Volume IV - Environmental Assessment & Environmental Monitoring Programs

Hazardous Waste Management Facility Operating License Renewal Application

Petro-Chem Processing Group of Nortru, LLC (Petro-Chem)
MID 980 615 298; Waste Data Systems Number 399102
421 Lycaste Street, Detroit, Michigan

Prepared for
Petro-Chem Processing Group of Nortru, LLC (Petro-Chem)

June 2022

Proj. No. 22821113.05

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VOLUME I – General

VOLUME II – Photos & Drawings

VOLUME III - Hydrogeologic

VOLUME IV – Environmental Assessment & Monitoring

VOLUME V – Waste Management Systems

Section 1

Environmental Assessment (B4)

FORM EQP 5111 ATTACHMENT TEMPLATE B4
ENVIRONMENTAL ASSESSMENT

The administrative rules promulgated pursuant to Part 111, Hazardous Waste Management, of Michigan's Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (Act 451) §324.11118(3) and R 299.9504(1)(e) and R 299.9504(1)(b) establish requirements for conducting environmental assessments at hazardous waste management facilities. Before receiving an operating license, owners and operators of hazardous waste treatment, storage, or disposal facilities must evaluate the (proposed) facility's impact on air, water, or other natural resources of the state. The evaluation must also include a failure mode assessment. All references to 40 CFR citations specified herein are adopted by reference in R 299.11003.

This license application template addresses requirements for an environmental assessment for hazardous waste management units at the Petro-Chem facility.

TECHNIQUES

INTRODUCTION

This environmental assessment for Petro-Chem describes current conditions, environmental impacts, and applicable exposure information for landfills and surface impoundments. The goals of the environmental assessment are to describe and discuss (1) the probable impact of the facility on natural resources, human life, and all environmental elements that affect these values; (2) probable unavoidable adverse effects of the facility; (3) alternatives for accomplishing the same objective; and (4) possible modifications that would minimize adverse effects.

The objective of the Petro-Chem facility is to take hazardous waste streams and repurpose this waste to be a fuel for other industrial operations through blending operations on site. This is beneficial and preferred over incineration and other waste disposal methods. Incineration and other waste disposal methods are not conducted on site. The Detroit Petro-Chem facility is not a final disposal location for any waste streams.

B4.A CURRENT CONDITIONS

B4.A.1 Facility Description

Petro-Chem operates a waste treatment, storage, and disposal facility located at 421 Lycaste Avenue in Detroit (Wayne County), Michigan. The operations are located in an industrial setting on approximately 20 acres of land at the corner of Lycaste and Freud Streets. Waste handling activities include off-loading of waste from tanker trucks, storage and blending of the waste in a series of twenty-one storage and blending tanks, and loading of the blended waste back into tanker trucks. Additional waste handling operations consist of offloading waste from drums and small containers (such as lab-pack wastes) by pumping, vacuuming or pouring.

Petro-Chem is permitted to receive a wide range of waste codes. Primarily, the facility handles liquid, solid, and semi-solid organic wastes, including spent solvents, paints, sludges and various other organic materials from the petrochemical, automobile, paint, and other nearby industries. The wastes are received in bulk (tanker trucks) and containers and are processed for reuse (majority) or for off-site disposal at licensed disposal facilities. The site features consist of administrative offices, laboratories, several large concrete-paved tank farms housing more than 40 aboveground storage tanks, paved loading and unloading areas, container handling areas, a maintenance garage for plant and trucking activities and a container handling building. The site operates 24 hours per day, seven days per week. A topographical map and a Facility layout drawing have been provided in Volume IV, Section 1, Appendix B4.1 and Appendix B4.2. Copies of relevant facility permits have been provided in provided Volume, IV, Section 1, Appendix B4.3.

B4.A.2 Description of Existing Environmental Conditions

A description of existing environmental conditions at the facility and any surrounding areas that may be affected by the facility is included in this section. Detailed information is provided in Volume III Form B3 and is not repeated here; however, references to appropriate attachment templates are provided. Maps, photographs, and other relevant information that are not included in other templates are included in this section. Important ecological relationships, functions, and interdependence of physical environmental elements and social and economic elements are discussed. Factual information from publications, reports, or personal communications is documented, with sources cited.

B4.A.2(a) Climate

Detroit typically has a Midwestern humid continental seasonal climate, which is influenced by the Great Lakes. There are four distinct seasons; winters are cold with moderate to heavy snowfall, while summers can be warm and humid. The area experiences “lake effect” weather, primarily in the form of increased cloudiness during late fall and early winter. The highest average temperature is in July at 85° F (29° C), while the lowest average temperature is in January at 20° F (−7°C). Summer temperatures can exceed 90° F (32° C), and winter temperatures can drop well below 0° F (−18° C). The average windspeed for the Detroit area is approximately 4.4 miles per hour, from a southwesterly direction (weatherunderground.com and weather.com). Average monthly precipitation ranges from 2 to 4 inches (5 to 10 cm), with the heaviest occurring during the summer months. Snowfall, which normally occurs from November to April, ranges from 1 to 10 inches (2.5 to 25 cm) per month.

B4.A.2(b) Topography

Petro-Chem is located in an urban and highly developed, industrialized area. There are residential homes to the south of the facility. Based on review of the USGS 7.5 minute, Belle Isle, Michigan Quadrangle topographic map, there are no bodies of surface water located within a half-mile radius of the facility. The closest surface water body is the Detroit River located over 2,900 feet south of the facility, and the groundwater beneath the subject property flows toward the north, east, and west away from the Detroit River. In addition, the general surface topography of the area is flat. Topographic and location maps have been provided with the Part A application in Volume I, Section 1. Maps are also provided in Volume IV, Section 1, Appendix B4.1 and B4.2.

B4.A.2(c) Geology

Petro-Chem is located at an elevation of approximately 580 feet above mean sea level (msl) on flat terrain. The facility overlies glacial deposits, which are consistent with regional depositional patterns. According to soil borings taken during construction of groundwater monitoring wells, the soils encountered beneath the property can be divided into a mixed-fill unit, a peat unit, and a clay unit. Copies of the soil borings are included in Appendix B4.2. The three- to ten-feet thick mixed-fill unit consists of sand, cinders, peat, brick, fine ash, and fibrous materials. The peat unit varies from dark brown to very soft black peat. The thickness of the peat unit is inversely correlated to the thickness of the mixed-fill unit. In areas where the peat unit is thicker, the mixed-fill is less thick and vice-versa. The clay unit lies immediately beneath the mixed-fill and peat unit. The clay appears to be homogeneous at least to a depth of 30 feet below ground surface (bgs). These types of clays have estimated permeability between 3.6 x 10-8 and 8.5 x 10-8 cm per second, thus providing some protection against seepage into the soils and shallow groundwater of potential spill or leaks. The depth to ground water ranges from 5 to 11 feet bgs and the direction of the groundwater gradient is north, east, and west. Refer to Volume III, EGLE Form B3, Hydrogeological Report for additional information.

B4.A.2(d) Soils

Based on the results of previous investigations, soil conditions can be summarized as a layer of mixed-fill from ground surface to approximately 5 feet bgs, overlying an approximately 5 foot thick peat unit, which overlies a clay unit. Lenses of minor sand or sandy-clay were observed within the peat layer during onsite sampling activities. The thick clay unit is well-documented as a regional confining layer. Additional information pertaining to the soils can be found in B4.A.2(c). Refer to Volume III, EGLE Form B3, Hydrogeological Report for additional information.

B4.A.2(e) Hydrology

Based on previous investigations conducted at the Petro-Chem facility, the depth to groundwater at the site ranges from 5 to 11 feet bgs and the direction of the groundwater gradient is north, east, and west. Groundwater encountered at this depth is probably perched and has a low groundwater yield. Perched groundwater at the site is located within the peat layer.

The upper layer of mixed-fill material may be capable of yielding an adequate volume of water; but this water would most likely be from surface runoff and sustaining a flow for a period of time. Similarly, the perched groundwater in the peat layer is also intermittent in yield. Both layers would likely be of poor quality (i.e., not suitable for drinking purposes). The underlying clay unit is not capable of yielding significant amounts of groundwater to wells.

Surface water runoff from the facility is discharged to a combined sewer system that discharges to the Detroit Water and Sewerage Department. The closest surface water body, the Detroit River, is over a half-mile south of the facility.

The facility’s groundwater monitoring program has found elevated concentrations of methyl tertiary butyl ether (MTBE) in several samples. The facility has been investigating the source of the MTBE. Additional information and findings from the study will be sent directly to EGLE as outlined in the approved January 18, 2010 MTBE investigation work plan. This work plan has been provided to EGLE. An electronic copy will be provided up on request.

Refer to Volume III, EGLE Form B3, Hydrogeological Report for additional information.

B4.A.2(f) Land Use and Zoning

Petro-Chem is located in an industrialized area on the east side of Detroit in Wayne County, Michigan. Currently, the northern, eastern and western adjacent properties are industrial in use. South of the facility are residential homes. Historically, the entire surrounding area was industrial in use. The homes built to the south of the facility are built on land that was previously utilized for industrial purposes.

B4.A.2(g) Historical or Archaeological Resources

The current facility archaeological component has little potential to adversely affect significant archaeological resources since the ground has been disturbed during construction of the original building, additions, parking and driveways.

Petro-Chem has not been made aware of any historical or archaeological resources identified at the subject property or in the surrounding area since the previous investigation was conducted as part of the previous permit application.

B4.A.2(h) Social Environment

The social environment, in terms of demographics and infrastructure of the area, is discussed in the following two subsections.

B4.A.2(h)(i) Demographics

The facility is located in a highly developed and industrialized area. According to the 2020 census of Detroit, Michigan, 54% of the population is between the ages of 18 and 65 years old. The population is approximately 77% African American, 14% Caucasian, 7.7% Hispanic or Latino, 1.9% Asian and 2.4% other. In Detroit the unemployment rate has been reported to be 4.6 to 6.9% over the between March 2021 and March 2022 per the US Bureau of Labor and Statistics. DTE is the largest local employer in the area of the Petro-Chem facility. The Petro-Chem facility employs approximately 85 people. The continued operation of the waste handling facility will not negatively impact the local demographics.

B4.A.2(h)(ii) Infrastructure

The existing facility currently has access to city water, sanitary sewer, storm sewer, natural gas, power, and telephone. These utilities are maintained by the providers.

Wastes generated at the facility or that are unable to be effectively treated at the facility are disposed of through off-site licensed waste disposal facilities.

Petro-Chem maintains a comprehensive program for management of hazardous and non-hazardous streams that are generated.

Water is supplied to the property from the Great Lakes Water Authority (GLWA), previously the Detroit Water and Sewage Department (DWSD).

Storm water from the facility discharges to the combined sewer system operated by GLWA.

Sanitary wastewater from the property is collected and discharged to GLWA, which has adequate capacity to handle the flow.

There will be no need to expand utility needs for the future operation of the facility.

There is one school, Keeting School, two public parks (Maheras-Gentry Park and Stockton park), and the St. Jean boat launch within a one-mile radius of the facility. Refer to Volume IV, Section 1, Figure B4.1.

Local law enforcement is handled by the City of Detroit Police Department.

B4.A.2(i) Transportation

The Petro-Chem is currently located on the corner of Freud and Lycaste Streets in Detroit (Wayne County), Michigan. Parking for employees is provided in on site paved parking areas. The majority of waste materials transported to and from the site are in tanker trucks or semi-trailers. A railroad is located on the eastern adjoining property and may be used in the future to unload waste materials to tanker trucks. Petro-Chem is located in a highly developed and urban area. The highways and surface streets in the area are designed for high traffic loads. Refer to Figure B4.1 in Volume IV, Section1, Appendix B4.1.

B4.A.2(j) Air Quality

Ambient air quality in the area is in attainment with national ambient air quality standards with the exception of PM 2.5 (fine particles). The facility operates under the Michigan Air Use Permit to Install 2019 PTI 6-19 N0731. Air emissions from the facility are primarily from the offloading and loading of solvents from tanker trucks and the aboveground storage tanks. A copy of the permit is included in Appendix B4.4. The Petro-Chem facility is located in a highly industrialized area. The surrounding properties have the potential to emit air contaminants associated with onsite activities.

The prevailing winds generally blow towards the northeastern direction toward heavily industrial areas. There are no visible emissions on site. Solvent odors can be detected on site but are not noticeable off the property. Petro-Chem has installed an air-meteorological survey station which monitors and records wind speed and direction, temperature, humidity, etc., in order to better control emissions generated at the facility. Additionally, Petro-Chem conducts fence line ambient air monitoring on the northern, western, southern and eastern sides of the property. Additional information on this monitoring plan can be found in the 2010 Ambient Air Monitoring plan is provided in Volume IV, Section 2, Appendix B5.0 of this permit application.

B4.A.2(k) Noise

Noise levels below 65 decibels (dB) are normally considered acceptable in suitable living environments. Responses to noise vary, depending on the type and characteristics of the noise, the expected level of noise, the distance between the noise source and the receptor, the receptor’s sensitivity, and the time of day. The table below lists the sound levels of some familiar sources:

Sound Levels of Various Sources	
Source	Sound Level (dB)
Near jet plane at takeoff	140
Gun muzzle blast	140
Threshold of pain	120
Loud music	115
Car horn	115
Thunder	110

Sound Levels of Various Sources	
Source	Sound Level (dB)
Chainsaw	100
Lawn mower	90
Jack hammer	88
Dozer	85
Backhoe	80
Alarm clock	75
Normal conversation	60
Light traffic	50
Refrigerator	40
Rustle of leaves	20
Normal breathing	10

Operation of the Petro-Chem facility involves the movement of workers and truck traffic. Although noise levels would be highest during the day, there would be noise levels during night time as well. These noise levels would not be expected to extend far beyond the boundaries of the site.

B4.A.2(l) Appearance and Aesthetics

The Petro-Chem facility is located in a highly developed and industrialized area. The facility is primarily covered with building or asphalt/concrete. There are limited landscaped areas or areas with large amounts of vegetation. There are no visually pleasing landscapes or views and no unique natural or man-made features associated with the facility.

B4.A.2(m) Terrestrial Ecosystem

The characteristics of the terrestrial ecosystem, in terms of flora, fauna, rare or endangered species, and critical habitat are described in the following subsections.

B4.A.2(m)(i) Flora

The Petro-Chem facility is located in a highly developed and industrialized area. Approximately 99 percent of the facility is concrete or gravel covered. The remaining areas are improved with native grasses. Surrounding areas are industrial in development, with the exception of the southern residential community that has landscaped areas.

B4.A.2(m)(ii) Fauna

Wildlife at the facility is dominated by human tolerant species. Animal species found in the area would be limited to species such as the American robin, house sparrows, and squirrels.

B4.A.2(m)(iii) Rare or Endangered Species

Research identified the following endangered species located in Wayne County. The species have not been seen on or near the Petro-Chem facility.

Species	Status	Habitat
Indiana bat *(Myotis sodalist)*	Endangered	Summer habitat includes small to medium river and stream corridors with well developed riparian woods; woodlots within 1 to 3 miles of small to medium rivers and streams; and upland forests. Caves and mines as hibernacula.
Eastern massasauga *(Sistrurus catenatus catenatus)*	Candidate	Not provided in research source
Eastern prairie fringed orchid (*Plantathera leucophaea*)	Threatened	Mesic to wet prairies and meadows
Source: United States Fish and Wildlife Endangered Species Program (http://www.fws.gov/midwest/Endangered/lists/michigan-cty.html)		

B4.A.2(m)(iv) Critical Habitat

The facility is located in a highly developed and industrialized area. No critical habitats have been identified for the survival of local species

B4.A.2(n) Aquatic Ecosystem

The characteristics of the aquatic ecosystem, in terms of flora, fauna, rare or endangered species, and critical habitat are described in the following subsections.

B4.A.2(n)(i) Flora

The Petro-Chem facility is not located within a half-mile of a surface water body. There is no aquatic vegetation on or near the facility. The Detroit River is located south of the facility within a one-mile radius. Aquatic vegetation associated with a typical Midwestern River, e.g., plankton, is present.

B4.A.2(n)(ii) Fauna

The Petro-Chem facility is not located within a half-mile of a surface water body. There is no aquatic animal species on or near the facility. The Detroit River is located south of the facility within a one-mile radius. Aquatic animal species associated with a typical Midwestern river, e.g., fish, are present.

B4.A.2(n)(iii) Rare or Endangered Species

Species	Status	Habitat
Northern riffleshell (Dysnomia torulosa rangiana)	Endangered	*Large streams and small rivers in firm sand of riffle areas; also occurs in Lake Erie*
Rayed Bean Mussel (Villosa fabalis)	Candidate	Not provided in research source
Source: United States Fish and Wildlife Endangered Species Program (http://www.fws.gov/midwest/Endangered/lists/michigan-cty.html)		

B4.A.2(n)(iv) Critical Habitat

The facility is located in a highly developed and industrialized area. No critical habitats have been identified for the survival of aquatic species in the area

B4.B ENVIRONMENTAL IMPACTS OF THE FACILITY

The continued operation of the facility has a minimum potential to impact or change the environment of the area surrounding the facility during normal operation. However, during failure mode the facility does have the potential to impact or change the environment of the area surrounding the facility.

Petro-Chem has implemented standard operating procedures to minimize the potential for a release of materials into the environment. In addition, Petro-Chem has engineered the structural elements of the property to prevent a damaging release of material into the environment and minimize impact to groundwater, air and soil. Due to the nature of the operations on site there will be releases of contaminates in to the ambient air. Petro-Chem has received a permit to govern these operations and minimize impact on the environment.

Failure mode would indicate that an accidental release or incident would have occurred despite the standard operating procedures and structural controls in place for operation. Groundwater and ambient air could be negatively impacted by an operational failure, due to the nature of the materials on site. Petro-Chem has made efforts to plan for and mitigate environmental impacts during operational failures. Structural controls have been put into place to minimize impact to groundwater and air during operational failures. In addition, it should be noted that an operation failure is an unlikely event.

B4.C EXPOSURE INFORMATION REPORT FOR LANDFILLS AND SURFACE IMPOUNDMENTS

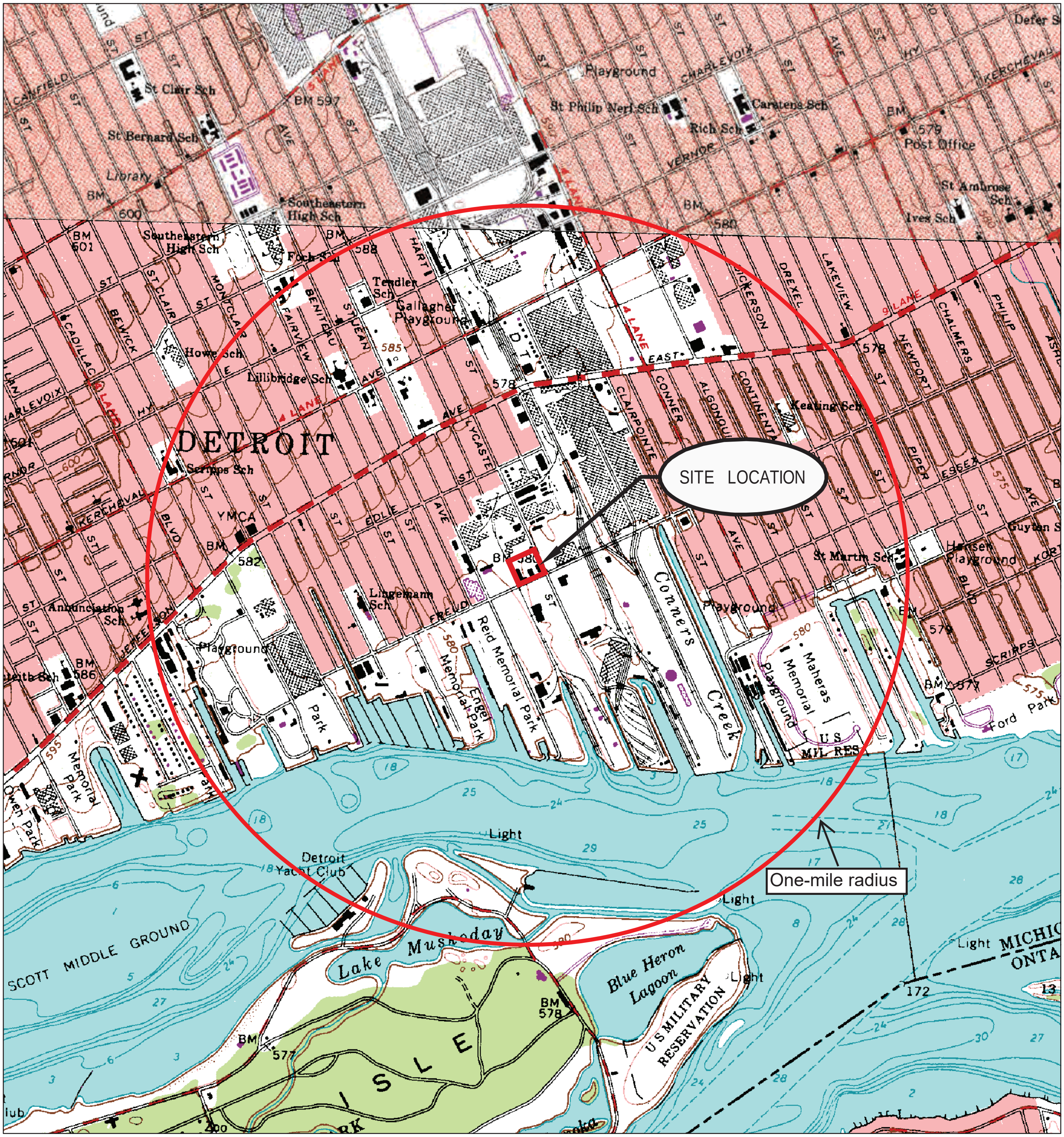
Petro-Chem does not operate landfills or surface impoundments on site.

B4.D EVALUATION OF ALTERNATE HAZARDOUS WASTE MANAGEMENT TECHNOLOGIES

Petro-Chem operations are practical and economically viable hazardous waste management methods that will protect public health and the environment. The primary operation of the facility is the blending of hazardous wastes to be reused as fuel for industrial operations. This is a beneficial process that reduces the amount of virgin fuels required for industrial purposes. Petro-Chem has not been made aware of any alternative hazardous waste management methods identified since the previous investigation was conducted as part of the previous permit application.

Appendix B4.1

Topo Map



QUADRANGLE LOCATION

Scale 1:24000

0 1/2 1 MILE

1000 0 1000 2000 3000 FEET

(SOURCE OF MAP IS USGS 7.5 MINUTE QUADRANGLE MAP, BELLE ISLE(1980), MICHIGAN)

N

CHECK BY	KLW
DRAWN BY	JL
DATE	3/25/2010
SCALE	AS SHOWN
CAD NO.	109200.02_A
PRJ NO.	11009-109200.02

SITE LOCATION MAP

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

BUREAU VERITAS

FIGURE

B4.1

Appendix B4.2

Site Map & Logs

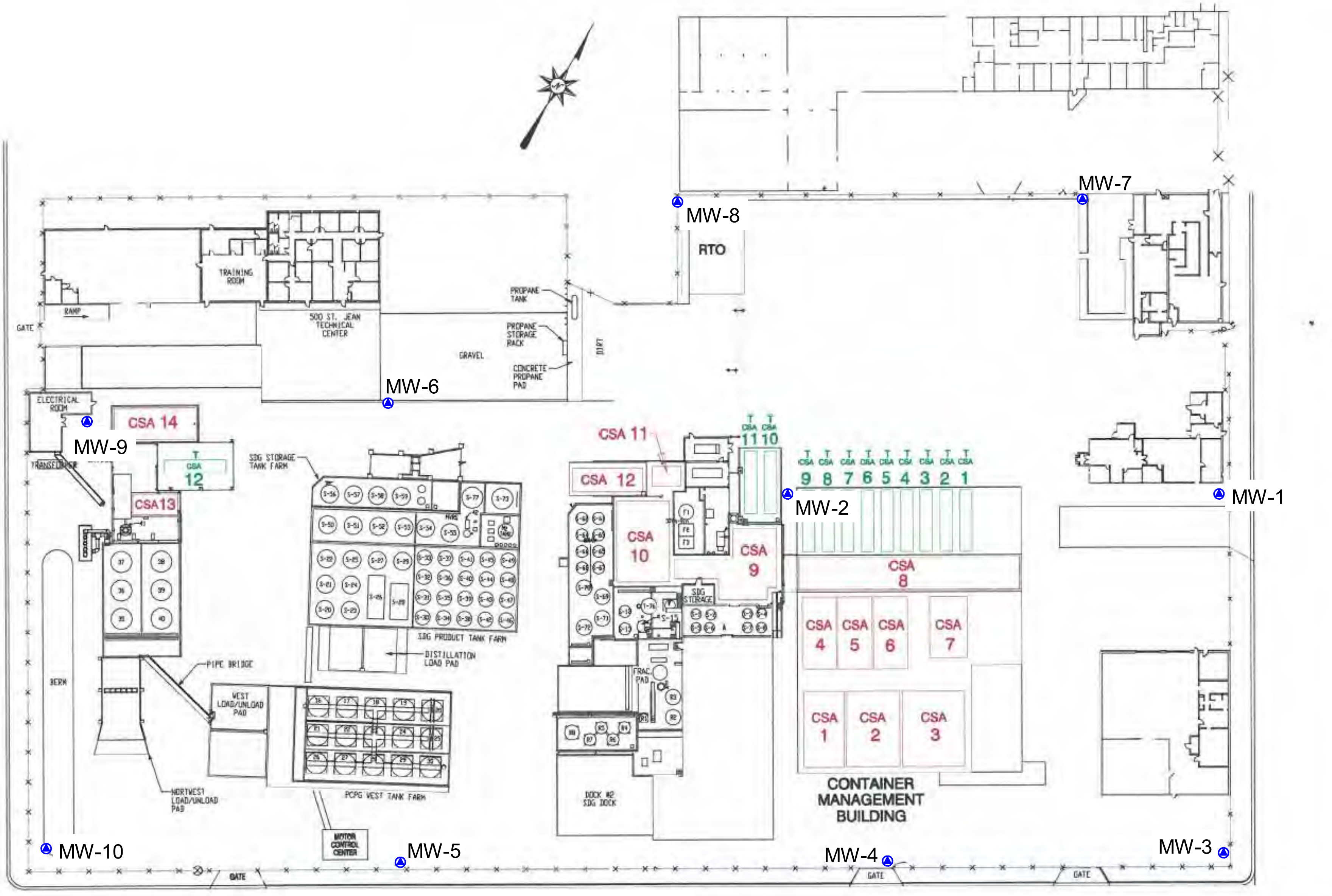


Figure B4.2
Site map with monitoring well locations

BUREAU VERITAS

Petro-Chem Processing Group
421 Lycaste Street
Detroit, Michigan

Project No. 11010-000175.00

Last Revision:
October 28, 2010

ATTACHMENT 1
SOIL BORING LOGS
PETRO-CHEM PROCESSING, INC.

HARTLEY & ASSOCIATES, P.C.

8621 KRATAGE AVENUE UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No. Well #1
Ground Surface Elev.
Datum
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068
Client Environmental Research Group
Ann Arbor, Michigan
Date Drilled 10-21-82
Driller L. Hartley
Drilling Method 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W.L.	
	2						
	4				Loose Moist Brown-Black Clayey Sand, Cinders, and Broken Concrete FILL		
	6	AS					
	8			8.5			
Well Screen	10			10.0	Very Soft Wet Black Peat Muck	▽	Water Level 9.9'
	12				Soft Wet Gray Clay		
	14			14.5			
	16				Stiff Moist Brown Sandy Clay		
	18	SS	8 12 15	18.0			
					End of Boring		
	20						
	22						
	24						
	26						

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S. - Sectional Liner Sample
A.S. - Auger Sample
C.C.P. - Continuous Cone Penetration Test

"No" - Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30".
(12" Depth Increments

W.L. - Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
nd - Natural Density in P.C.F.

HARTLEY & ASSOCIATES, P.C.

8821 KRATAGE AVENUE UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No.	Well #2	H & A Job No.	82-068
Ground Surface Elev.		Client	Environmental Research Group Ann Arbor, Michigan
Datum		Date Drilled	10-21-82
Project	Petro-Chem Processing, Inc. 421 Lycaste Detroit, Michigan	Order	L. Hartley
		Drilling Method	4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
	2			3.2	Loose Moist Black Sand FILL with Assorted Chemicals		
	4			5.0	Loose Wet Brown-Black Clayey Medium to Coarse Sand FILL	▽	Water Level 4.7'
	6	AS					
	8			10.7	Soft Damp Brown Peat		
Well Screen	10 12	SS	2 3 4	12.0	Soft Wet Gray Sandy Clay		No Recovery
	14	SS	8 8 13	14.0	Stiff Moist Gray-Brown Sandy Clay		
	16 18 20 22 24 28				End of Boring		

MPLE TYPES
S. - 2" O.D. Split Spoon Sample
S.-Sectional Liner Sample

"No"-Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30".

W.L.-Water Level
w - Moisture Content %
qu - Unconfined Compressive Strength in P.S.F.

TEST BORING REPORT

BORING No. Well #2-C
H & A Job No. 82-068-4
Ground Surface Elev.
Client TMA/ERG
Ann Arbor, Michigan
Datum
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan
Date Drilled 5-21-87
Driller L. Hartley
Drilling Method: 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
	2			3.0	Loose Black Sand FILL with Cinders, Gravel, and Peat		
	4 6			8.0	Soft Wet Dark Brown Peat	▽	Water Level 5.0'
	8 10	Well Screen		10.0	Soft Wet Gray Silty Clay		
	12 14 16 18 20 22 24 26				End of Boring		

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S.-Sectional Liner Sample
A.S.-Auger Sample
C.C.P.-Continuous Cone Penetration Test

"No"-Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30". (12" Depth Increments during C.C.P. Tests)

W.L.-Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
nd - Natural Density in P.C.F.

SHEET 1 OF 3

HARTLEY & ASSOCIATES, P. C.
3821 KRATAGE AVENUE
UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No. Well #3
Ground Surface Elev.
Datum
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068
Client Environmental Research Group
Ann Arbor, Michigan
Date Drilled 10-21-82
Driller L. Hartley
Drilling Method 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
				1.0	Loose Dark Brown Medium Sand FILL		
	2				Loose Moist Black Cinders and Gray Ashes FILL		
				4.0			
	4				Loose Damp Brown Cinders and Ashes FILL		
	6	AS					
	8			9.2			
Well Screen	10			10.0	Soft Wet Black Peat Muck		
					Plastic Damp Gray Sandy Clay		
	12	SS	2 3 3	13.5			
	14				End of Boring		Boring was Dry on Completion.
	16						
	18						
	20						
	22						
	24						
	26						

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S. - Sectional Liner Sample

"No" - Number of Blows Required to Drive Sampler into Soil in 6" Dozen Increments, using 140 lb Hammer Dropping 30".

W.L. - Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
[illegible] in P.C.F.

HARTLEY & ASSOCIATES, P. C.

TEST BORING REPORT

BORING No.	Observation Well 3-B **	H & A Job No.	82-068-5
Ground Surface Elev.		Client	TMA/ERG Ann Arbor, Michigan
Datum		Date Drilled	1-31-89
Project	Replacement of O.W. 3-A Petro-Chem Processing, Inc. Detroit, Michigan	Driller	L. Hartley
		Drilling Method:	4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE		STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
		TYPE	No.				
Concrete					Loose Moist Dark Brown Sand, Cinders, and Ashes FILL with Clinkers and Brick		
Bentonite	2						
	4						
Silica Sand	6						
Well Screen	8			9.8			Boring was Dry on Completion.
	10			10.0	Loose Wet Rusty Sand and Fine Gravel FILL		
Silica Sand				11.0	Soft Wet Gray Sandy Clay		
	12			13.0	Plastic Damp Gray Silty Clay		
	14				End of Boring		
	16				** Located 6' East of Observation Well 3-A		
	18						
	20						
	22						
	24						
	26						

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S - Sectional Liner Sample

"No" - Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30".

W.L. - Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
Natural Density in P.C.F.

HARTLEY & ASSOCIATES, P.C.

8821 KRATAGE AVENUE UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No. Well #4

Ground Surface Elev. --

Datum

Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068

Client Environmental Research Grou
Ann Arbor, Michigan

Date Drilled 10-21-82

Driller L. Hartley

Drilling Method 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
	2 4			5.0	Loose Moist Dark Brown Cinders and Ashes FILL	▽	Water Level 5.0'
	8	AS		6.5	Loose Wet Black Cinders FILL with Heavy Chemical Odor		
	8			10.2	Very Soft Wet Dark Brown Peat		
Well Screen	10 12	SS	2 2 2	12.0	Very Soft Wet Gray-Black Clay with Seams of Brown Fine Sand		
				12.5	Soft Moist Gray Silty Clay		
	14 16 18 20 22 24 26				End of Boring		

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S. - Sectional Liner Sample
A.S. - Auger Sample
C.C.P. - Continuous Cone Penetration Test

"No" - Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30".
(12" Depth Increments

W.L. - Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
γd - Natural Density in P.C.F.

4 6

HARTLEY & ASSOCIATES, P. C.

5821 KRATAGE AVENUE UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No.	Well #5	H & A Job No.	82-068
Ground Surface Elev.		Client	Environmental Research Gro Ann Arbor, Michigan
Datum		Date Drilled	10-21-82
Project	Petro-Chem Processing, Inc. 421 Lycaste Detroit, Michigan	Driller	L. Hartley
		Drilling Method	4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W.L.	
	2			3.4	Loose Moist Dark Brown Medium Sand FILL	▽	Water Level 3.8
	4 6	AS		6.5	Loose Wet Black Sand and Brown Cinders FILL		
				8.0	Soft Wet Black Peat Muck		
11 Screen	8	AS		10.0	Loose Wet Gray Medium Sand		
	10 12	SS	2 3 3	12.0	Plastic Damp Gray Sandy Clay		
	14 16 18 20 22 24 26				End of Boring		

MPLE TYPES

"No"-Number of Blows Required to Drive Sampler into Soil in 6" Depth

W.L.-Water Level
w - Moisture Content, %
- Unconfined Compress

HARTLEY & ASSOCIATES, P. C.

Sectior
Revised 03/01/

TEST BORING REPORT

BORING No. Well #5-A
Ground Surface Elev.
Datum
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068-4
Client TMA/ERG
Ann Arbor, Michigan
Date Drilled 5-21-87
Driller L. Hartley
Drilling Method: 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W.L.	
				0.4	Loose Sand and Cinders FILL		
		AS		3.5	Firm Moist Brown Silty Clay FILL		
	5	AS		6.3	Loose Wet Dark Brown Sand and Cinders FILL, with Pieces of Brick and Broken Glass	∇	Water Level 5.0'
Well Screen		AS		8.5	Soft Wet Brown Fibrous Peat		
		AS		9.5	Soft Wet Dark Brown Peat Muck		
	10	AS		12.0	Loose Wet Gray Silty Fine Sand and Sandy Silt		
	15	AS		15.4	Firm Damp Gray Silty Clay		
	20	AS		21.0	Stiff Moist Brown Sandy Clay with Pebbles		
	25 30	AS		30.0	Firm Damp Gray Silty Clay with Traces of Sand		
					End of Boring		

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S.-Sectional Liner Sample
A.S.-Auger Sample
C.C.P.-Continuous Cone Penetration Test

"No"-Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30". (12" Depth Increments during C.C.P. Tests)

W.L.-Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
nd - Natural Density in P.C.F.

SHEET 2 OF 3

HARTLEY & ASSOCIATES, P.C.

TEST BORING REPORT

BORING No. Observation Well 5-B **
Ground Surface Elev.
Datum
Project Replacement of O.W. 5-A
Petro-Chem Processing, Inc.
Detroit, Michigan

H & A Job No. 82-068-5
Client TMA/ERG
Ann Arbor, Michigan
Date Drilled 1-31-89
Driller L. Hartley
Drilling Method: 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
Concrete				1.0	Firm Mottled Gray Silty Clay FILL		
Bentonite	2 4				Loose Moist Dark Brown-- Cinders and Ashes FILL		
					Becomes Wet----	▽	Water Level 5.5' at Completion.
Silica Sand	6			6.8			
	8			9.2	Soft Wet Dark Brown Peat		
Well Screen	10			11.5	Soft Wet Gray-Brown Sandy Marl		
Silica Sand	12			13.0	Plastic Damp Gray Silty Clay		
	14 16 18 20 22 24 26				End of Boring ** Located 2' South of Observation Well 5-A		

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S.-Sectional Liner Sample
A.S. Auger Sample
C.C.P.-Continuous Cone Penetration Test

"No"-Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30".
(12" Depth Increments

W.L.-Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
nd - Natural Density in P.C.F

HARTLEY & ASSOCIATES, P.C.

6821 KRATAGE AVENUE UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No. Well #6
Ground Surface Elev.
Datum
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068
Client Environmental Research Group
Ann Arbor, Michigan
Date Drilled 10-21-82
Driller L. Hartley
Drilling Method 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W.L.	
	2			2.0	Loose Moist Dark Brown Medium Sand and Cinders FILL		
	4	AS		4.5	Loose Wet Black Cinders FILL	▽	Water Level 3.9'
Well Screen	6	AS		8.0	Very Soft Wet Black Sandy Peat		
	8 10	SS	4 7 12	10.0	Stiff Moist Gray Sandy Clay		
	12 14 16 18 20 22 24 26				End of Boring		

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S. - Sectional Liner Sample

"No" - Number of Blows Required to Drive Sampler into Soil in 6" Depth increments, using 140 lb Hammer Dropping 30".

W.L. - Water Level
w - Moisture Content %
qu - Unconfined Compressive Strength in P.S.F.
γd - Natural Density in P.C.F.

HARTLEY & ASSOCIATES, P.C.

Section
Revised 03/01/

TEST BORING REPORT

BORING No. Well #6-A
Ground Surface Elev.
Datum
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068-4
Client TMA/ERG
Ann Arbor, Michigan
Date Drilled 5-21-87
Driller L. Hartley
Drilling Method: 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
	5			7.0	Loose Moist Dark Brown Sand, Cinders, Brick, and Broken Concrete FILL	▽	Water Level 6.7'
Well Screen				9.0	Soft Wet Dark Brown Peat		
	10			12.1	Soft Wet Gray Silty Clay		
				14.7	Stiff Moist Gray Silty Clay		
	15			18.0	Firm Moist Gray-Brown Sandy Clay with Traces of Gravel		
				19.5	Firm Damp Gray-Brown Silty Clay		
	20 25			30.0	Plastic Wet Gray Silty Clay		
	30				End of Boring		

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S.-Sectional Liner Sample
A.S.-Auger Sample
C.C.P.-Continuous Cone Penetration Test

"No"-Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30".
(12" Depth Increments during C.C.P. Tests)

W.L.-Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
nd - Natural Density in P.C.F.

SHEET 3 OF 3

HARTLEY & ASSOCIATES, P. C.

8821 KRATAGE AVENUE UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No. Well #7
Casing Top ~~Ground Surface~~ Elev. 99.89
Datum Top of Well #1 = 100.00
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068-2
Client Environmental Research Group,
Ann Arbor, Michigan
Date Drilled 8-29-85
Driller L. Hartley
Drilling Method: 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
	2			3.0	Firm Moist Brown Silty Clay FILL with Seams of Dark Brown Ashes		
	4 6			6.4	Firm Moist Brown Silty Clay FILL		
		Well Screen		7.1	Soft Wet Dark Brown Fibrous Peat	▽	Water Level 7.0'
	8			8.4	Soft Wet Black Silty Peat with Strong Sulfur Odor		
				9.4	Loose Wet Gray Silty Fine to Medium Sand		
	10 12			12.0	Soft Wet Gray Silty Clay		
				13.0	Firm Moist Gray Silty Clay		
	14 16 18 20 22 24 26				End of Boring		

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S.-Sectional Liner Sample
A.S.-Auger Sample
C.C.P.-Continuous Cone Penetration Test

"No"-Number of Blows Required to Drive Sampler into Soil In 6" Depth Increments, using 140 lb Hammer Dropping 30". (12" Depth Increments during C.C.P. Tests)

W.L.-Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
nd - Natural Density in P.C.F.

SHEET 1 OF 4

HARTLEY & ASSOCIATES, P.C.
8821 KRATAGE AVENUE UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No. Well #8
~~Ground Surface~~ Casing Top Elev. 99.77
Datum Top of Well #1 = 100.00
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068-2
Client Environmental Research Group,
Ann Arbor, Michigan
Date Drilled 8-29-85
Driller L. Hartley
Drilling Method: 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
				0.8	Crushed Limestone FILL		
	2			3.0	Loose Moist Brown-Black Sand, Cinders, and Gravel FILL		
	4			3.5	Soft Wet Gray-Brown Silty Clay	▽	Water Level 3.8'
				5.4	Loose Wet Dark Brown Medium Sand		
	6			6.1	Soft Wet Dark Brown Peat with Strong Petroleum Odor		
				7.1	Very Soft Wet Black Sandy Peat		
	8	Well Screen		7.9	Loose Wet Brown Medium Sand		
				9.0	Loose Wet Gray Silty Fine Sand		
	10			10.0	Plastic Moist Gray Sandy Clay		
					End of Boring		
	12						
	14						
	16						
	18						
	20						
	22						
	24						
	26						

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S.-Sectional Liner Sample
A.S.-Auger Sample
C.C.P.-Continuous Cone Penetration Test

"No"-Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30".
(12" Depth Increments during C.C.P. Tests)

W.L.-Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
nd - Natural Density in P.C.F.

SHEET 2 OF 4

HARTLEY & ASSOCIATES, P. C.
8821 KRATAGE AVENUE UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No. Well #9
Casing Top ~~Ground Surface~~ Elev. 101.24
Datum Top of Well #1 = 100.00
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068-2
Client Environmental Research Group
Ann Arbor, Michigan
Date Drilled 8-29-85
Driller L. Hartley
Drilling Method: 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
	2			3.0	Loose Moist Dark Brown Sand, Cinders, and Ashes FILL		
	4			3.8	Loose Moist Brown Medium Sand FILL		
	6			7.6	Loose Damp Dark Brown Sand FILL with Cinders and Glass	▽	Water Level 7.3'
	8	Well Screen		~~8.0~~	Soft Wet Brown Fibrous Peat		
	10			10.0	Very Soft Wet Dark Brown Peat Muck		
				10.6	Loose Wet Gray Silty Fine Sand		
				~~11.0~~	Loose Damp Gray Clayey Silt		
	12			12.5	Loose Wet Gray Sandy Sily		
	14				End of Boring		
	16						
	18						
	20						
	22						
	24						
	26						

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S.-Sectional Liner Sample
A.S.-Auger Sample
C.C.P.-Continuous Cone Penetration Test

"No"-Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30".
(12" Depth Increments during C.C.P. Tests)

W.L.-Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
nd - Natural Density in P.C.F.

SHEET 3 OF 4

HARTLEY & ASSOCIATES, P. C.

8821 KRATAGE AVENUE UNION LAKE, MICHIGAN 48085

TEST BORING REPORT

BORING No. Well #10
Casing Top Elev. 99.68
Datum Top of Well #1 = 100.00
Project Petro-Chem Processing, Inc.
421 Lycaste
Detroit, Michigan

H & A Job No. 82-068-2
Client Environmental Research Group,
Ann Arbor, Michigan
Date Drilled 8-29-85
Driller L. Hartley
Drilling Method: 4" Auger on A.T.V.

ELEV.	DEPTH IN FEET	SAMPLE TYPE	SAMPLE No.	STRATA CHANGE	SOIL CLASSIFICATION	W. L.	
	2			2.0	Loose Dark Brown Sand, Cinders, Brick and Ashes FILL		
	4 6			7.4	Loose Wet Gray-Brown-White Ashes, Sand, and Cinders FILL with Broken Glass	▽	Water Level 6.0'
	8	Well Screen		8.0	Soft Wet Brown Fibrous Peat		
				9.0	Soft Wet Black Peat		
				9.7	Very Soft Dark Brown Peat Muck		
	10			10.0	Loose Wet Gray Sandy Silt		
	12 14 16 18 20 22 24 26				End of Boring		

SAMPLE TYPES
S.S. - 2" O.D. Split Spoon Sample
L.S.-Sectional Liner Sample
A.S.-Auger Sample
C.C.P.-Continuous Cone Penetration Test

"No"-Number of Blows Required to Drive Sampler into Soil in 6" Depth Increments, using 140 lb Hammer Dropping 30".
(12" Depth Increments during C.C.P. Tests)

W.L.-Water Level
w - Moisture Content, %
qu - Unconfined Compressive Strength in P.S.F.
nd - Natural Density in P.C.F.

SHEET 4 OF 4

WW Engineering & Science

Log of Boring

Page 1 of 2

Project No. 83104

Client Petro-Chem Processing, Inc.
Location Detroit, MI
Logged By N. Marcelletti
Contractor CTI Associates
Driller J. Springstead

Boring Designation DB-1A
Start Date 2-4-91 Completed 2-5-91
Ground Surface Elevation : approximately 578.8 feet based on site USGS elevation map prepared 1991.

Drilling Method(s)	Depth Range
6 1/4" Hollow Stem Auger	0-15.0 feet
Rotary wash with 3-3/4" roller bit	15-30 feet

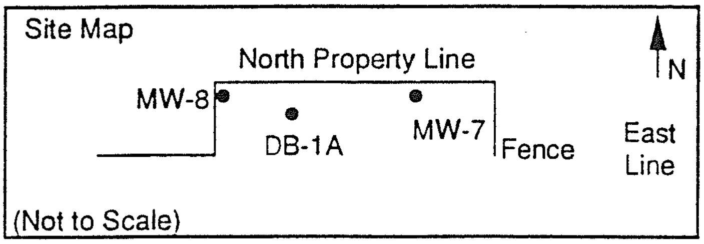
Sampling Method(s)	Depth Range
2-inch Split Spoon	1.5-3.5 foot intervals
3-inch Shelby Tube	13.0' to15.0' and 23.0' to 25.5'

Grouting Material/Method	Depth Range
Cement and Bentonite	0-30.0 feet

Water Level Data
Water encountered at 8.0 feet during drilling.

General Notes
4-inch steel drilling casing set from 0-15 feet and cemented in borehole

Site Map



(Not to Scale)

Borehole Depth (feet)	Sample Type and Number	Depth of Sample Tip (feet)	Sample Recovered (inches)	Hammer Blows (6-Inch Intervals)	Depth of Borehole Casing (feet)	Field Data	Field Data	Graphic Log	Depth (feet)	Field Sample Descriptions
				13 22						
1	S-1	2.0	18	25 10					2.5	FILL: Compact Black FINE TO MEDIUM SAND, some coarse gravel, light brown silty clay, wood fragments, moist
2				4 8						
3	S-2	3.0	18	11 8						
4				2 3						
5	S-3	5.0	18	3 2						
6	S-4	7.0	16	2 4						
7				1			▽			
8	S-5	9.0	15	2 3					8.4	Medium Black PEAT, with brown fine sand seams, moist
9										
10				3 6						
11	S-6	11.5	15	9 2						
12	S-7	13.0	14	7 8						
13										
14	ST-1	15.0	24	pushed	15.0					
15				6 12						
16	S-8	16.5	16	15 6	15.0					
17	S-9	18.0	16	13 16	15.0					
18				6 8						
19	S-10	19.5	16	12 2	15.0					Very Stiff Gray SILTY CLAY,occasional wood fragments, moist
20										

(Continued on Page 2)

WW Engineering & Science

Log of Boring

Page 2 of 2
Project No. 83104

Client Petro-Chem Processing, Inc.
Location Detroit, MI

Boring Designation DB-1A
Start Date 2-4-91 Completed 2-5-91
Ground Surface Elevation : approximately 578.8 feet based on site USGS elevation map prepared 1991.

Borehole Depth (feet)	Sample Type and Number	Depth of Sample Tip (feet)	Sample Recovered (inches)	Hammer Blows (6-Inch Intervals)	Depth of Borehole Casing (feet)	Field Data	Field Data	Graphic Log	Depth (feet)	Field Sample Descriptions
21	S-11	21.0		3 4	15.0				21.0	Very Stiff Gray SILTY CLAY,occasional wood fragments, moist
22										
23	ST--	23.0	0	Pushed-No Recovery						
24										
25	ST-2	25.5	30	Pushed						
26										
27	S-14	27.0	18	2 3 4	15.0					
28	S-15	28.5	18	2 3 5	15.0					
29										Medium Gray SILTY CLAY, moist
30	S-16	30.0	18	1 2 4	15.0				30.0	END OF BORING
1										
2										
3										
4										
5										
6										
7										
8										
9										
0										
1										
2										
3										
4										
5										
6										
7										
8										
9										
0										

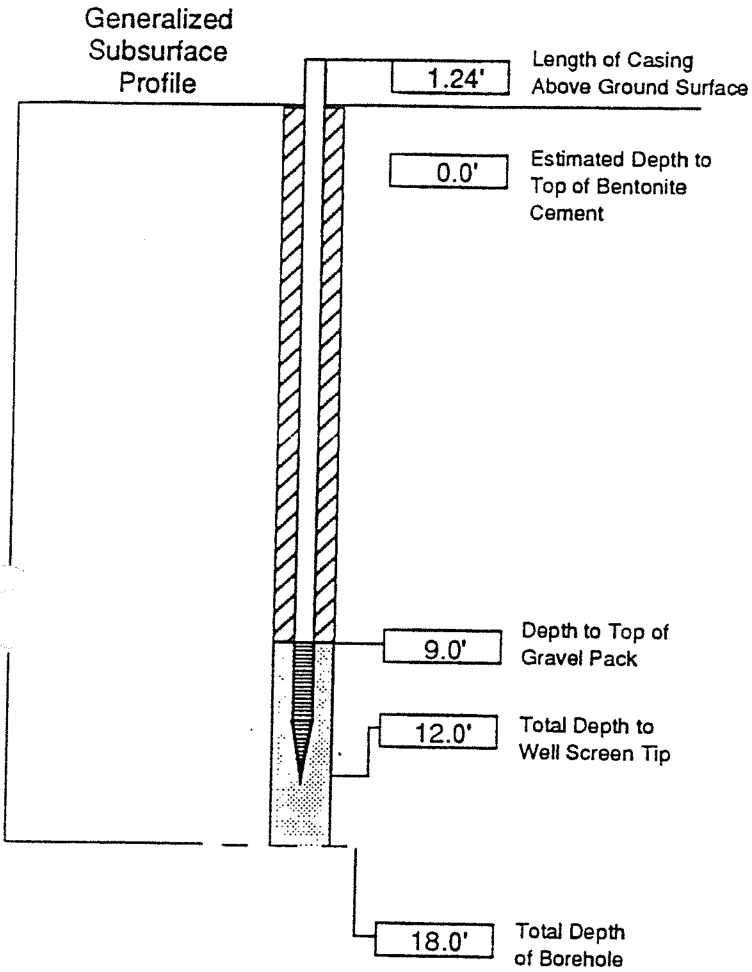
ATTACHMENT 2
REVISED SOIL BORING LOGS
PETRO-CHEM PROCESSING, INC.

Project Name: Petro-Chem Processing, Inc.

Log of Well Installation

Well Description: Monitoring Well OW-1
Date(s) of Installation 10/21/82

Top of Casing Elevation: 582.316
Ground Surface Elevation: 581.076
Well Screen Tip Elevation: 569.076



Well Casing

Diameter: 2"
Total Length: 9'
Material: Galvanized
Cap (Y/N) Yes

Well Screen

Diameter: 2"
Length: 3'
Mesh: Not Available
Material: Stainless Steel with Iron Core
Screen Plug (Y/N): Yes

Inspector: K. Campbell/P. Baxter
Contractor Environmental Research Group
Driller: Hartley & Assoc., P.C.
Drilling Equipment: 4" Auger on A.T.V.

Water Level Data

Datum: 580.226 BM #54-254B

Date	Water Level Elevation
9/1/83	569.606
3/5/84	569.956
11/12/84	569.816
10/4/88	570.336
11/1/89	570.246

Atterburg Limits: CL
Blow Counts : 8/12/15 at 16.5' to 18.0'

Notes: See site map for location of monitoring well.

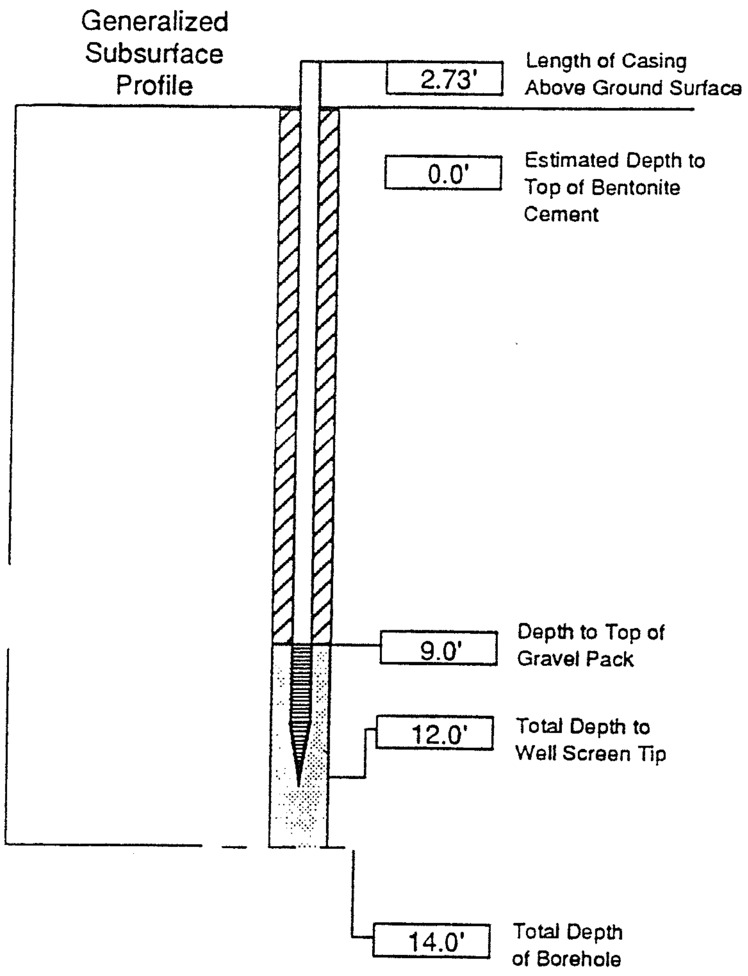
Figure

WW Engineering & Science

Project Name: Petro-Chem Processing, Inc.

Log of Well Installation

Well Description: Monitoring Well OW-2
Date(s) of Installation 10/21/82



Top of Casing Elevation: 582.046
Ground Surface Elevation: 579.316
Well Screen Tip Elevation: 567.316

Well Casing

Diameter: 2"
Total Length: 9'
Material: Galvanized
Cap (Y/N) Yes

Well Screen

Diameter: 2"
Length: 3'
Mesh: Not Available
Material: Stainless Steel with Iron Core
Screen Plug (Y/N): Yes

Inspector: K. Campbell/P. Baxter
Contractor Environmental Research Group
Driller: Hartley & Assoc., P.C.
Drilling Equipment: 4" Auger on A.T.V.

Water Level Data

Datum: 580.226 BM #54-254B

Date	Water Level Elevation
9/1/83	573.306
3/5/84 (a)	572.716
11/12/84	572.046
10/4/88 (b)	571.356
11/1/89	571.706

Atterburg Limits: CL
Blow Counts : 2/3/8 at 11' Below Grade
4/8/13 at 12.3' Below Grade

Notes: See site map for location of monitoring well.
(a) Well OW-2 was damaged, removed and replaced by a new well OW-2A in the same location.
(b) Well OW-2C replaced previous well OW-2B which was installed in 1986.

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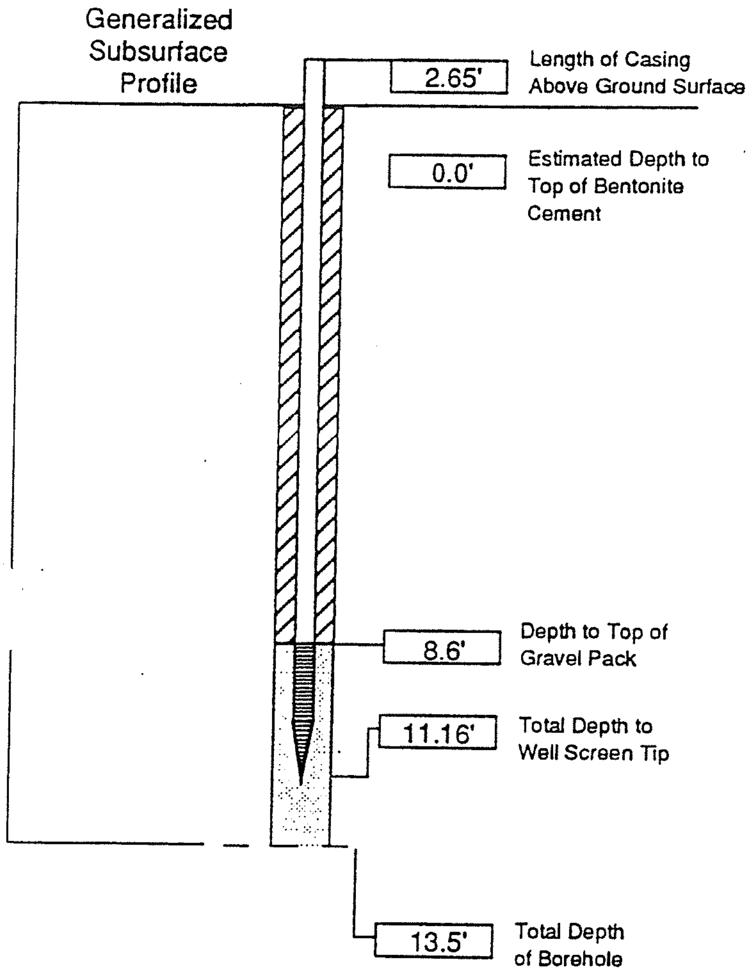
Project Name: Petro-Chem Processing, Inc.

Log of Well Installation

Well Description: Monitoring Well OW-3
Date(s) of Installation 10/21/82



Top of Casing Elevation: 582.766
Ground Surface Elevation: 580.116
Well Screen Tip Elevation: 568.316

Well Casing
Diameter: 2"
Total Length: 8.5'
Material: Galvanized
Cap (Y/N) Yes

Well Screen
Diameter: 2"
Length: 3'
Mesh: Not Available
Material: Stainless Steel with Iron Core
Screen Plug (Y/N): Yes

Inspector: K. Campbell/P. Baxter
Contractor Environmental Research Group
Driller: Hartley & Assoc., P.C.
Drilling Equipment: 4" Auger on A.T.V.

Water Level Data

Datum: 580.226 BM #54-254B

Date	Water Level Elevation
9/1/83	568.106
3/5/84	568.026
11/12/84	568.026
10/4/88 (a)	568.386
11/1/89 (b)	Dry

Atterburg Limits: CL
Blow Counts : 2/3/3 at 12' to 13.5'
Permeability: 3.6 x 10^{-8} cm/sec

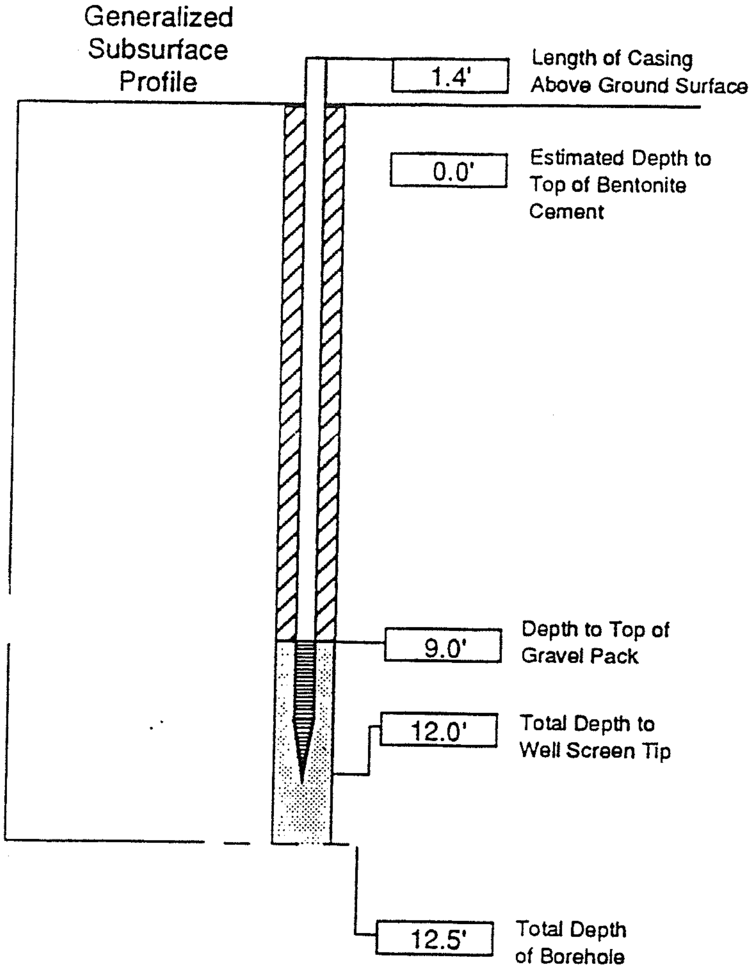
Notes: See site map for location of monitoring well.
(a) Well OW-3 was replaced by OW-3A in 1986.
(b) Well OW-3A was replaced by OW-3B on January 31, 1989. This well was located 6' east of Well OW-3A.

Figure

Project Name: Petro-Chem Processing, Inc.

Log of Well Installation

Well Description: Monitoring Well OW-4
Date(s) of Installation 10/21/82



Top of Casing Elevation:	581.196
Ground Surface Elevation:	579.796
Well Screen Tip Elevation:	567.796

Well Casing

Diameter: 2"
Total Length: 9'
Material: Galvanized
Cap (Y/N) Yes

Well Screen

Diameter: 2"
Length: 3'
Mesh: Not Available
Material: Stainless Steel with Iron Core
Screen Plug (Y/N): Yes

Inspector: K. Campbell/P. Baxter
Contractor Environmental Research Group
Driller: Hartley & Assoc., P.C.
Drilling Equipment: 4" Auger on A.T.V.

Water Level Data

Datum: 580.226 BM #54-254B

Date	Water Level Elevation
9/1/83	574.156
3/5/84	574.046
11/12/84	573.936
10/4/88	574.346
11/1/89	574.086

Atterburg Limits: CL
Blow Counts : 2/2/2 at 11' to 12.5'

Notes: See site map for location of monitoring well.

Figure

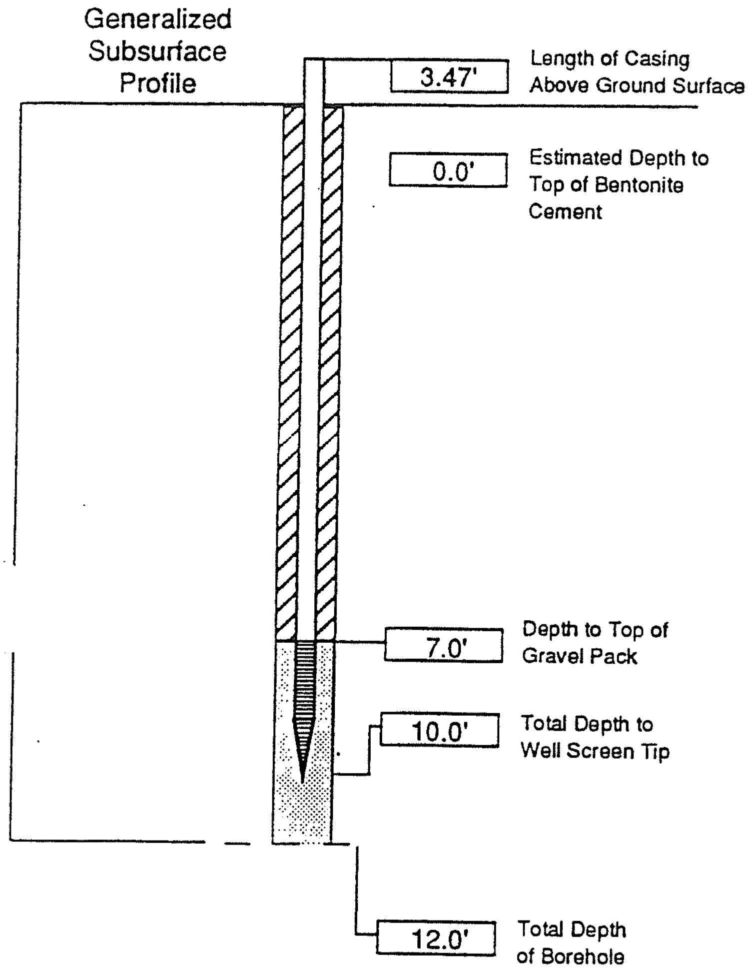
WW Engineering & Science

Project Name: Petro-Chem Processing, Inc.

Log of Well Installation

Well Description: Monitoring Well OW-5

Date(s) of Installation 10/21/82



Top of Casing Elevation: 581.986

Ground Surface Elevation: 578.516

Well Screen Tip Elevation: 571.516

Well Casing

Diameter: 2"
Total Length: 7.0'
Material: Galvanized
Cap (Y/N) Yes

Well Screen

Diameter: 2"
Length: 3'
Mesh: Not Available
Material: Stainless Steel with Iron Core
Screen Plug (Y/N): Yes

Inspector: K. Campbell/P. Baxter
Contractor Environmental Research Group
Driller: Hartley & Assoc., P.C.
Drilling Equipment: 4" Auger on A.T.V.

Water Level Data

Datum: 580.226 BM #54-254B

Date	Water Level Elevation
9/1/83	571.306
3/5/84	572.026
11/12/84	571.686

Atterburg Limits: CL
Blow Counts : 2/3/3 at 10.5' to 12.0'
Permeability: 8.5 x 10 $^{-8}$ cm/sec

Notes: See site map for location of monitoring well.

Figure

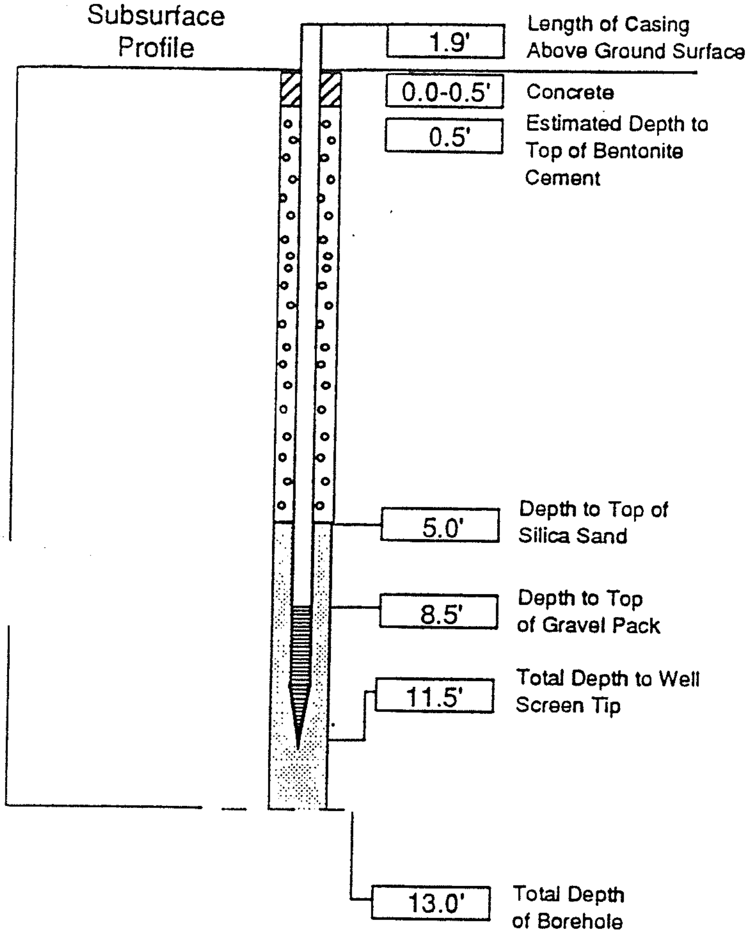
WW Engineering & Science

Project Name: Petro-Chem Processing, Inc.

Log of Well Installation

Well Description: Monitoring Well OW-5B
Date(s) of Installation 1/31/89

Generalized Subsurface Profile



Top of Casing Elevation: 581.986
Ground Surface Elevation: 578.516
Well Screen Tip Elevation: 571.516

Well Casing

Diameter: 2"
Total Length: 8.5'
Material: Galvanized
Cap (Y/N) Yes

Well Screen

Diameter: 2"
Length: 3'
Mesh: Not Available
Material: Stainless Steel with Iron Core
Screen Plug (Y/N): Yes

Inspector: K. Campbell/P. Baxter
Contractor Environmental Research Group
Driller: Hartley & Assoc., P.C.
Drilling Equipment: 4" Auger on A.T.V.

Water Level Data

Datum: 580.226 BM #54-254B

Date	Water Level Elevation
1/31/89	572.446

Atterburg Limits: CL

Notes: See site map for location of monitoring well.
Well OW-5B is located 2' south of OW-5A

Figure

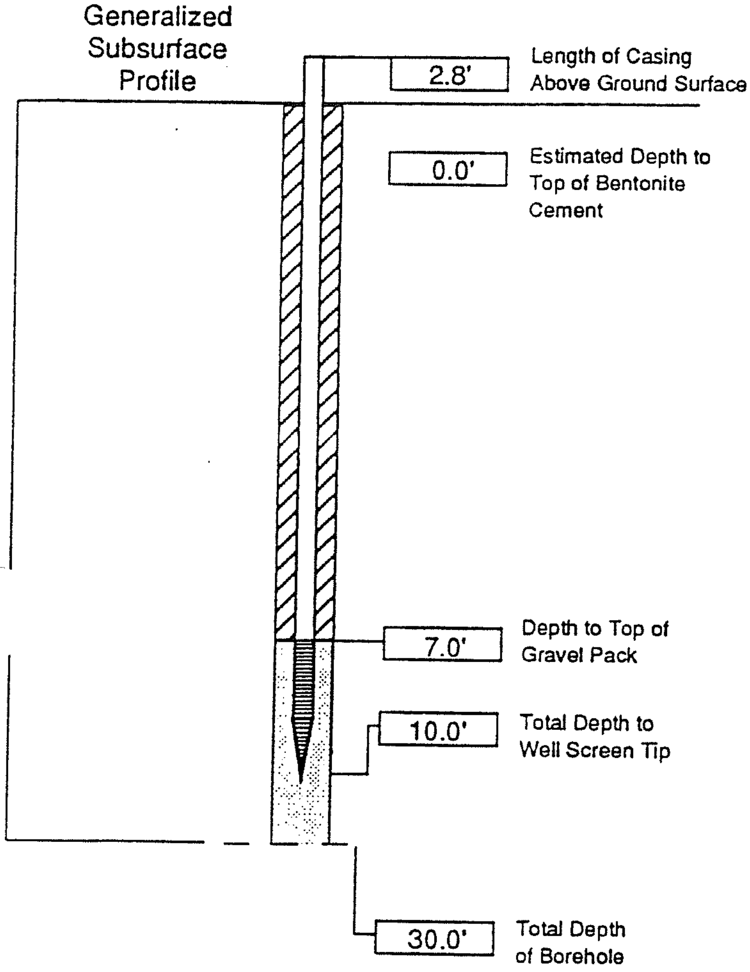
WW Engineering & Science

Project Name: Petro-Chem Processing, Inc.

Log of Well Installation

Well Description: Monitoring Well OW-6A

Date(s) of Installation 5/21/82



2.8' Length of Casing Above Ground Surface

0.0' Estimated Depth to Top of Bentonite Cement

7.0' Depth to Top of Gravel Pack

10.0' Total Depth to Well Screen Tip

30.0' Total Depth of Borehole

Top of Casing Elevation:	583.876
Ground Surface Elevation:	581.076
Well Screen Tip Elevation:	571.076

Well Casing

Diameter: 2"

Total Length: 7.0'

Material: Galvanized

Cap (Y/N) Yes

Well Screen

Diameter: 2"

Length: 3'

Mesh: Not Available

Material: Stainless Steel with Iron Core

Screen Plug (Y/N): Yes

Inspector: K. Campbell/P. Baxter

Contractor Environmental Research Group

Driller: Hartley & Assoc., P.C.

Drilling Equipment: 4" Auger on A.T.V.

Water Level Data

Datum: 580.226 BM #54-254B

Date	Water Level Elevation
11/1/89	571.356

Atterburg Limits: CL

Permeability: 3.8 x 10^{-8} cem/sec

Notes: See site map for location of monitoring well.

Figure

WW Engineering & Science

Log of Boring

Page 1 of 2

Project No. 83104

Client Petro-Chem Processing, Inc.
Location Detroit, MI
Logged By N. Marcelletti
Contractor CTI Associates
Driller J. Springstead

Boring Designation DB-1A
Start Date 2-4-91 Completed 2-5-91
Ground Surface Elevation : approximately 578.8 feet based on site USGS elevation map prepared 1991.

Drilling Method(s)	Depth Range
6 1/4" Hollow Stem Auger	0-15.0 feet
Rotary wash with 3-3/4" roller bit	15-30 feet

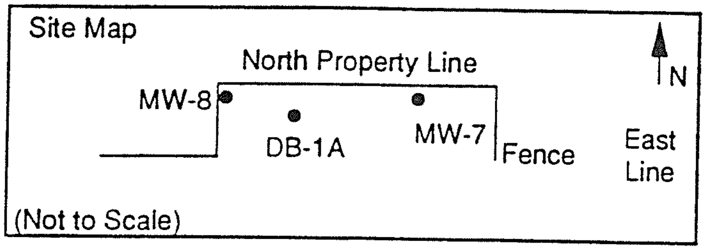
Sampling Method(s)	Depth Range
2-inch Split Spoon	1.5-3.5 foot intervals
3-inch Shelby Tube	13.0' to15.0' and 23.0' to 25.5'

Grouting Material/Method	Depth Range
Cement and Bentonite	0-30.0 feet

Water Level Data
Water encountered at 8.0 feet during drilling.

General Notes
4-inch steel drilling casing set from 0-15 feet and cemented in borehole

Site Map



Borehole Depth (feet)	Sample Type and Number	Depth of Sample Tip (feet)	Sample Recovered (inches)	Hammer Blows (6-Inch Intervals)	Depth of Borehole Casing (feet)	Field Data	Field Data	Graphic Log	Depth (feet)	Subsurface Description (incorporates soil sample test data)
1				13 22						
2	S-1	2.0	18	25 10					2.5	FILL: Compact Black FINE TO MEDIUM SAND, some coarse gravel, light brown silty clay, wood fragments, moist
3	S-2	3.0	18	4 8 11 8						
4										
5	S-3	5.0	18	2 3 3 2						
6										
7	S-4	7.0	16	2 4						
8							▽		8.4	Medium Black PEAT, with brown fine sand seams, moist
9	S-5	9.0	15	1 2 3						
10										
11	S-6	11.5	15	3 6 9 2						
12										
13	S-7	13.0	14	7 8						
14										
15	ST-1	15.0	24	pushed	15.0					
16	S-8	16.5	16	6 12 15 6	15.0					
17										
18	S-9	18.0	16	13 16	15.0					
19	S-10	19.5	16	6 8 12 2	15.0					Very Stiff Gray SILTY CLAY with little to some Sand, occasional wood fragments, moist
20										

(Continued on Page 2)

WW Engineering & Science

Log of Boring

Page 2 of 2

Project No. 83104

Client Petro-Chem Processing, Inc.
Location Detroit, MI

Boring Designation DB-1A
Start Date 2-4-91 Completed 2-5-91
Ground Surface Elevation : approximately 578.8 feet based on site USGS elevation map prepared 1991.

Borehole Depth (feet)	Sample Type and Number	Depth of Sample Tip (feet)	Sample Recovered (inches)	Hammer Blows (6-Inch Intervals)	Depth of Borehole Casing (feet)	Field Data	Field Data	Graphic Log	Depth (feet)	Subsurface Description
21	S-11	21.0		3 4	15.0				21.0	Very Stiff Gray SILTY CLAY with little to some Sand, occasional wood fragments, moist
22										
23	ST--	23.0	0	Pushed-No Recovery						
24										
25	ST-2	25.5	30	Pushed						
26										
27	S-14	27.0	18	2 3 4	15.0					
28	S-15	28.5	18	2 3 5	15.0					
29										Medium Gray SILTY CLAY with some Sand and trace Gravel, moist
30	S-16	30.0	18	1 2 4	15.0				30.0	
1										END OF BORING
2										
3										
4										
5										
6										
7										
8										
9										
0										
1										
2										
3										
4										
5										
6										
7										
8										
9										
0										

Appendix B4.3

Permits

STATE OF MICHIGAN
DEPARTMENT OF ENVIRONMENTAL QUALITY
LANSING

GRETCHEN WHITMER
GOVERNOR

LIESL EICHLER CLARK
DIRECTOR

February 12, 2019

RECEIVED
[illegible]
BY:

Mr. Edward C. Burk, Compliance Manager
Stericycle Environmental Solutions
515 Lycaste Street
Detroit, Michigan 48214

Dear Mr. Burk:

SUBJECT: Modification 2, Updated Site Figure, Hazardous Waste Management Facility Operating License; Petro-Chem Processing Group of Nortru, LLC, Detroit, Michigan; MID 980 615 298

The Michigan Department of Environmental Quality (MDEQ), Waste Management and Radiological Protection Division (WMRPD), Hazardous Waste Section (HWS), has reviewed the attached revised site figure, Figure 251, received July 24, 2018, via email for the Petro-Chem Processing Group of Nortru, LLC (PCPG) facility located at 421 Lycaste Street in Detroit, Michigan. This is an administrative and informational change to the hazardous waste management facility operating license (License), issued December 18, 2012, pursuant to Rule (R) 299.9519(5)(a)(i) of the administrative rules promulgated pursuant to Part 111, Hazardous Waste Management, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended; and constitutes a minor modification to the License. The revised Figure 251 has been added to Attachment 6, Engineering Plans and Specifications, of the License; and the corresponding conditions in Parts III and IV of the License boilerplate have been updated to include the appropriate references. Please see the attached track changes and clean copies of the modified boilerplate conditions for further clarification.

In accordance with R 299.9519(6)(b), PCPG is required to send notice of minor modifications to all persons on the facility mailing list and to the appropriate units of state and local government. Such notice must be provided within 90 calendar days of this approval. The updated facility mailing list is enclosed. Please notify the WMRPD of any addresses on the facility mailing list that are returned to sender and provide a scan of the returns or the original envelope for our records.

Should you have any questions regarding this License amendment, please contact Mr. Dan Dailey, Environmental Engineer Specialist, Permit and Corrective Action Unit, HWS, WMRPD, at 517-242-7261; daileyd@michigan.gov; or MDEQ, WMRPD, P.O. Box 30241, Lansing, Michigan 48909-7741; or you may contact me.

Sincerely,

Allan B. Taylor

Allan B. Taylor, Manager
Hazardous Waste Section
Waste Management and Radiological
Protection Division
517-614-7335

Enclosures

cc/enc: Mr. Allen Jones, Stericycle Environmental Solutions
Ms. Tracy Kecskemeti, DEQ
Ms. Virginia Himich, DEQ
Ms. Jeanette Noechel, DEQ
Mr. Dan Dailey, DEQ
Operating License File

State of Michigan
Department of Environmental Quality
HAZARDOUS WASTE MANAGEMENT FACILITY OPERATING LICENSE

NAME OF LICENSEE: Petro-Chem Processing Group of Nortru, LLC

NAME OF FACILITY OWNER: Nortru, LLC

NAME OF FACILITY OPERATOR: Petro-Chem Processing Group of Nortru, LLC

NAME OF TITLEHOLDER OF LAND: Nortru, LLC

FACILITY NAME: Petro-Chem Processing Group of Nortru, LLC

FACILITY LOCATION: 421 Lycaste, Detroit, Michigan 48214

EPA IDENTIFICATION (ID) NUMBER: MID 980 615 298

EFFECTIVE DATE: December 18, 2012

REAPPLICATION DATE: June 21, 2022

EXPIRATION DATE: December 18, 2022

AUTHORIZED ACTIVITIES

Pursuant to Part 111, Hazardous Waste Management, of Michigan's Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (Act 451), being §§324.11101 to 324.11153 of the Michigan Compiled Laws, and the hazardous waste management administrative rules (hereafter called the "rules") promulgated thereunder, being R 299.9101 *et. seq.* of the Michigan Administrative Code, by the Michigan Department of Environmental Quality (DEQ), an operating license (hereafter called the "license") is issued to Petro-Chem Processing Group of Nortru, LLC (hereafter called the "licensee") to operate a hazardous waste management facility (hereafter called the "facility") located at latitude 42° 22' 1" and longitude 82° 57' 55". The licensee is authorized to conduct the following hazardous waste management activities:

- ☒ STORAGE
  - ☒ Container
  - ☒ Tank
  - ☐ Waste Pile
  - ☐ Surface Impoundment
  - ☐ Drip Pad
- ☒ TREATMENT
  - ☐ Container
  - ☒ Tank
  - ☐ Surface Impoundment
  - ☐ Incinerator
  - ☐ Other:
- ☐ DISPOSAL
  - ☐ Landfill
  - ☐ Land Application
  - ☐ Surface Impoundment
- ☐ POSTCLOSURE
  - ☐ Tank
  - ☐ Surface Impoundment
  - ☐ Landfill
  - ☐ Waste Pile

APPLICABLE REGULATIONS AND LICENSE APPROVAL

The conditions of this license were developed in accordance with the applicable provisions of the rules, effective March 17, 2008. The licensee shall comply with all terms and conditions of this license, Part 111, and its rules. This license consists of the 20 pages of conditions attached hereto (including those in Attachments 1 through 11) and the applicable regulations contained in R 299.9101 through R 299.11008. For purposes of compliance with this license, applicable rules are those that are in effect on the date of issuance of this license in accordance with R 299.9521(3)(a).

This license is based on the information in the license application submitted on May 18, 2009, and any subsequent amendments (hereafter referred to as the "application"). Pursuant to R 299.9519(11)(c), the license may be revoked if the licensee fails, in the application or during the license issuance process, to disclose fully all relevant facts or, at any time, misrepresents any relevant facts. As specified in R 299.9519(1), the facility shall be constructed, operated, and maintained in accordance with Part 111 of Act 451, the rules, and this license.

This license is effective on the date of issuance and shall remain in effect for 10 years from the date of issuance, unless revoked pursuant to R 299.9519 or continued in effect as provided by the Michigan Administrative Procedures Act, 1969 PA 306, as amended (Act 306).

Amendment 2 issued this 12th day of February, 2019

by Allan B. Taylor
Allan B. Taylor, Manager
Hazardous Waste Section
Waste Management and Radiological Protection Division

HAZARDOUS WASTE MANAGEMENT FACILITY OPERATING LICENSE
FOR

Petro-Chem Processing Group of Nortru, LLC
MID 980 615 298

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PART IV: TANK SYSTEM STORAGE AND TREATMENT CONDITIONS

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PART VI: CORRECTIVE ACTION CONDITIONS

PART VII: SCHEDULE OF COMPLIANCE

LIST OF ATTACHMENTS

PART I
STANDARD CONDITIONS

A. TERMINOLOGY AND REFERENCES

Throughout this license, the term "Office" means the Office of Waste Management and Radiological Protection within the DEQ responsible for administering Part 111 of Act 451 and the rules. Throughout this license, "Director" means the Director of the DEQ or the Director's duly authorized designee such as the Office Chief. All of the provisions of Title 40 of the Code of Federal Regulations (CFR) referenced in this license are adopted by reference in R 299.11003.

B. EFFECT OF LICENSE

Except as otherwise provided by law, any treatment, storage, or disposal of hazardous waste not specifically authorized in this license is prohibited. Issuance of this license does not authorize any injury to persons or property, any invasion of other private rights, or any infringement of federal, state, or local law or regulations {R 299.9516(8)}; nor does it obviate the necessity of obtaining such permits or approvals from other units of government as may be required by law. Compliance with the terms of this license does not constitute a warranty or representation of any kind by the DEQ, nor does the DEQ intend that compliance with this license constitutes a defense to any order issued or any action brought under Act 451 or any other applicable state statute or §106(a) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) {42 U.S.C. 9606(a)}, the Resource Conservation and Recovery Act of 1976, as amended (RCRA), and its rules, or any other applicable federal statute. The licensee, however, does not represent that it will not argue that compliance with the terms of this license may be a defense to such future regulatory actions. Each attachment to this license is a part of, and is incorporated into, this license and is deemed an enforceable part of the license.

C. SEVERABILITY

The provisions of this license are severable, and if any provision of this license, or the application of any provision of this license to any circumstance, is held invalid, the application of such provision to other circumstances and the remainder of this license shall not be affected thereby.

D. RESPONSIBILITIES

1. The licensee shall comply with Part 111 of Act 451, the rules, and all conditions of this license, except to the extent authorized by the DEQ pursuant to the terms of an emergency operating license. Any license noncompliance, except to the extent authorized by the DEQ pursuant to the terms of an emergency operating license, constitutes a violation of Part 111 of Act 451 and is grounds for enforcement action, license revocation, license modification, or denial of a license renewal application. {§§324.11148, 324.11150, and 324.11151 of Act 451 and R 299.9521(1)(a) and (c) and (3)(a) and (b) and 40 CFR §270.30(a)}

2. If the licensee wishes to continue an activity regulated by this license after the expiration date of this license, the licensee shall submit a complete application for a new license to the Office Chief at least 180 days before this license expires, **June 21, 2022**, unless an extension is granted pursuant to R 299.9510(5). To the extent the licensee makes a timely and sufficient application for renewal of this license, this license and all conditions herein will remain in effect beyond the license expiration date and shall not expire until a decision on the application is finally made by the DEQ, and if the application is denied or the terms of the new license are limited, until the last day for applying for judicial review of the new license or a later date fixed

by order of the reviewing court consistent with §91(2) of Act 306. {R 299.9521(1)(a) and (c) and (3)(a) and 40 CFR §270.30(b)}

3. The licensee shall comply with the conditions specified in R 299.9521(1)(b)(i) to (iii) and 40 CFR §270.30(c) through (k), (l)(2), (3), (5), (7), and (11), and (m). {§§11123(3), 11146(1) and (2), and 11148(1) of Act 451 and R 299.9501(1), R 299.9516, R 299.9519, R 299.9521(1)(a) and (b) and (3)(a) and (b), R 299.9522, and R 299.9525}

4. The licensee shall give notice to the Office Chief as soon as possible prior to any planned physical alterations or additions to the licensed facility. {R 299.9501 and R 299.9519 and Part 6 of the Part 111 Rules}

E. SUBMITTAL DEADLINES

When the deadline for submittals required under this license falls on a weekend or legal state holiday, the deadline shall be extended to the next regular business day. This extension does not apply to the deadline for financial mechanisms and associated renewals, replacements, and extensions of financial mechanisms required under this license. The licensee may request extension of the deadlines for submittals required under this license. The licensee shall submit such requests at least five business days prior to the existing deadline for review and approval by the Office Chief. Written extension requests shall include justification for each extension. {R 299.9519 and R 299.9521(3)(a)}

PART II
GENERAL OPERATING CONDITIONS

A. GENERAL WASTE ANALYSIS

The licensee shall ensure that any waste managed at the facility has been properly characterized pursuant to R 299.9302 and comply with the procedures described in the attached Waste Analysis Plan, Attachment 1, of this license. {R 299.9605(1), and 40 CFR §264.13}

B. SECURITY

The licensee shall comply with the barrier, surveillance, and signage requirements of R 299.9605(1) and 40 CFR §264.14.

C. GENERAL INSPECTION REQUIREMENTS

1. The licensee shall inspect the facility in accordance with the Inspection Schedule, Attachment 2, of this license and comply with the inspection requirements of R 299.9605(1) and 40 CFR §264.15.

2. The licensee shall develop and implement a procedure to ensure compliance with the requirements of R 299.9605(2) regarding transport vehicles and other containers leaving the facility.

D. PERSONNEL TRAINING

The licensee shall comply with the personnel training requirements of R 299.9605 and 40 CFR §264.16. The Personnel Training Program, Attachment 3, of this license shall, at a minimum, cover all items in R 299.9605 and 40 CFR §264.16.

E. PREPAREDNESS AND PREVENTION

The licensee shall comply with the preparedness and prevention requirements of R 299.9606 and 40 CFR Part 264, Subpart C.

F. CONTINGENCY PLAN

The licensee shall comply with the contingency plan requirements of R 299.9607 and 40 CFR Part 264, Subpart D. The Contingency Plan, Attachment 4, of this license and the prescribed emergency procedures shall be immediately implemented by the licensee whenever there is a fire, explosion, or other release of hazardous waste or hazardous waste constituents that threatens or could threaten human health or the environment, or if the licensee has knowledge that a spill has reached surface water or groundwater.

G. DUTY TO MITIGATE

Upon notification from the Office Chief or his or her designee that an activity at the facility may present an imminent and substantial endangerment to human health or the environment, the licensee shall immediately comply with an order issued by the Office Chief pursuant to §11148(1) of Act 451 to halt such activity and conduct other activities as required by the Office Chief to eliminate the said endangerment. The licensee shall not resume the halted activity without the prior written approval from the Office Chief. {§11148 of Act 451 and R 299.9521(3)(b)}

H. MANIFEST SYSTEM

The licensee shall comply with the manifest requirements of R 299.9304, R 299.9305, and R 299.9608.

I. RECORD KEEPING AND REPORTING

1. The licensee shall comply with the written operating record and monthly operating report (EQP 5142 form) requirements of R 299.9609 and 40 CFR §264.73 and Part 264, Appendix I, and R 299.9610(3), respectively. The monthly operating report shall be submitted on EQP 5142 form provided by the Office Chief, or an equivalent form that has been approved by the Office Chief.

2. The licensee shall comply with the biennial report requirements of R 299.9610. {R 299.9521(1)(a) and 40 CFR §270.30(l)(9)}

3. The licensee shall submit the results of all environmental monitoring required by this license and any additional environmental sampling or analysis conducted beyond that required by this license, in the form of an Environmental Monitoring Report to the Office Chief within 60 days after any sample collection. {R 299.9521(1)(a) and R 299.9521(3)(b) and 40 CFR §270.30(l)(4)}

4. The licensee shall provide environmental monitoring information or data that is required pursuant to this license to an authorized representative of an environmental or emergency response department of the city of Detroit or county of Wayne who requests such information or data and that has jurisdiction over the facility. Such information or data shall be made available on the same day the licensee forwards this information to the Office Chief. {R 299.9521(3)(b)}

5. The licensee shall immediately report to the Office Chief any noncompliance with the license that may endanger human health or the environment by doing both of the following:

    a. The licensee shall immediately notify the Office Chief at 517-335-2690, if the noncompliance occurs Monday through Friday during the period of 8:00 a.m. to 5:00 p.m., except state holidays, or by calling the DEQ Pollution Emergency Alerting System (PEAS) at 1-800-292-4706 during all other times. This notice shall include the following:

        (i) Information concerning the fire, explosion, release, or discharge of any hazardous waste or hazardous waste constituent that could threaten human health or the environment, that has reached surface water or groundwater, or that may endanger public drinking water supplies or the environment; and

        (ii) A description of the occurrence and its cause, including all of the information outlined in R 299.9607(2)(a)-(i).

    b. The licensee shall also follow up the verbal notice by providing a written report to the Office Chief within five days of the time the licensee becomes aware of the circumstances. The written report shall contain all of the information in Condition II.I.5.a.(i)-(ii) of this license along with a description of the noncompliance and its cause; the periods of noncompliance (including exact dates and times); whether the noncompliance has been corrected and, if not, the anticipated time it is expected to continue; and steps taken or planned to reduce, eliminate, and prevent recurrence of the noncompliance and when those activities occurred or will occur. The Office Chief may waive the 5-day written notice requirement in favor of submittal of a written report within 15 days of the time the licensee becomes aware of the circumstances.

{R 299.9521(1)(a) and R 299.9607 and 40 CFR §270.30(l)(6)}

6. The licensee shall report all other instances of noncompliance with this license, Part 111 of Act 451, the rules, and any other applicable environmental laws or rules that apply to the licensed facility at the time monitoring reports required by this license are submitted or within 30 days, whichever is sooner. The reports shall contain the information listed in Condition II.I.5. of this license. {R 299.9521(1)(a) and 40 CFR §270.30(l)(10)}

7. The licensee may make minor modifications to the forms contained in the attachments to this license. The modifications may include changing the format, updating existing references and information, adding necessary information, and changing certification and notification information in accordance with Part 111 of Act 451 and its rules and RCRA and its regulations. The licensee shall submit the modifications to the Office Chief prior to implementing the use of the modified form(s). If the Office Chief does not reject or require revision of the modified form(s) within 14 days of receipt, the licensee shall implement use of the modified form(s) and the form(s) shall be incorporated into this license as a replacement for the existing form(s).

J. CLOSURE

The licensee shall comply with the closure requirements of R 299.9613. The licensee shall close the facility in accordance with the Closure Plan, Attachment 5, of this license, all other applicable requirements of this license, and all other applicable laws. {R 299.9613 and 40 CFR Part 264, Subpart G, except 40 CFR §§264.112(d)(1), 264.115, and 264.120}

K. FINANCIAL ASSURANCE FOR CLOSURE

1. On the effective date of this license, the facility closure cost estimate is $1,946,093. The licensee shall keep this estimate current as required under R 299.9702 and 40 CFR §264.142.

2. The licensee shall continuously maintain financial assurance for the current closure cost estimate as required under R 299.9703.

L. FINANCIAL ASSURANCE FOR CORRECTIVE ACTION

1. The licensee shall establish a cost estimate(s) for completing corrective actions at the facility for the cost of performing corrective actions at such time as work plans are submitted, as required by Part VI of this license. The licensee shall keep the corrective action cost estimate current as required under R 299.9712.

2. The licensee shall continuously maintain financial assurance for corrective action as required under R 299.9713.

M. FINANCIAL REPSONSIBILITY FOR LIABILITY COVERAGE

The licensee shall continuously maintain liability coverage for sudden and accidental occurrences, as required by R 299.9710.

N. WASTE MINIMIZATION

The licensee shall certify, at least annually, that the licensee has a hazardous waste minimization program in place. {R 299.9609(1)(a), 40 CFR §264.73(b)(9), §3005(h) of RCRA, and 42 U.S.C. §6925(h)}

O. LAND DISPOSAL RESTRICTIONS

The licensee shall comply with all of the requirements of 40 CFR Part 268. {R 299.9627 and 40 CFR Part 268}

P. AIR EMISSION STANDARDS

1. The licensee shall comply with the requirements of 40 CFR Part 264, Subpart AA, regarding air emission standards for process vents; Subpart BB, regarding air emission standards for equipment leaks; and Subpart CC, regarding air emission standards for tanks, surface impoundments, and containers.
2. The licensee shall notify the Office Chief of any waste management units that become subject to the requirements of 40 CFR Part 264, Subparts AA, BB, and/or CC within 30 days of the start of the regulated activity.

{R 299.9630, R 299.9631, and R 299.9634 and 40 CFR Part 264, Subparts AA, BB, and CC}

Q. DOCUMENTS TO BE MAINTAINED AT THE FACILITY

The licensee shall maintain at the facility the following documents and amendments required by this license, until closure/postclosure is completed, certified by an independent registered professional engineer, and the facility is released from financial assurance requirements for closure/postclosure by the Director:

1. Waste Analysis Plan, including Quality Assurance/Quality Control (QA/QC) Plans.
2. Inspection Schedules and records.
3. Personnel Training Program documents and records.
4. Contingency Plan.
5. Closure Plan.
6. Cost estimates for facility closure, and corrective action and copies of related financial assurance documents.
7. Operating record.
8. Site Security Plan.
9. Facility engineering plans and specifications.
10. Record keeping procedures.
11. Environmental monitoring plans, including Sampling and Analysis Plans and QA/QC Plans.
12. Environmental monitoring data and statistical records.
13. Preventative procedures (Personnel Protection Plan).
14. Hazardous waste minimization program certification.

{R 299.9521(3)(a)}

R. ENGINEERING PLANS

The licensee shall construct, operate, and maintain the facility in accordance with the Engineering Plans and Specifications, Attachment 6, of this license, and any modifications to those plans shall be made in accordance with this license

PART III
CONTAINER STORAGE CONDITIONS

A. COVERAGE OF LICENSE

The hazardous waste container storage areas at the facility shown in Drawings 251, A-1, SUP A-1, A-2, SUP A-2, A-3, SUP A-3, A-4, SUP A-4, A-9, F-1, F-2, G-1, G-2, G-3, G-4, G-5, M-1, M-2, M-3, M-3A, M-4, S-1, S-2, S-4, S-5, S-6, 071, 072, 073, PCPI-63, PCPI-63B, PCPI-91, PCPI-153, and PCPI-154 are covered by this license. Any expansion or enlargement beyond the facility boundary shown in Drawing G-2 or beyond the 385,399 gallon storage design capacity requires a new expansion license from the Director. Drawings 251, A-1, SUP A-1, A-2, SUP A-2, A-3, SUP A-3, A-4, SUP A-4, A-9, F-1, F-2, G-1, G-2, G-3, G-4, G-5, M-1, M-2, M-3, M-3A, M-4, S-1, S-2, S-4, S-5, S-6, 071, 072, 073, PCPI-63, PCPI-63B, PCPI-91, PCPI-153, and PCPI-154 are incorporated into this license as part of the Engineering Plans and Specifications, Attachment 6, of this license. {R 299.9521(1)(b)}

B. WASTE IDENTIFICATION AND QUANTITY

1. The licensee may store no more than a total volume of 385,399 gallons of the hazardous wastes listed in the Appendices of Attachment 5 of this license in containers at the facility, subject to the terms of this license. The maximum number of containers of hazardous waste that may be stored at the facility is 7,195, 55-gallon container equivalents. {R 299.9521(2)(d)}

2. Storage of hazardous waste in containers by the licensee is limited to the following specified areas as shown on Drawings 251, A-1, F-2, G-3, M-3A, S-1, PCPI-63, PCPI-91, and PCPI-153 in the Engineering Plans and Specifications, Attachment 6, of this license:

Storage Area Description	Maximum Inventory Allowed
Truck Staging Area (Up to 72 hours Only)	363 containers or 20,000 gallons
Tank Storage Area 1 (TS1) Transfer Pad during waste fingerprinting and offloading (Up to 72 hours Only)	Up to 6 Tanker Truck Trailers or Up to 3 Tanker Truck Trailers and Up to 3 Super Tanker Truck Trailers or 54,000 gallons
TS2 Transfer Pad during waste fingerprinting and offloading (Up to 72 hours Only)	Up to 2 Super Tanker Truck Trailers or 24,000 gallons
First Floor Operations Building – North Storage	700 containers or 38,500 gallons
CMB Container Storage Areas	3,888 containers or 213,840 gallons
CMB Roll-Off Storage	1 roll-off box or 8,080 gallons
CMB Temporary Storage (Up to 72 hours only – TS3 Transfer Pad, TS4 Transfer Pad, QA/QC Area, Pump Room)	675 containers or 37,119 gallons
Drum Dock #3	300 containers or 16,500 gallons
Drum Dock #4	147 containers or 8,080 gallons
SBS Container Storage Room	272 containers or 14,960 gallons
SBS Solids Storage Area (Solids Only)	1 roll-off box or 8,080 gallons
SBS Dock Storage Area	368 containers or 20,240 gallons
Total Facility Authorized Container Storage Capacity	**385,399 gallons**

C. USE AND MANAGEMENT OF CONTAINERS

1. The licensee shall manage all containers in compliance with R 299.9521(3)(b), R 299.9614, and R 299.9627 and 40 CFR §§264.171, 264.172, 264.173, and 268.50(a)(2)(i).

2. The licensee shall only place containers, stacked no greater than two high, into the hazardous waste container storage areas referenced in Condition III.A. and B. of this license in accordance with the configuration shown in Drawings 251, A-1, F-2, G-3, M-3A, S-1, PCPI-63, PCPI-91, and PCPI-153 in the Engineering Plans and Specifications, Attachment 6, of this license or an alternate configuration approved by the Office Chief. {R 299.9521(3)(b)}

3. The licensee shall operate and maintain the containment system in accordance with the requirements of R 299.9614 and 40 CFR §264.175, and the Engineering Plans and Specifications, Attachment 6, of this license.

D. SPECIAL REQUIREMENTS FOR IGNITABLE OR REACTIVE WASTES

1. The licensee shall locate containers holding ignitable or reactive wastes in accordance with R 299.9614 and 40 CFR §264.176.

2. The licensee shall take precautions to prevent the accidental ignition or reaction of ignitable or reactive wastes by following the procedures specified in Attachments 7, 9, and 10 of this license, where applicable. The licensee shall document compliance with this condition and place this documentation in the operating record. {R 299.9605 and 40 CFR §264.17(a) and (c)}

E. SPECIAL REQUIREMENTS FOR INCOMPATIBLE WASTES OR MATERIALS

1. Prior to placing incompatible wastes or incompatible wastes and materials in the same container, the licensee shall comply with R 299.9605 and 40 CFR §264.17(b) by following the procedures specified in Attachments 7, 9, and 10 of this license. {R 299.9521(2)(d) and (3)(b)}

2. The licensee shall prevent the placement of hazardous waste in an unwashed container that previously held an incompatible waste or material. {R 299.9614 and 40 CFR §264.177(b)}

3. The licensee shall document compliance with Conditions III.E.1. and III.E.2. of this license and place this documentation in the operating record. {R 299.9605 and 40 CFR §264.17(c)}

4. The licensee shall separate containers of incompatible wastes as indicated in the procedures contained in Attachments 7 and 9 of this license. {R 299.9614 and 40 CFR §264.177(c)}

F. DISPOSITION OF ACCUMULATED LIQUIDS

The licensee shall remove all liquids accumulated in the containment system within 24 hours of detection and manage the liquids in accordance with the requirements of Part 111 of Act 451 and the rules, as specified in the Use and Management of Containers, Attachment 7, of this license. {R 299.9521(3)(b) and R 299.9614(1)(a) and 40 CFR §264.175(b)(5)}

PART IV
TANK SYSTEM STORAGE AND TREATMENT CONDITIONS

A. COVERAGE OF LICENSE

The hazardous waste tank system storage and treatment areas at the facility shown in Drawings 251, A-1, A-4, G-2, G-3, G-5, M-3A, 071, 072, 073, TK001, TK002, PCPI-58, PCPI-58B, PCPI-58C, PCPI-59, PCPI-60, PCPI-79, PCPI-116B, PCPI-174, PCPI-192, PCPI-193, PCPI-194, PCPI-196B, and PCPI-572A are covered by this license. Any expansion or enlargement beyond the facility boundary shown in Drawings G-2 or beyond the 646,956-gallon tank system storage design capacity requires a new expansion license from the Director. Drawings 251, A-1, A-4, G-2, G-3, G-5, M-3A, 071, 072, 073, TK001, TK002, PCPI-58, PCPI-58B, PCPI-58C, PCPI-59, PCPI-60, PCPI-79, PCPI-116B, PCPI-174, PCPI-192, PCPI-193, PCPI-194, PCPI-196B, and PCPI-572A are incorporated into this license as the Engineering Plans and Specifications, Attachment 6,of this license. {R 299.9521(1)(b)}

B. WASTE IDENTIFICATION AND QUANTITY

1. The licensee may store no more than a total volume of 646,956 gallons of the hazardous wastes listed in the Appendices of Attachment 5 of this license in the tank systems identified as Tank Systems 1, 2, and 3 and the CMB Tanks in Attachments 8 and 9, subject to the terms of this license. {R 299.9521(2)(d)}

2.

Tank System Description	Maximum Inventory Allowed
Tank System 1: Tanks 16-30	28,000 gallons each; 420,000 gallons total
Tank System 2: Tanks 35-40	28,000 gallons each; 168,000 gallons total
Tank System 3: Tanks S69, S70	13,277 gallons each; 26,554 gallons total
Tank System 3: Tanks S71, S72	10,201 gallons each; 20,402 gallons total
CMB Tanks: TK 001, TK 002	6,000 gallons each; 12,000 gallons total
Total Authorized Tank Storage Capacity	**646,956 gallons**

C. WASTE TREATMENT CAPACITY AND METHODS

1. The licensee may treat no more than a total volume of 155,000 gallons per day of the hazardous wastes listed in the Appendices of Attachment 5 of this license in the tank systems identified as Tanks S69, S70, S71, S72 (Fuel Blending and Spent Solvent Reclamation), 16-30 (Fuel Blending), and 35-40 (Fuel Blending) in Tables 1 and 2 of the Process Descriptions, Attachment 9,of this license and Drawings 251, A-1, A-4, G-2, G-3, G-5, M-3A, 071, 072, 073, TK001, TK002, PCPI-58, PCPI-58B, PCPI-58C, PCPI-59, PCPI-60, PCPI-79, PCPI-116B, PCPI-174, PCPI-192, PCPI-193, PCPI-194, PCPI-196B, and PCPI-572A in the Engineering Plans and Specifications, Attachment 6, of this license subject to the license terms. {R 299.9521(2)(d) and (3)(a) and (b)}

2. The licensee may only conduct the treatment methods specified in the Treatment Process Description, Attachment 10, of this license subject to the license terms. {R 299.9521(2)(d) and (3)(a) and (b)}

D. DESIGN, CONTAINMENT, AND ASSESSMENT OF TANK SYSTEMS

The licensee shall operate and maintain all tank systems in accordance with the applicable requirements of R 299.9615 and 40 CFR §§264.193 and 264.194, and in accordance with the Engineering Plans and Specifications, Attachment 6, of this license.

E. MANAGEMENT OF TANK SYSTEMS

1. The licensee shall label and manage the tank systems in accordance with the requirements of R 299.9615 and R 299.9627, 40 CFR §§264.194, 264.196, and 268.50(a)(2)(ii), R 29.4101 to R 29.4504 pursuant to the provisions of the Fire Prevention Act, 1941 PA 207, as amended, National Fire Protection Association (NFPA) Standard No. 704, and the spill and overfill prevention procedures specified in the Tank systems, Attachment 8, of this license. {R 299.9615}

2. The licensee shall conduct the treatment of hazardous wastes in accordance with the methods and procedures specified in the Treatment Process Description, Attachment 10, of this license. {R 299.9633}

F. SPECIAL REQUIREMENTS FOR IGNITABLE OR REACTIVE WASTES

1. The licensee shall not place ignitable or reactive waste in a tank system unless the procedures described in Attachments 8 and 9 of this license are followed. The licensee shall document compliance with this condition and place this documentation in the operating record. {R 299.9605, R 299.9609, R 299.9615 and 40 CFR §§264.17(c), 264.73(b)(3), and 264.198(a)}

2. The licensee shall maintain the protective distances between the tank systems and any public ways, streets, alleys, or adjoining property lines that can be built upon, as required in Tables 2-1 through 2-6 of the NFPA's "Flammable and Combustible Liquids Code" (1977 or 1981) as specified in Attachments 8 and 9 of this license, and as required by R 299.9615 and 40 CFR §264.198(b).

G. SPECIAL REQUIREMENTS FOR INCOMPATIBLE WASTES OR MATERIALS

The licensee shall not place incompatible wastes or incompatible wastes and materials, in the same tank system or place hazardous waste in a tank system that has not been decontaminated and that previously held an incompatible waste or material unless the procedures specified in Attachments 8, 9, and 10 of this license are followed, as required by R 299.9615 and 40 CFR §264.17(b). The licensee shall document compliance with this condition and place this documentation in the operating record. {R 299.9609 and R 299.9615 and 40 CFR §§264.17(c), 264.73(b)(3), and 264.199}

H. DISPOSITION OF ACCUMULATED LIQUIDS

The licensee shall remove spilled or leaked waste and accumulated precipitation from the tank system within 24 hours of detection and manage it in accordance with the requirements of Part 111 of Act 451 and the rules, and the procedures in the Tank Systems, Attachment 8, of this license. {R 299.9521(3)(b), R 299.9615, and 40 CFR §264.193(c)(4)}

PART V
ENVIRONMENTAL MONITORING CONDITIONS

A. GROUNDWATER MONITORING PROGRAM

1. The licensee shall conduct a semiannual corrective action monitoring program. Under this program, the licensee shall operate and maintain a groundwater monitoring system in accordance with the Groundwater Monitoring Programs, Sampling and Analysis Plan (SAP) of Attachment 11, of this license. {R 299.9611(2)(a) and (b), R 299.9612, and R 299.9629 and 40 CFR Part 264, Subpart F, excluding 40 CFR §§264.94(a)(2) and (3), 264.94(b) and (c), 264.100, and 264.101}

2. The licensee shall submit proposed revisions to the SAP to the Office Chief for approval prior to implementation and shall revise any other affected document accordingly. If approved, the revisions to the SAP shall become part of this license without the need for a minor license modification. {R 299.9519(5)(c)(ii), R 299.9611(2)(a), and R 299.9612 and 40 CFR §264.97(d) and (e)}

3. Water removed from each monitoring well shall be managed as specified on page 4 of the Environmental Monitoring Programs, Attachment 11, of this license. {R 299.9521(3)(b)}

4. The licensee shall submit an annual groundwater report to the Office Chief no later than March 1st of each year for the previous calendar year's activities. At a minimum, the report shall include the following information:

   a. A narrative summary of the previous calendar year's sampling events, including sampling event dates, the identification of any significant problems with respect to SAP procedures, and copies of field log sheets.

   b. A determination of the groundwater flow rate and direction in the monitored zone, including the preparation of a groundwater level contour map from this data.

   c. A summary of groundwater quality data results, including a narrative summary of results and trends, isochems, data graphs, and data tables.

   d. A presentation of the statistical analysis of the data and the identification of any statistically significant trends pursuant to Condition V.A.5. of this license.

   e. An analysis and discussion of laboratory and field related QA/QC information. This shall include results of equipment, field, and trip blanks and discussion and evaluation of the adequacy of the data with respect to SAP specifications and requirements.

   {R 299.9521(3)(b) and R 299.9612(1) and 40 CFR §264.97(j)}

5. Within 60 days of each sampling of each monitoring well, the licensee shall determine if a statistically significant increase has occurred compared to background levels for each primary parameter described in Section B5.A.3(a), and listed in the volatile organic compounds and semi-volatile compounds analyte lists, of the Environmental Monitoring Programs, Attachment 11, of this license. This statistical test will be conducted as follows:

   a. The nonparametric Mann-Kendell test will be applied to each well individually (intra well).

6. The licensee shall submit the results of groundwater monitoring required by this license in the form of an Environmental Monitoring Report to the Office Chief within 60 days after any sample collection. This report must include:

   a. A brief summary describing whether contaminant trends are increasing, decreasing, or remaining steady.

   b. Data summary table and laboratory analytical data.

   c. Identification of any tentatively identified compounds (TICs).

7. In the event that the Office Chief determines from the findings of Conditions V.A.5. of this license that a statistically significant increase (or change in pH) in hazardous constituents has occurred in the groundwater and the Director finds, in accordance with §11148 of Act 451, that the increase (or change in pH) may present an imminent and substantial hazard to the health of persons or to the natural resources, or is endangering or causing damage to public health or the environment, the licensee shall immediately comply with an order issued by the Director pursuant to §11148(1) of Act 451 to cease waste receipt, storage, and treatment at the affected units and conduct other activities as required by the Director to eliminate the said endangerment. {R 299.9612(1)(g)}

B. AMBIENT AIR MONITORING PROGRAM

The licensee shall conduct ambient air monitoring in accordance with the program specified in the Environmental Monitoring Programs, Attachment 11, of this license within 30 days after the issuance of this license. {R 299.9611(2)(c)}

PART VI
CORRECTIVE ACTION CONDITIONS

A. CORRECTIVE ACTION AT THE FACILITY

1. The licensee shall implement corrective action for all releases of a contaminant from any waste management units (WMUs) at the facility, regardless of when the contaminant may have been placed in or released from the WMU. For the purposes of this license, the term "corrective action" means an action determined by the Office Chief to be necessary to protect the public health, safety, welfare, or the environment, and includes, but is not limited to, investigation, evaluation, cleanup, removal, remediation, monitoring, containment, isolation, treatment, storage, management, temporary relocation of people, and provision of alternative water supplies, or any corrective action allowed under Title II of the federal Solid Waste Disposal Act, PL 89-272, as amended, or regulations promulgated pursuant to that act. For the purposes of this license, the process outlined in Part 111 of Act 451 and the environmental protection standards adopted in R 299.9629 shall be used to satisfy the corrective action obligations under this license. {§§11102 and 11115a of Act 451 and R 299.9629}

2. To the extent that a release of a hazardous substance, as defined in §20101(t) of Act 451, that is not also a contaminant, as defined in §11102(2) of Act 451, is discovered while performing corrective action under this license, the licensee shall take concurrent actions as necessary to address the Part 201, Environmental Remediation, of Act 451 remedial obligations for that release. {R 299.9521(3)(b)}

B. CORRECTIVE ACTION BEYOND THE FACILITY BOUNDARY

The licensee shall implement corrective action beyond the facility in accordance with §11115a of Act 451 and R 299.9629(2).

C. IDENTIFICATION OF WASTE MANAGEMENT UNITS AND AREAS OF CONCERN

The WMUs and areas of concern (AOCs) at the facility are identified below and shown on Drawing G-1 and the Area of Concern Map in the Engineering Plans and Specifications, Attachment 6, of this license.

1. The following WMU and AOCs, identified in the Evaluation of Part 201 Exposure Pathways (2007) and the RCRA Facility Investigation Report (2011), require further corrective action at this time that includes, at a minimum, further investigation to determine the nature and extent of the release in accordance with Condition VI.D. of this license.

WMU Number 15:	Former Container Processing System
AOC Number 1:	Soil Volatilization to Indoor Air Exceedences
AOC Number 2:	Soil Volatilization to Ambient Air Exceedences
AOC Number 3:	MTBE Release to Site Wide Groundwater

2. The following WMUs do not require corrective action at this time as they are currently operating pursuant to the act and its rules with no evidence of a release of any contaminants. Corrective action may be required when any of the units undergo final closure.

WMU Number 16:	West Tank Farm
WMU Number 17:	Northwest Tank Farm
WMU Number 18:	Super Blender System
WMU Number 19:	Site Paving Areas

{§§11102 and 11115a of Act 451 and R 299.9521(3)(b) and R 299.9629}

3. Within 30 days of discovery of a new WMU or a release of a contaminant from a new WMU, the licensee shall provide written notification to the Office Chief. The written notification shall include all of the following information:

   a. The location of the unit on the facility topographic map.

   b. The designation of the type of unit.

   c. The general dimensions and structural description, including any available drawings of the unit.

   d. The dates the unit was operated.

   e. Specification of all waste(s) that have been managed in the unit.

   f. All available information pertaining to any release of a contaminant from the unit.

4. Based on a review of all of the information provided in Condition VI.C.3. of this license, the Office Chief may require corrective action for the newly-identified WMU. The licensee shall submit a written Investigation Work Plan to the Office Chief within 60 days of written notification by the Office Chief that corrective action for the unit is required.

   {§§11102 and 11115a of Act 451 and R 299.9504(1), R 299.9508(1)(b), and R 299.9629 and 40 CFR §270.14(d)}

D. CORRECTIVE ACTION INVESTIGATION

The licensee shall conduct a Corrective Action Investigation to determine if a release of a contaminant(s) from any of the WMUs identified in Condition VI.C. of this license has occurred and, if a release(s) has occurred, evaluate the nature and extent of the release(s). The licensee shall submit a written Corrective Action Investigation Work Plan, Corrective Action Investigation Final Report documenting compliance with the approved Work Plan and supporting further corrective action at the facility, and Corrective Action Investigation progress reports to the Office Chief for review and approval in accordance with Condition VI.K. of this license. The Office Chief will approve, modify and approve, or provide a Notice of Deficiency (NOD) for the Work Plan and Final Report. Upon approval, the Work Plan and Final Report become enforceable conditions of this license. {§§11102 and 11115a of Act 451 and R 299.9629}

E. INTERIM MEASURES

The licensee shall conduct interim measures (IMs) at the facility, if determined necessary by the licensee or the Office Chief, to cleanup or remove a released contaminant or to take other actions, prior to the implementation of corrective action measures, as may be necessary to prevent, minimize, or mitigate injury to the public health, safety, or welfare, or to the environment. The licensee shall submit a written IM Work Plan, an IM Final Report documenting compliance with the approved Work Plan and supporting further corrective action at the facility, and IM progress reports to the Office Chief for review and approval in accordance with Condition VI.K. of this license. The Office Chief will approve, modify and approve, or provide an NOD for the Work Plan and Final Report. Upon approval, the Work Plan and Final Report become enforceable conditions of this license. {§§11102 and 11115a of Act 451 and R 299.9629}

F. DETERMINATION OF NO FURTHER ACTION

1. The licensee shall continue corrective action measures to the extent necessary to ensure that the applicable environmental protection standards adopted in Part 111 of Act 451 are met, if the limits are not less stringent than allowed pursuant to the provisions of RCRA.

2. Based on the results of the Corrective Action Investigation and other relevant information, the licensee shall submit a written request for a license minor modification to the Office Chief if the licensee wishes to terminate corrective action for a specific WMU identified in Condition VI.C. of this license. The licensee must demonstrate that there have been no releases of a contaminant(s) from the WMU and that the WMU does not pose a threat to public health, safety, welfare, or the environment.

3. Based on the results of the Corrective Action Investigation and other relevant information, the licensee shall submit a written request for a license major modification to the Office Chief if the licensee wishes to terminate facility-wide corrective action. The licensee must conclusively demonstrate that there have been no releases of a contaminant(s) from any of the WMUs at the facility and that none of the WMUs pose a threat to public health, safety, welfare, or the environment.

4. If, based upon a review of the licensee's request for a license modification pursuant to Condition VI.F.2. or VI.F.3. of this license, the results of the completed Corrective Action Investigation, and other relevant information, the Office Chief determines that the releases, or suspected releases, of a contaminant(s) do not exist and that the WMU(s) do not pose a threat to public health, safety, welfare, or the environment, the Office Chief will approve the requested modification, subject to conditions VI.F.5. and VI.F.6., below.

5. A determination of no further action shall not preclude the Office Chief from requiring continued or periodic monitoring of air, soil, groundwater, or surface water, if necessary, to protect public health, safety, welfare, or the environment, when facility-specific circumstances indicate that potential or actual releases of a contaminant(s) may occur.

6. A determination of no further action shall not preclude the Office Chief from requiring further corrective action at a later date, if new information or subsequent analysis indicates that a release or potential release of a contaminant(s) from a WMU at the facility may pose a threat to public health, safety, welfare, or the environment. The Office Chief will initiate the necessary license modifications if further corrective action is required at a later date.

{§§11102 and 11115a of Act 451 and R 299.9629(2)}

G. CORRECTIVE MEASURES STUDY

If the Office Chief determines, based on the results of the Corrective Action Investigation and other relevant information, that response activities are necessary, the Office Chief will notify the licensee in writing that a Corrective Measures Study (CMS) is required. If required by the Office Chief, the licensee shall conduct a CMS to develop and evaluate the response activity alternative(s) necessary to address the release(s) of a contaminant(s) or hazardous substances and the WMU(s) that are identified in the approved Corrective Action Investigation Final Report as requiring final response activities. The licensee shall submit a written CMS Work Plan, an CMS Final Report documenting compliance with the approved Work Plan and supporting further corrective action at the facility, and CMS progress reports to the Office Chief for review and approval in accordance with Condition VI.K. of this license. The Office Chief will approve, modify and approve, or provide an NOD for the Work

Plan and Final Report. Upon approval, the Work Plan and Final Report become enforceable conditions of this license. {§§11102 and 11115a of Act 451 and R 299.9629}

H. CORRECTIVE MEASURES IMPLEMENTATION

1. The licensee shall implement final corrective action measures based on the CMS Final Report approved by the Office Chief. The licensee shall submit a written Corrective Measures Implementation (CMI) Work Plan to the Office Chief for review and approval. The licensee shall also submit a written CMI Final Report documenting compliance with the approved CMI Work Plan and providing justification that the corrective action measures may cease and CMI progress reports to the Office Chief for review and approval in accordance with Condition VI.K. of this license. The Office Chief will approve, modify and approve, or provide an NOD for the Work Plan and Final Report. Upon approval, the Work Plan and Final Report become enforceable conditions of this license.

2. The Office will provide notice of its draft decision on the CMI Work Plan to persons on the facility mailing list and provide an opportunity for a public hearing.

3. The licensee shall implement the approved CMI Work Plan within 60 days of receipt of the Office Chief's written approval of the CMI Work Plan.

{§§11102 and 11115a of Act 451 and R 299.9629}

I. CORRECTIVE ACTION MANAGEMENT UNITS

If applicable, the licensee shall comply with the requirements of R 299.9635 in order to designate an area at the facility as a corrective action management unit for implementation of corrective action remedies. {R 299.9521(3)(a)}

J. TEMPORARY UNITS

If applicable, the licensee shall comply with the requirements of R 299.9636 in order to designate tank or container storage units used for the treatment or storage of remediation wastes as temporary units for implementation of corrective action remedies. {R 299.9521(3)(a)}

K. SUMMARY OF CORRECTIVE ACTION SUBMITTALS

The licensee shall submit the required corrective action documents in accordance with Conditions VI.D., VI.E., VI.G., and VI.H. of this license and the schedule below.

CORRECTIVE ACTION DOCUMENT	SUBMITTAL DEADLINE
Written notification of new release of contaminant from existing WMU, new WMU, or release of contaminant from new WMU	Within 30 days of discovery
Corrective Action Investigation Work Plan for newly-identified release of contaminant from existing WMU, new WMU, or release of a contaminant from a new WMU	Within 60 days of receipt of written notification that response activity is required

CORRECTIVE ACTION DOCUMENT	SUBMITTAL DEADLINE
Corrective Action Investigation Work Plan for existing WMUs, AOCs, and contaminant releases	Within 60 days of the effective date of this license
Revised Corrective Action Investigation Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Work Plan NOD
Corrective Action Investigation progress reports	Within 90 days of initiation of the investigation and every 90 days thereafter, unless otherwise approved
Corrective Action Investigation Final Report for WMUs and contaminant releases	Within 60 days of completion of investigation
Revised Corrective Action Investigation Final Report for WMUs and contaminant releases	Within 60 days of receipt of Final Report NOD
IM Work Plan for WMUs and contaminant releases	Within 60 days of receipt of notification that Work Plan is required
Revised IM Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Work Plan NOD
IM progress reports	Within 90 days of initiation of the IM and every 90 days thereafter, unless otherwise approved
IM Final Report for WMUs and contaminant releases	Within 60 days of completion of the IM
Revised IM Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Final Report NOD
CMS Work Plan for WMUs and contaminant releases	Within 60 days of receipt of notification that CMS is required
Revised CMS Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Work Plan NOD
CMS progress reports	Within 90 days of initiation of the CMS and every 90 days thereafter, unless otherwise approved
CMS Final Report for WMUs and contaminant releases	Within 60 days of completion of the CMS
Revised CMS Final Report for WMUs and contaminant releases	Within 60 days of receipt of Final Report NOD
CMI Work Plan for WMUs and contaminant releases	Within 60 days of approval of the CMS Final Report
Revised CMI Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Work Plan NOD
CMI Work Plan progress reports	Within 90 days of implementation of Work Plan and

CORRECTIVE ACTION DOCUMENT	SUBMITTAL DEADLINE
	every 90 days thereafter, unless otherwise approved
CMI Final Report for remediated WMUs and contaminant releases	Within 60 days after corrective action measures have been completed and cleanup criteria have been met
Revised CMI Final Report for WMUs and contaminant releases	Within 60 days of receipt of Final Report NOD

L. CORRECTIVE ACTION DOCUMENTS RETENTION

The licensee shall maintain all corrective action documents required by this license at the facility. The documents shall be maintained for the operating life of the facility or until the facility is released from financial assurance requirements for corrective action by the Director, whichever is longer. The licensee shall offer such documents to the Office Chief prior to discarding those documents. {§§11102 and 11115a of Act 451 and R 299.9521(3)(b) and R 299.9629}

PART VII
SCHEDULE OF COMPLIANCE

A. NEW CONSTRUCTION

1. Construction Schedule: The licensee shall initiate construction of 10,341 gallons of excess available storage capacity in the form of hazardous waste container or tank storage units within 3 years after the effective date of this license. This license condition remains valid for a period of 5 years from the effective date of this license if construction is initiated within the 3-year period and proceeds in a continuous manner. Extensions may be granted by the Office Chief if unexpected construction delays occur beyond the control of the licensee.

2. Plan Submittal and Review: Prior to construction of excess storage capacity, the licensee shall submit engineering plans of all storage equipment and containment structures to the Office Chief for review and approval. The plans shall be prepared and sealed by a registered professional engineer and shall include all of the following information:

   a. Plan views, elevations, sections, and supplementary views that, together with general layout drawings, provide working information for the review of the storage process.

   b. Specifications on all construction materials and installation methods.

   c. The basis of design for all storage equipment and containment structures.

   d. A flow diagram of the storage process.

   e. The design capacity of the storage process.

   {R 299.9504(1)(g)}

3. Notification of Start of Construction: The licensee shall notify the Office Chief as soon as possible, but no later than seven days prior to beginning construction of excess storage capacity approved pursuant to Condition VII.A.2. of this license.

4. Progress Reports: Starting within 90 days after the effective date of the license, and quarterly thereafter, the licensee shall submit progress reports to the Office Chief detailing the status of construction completion and the expected construction activities during the next 90-day reporting period. The licensee shall continue to provide these progress reports until the letter required in condition VII.5., below, has been provided to the Office Chief.

5. Certification and Inspection: The licensee shall not store hazardous waste in the portion of the facility constructed pursuant to this part of the license until:

   a. The licensee has submitted, to the Office Chief, by certified mail or hand delivery, a letter signed by the licensee and a registered professional engineer stating that the excess available storage capacity at the facility has been constructed in compliance with the license and approved plans, and

   b. The RMD has inspected the modified facility and issued a determination that the construction is in compliance with the conditions of the license.

6. Forfeiture: Any claim by the licensee to the 10,341 gallon excess available storage capacity authorized by this license Condition VII.A., but not constructed in accordance with the deadlines to begin and complete construction in Condition VII.A.1. shall be forfeited.

{R 299.9504(1)(g), R 299.9508, and R 299.9516}

State of Michigan
Department of Environmental Quality

HAZARDOUS WASTE MANAGEMENT FACILITY OPERATING LICENSE

NAME OF LICENSEE: Petro-Chem Processing Group of Nortru, LLC

NAME OF FACILITY OWNER: Nortru, LLC

NAME OF FACILITY OPERATOR: Petro-Chem Processing Group of Nortru, LLC

NAME OF TITLEHOLDER OF LAND: Nortru, LLC

FACILITY NAME: Petro-Chem Processing Group of Nortru, LLC

FACILITY LOCATION: 421 Lycaste, Detroit, Michigan 48214

EPA IDENTIFICATION (ID) NUMBER: MID 980 615 298 EFFECTIVE DATE: December 18, 2012

REAPPLICATION DATE: June 21, 2022 EXPIRATION DATE: December 18, 2022

AUTHORIZED ACTIVITIES

Pursuant to Part 111, Hazardous Waste Management, of Michigan's Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (Act 451), being §§324.11101 to 324.11153 of the Michigan Compiled Laws, and the hazardous waste management administrative rules (hereafter called the "rules") promulgated thereunder, being R 299.9101 *et. seq.* of the Michigan Administrative Code, by the Michigan Department of Environmental Quality (DEQ), an operating license (hereafter called the "license") is issued to Petro-Chem Processing Group of Nortru, LLC (hereafter called the "licensee") to operate a hazardous waste management facility (hereafter called the "facility") located at latitude 42° 22' 1" and longitude 82° 57' 55". The licensee is authorized to conduct the following hazardous waste management activities:

- ☒ STORAGE
  - ☒ Container
  - ☒ Tank
  - ☐ Waste Pile
  - ☐ Surface Impoundment
  - ☐ Drip Pad
- ☒ TREATMENT
  - ☐ Container
  - ☒ Tank
  - ☐ Surface Impoundment
  - ☐ Incinerator
  - ☐ Other:
- ☐ DISPOSAL
  - ☐ Landfill
  - ☐ Land Application
  - ☐ Surface Impoundment
- ☐ POSTCLOSURE
  - ☐ Tank
  - ☐ Surface Impoundment
  - ☐ Landfill
  - ☐ Waste Pile

APPLICABLE REGULATIONS AND LICENSE APPROVAL

The conditions of this license were developed in accordance with the applicable provisions of the rules, effective March 17, 2008. The licensee shall comply with all terms and conditions of this license, Part 111, and its rules. This license consists of the 20 pages of conditions attached hereto (including those in Attachments 1 through 11) and the applicable regulations contained in R 299.9101 through R 299.11008. For purposes of compliance with this license, applicable rules are those that are in effect on the date of issuance of this license in accordance with R 299.9521(3)(a).

This license is based on the information in the license application submitted on May 18, 2009, and any subsequent amendments (hereafter referred to as the "application"). Pursuant to R 299.9519(11)(c), the license may be revoked if the licensee fails, in the application or during the license issuance process, to disclose fully all relevant facts or, at any time, misrepresents any relevant facts. As specified in R 299.9519(1), the facility shall be constructed, operated, and maintained in accordance with Part 111 of Act 451, the rules, and this license.

This license is effective on the date of issuance and shall remain in effect for 10 years from the date of issuance, unless revoked pursuant to R 299.9519 or continued in effect as provided by the Michigan Administrative Procedures Act, 1969 PA 306, as amended (Act 306).

Amendment 2 issued this 12th day of February, 2019

by Allan B. Taylor
Allan B. Taylor, Manager
Hazardous Waste Section
Waste Management and Radiological Protection Division

HAZARDOUS WASTE MANAGEMENT FACILITY OPERATING LICENSE
FOR

Petro-Chem Processing Group of Nortru, LLC
MID 980 615 298

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PART I
STANDARD CONDITIONS

A. TERMINOLOGY AND REFERENCES

Throughout this license, the term "Office" means the Office of Waste Management and Radiological Protection within the DEQ responsible for administering Part 111 of Act 451 and the rules. Throughout this license, "Director" means the Director of the DEQ or the Director's duly authorized designee such as the Office Chief. All of the provisions of Title 40 of the Code of Federal Regulations (CFR) referenced in this license are adopted by reference in R 299.11003.

B. EFFECT OF LICENSE

Except as otherwise provided by law, any treatment, storage, or disposal of hazardous waste not specifically authorized in this license is prohibited. Issuance of this license does not authorize any injury to persons or property, any invasion of other private rights, or any infringement of federal, state, or local law or regulations {R 299.9516(8)}; nor does it obviate the necessity of obtaining such permits or approvals from other units of government as may be required by law. Compliance with the terms of this license does not constitute a warranty or representation of any kind by the DEQ, nor does the DEQ intend that compliance with this license constitutes a defense to any order issued or any action brought under Act 451 or any other applicable state statute or §106(a) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) {42 U.S.C. 9606(a)}, the Resource Conservation and Recovery Act of 1976, as amended (RCRA), and its rules, or any other applicable federal statute. The licensee, however, does not represent that it will not argue that compliance with the terms of this license may be a defense to such future regulatory actions. Each attachment to this license is a part of, and is incorporated into, this license and is deemed an enforceable part of the license.

C. SEVERABILITY

The provisions of this license are severable, and if any provision of this license, or the application of any provision of this license to any circumstance, is held invalid, the application of such provision to other circumstances and the remainder of this license shall not be affected thereby.

D. RESPONSIBILITIES

1. The licensee shall comply with Part 111 of Act 451, the rules, and all conditions of this license, except to the extent authorized by the DEQ pursuant to the terms of an emergency operating license. Any license noncompliance, except to the extent authorized by the DEQ pursuant to the terms of an emergency operating license, constitutes a violation of Part 111 of Act 451 and is grounds for enforcement action, license revocation, license modification, or denial of a license renewal application. {§§324.11148, 324.11150, and 324.11151 of Act 451 and R 299.9521(1)(a) and (c) and (3)(a) and (b) and 40 CFR §270.30(a)}

2. If the licensee wishes to continue an activity regulated by this license after the expiration date of this license, the licensee shall submit a complete application for a new license to the Office Chief at least 180 days before this license expires, **June 21, 2022**, unless an extension is granted pursuant to R 299.9510(5). To the extent the licensee makes a timely and sufficient application for renewal of this license, this license and all conditions herein will remain in effect beyond the license expiration date and shall not expire until a decision on the application is finally made by the DEQ, and if the application is denied or the terms of the new license are limited, until the last day for applying for judicial review of the new license or a later date fixed

by order of the reviewing court consistent with §91(2) of Act 306. {R 299.9521(1)(a) and (c) and (3)(a) and 40 CFR §270.30(b)}

3. The licensee shall comply with the conditions specified in R 299.9521(1)(b)(i) to (iii) and 40 CFR §270.30(c) through (k), (l)(2), (3), (5), (7), and (11), and (m). {§§11123(3), 11146(1) and (2), and 11148(1) of Act 451 and R 299.9501(1), R 299.9516, R 299.9519, R 299.9521(1)(a) and (b) and (3)(a) and (b), R 299.9522, and R 299.9525}

4. The licensee shall give notice to the Office Chief as soon as possible prior to any planned physical alterations or additions to the licensed facility. {R 299.9501 and R 299.9519 and Part 6 of the Part 111 Rules}

E. SUBMITTAL DEADLINES

When the deadline for submittals required under this license falls on a weekend or legal state holiday, the deadline shall be extended to the next regular business day. This extension does not apply to the deadline for financial mechanisms and associated renewals, replacements, and extensions of financial mechanisms required under this license. The licensee may request extension of the deadlines for submittals required under this license. The licensee shall submit such requests at least five business days prior to the existing deadline for review and approval by the Office Chief. Written extension requests shall include justification for each extension. {R 299.9519 and R 299.9521(3)(a)}

PART II
GENERAL OPERATING CONDITIONS

A. GENERAL WASTE ANALYSIS

The licensee shall ensure that any waste managed at the facility has been properly characterized pursuant to R 299.9302 and comply with the procedures described in the attached Waste Analysis Plan, Attachment 1, of this license. {R 299.9605(1), and 40 CFR §264.13}

B. SECURITY

The licensee shall comply with the barrier, surveillance, and signage requirements of R 299.9605(1) and 40 CFR §264.14.

C. GENERAL INSPECTION REQUIREMENTS

1. The licensee shall inspect the facility in accordance with the Inspection Schedule, Attachment 2, of this license and comply with the inspection requirements of R 299.9605(1) and 40 CFR §264.15.
2. The licensee shall develop and implement a procedure to ensure compliance with the requirements of R 299.9605(2) regarding transport vehicles and other containers leaving the facility.

D. PERSONNEL TRAINING

The licensee shall comply with the personnel training requirements of R 299.9605 and 40 CFR §264.16. The Personnel Training Program, Attachment 3, of this license shall, at a minimum, cover all items in R 299.9605 and 40 CFR §264.16.

E. PREPAREDNESS AND PREVENTION

The licensee shall comply with the preparedness and prevention requirements of R 299.9606 and 40 CFR Part 264, Subpart C.

F. CONTINGENCY PLAN

The licensee shall comply with the contingency plan requirements of R 299.9607 and 40 CFR Part 264, Subpart D. The Contingency Plan, Attachment 4, of this license and the prescribed emergency procedures shall be immediately implemented by the licensee whenever there is a fire, explosion, or other release of hazardous waste or hazardous waste constituents that threatens or could threaten human health or the environment, or if the licensee has knowledge that a spill has reached surface water or groundwater.

G. DUTY TO MITIGATE

Upon notification from the Office Chief or his or her designee that an activity at the facility may present an imminent and substantial endangerment to human health or the environment, the licensee shall immediately comply with an order issued by the Office Chief pursuant to §11148(1) of Act 451 to halt such activity and conduct other activities as required by the Office Chief to eliminate the said endangerment. The licensee shall not resume the halted activity without the prior written approval from the Office Chief. {§11148 of Act 451 and R 299.9521(3)(b)}

H. MANIFEST SYSTEM

The licensee shall comply with the manifest requirements of R 299.9304, R 299.9305, and R 299.9608.

I. RECORD KEEPING AND REPORTING

1. The licensee shall comply with the written operating record and monthly operating report (EQP 5142 form) requirements of R 299.9609 and 40 CFR §264.73 and Part 264, Appendix I, and R 299.9610(3), respectively. The monthly operating report shall be submitted on EQP 5142 form provided by the Office Chief, or an equivalent form that has been approved by the Office Chief.

2. The licensee shall comply with the biennial report requirements of R 299.9610. {R 299.9521(1)(a) and 40 CFR §270.30(l)(9)}

3. The licensee shall submit the results of all environmental monitoring required by this license and any additional environmental sampling or analysis conducted beyond that required by this license, in the form of an Environmental Monitoring Report to the Office Chief within 60 days after any sample collection. {R 299.9521(1)(a) and R 299.9521(3)(b) and 40 CFR §270.30(l)(4)}

4. The licensee shall provide environmental monitoring information or data that is required pursuant to this license to an authorized representative of an environmental or emergency response department of the city of Detroit or county of Wayne who requests such information or data and that has jurisdiction over the facility. Such information or data shall be made available on the same day the licensee forwards this information to the Office Chief. {R 299.9521(3)(b)}

5. The licensee shall immediately report to the Office Chief any noncompliance with the license that may endanger human health or the environment by doing both of the following:

    a. The licensee shall immediately notify the Office Chief at 517-335-2690, if the noncompliance occurs Monday through Friday during the period of 8:00 a.m. to 5:00 p.m., except state holidays, or by calling the DEQ Pollution Emergency Alerting System (PEAS) at 1-800-292-4706 during all other times. This notice shall include the following:

        (i) Information concerning the fire, explosion, release, or discharge of any hazardous waste or hazardous waste constituent that could threaten human health or the environment, that has reached surface water or groundwater, or that may endanger public drinking water supplies or the environment; and

        (ii) A description of the occurrence and its cause, including all of the information outlined in R 299.9607(2)(a)-(i).

    b. The licensee shall also follow up the verbal notice by providing a written report to the Office Chief within five days of the time the licensee becomes aware of the circumstances. The written report shall contain all of the information in Condition II.I.5.a.(i)-(ii) of this license along with a description of the noncompliance and its cause; the periods of noncompliance (including exact dates and times); whether the noncompliance has been corrected and, if not, the anticipated time it is expected to continue; and steps taken or planned to reduce, eliminate, and prevent recurrence of the noncompliance and when those activities occurred or will occur. The Office Chief may waive the 5-day written notice requirement in favor of submittal of a written report within 15 days of the time the licensee becomes aware of the circumstances.

{R 299.9521(1)(a) and R 299.9607 and 40 CFR §270.30(l)(6)}

6. The licensee shall report all other instances of noncompliance with this license, Part 111 of Act 451, the rules, and any other applicable environmental laws or rules that apply to the licensed facility at the time monitoring reports required by this license are submitted or within 30 days, whichever is sooner. The reports shall contain the information listed in Condition II.I.5. of this license. {R 299.9521(1)(a) and 40 CFR §270.30(l)(10)}

7. The licensee may make minor modifications to the forms contained in the attachments to this license. The modifications may include changing the format, updating existing references and information, adding necessary information, and changing certification and notification information in accordance with Part 111 of Act 451 and its rules and RCRA and its regulations. The licensee shall submit the modifications to the Office Chief prior to implementing the use of the modified form(s). If the Office Chief does not reject or require revision of the modified form(s) within 14 days of receipt, the licensee shall implement use of the modified form(s) and the form(s) shall be incorporated into this license as a replacement for the existing form(s).

J. CLOSURE

The licensee shall comply with the closure requirements of R 299.9613. The licensee shall close the facility in accordance with the Closure Plan, Attachment 5, of this license, all other applicable requirements of this license, and all other applicable laws. {R 299.9613 and 40 CFR Part 264, Subpart G, except 40 CFR §§264.112(d)(1), 264.115, and 264.120}

K. FINANCIAL ASSURANCE FOR CLOSURE

1. On the effective date of this license, the facility closure cost estimate is $1,946,093**.** The licensee shall keep this estimate current as required under R 299.9702 and 40 CFR §264.142.

2. The licensee shall continuously maintain financial assurance for the current closure cost estimate as required under R 299.9703.

L. FINANCIAL ASSURANCE FOR CORRECTIVE ACTION

1. The licensee shall establish a cost estimate(s) for completing corrective actions at the facility for the cost of performing corrective actions at such time as work plans are submitted, as required by Part VI of this license. The licensee shall keep the corrective action cost estimate current as required under R 299.9712.

2. The licensee shall continuously maintain financial assurance for corrective action as required under R 299.9713.

M. FINANCIAL REPSONSIBILITY FOR LIABILITY COVERAGE

The licensee shall continuously maintain liability coverage for sudden and accidental occurrences, as required by R 299.9710.

N. WASTE MINIMIZATION

The licensee shall certify, at least annually, that the licensee has a hazardous waste minimization program in place. {R 299.9609(1)(a), 40 CFR §264.73(b)(9), §3005(h) of RCRA, and 42 U.S.C. §6925(h)}

O. LAND DISPOSAL RESTRICTIONS

The licensee shall comply with all of the requirements of 40 CFR Part 268. {R 299.9627 and 40 CFR Part 268}

P. AIR EMISSION STANDARDS

1. The licensee shall comply with the requirements of 40 CFR Part 264, Subpart AA, regarding air emission standards for process vents; Subpart BB, regarding air emission standards for equipment leaks; and Subpart CC, regarding air emission standards for tanks, surface impoundments, and containers.
2. The licensee shall notify the Office Chief of any waste management units that become subject to the requirements of 40 CFR Part 264, Subparts AA, BB, and/or CC within 30 days of the start of the regulated activity.

{R 299.9630, R 299.9631, and R 299.9634 and 40 CFR Part 264, Subparts AA, BB, and CC}

Q. DOCUMENTS TO BE MAINTAINED AT THE FACILITY

The licensee shall maintain at the facility the following documents and amendments required by this license, until closure/postclosure is completed, certified by an independent registered professional engineer, and the facility is released from financial assurance requirements for closure/postclosure by the Director:

1. Waste Analysis Plan, including Quality Assurance/Quality Control (QA/QC) Plans.
2. Inspection Schedules and records.
3. Personnel Training Program documents and records.
4. Contingency Plan.
5. Closure Plan.
6. Cost estimates for facility closure, and corrective action and copies of related financial assurance documents.
7. Operating record.
8. Site Security Plan.
9. Facility engineering plans and specifications.
10. Record keeping procedures.
11. Environmental monitoring plans, including Sampling and Analysis Plans and QA/QC Plans.
12. Environmental monitoring data and statistical records.
13. Preventative procedures (Personnel Protection Plan).
14. Hazardous waste minimization program certification.

{R 299.9521(3)(a)}

R. ENGINEERING PLANS

The licensee shall construct, operate, and maintain the facility in accordance with the Engineering Plans and Specifications, Attachment 6, of this license, and any modifications to those plans shall be made in accordance with this license

PART III
CONTAINER STORAGE CONDITIONS

A. COVERAGE OF LICENSE

The hazardous waste container storage areas at the facility shown in Drawings 251, A-1, SUP A-1, A-2, SUP A-2, A-3, SUP A-3, A-4, SUP A-4, A-9, F-1, F-2, G-1, G-2, G-3, G-4, G-5, M-1, M-2, M-3, M-3A, M-4, S-1, S-2, S-4, S-5, S-6, 071, 072, 073, PCPI-63, PCPI-63B, PCPI-91, PCPI-153, and PCPI-154 are covered by this license. Any expansion or enlargement beyond the facility boundary shown in Drawing G-2 or beyond the 385,399 gallon storage design capacity requires a new expansion license from the Director. Drawings 251, A-1, SUP A-1, A-2, SUP A-2, A-3, SUP A-3, A-4, SUP A-4, A-9, F-1, F-2, G-1, G-2, G-3, G-4, G-5, M-1, M-2, M-3, M-3A, M-4, S-1, S-2, S-4, S-5, S-6, 071, 072, 073, PCPI-63, PCPI-63B, PCPI-91, PCPI-153, and PCPI-154 are incorporated into this license as part of the Engineering Plans and Specifications, Attachment 6, of this license. {R 299.9521(1)(b)}

B. WASTE IDENTIFICATION AND QUANTITY

1. The licensee may store no more than a total volume of 385,399 gallons of the hazardous wastes listed in the Appendices of Attachment 5 of this license in containers at the facility, subject to the terms of this license. The maximum number of containers of hazardous waste that may be stored at the facility is 7,195, 55-gallon container equivalents. {R 299.9521(2)(d)}

2. Storage of hazardous waste in containers by the licensee is limited to the following specified areas as shown on Drawings 251, A-1, F-2, G-3, M-3A, S-1, PCPI-63, PCPI-91, and PCPI-153 in the Engineering Plans and Specifications, Attachment 6, of this license:

Storage Area Description	Maximum Inventory Allowed
Truck Staging Area (Up to 72 hours Only)	363 containers or 20,000 gallons
Tank Storage Area 1 (TS1) Transfer Pad during waste fingerprinting and offloading (Up to 72 hours Only)	Up to 6 Tanker Truck Trailers or Up to 3 Tanker Truck Trailers and Up to 3 Super Tanker Truck Trailers or 54,000 gallons
TS2 Transfer Pad during waste fingerprinting and offloading (Up to 72 hours Only)	Up to 2 Super Tanker Truck Trailers or 24,000 gallons
First Floor Operations Building – North Storage	700 containers or 38,500 gallons
CMB Container Storage Areas	3,888 containers or 213,840 gallons
CMB Roll-Off Storage	1 roll-off box or 8,080 gallons
CMB Temporary Storage (Up to 72 hours only – TS3 Transfer Pad, TS4 Transfer Pad, QA/QC Area, Pump Room)	675 containers or 37,119 gallons
Drum Dock #3	300 containers or 16,500 gallons
Drum Dock #4	147 containers or 8,080 gallons
SBS Container Storage Room	272 containers or 14,960 gallons
SBS Solids Storage Area (Solids Only)	1 roll-off box or 8,080 gallons
SBS Dock Storage Area	368 containers or 20,240 gallons
Total Facility Authorized Container Storage Capacity	**385,399 gallons**

C. USE AND MANAGEMENT OF CONTAINERS

1. The licensee shall manage all containers in compliance with R 299.9521(3)(b), R 299.9614, and R 299.9627 and 40 CFR §§264.171, 264.172, 264.173, and 268.50(a)(2)(i).

2. The licensee shall only place containers, stacked no greater than two high, into the hazardous waste container storage areas referenced in Condition III.A. and B. of this license in accordance with the configuration shown in Drawings 251, A-1, F-2, G-3, M-3A, S-1, PCPI-63, PCPI-91, and PCPI-153 in the Engineering Plans and Specifications, Attachment 6, of this license or an alternate configuration approved by the Office Chief. {R 299.9521(3)(b)}

3. The licensee shall operate and maintain the containment system in accordance with the requirements of R 299.9614 and 40 CFR §264.175, and the Engineering Plans and Specifications, Attachment 6, of this license.

D. SPECIAL REQUIREMENTS FOR IGNITABLE OR REACTIVE WASTES

1. The licensee shall locate containers holding ignitable or reactive wastes in accordance with R 299.9614 and 40 CFR §264.176.

2. The licensee shall take precautions to prevent the accidental ignition or reaction of ignitable or reactive wastes by following the procedures specified in Attachments 7, 9, and 10 of this license, where applicable. The licensee shall document compliance with this condition and place this documentation in the operating record. {R 299.9605 and 40 CFR §264.17(a) and (c)}

E. SPECIAL REQUIREMENTS FOR INCOMPATIBLE WASTES OR MATERIALS

1. Prior to placing incompatible wastes or incompatible wastes and materials in the same container, the licensee shall comply with R 299.9605 and 40 CFR §264.17(b) by following the procedures specified in Attachments 7, 9, and 10 of this license. {R 299.9521(2)(d) and (3)(b)}

2. The licensee shall prevent the placement of hazardous waste in an unwashed container that previously held an incompatible waste or material. {R 299.9614 and 40 CFR §264.177(b)}

3. The licensee shall document compliance with Conditions III.E.1. and III.E.2. of this license and place this documentation in the operating record. {R 299.9605 and 40 CFR §264.17(c)}

4. The licensee shall separate containers of incompatible wastes as indicated in the procedures contained in Attachments 7 and 9 of this license. {R 299.9614 and 40 CFR §264.177(c)}

F. DISPOSITION OF ACCUMULATED LIQUIDS

The licensee shall remove all liquids accumulated in the containment system within 24 hours of detection and manage the liquids in accordance with the requirements of Part 111 of Act 451 and the rules, as specified in the Use and Management of Containers, Attachment 7, of this license. {R 299.9521(3)(b) and R 299.9614(1)(a) and 40 CFR §264.175(b)(5)}

PART IV
TANK SYSTEM STORAGE AND TREATMENT CONDITIONS

A. COVERAGE OF LICENSE

The hazardous waste tank system storage and treatment areas at the facility shown in Drawings 251, A-1, A-4, G-2, G-3, G-5, M-3A, 071, 072, 073, TK001, TK002, PCPI-58, PCPI-58B, PCPI-58C, PCPI-59, PCPI-60, PCPI-79, PCPI-116B, PCPI-174, PCPI-192, PCPI-193, PCPI-194, PCPI-196B, and PCPI-572A are covered by this license. Any expansion or enlargement beyond the facility boundary shown in Drawings G-2 or beyond the 646,956-gallon tank system storage design capacity requires a new expansion license from the Director. Drawings 251, A-1, A-4, G-2, G-3, G-5, M-3A, 071, 072, 073, TK001, TK002, PCPI-58, PCPI-58B, PCPI-58C, PCPI-59, PCPI-60, PCPI-79, PCPI-116B, PCPI-174, PCPI-192, PCPI-193, PCPI-194, PCPI-196B, and PCPI-572A are incorporated into this license as the Engineering Plans and Specifications, Attachment 6,of this license. {R 299.9521(1)(b)}

B. WASTE IDENTIFICATION AND QUANTITY

1. The licensee may store no more than a total volume of 646,956 gallons of the hazardous wastes listed in the Appendices of Attachment 5 of this license in the tank systems identified as Tank Systems 1, 2, and 3 and the CMB Tanks in Attachments 8 and 9, subject to the terms of this license. {R 299.9521(2)(d)}

2.

Tank System Description	**Maximum Inventory Allowed**
Tank System 1: Tanks 16-30	28,000 gallons each; 420,000 gallons total
Tank System 2: Tanks 35-40	28,000 gallons each; 168,000 gallons total
Tank System 3: Tanks S69, S70	13,277 gallons each; 26,554 gallons total
Tank System 3: Tanks S71, S72	10,201 gallons each; 20,402 gallons total
CMB Tanks: TK 001, TK 002	6,000 gallons each; 12,000 gallons total
Total Authorized Tank Storage Capacity	**646,956 gallons**

C. WASTE TREATMENT CAPACITY AND METHODS

1. The licensee may treat no more than a total volume of 155,000 gallons per day of the hazardous wastes listed in the Appendices of Attachment 5 of this license in the tank systems identified as Tanks S69, S70, S71, S72 (Fuel Blending and Spent Solvent Reclamation), 16-30 (Fuel Blending), and 35-40 (Fuel Blending) in Tables 1 and 2 of the Process Descriptions, Attachment 9,of this license and Drawings 251, A-1, A-4, G-2, G-3, G-5, M-3A, 071, 072, 073, TK001, TK002, PCPI-58, PCPI-58B, PCPI-58C, PCPI-59, PCPI-60, PCPI-79, PCPI-116B, PCPI-174, PCPI-192, PCPI-193, PCPI-194, PCPI-196B, and PCPI-572A in the Engineering Plans and Specifications, Attachment 6, of this license subject to the license terms. {R 299.9521(2)(d) and (3)(a) and (b)}

2. The licensee may only conduct the treatment methods specified in the Treatment Process Description, Attachment 10, of this license subject to the license terms. {R 299.9521(2)(d) and (3)(a) and (b)}

D. DESIGN, CONTAINMENT, AND ASSESSMENT OF TANK SYSTEMS

The licensee shall operate and maintain all tank systems in accordance with the applicable requirements of R 299.9615 and 40 CFR §§264.193 and 264.194, and in accordance with the Engineering Plans and Specifications, Attachment 6, of this license.

E. MANAGEMENT OF TANK SYSTEMS

1. The licensee shall label and manage the tank systems in accordance with the requirements of R 299.9615 and R 299.9627, 40 CFR §§264.194, 264.196, and 268.50(a)(2)(ii), R 29.4101 to R 29.4504 pursuant to the provisions of the Fire Prevention Act, 1941 PA 207, as amended, National Fire Protection Association (NFPA) Standard No. 704, and the spill and overfill prevention procedures specified in the Tank systems, Attachment 8, of this license. {R 299.9615}

2. The licensee shall conduct the treatment of hazardous wastes in accordance with the methods and procedures specified in the Treatment Process Description, Attachment 10, of this license. {R 299.9633}

F. SPECIAL REQUIREMENTS FOR IGNITABLE OR REACTIVE WASTES

1. The licensee shall not place ignitable or reactive waste in a tank system unless the procedures described in Attachments 8 and 9 of this license are followed. The licensee shall document compliance with this condition and place this documentation in the operating record. {R 299.9605, R 299.9609, R 299.9615 and 40 CFR §§264.17(c), 264.73(b)(3), and 264.198(a)}

2. The licensee shall maintain the protective distances between the tank systems and any public ways, streets, alleys, or adjoining property lines that can be built upon, as required in Tables 2-1 through 2-6 of the NFPA's "Flammable and Combustible Liquids Code" (1977 or 1981) as specified in Attachments 8 and 9 of this license, and as required by R 299.9615 and 40 CFR §264.198(b).

G. SPECIAL REQUIREMENTS FOR INCOMPATIBLE WASTES OR MATERIALS

The licensee shall not place incompatible wastes or incompatible wastes and materials, in the same tank system or place hazardous waste in a tank system that has not been decontaminated and that previously held an incompatible waste or material unless the procedures specified in Attachments 8, 9, and 10 of this license are followed, as required by R 299.9615 and 40 CFR §264.17(b). The licensee shall document compliance with this condition and place this documentation in the operating record. {R 299.9609 and R 299.9615 and 40 CFR §§264.17(c), 264.73(b)(3), and 264.199}

H. DISPOSITION OF ACCUMULATED LIQUIDS

The licensee shall remove spilled or leaked waste and accumulated precipitation from the tank system within 24 hours of detection and manage it in accordance with the requirements of Part 111 of Act 451 and the rules, and the procedures in the Tank Systems, Attachment 8, of this license. {R 299.9521(3)(b), R 299.9615, and 40 CFR §264.193(c)(4)}

PART V
ENVIRONMENTAL MONITORING CONDITIONS

A. GROUNDWATER MONITORING PROGRAM

1. The licensee shall conduct a semiannual corrective action monitoring program. Under this program, the licensee shall operate and maintain a groundwater monitoring system in accordance with the Groundwater Monitoring Programs, Sampling and Analysis Plan (SAP) of Attachment 11, of this license. {R 299.9611(2)(a) and (b), R 299.9612, and R 299.9629 and 40 CFR Part 264, Subpart F, excluding 40 CFR §§264.94(a)(2) and (3), 264.94(b) and (c), 264.100, and 264.101}

2. The licensee shall submit proposed revisions to the SAP to the Office Chief for approval prior to implementation and shall revise any other affected document accordingly. If approved, the revisions to the SAP shall become part of this license without the need for a minor license modification. {R 299.9519(5)(c)(ii), R 299.9611(2)(a), and R 299.9612 and 40 CFR §264.97(d) and (e)}

3. Water removed from each monitoring well shall be managed as specified on page 4 of the Environmental Monitoring Programs, Attachment 11, of this license. {R 299.9521(3)(b)}

4. The licensee shall submit an annual groundwater report to the Office Chief no later than March 1st of each year for the previous calendar year's activities. At a minimum, the report shall include the following information:

   a. A narrative summary of the previous calendar year's sampling events, including sampling event dates, the identification of any significant problems with respect to SAP procedures, and copies of field log sheets.

   b. A determination of the groundwater flow rate and direction in the monitored zone, including the preparation of a groundwater level contour map from this data.

   c. A summary of groundwater quality data results, including a narrative summary of results and trends, isochems, data graphs, and data tables.

   d. A presentation of the statistical analysis of the data and the identification of any statistically significant trends pursuant to Condition V.A.5. of this license.

   e. An analysis and discussion of laboratory and field related QA/QC information. This shall include results of equipment, field, and trip blanks and discussion and evaluation of the adequacy of the data with respect to SAP specifications and requirements.

   {R 299.9521(3)(b) and R 299.9612(1) and 40 CFR §264.97(j)}

5. Within 60 days of each sampling of each monitoring well, the licensee shall determine if a statistically significant increase has occurred compared to background levels for each primary parameter described in Section B5.A.3(a), and listed in the volatile organic compounds and semi-volatile compounds analyte lists, of the Environmental Monitoring Programs, Attachment 11, of this license. This statistical test will be conducted as follows:

   a. The nonparametric Mann-Kendell test will be applied to each well individually (intra well).

6. The licensee shall submit the results of groundwater monitoring required by this license in the form of an Environmental Monitoring Report to the Office Chief within 60 days after any sample collection. This report must include:

   a. A brief summary describing whether contaminant trends are increasing, decreasing, or remaining steady.

   b. Data summary table and laboratory analytical data.

   c. Identification of any tentatively identified compounds (TICs).

7. In the event that the Office Chief determines from the findings of Conditions V.A.5. of this license that a statistically significant increase (or change in pH) in hazardous constituents has occurred in the groundwater and the Director finds, in accordance with §11148 of Act 451, that the increase (or change in pH) may present an imminent and substantial hazard to the health of persons or to the natural resources, or is endangering or causing damage to public health or the environment, the licensee shall immediately comply with an order issued by the Director pursuant to §11148(1) of Act 451 to cease waste receipt, storage, and treatment at the affected units and conduct other activities as required by the Director to eliminate the said endangerment. {R 299.9612(1)(g)}

B. AMBIENT AIR MONITORING PROGRAM

The licensee shall conduct ambient air monitoring in accordance with the program specified in the Environmental Monitoring Programs, Attachment 11, of this license within 30 days after the issuance of this license. {R 299.9611(2)(c)}

PART VI
CORRECTIVE ACTION CONDITIONS

A. CORRECTIVE ACTION AT THE FACILITY

1. The licensee shall implement corrective action for all releases of a contaminant from any waste management units (WMUs) at the facility, regardless of when the contaminant may have been placed in or released from the WMU. For the purposes of this license, the term "corrective action" means an action determined by the Office Chief to be necessary to protect the public health, safety, welfare, or the environment, and includes, but is not limited to, investigation, evaluation, cleanup, removal, remediation, monitoring, containment, isolation, treatment, storage, management, temporary relocation of people, and provision of alternative water supplies, or any corrective action allowed under Title II of the federal Solid Waste Disposal Act, PL 89-272, as amended, or regulations promulgated pursuant to that act. For the purposes of this license, the process outlined in Part 111 of Act 451 and the environmental protection standards adopted in R 299.9629 shall be used to satisfy the corrective action obligations under this license. {§§11102 and 11115a of Act 451 and R 299.9629}

2. To the extent that a release of a hazardous substance, as defined in §20101(t) of Act 451, that is not also a contaminant, as defined in §11102(2) of Act 451, is discovered while performing corrective action under this license, the licensee shall take concurrent actions as necessary to address the Part 201, Environmental Remediation, of Act 451 remedial obligations for that release. {R 299.9521(3)(b)}

B. CORRECTIVE ACTION BEYOND THE FACILITY BOUNDARY

The licensee shall implement corrective action beyond the facility in accordance with §11115a of Act 451 and R 299.9629(2).

C. IDENTIFICATION OF WASTE MANAGEMENT UNITS AND AREAS OF CONCERN

The WMUs and areas of concern (AOCs) at the facility are identified below and shown on Drawing G-1 and the Area of Concern Map in the Engineering Plans and Specifications, Attachment 6, of this license.

1. The following WMU and AOCs, identified in the Evaluation of Part 201 Exposure Pathways (2007) and the RCRA Facility Investigation Report (2011), require further corrective action at this time that includes, at a minimum, further investigation to determine the nature and extent of the release in accordance with Condition VI.D. of this license.

WMU Number 15:	Former Container Processing System
AOC Number 1:	Soil Volatilization to Indoor Air Exceedences
AOC Number 2:	Soil Volatilization to Ambient Air Exceedences
AOC Number 3:	MTBE Release to Site Wide Groundwater

2. The following WMUs do not require corrective action at this time as they are currently operating pursuant to the act and its rules with no evidence of a release of any contaminants. Corrective action may be required when any of the units undergo final closure.

WMU Number 16:	West Tank Farm
WMU Number 17:	Northwest Tank Farm
WMU Number 18:	Super Blender System
WMU Number 19:	Site Paving Areas

{§§11102 and 11115a of Act 451 and R 299.9521(3)(b) and R 299.9629}

3. Within 30 days of discovery of a new WMU or a release of a contaminant from a new WMU, the licensee shall provide written notification to the Office Chief. The written notification shall include all of the following information:

   a. The location of the unit on the facility topographic map.

   b. The designation of the type of unit.

   c. The general dimensions and structural description, including any available drawings of the unit.

   d. The dates the unit was operated.

   e. Specification of all waste(s) that have been managed in the unit.

   f. All available information pertaining to any release of a contaminant from the unit.

4. Based on a review of all of the information provided in Condition VI.C.3. of this license, the Office Chief may require corrective action for the newly-identified WMU. The licensee shall submit a written Investigation Work Plan to the Office Chief within 60 days of written notification by the Office Chief that corrective action for the unit is required.

   {§§11102 and 11115a of Act 451 and R 299.9504(1), R 299.9508(1)(b), and R 299.9629 and 40 CFR §270.14(d)}

D. CORRECTIVE ACTION INVESTIGATION

The licensee shall conduct a Corrective Action Investigation to determine if a release of a contaminant(s) from any of the WMUs identified in Condition VI.C. of this license has occurred and, if a release(s) has occurred, evaluate the nature and extent of the release(s). The licensee shall submit a written Corrective Action Investigation Work Plan, Corrective Action Investigation Final Report documenting compliance with the approved Work Plan and supporting further corrective action at the facility, and Corrective Action Investigation progress reports to the Office Chief for review and approval in accordance with Condition VI.K. of this license. The Office Chief will approve, modify and approve, or provide a Notice of Deficiency (NOD) for the Work Plan and Final Report. Upon approval, the Work Plan and Final Report become enforceable conditions of this license. {§§11102 and 11115a of Act 451 and R 299.9629}

E. INTERIM MEASURES

The licensee shall conduct interim measures (IMs) at the facility, if determined necessary by the licensee or the Office Chief, to cleanup or remove a released contaminant or to take other actions, prior to the implementation of corrective action measures, as may be necessary to prevent, minimize, or mitigate injury to the public health, safety, or welfare, or to the environment. The licensee shall submit a written IM Work Plan, an IM Final Report documenting compliance with the approved Work Plan and supporting further corrective action at the facility, and IM progress reports to the Office Chief for review and approval in accordance with Condition VI.K. of this license. The Office Chief will approve, modify and approve, or provide an NOD for the Work Plan and Final Report. Upon approval, the Work Plan and Final Report become enforceable conditions of this license. {§§11102 and 11115a of Act 451 and R 299.9629}

F. DETERMINATION OF NO FURTHER ACTION

1. The licensee shall continue corrective action measures to the extent necessary to ensure that the applicable environmental protection standards adopted in Part 111 of Act 451 are met, if the limits are not less stringent than allowed pursuant to the provisions of RCRA.

2. Based on the results of the Corrective Action Investigation and other relevant information, the licensee shall submit a written request for a license minor modification to the Office Chief if the licensee wishes to terminate corrective action for a specific WMU identified in Condition VI.C. of this license. The licensee must demonstrate that there have been no releases of a contaminant(s) from the WMU and that the WMU does not pose a threat to public health, safety, welfare, or the environment.

3. Based on the results of the Corrective Action Investigation and other relevant information, the licensee shall submit a written request for a license major modification to the Office Chief if the licensee wishes to terminate facility-wide corrective action. The licensee must conclusively demonstrate that there have been no releases of a contaminant(s) from any of the WMUs at the facility and that none of the WMUs pose a threat to public health, safety, welfare, or the environment.

4. If, based upon a review of the licensee's request for a license modification pursuant to Condition VI.F.2. or VI.F.3. of this license, the results of the completed Corrective Action Investigation, and other relevant information, the Office Chief determines that the releases, or suspected releases, of a contaminant(s) do not exist and that the WMU(s) do not pose a threat to public health, safety, welfare, or the environment, the Office Chief will approve the requested modification, subject to conditions VI.F.5. and VI.F.6., below.

5. A determination of no further action shall not preclude the Office Chief from requiring continued or periodic monitoring of air, soil, groundwater, or surface water, if necessary, to protect public health, safety, welfare, or the environment, when facility-specific circumstances indicate that potential or actual releases of a contaminant(s) may occur.

6. A determination of no further action shall not preclude the Office Chief from requiring further corrective action at a later date, if new information or subsequent analysis indicates that a release or potential release of a contaminant(s) from a WMU at the facility may pose a threat to public health, safety, welfare, or the environment. The Office Chief will initiate the necessary license modifications if further corrective action is required at a later date.

{§§11102 and 11115a of Act 451 and R 299.9629(2)}

G. CORRECTIVE MEASURES STUDY

If the Office Chief determines, based on the results of the Corrective Action Investigation and other relevant information, that response activities are necessary, the Office Chief will notify the licensee in writing that a Corrective Measures Study (CMS) is required. If required by the Office Chief, the licensee shall conduct a CMS to develop and evaluate the response activity alternative(s) necessary to address the release(s) of a contaminant(s) or hazardous substances and the WMU(s) that are identified in the approved Corrective Action Investigation Final Report as requiring final response activities. The licensee shall submit a written CMS Work Plan, an CMS Final Report documenting compliance with the approved Work Plan and supporting further corrective action at the facility, and CMS progress reports to the Office Chief for review and approval in accordance with Condition VI.K. of this license. The Office Chief will approve, modify and approve, or provide an NOD for the Work

Plan and Final Report. Upon approval, the Work Plan and Final Report become enforceable conditions of this license. {§§11102 and 11115a of Act 451 and R 299.9629}

H. CORRECTIVE MEASURES IMPLEMENTATION

1. The licensee shall implement final corrective action measures based on the CMS Final Report approved by the Office Chief. The licensee shall submit a written Corrective Measures Implementation (CMI) Work Plan to the Office Chief for review and approval. The licensee shall also submit a written CMI Final Report documenting compliance with the approved CMI Work Plan and providing justification that the corrective action measures may cease and CMI progress reports to the Office Chief for review and approval in accordance with Condition VI.K. of this license. The Office Chief will approve, modify and approve, or provide an NOD for the Work Plan and Final Report. Upon approval, the Work Plan and Final Report become enforceable conditions of this license.

2. The Office will provide notice of its draft decision on the CMI Work Plan to persons on the facility mailing list and provide an opportunity for a public hearing.

3. The licensee shall implement the approved CMI Work Plan within 60 days of receipt of the Office Chief's written approval of the CMI Work Plan.

{§§11102 and 11115a of Act 451 and R 299.9629}

I. CORRECTIVE ACTION MANAGEMENT UNITS

If applicable, the licensee shall comply with the requirements of R 299.9635 in order to designate an area at the facility as a corrective action management unit for implementation of corrective action remedies. {R 299.9521(3)(a)}

J. TEMPORARY UNITS

If applicable, the licensee shall comply with the requirements of R 299.9636 in order to designate tank or container storage units used for the treatment or storage of remediation wastes as temporary units for implementation of corrective action remedies. {R 299.9521(3)(a)}

K. SUMMARY OF CORRECTIVE ACTION SUBMITTALS

The licensee shall submit the required corrective action documents in accordance with Conditions VI.D., VI.E., VI.G., and VI.H. of this license and the schedule below.

CORRECTIVE ACTION DOCUMENT	SUBMITTAL DEADLINE
Written notification of new release of contaminant from existing WMU, new WMU, or release of contaminant from new WMU	Within 30 days of discovery
Corrective Action Investigation Work Plan for newly-identified release of contaminant from existing WMU, new WMU, or release of a contaminant from a new WMU	Within 60 days of receipt of written notification that response activity is required

CORRECTIVE ACTION DOCUMENT	SUBMITTAL DEADLINE
Corrective Action Investigation Work Plan for existing WMUs, AOCs, and contaminant releases	Within 60 days of the effective date of this license
Revised Corrective Action Investigation Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Work Plan NOD
Corrective Action Investigation progress reports	Within 90 days of initiation of the investigation and every 90 days thereafter, unless otherwise approved
Corrective Action Investigation Final Report for WMUs and contaminant releases	Within 60 days of completion of investigation
Revised Corrective Action Investigation Final Report for WMUs and contaminant releases	Within 60 days of receipt of Final Report NOD
IM Work Plan for WMUs and contaminant releases	Within 60 days of receipt of notification that Work Plan is required
Revised IM Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Work Plan NOD
IM progress reports	Within 90 days of initiation of the IM and every 90 days thereafter, unless otherwise approved
IM Final Report for WMUs and contaminant releases	Within 60 days of completion of the IM
Revised IM Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Final Report NOD
CMS Work Plan for WMUs and contaminant releases	Within 60 days of receipt of notification that CMS is required
Revised CMS Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Work Plan NOD
CMS progress reports	Within 90 days of initiation of the CMS and every 90 days thereafter, unless otherwise approved
CMS Final Report for WMUs and contaminant releases	Within 60 days of completion of the CMS
Revised CMS Final Report for WMUs and contaminant releases	Within 60 days of receipt of Final Report NOD
CMI Work Plan for WMUs and contaminant releases	Within 60 days of approval of the CMS Final Report
Revised CMI Work Plan for WMUs and contaminant releases	Within 60 days of receipt of Work Plan NOD
CMI Work Plan progress reports	Within 90 days of implementation of Work Plan and

CORRECTIVE ACTION DOCUMENT	SUBMITTAL DEADLINE
	every 90 days thereafter, unless otherwise approved
CMI Final Report for remediated WMUs and contaminant releases	Within 60 days after corrective action measures have been completed and cleanup criteria have been met
Revised CMI Final Report for WMUs and contaminant releases	Within 60 days of receipt of Final Report NOD

L. CORRECTIVE ACTION DOCUMENTS RETENTION

The licensee shall maintain all corrective action documents required by this license at the facility. The documents shall be maintained for the operating life of the facility or until the facility is released from financial assurance requirements for corrective action by the Director, whichever is longer. The licensee shall offer such documents to the Office Chief prior to discarding those documents. {§§11102 and 11115a of Act 451 and R 299.9521(3)(b) and R 299.9629}

PART VII
SCHEDULE OF COMPLIANCE

A. NEW CONSTRUCTION

1. Construction Schedule: The licensee shall initiate construction of 10,341 gallons of excess available storage capacity in the form of hazardous waste container or tank storage units within 3 years after the effective date of this license. This license condition remains valid for a period of 5 years from the effective date of this license if construction is initiated within the 3-year period and proceeds in a continuous manner. Extensions may be granted by the Office Chief if unexpected construction delays occur beyond the control of the licensee.

2. Plan Submittal and Review: Prior to construction of excess storage capacity, the licensee shall submit engineering plans of all storage equipment and containment structures to the Office Chief for review and approval. The plans shall be prepared and sealed by a registered professional engineer and shall include all of the following information:

   a. Plan views, elevations, sections, and supplementary views that, together with general layout drawings, provide working information for the review of the storage process.

   b. Specifications on all construction materials and installation methods.

   c. The basis of design for all storage equipment and containment structures.

   d. A flow diagram of the storage process.

   e. The design capacity of the storage process.

   {R 299.9504(1)(g)}

3. Notification of Start of Construction: The licensee shall notify the Office Chief as soon as possible, but no later than seven days prior to beginning construction of excess storage capacity approved pursuant to Condition VII.A.2. of this license.

4. Progress Reports: Starting within 90 days after the effective date of the license, and quarterly thereafter, the licensee shall submit progress reports to the Office Chief detailing the status of construction completion and the expected construction activities during the next 90-day reporting period. The licensee shall continue to provide these progress reports until the letter required in condition VII.5., below, has been provided to the Office Chief.

5. Certification and Inspection: The licensee shall not store hazardous waste in the portion of the facility constructed pursuant to this part of the license until:

   a. The licensee has submitted, to the Office Chief, by certified mail or hand delivery, a letter signed by the licensee and a registered professional engineer stating that the excess available storage capacity at the facility has been constructed in compliance with the license and approved plans, and

   b. The RMD has inspected the modified facility and issued a determination that the construction is in compliance with the conditions of the license.

6. Forfeiture: Any claim by the licensee to the 10,341 gallon excess available storage capacity authorized by this license Condition VII.A., but not constructed in accordance with the deadlines to begin and complete construction in Condition VII.A.1. shall be forfeited.

{R 299.9504(1)(g), R 299.9508, and R 299.9516}

DEPARTMENT OF ENVIRONMENTAL QUALITY
AIR QUALITY DIVISION
ACTIVITY REPORT: On-site Inspection

N073155178

FACILITY: Nortru, LLC		**SRN / ID:** N0731
LOCATION: 421 LYCASTE, DETROIT		**DISTRICT:** Detroit
CITY: DETROIT		**COUNTY:** WAYNE
CONTACT: Ed Burk , Permitting Compliance Manager		**ACTIVITY DATE:** 09/24/2020
STAFF: Jonathan Lamb	**COMPLIANCE STATUS:** Compliance	**SOURCE CLASS:** SM OPT OUT
SUBJECT: Scheduled inspection FY 2020		
RESOLVED COMPLAINTS:		

DATE OF INSPECTION: September 24, 2020
INSPECTED BY: Jonathan Lamb, AQD-Detroit; Sam Liveson, AQD-Detroit
FACILITY PERSONNEL PRESENT: Ed Burke, Permitting Compliance Manager; Melanie Frohriep, Manager Facility Plant Operations; Angie Ebejer, Environmental Health and Safety.

SAFETY EQUIPMENT REQUIRED: Hard hat, steel-toed boots, and hi-visibility vest.

FACILITY BACKGROUND:

Clean Earth Environmental Solutions, LLC ("Clean Earth"), formerly Stericycle Environmental Solutions, is a waste processing and fuel blending facility located at 421 Lycaste St. (operations) and 515 Lycaste St. (offices) in Detroit, Michigan. The facility is licensed to transfer, store, and process hazardous and non-hazardous wastes, including solvents, waste fuels, paints, and household hazardous wastes. The facility was purchased by Clean Earth, Inc., a subsidiary of Harsco, Inc., in May 2020, at which time the name was changed from Stericycle Environmental Solutions to Clean Earth Environmental Solutions; previous facility names also include Nortru and Petro-Chem.

COMPLAINT/COMPLIANCE HISTORY:

The facility was found to be in noncompliance with several permit conditions during the most recent full compliance evaluation by AQD, completed on September 14, 2018, resulting in the issuance of a Violation Notice on June 11, 2019. The violations included failure to maintain accurate records and failure to perform negative pressure testing. At this time, the violations cited in the June 11, 2019 Violation Notice are considered to be resolved.

Based on its inspection on March 28, 2018, U.S. EPA issued a Finding of Violation (FOV) to "Stericycle, Inc." on June 18, 2018, for violations of 40 CFR Part 63, Subpart DD, 40 CFR Part 61, Subpart FF, and Renewable Operating Permit No. MI-ROP-N0731-2009. These violations included: failure to properly operate the vapor balance system, pressure relief valves, and sampling ports; failure to correctly calibrate VOC monitoring equipment and meet the performance criteria of Method 21 while monitoring; and failure to maintain vapor tight seals on delivery vessels. A copy of this FOV can be found in the facility file. At the time of writing, these violations remain unresolved. Based on a conversation with U.S. EPA Region V staff on November 17, 2020, U.S. EPA is currently in active enforcement negotiations with Clean Earth to resolve these violations.

Clean Earth is required to perform ambient air monitoring per its Part 111, Hazardous Waste Management operating license. The ambient monitoring results have shown periodic spikes of various compounds, including trichloroethylene (TCE), xylene, toluene, and methylene chloride. This issue is ongoing and is currently under evaluation by EGLE - Materials Management Division.

OUTSTANDING CONSENT ORDERS:

There are currently no outstanding consent orders. Facility entered into Consent Agreement and Final Order (CAFO) Docket No. CAA-05-2002-0020 with U.S. EPA on September 30, 2002 and operated under this CAFO until the CAFO was terminated by U.S. EPA on June 24, 2009.

PROCESS DESCRIPTION AND EQUIPMENT:

Clean Earth primarily performs fuel blending of solvent-based wastes, including paint solvents and solvent flush waste. The blended solvents are then sold to cement manufactures to be used as fuel for cement kilns. The facility also performs waste consolidation for off-site disposal.

Waste solvents are delivered to the facility via trucks, either in tankers or in containers (i.e., drums or totes). The offloading of wastes from tankers is performed in the TS1 and TS2 Transfer Pads, permitted under the flexible group FG-TruckTransfer. Drums and totes are unloaded using vac trucks, which are also unloaded in the TS1 and TS2 Transfer Pads. All offloading in the TS1 and TS2 Transfer Pads is performed using vapor balance to control emissions.

During the unloading of tankers and vac trucks, the waste solvents are pumped directly to blending tanks located in the TS1 and TS2 Tank Farms, which are permitted under FG-BlendingTanks. TS1 Tank Farm consists of fifteen 30,000-gallon vertical tanks (EU-TS1Tank 16 through EU-TS1Tank 30) and TS2 Tank Farm consists of six 30,000-gallon vertical tanks (EU-TS2Tank35 through EU-TS2Tank40). The individual tanks as well as the two tank farms are all connected with piping; the materials are transferred between tanks within the two tank farms so that all tanks contain approximately the same quantity and composition of blended material. All tanks in the TS1 and TS2 Tank Farms are equipped with agitators for blending and are controlled with an interconnecting vapor balance system, which equalizes the vapor pressure throughout the tank farms. The tanks are not heated and there is no treatment of material within the tanks, only blending. The contents of the tanks are sampled daily to determine the Btu content, halogen content, percent water, and specific gravity of the materials in the tanks; the tanks are also sampled monthly to determine the VOC and HAP content of the material. Facility personnel perform a daily visual inspection of the tanks to check the structural integrity, corrosion, leaks, valves/connectors, and secondary containment. The facility is also required to perform Leak Detection and Repair (LDAR) monitoring monthly to assure there are no fugitive emissions from equipment leaks.

The TS3 Tank Farm consists of four vertical tanks (two 13,277-gallon tanks and two 10,201-gallon tanks) which are subject to the Resource Recovery and Conservation Act (RCRA) and eight vertical 8,000-gallon tanks which are not subject to RCRA; these tanks are permitted as FG-TS3RCRATANKS and FG-TS3NONRCRATKS, respectively. The tanks are controlled by a vapor balance system. The TS3 Tank Farm had been idled for years but was reconditioned a couple years ago and re-permitted with the issuance of Permit to Install (PTI) No. 6-19; however, the TS3 Tank Farm has not yet been put into operation since the issuance of PTI No. 6-19 and therefore was not evaluated for compliance during this inspection.

The Container Management Building includes a drum segregation/storage area and a lab pack area. The lab pack area is used consolidate compatible small-quantity wastes, often from labs or retail stores, into larger quantities to ship off site for disposal; the facility is operating the lab pack area as exempt from permitting per Rule 284(2)(i). The facility previously operated a pump room located within the Container Management Building, but the pumping operation and associated storage tanks have ceased operation and are no longer permitted, though the tanks currently remain onsite (located outside the east wall of the Container Management Building).

The facility has a natural gas-fired boiler with a heat input of 12.6 MMBtu which is used for building and process heating; this boiler is exempt from permitting per Rule 282(2)(b)(i). There are two other boilers on site that are currently not in use; I was unable to obtain the heat input rating from the boiler plate, but the boilers appear to be similar in size or smaller than the 12.6 MMBtu boiler, so they should also meet the Rule 282(2)(b)(i) exemption.

APPLICABLE RULES/ PERMIT CONDITIONS:

The facility was issued Permit to Install (PTI) No. 6-19 on June 18, 2019, which set limits on emissions of hazardous air pollutants (HAPs) below major source thresholds. The facility had previously been determined to be a major source of HAPs and subject to the federal standards at 40 CFR 63, Subparts DD and EEEE; therefore, the facility was also subject to the Title V permitting program. Due to the rescission of U.S. EPA's "once in, always in" policy in 2018, the issuance of PTI No. 6-19 reclassified the facility as an area source of HAPs and a synthetic minor source (opt-out) with respect to the Title V program. Renewable Operating Permit (ROP) No. MI-ROP-N0731-2009 and PTI Nos. 84-04B, 84-04C, and 184-13 were voided upon issuance of PTI No. 6-19.

Clean Earth is also subject to the following federal standards:
- 40 CFR Part 61, Subpart FF – National Emission Standards for Benzene Waste Operations;
- 40 CFR Part 60, Subpart Kb – Standards of Performance for Volatile Liquid Storage Vessels (including Petroleum Liquid Storage Vessels) for which Construction, Reconstruction, or Modification Commenced after July 23, 1984.

Note: The facility is no longer subject to the following federal standards as an opt-out source under PTI No. 6-19:
- 40 CFR Part 63, Subpart DD – National Emission Standards for Hazardous Air Pollutants from Off-Site Waste and Recovery Operations;
- 40 CFR Part 63, Subpart EEEE – National Emission Standards for Hazardous Air Pollutants: Organic Liquids Distribution (Non-Gasoline).

For this inspection, records from June 2019 through August 2020 were reviewed in determining compliance with the applicable conditions of PTI No. 6-19. Copies of some of these records can be found in the facility file; other records were reviewed on site during the inspection:

PTI No. 6-19, Special Conditions

FG-BlendingTanks: Waste fuel storage tanks – all subject to 40 CFR Part 60 Subpart Kb and 40 CFR Part 61 Subpart FF. All material transfers are conducted using vapor balance. This includes the following emission units: EU-TS1Tank16, EU-TS1Tank17, EU-TS1Tank18, EU-TS1Tank19, EU-TS1Tank20, EU-TS1Tank21, EU-TS1Tank22, EU-TS1Tank23, EU-TS1Tank24, EU-TS1Tank25, EU-TS1Tank26, EU-TS1Tank27, EU-TS1Tank28, EU-TS1Tank29, EU-TS1Tank30, EU-TS2Tank35, EU-TS2Tank36, EU-TS2Tank37, EU-TS2Tank38, EU-TS2Tank39, EU-TS2Tank40

II. MATERIAL LIMITS

1. NOT EVALUATED. There have been no tank cleanouts performed since the last inspection, so this condition was not evaluated.

IV. DESIGN/EQUIPMENT PARAMETERS

1. IN COMPLIANCE. Based on the results of monthly inspections and monitoring, the conservation vents and vapor balance system for all tanks in FG-BlendingTanks appear to be properly installed, maintained, and operated in a satisfactory manner.
2. IN COMPLIANCE. Each tank is installed with high level alarms, pressure/vacuum relief valves, and pumps with automatic cut-off systems.

VI. MONITORING/RECORDKEEPING

1. IN COMPLIANCE. Facility performs inspections and monitoring of the tanks in FG-BlendingTanks in accordance with 40 CFR Part 60, Subparts A and Kb.
2. IN COMPLIANCE. The facility monitors the vapor pressure of the tanks in FG-BlendingTanks every six months, as required.
3. IN COMPLIANCE. The facility maintains all records of inspections and operating information for FG-BlendingTanks in accordance with 40 CFR Part 60, Subparts A and Kb.
4. IN COMPLIANCE. The facility maintains records of the dimensions and capacity of each tank, in accordance with 40 CFR Part 60, Subparts A and Kb.

5. IN COMPLIANCE. The facility maintains records of the vapor pressure of each tank. These records were reviewed on site during the inspection.
6. NOT EVALUATED. Past records indicate that the facility maintains the required records for all tank cleanouts; however, no tank cleanouts have been performed during this compliance period, so this condition was not evaluated during this inspection.

IX. OTHER REQUIREMENTS

1. IN COMPLIANCE. The facility appears to be in compliance with the applicable provisions of 40 CFR Part 60, Subparts A and Kb.

FG-TruckTransfer: Two tanker truck load/unloading pads, each with a vapor balance system. This includes the following emission units: EU-TS1TransferPad, EU-TS2TransferPad

II. MATERIAL LIMITS

1. IN COMPLIANCE. The facility did not exceed the permitted limit of 43,404,000 gallons of material transferred through FG-TruckTransfer per 12-month rolling time period. The highest amount of material transferred during the compliance period was 12,700,018 gallons for the 12-month time period ending December 2019. The total amount transferred at the time of inspection was 10,272,782 gallons for the 12-month rolling time period ending August 2020.

III. PROCESS/OPERATIONAL RESTRICTIONS

1. IN COMPLIANCE. The vapor balance system for FG-TruckTransfer is installed, maintained, and operated as required.
2. IN COMPLIANCE. The facility implements and maintains a malfunction abatement plan (MAP) for the loading rack and vapor balance system, as approved by AQD. The MAP has not required a revision since originally submitted. A copy of the MAP can be found in the facility file.
3. IN COMPLIANCE. The MAP was submitted to AQD within 90 days of issuance of PTI No. 6-19.

IV. DESIGN/EQUIPMENT PARAMETERS

1. IN COMPLIANCE. The facility does not load or unload any vessel unless the vapor balance system is installed and operated as described in this condition. The facility maintains these written procedures in an accessible location where transfers are performed.

VI. MONITORING/RECORDKEEPING

1. IN COMPLIANCE. The facility maintains records of the quantity of material, in gallons, transferred through FG-TruckTransfer on a monthly basis.
2. IN COMPLIANCE. All records are maintained in an acceptable format and made available by the 15th day of each calendar month.
3. IN COMPLIANCE. The facility maintains records of the total amount of each specific product transferred through FG-TruckTransfer on a monthly and 12-month rolling basis. A spot check of these records was performed on site during the inspection.
4. IN COMPLIANCE. The facility maintains records of all monitoring data and actions taken required by the MAP. These records were reviewed on site during the inspection.

FG-TS3NONRCRATANKS: Eight 8,000-gallon oil/oily water storage tanks in Tank System 3. All material transfers are conducted using vapor balance. These tanks are not subject to RCRA. These include the following emission units: EU-TS3TANK61, EU-TS3TANK62, EU-TS3TANK63, EU-TS3TANK64, EU-TS3TANK65, EU-TS3TANK66, EU-TS3TANK67, EU-TS3TANK68

NOT EVALUATED. This flexible group is currently not been in operation during this compliance evaluation period.

FG-TS3RCRATANKS: Four waste fuel storage and blending tanks (two 13,277 gallon and two 10,201 gallon) in Tank System 3. All material transfers are conducted using vapor balance. These tanks may also store alkaline wastes. These tanks are subject to RCRA. These include the following emission units: EU-TS3TANK69, EU-TS3TANK70, EU-TS3TANK71, EU-TS3TANK72

NOT EVALUATED. This flexible group has not been in operation during this compliance evaluation period.

FG-2019: All storage and blending tanks and all transfer pads as of PTI No. 6-19. These include the following emission units: EU-TS1Tank16, EU-TS1Tank17, EU-TS1Tank18, EU-TS1Tank19, EU-TS1Tank20, EU-TS1Tank21, EU-TS1Tank22, EU-TS1Tank23, EU-TS1Tank24, EU-TS1Tank25, EU-TS1Tank26, EU-TS1Tank27, EU-TS1Tank28, EU-TS1Tank29, EU-TS1Tank30, EU-TS2Tank35, EU-TS2Tank36, EU-TS2Tank37, EU-TS2Tank38, EU-TS2Tank39, EU-TS2Tank40, EU-TS3TANK61, EU-TS3TANK62, EU-TS3TANK63, EU-TS3TANK64, EU-TS3TANK65, EU-TS3TANK66, EU-TS3TANK67, EU-TS3TANK68, EU-TS3TANK69, EU-TS3TANK70, EU-TS3TANK71, EU-TS3TANK72, EU-TS1TransferPad, EU-TS2TransferPad

I. EMISSION LIMIT

1. IN COMPLIANCE. The facility did not exceed the permit limit of 6.9 tons of volatile organic compounds (VOCs) per 12-month rolling time period. The highest 12-month rolling total VOC emissions during the compliance period was 1.79 tons for the 12-month rolling time period ending in April 2020. The 12-month rolling total VOC emissions at the time of inspection was 1.75 tons for the 12-month rolling time period ending August 2020.

II. MATERIAL LIMIT

1. IN COMPLIANCE. The facility did not exceed the permit limit of 21,702,000 gallons of material received by tanker truck per 12-month rolling time period. The highest 12-month rolling total material received was 6,350,009 gallons in the 12-month time period ending December 2019. The 12-month total material received at the time of inspection was 5,136,391 gallons for the 12-month time period ending August 2020.

III. PROCESS/OPERATIONAL RESTRICTIONS

1. IN COMPLIANCE. The facility maintains and implements an approved malfunction abatement plan (MAP) for all vapor balance equipment in FG-2019, in accordance with this condition. The facility has not been required to revise the MAP since it was submitted to AQD.
2. IN COMPLIANCE. The facility implements and maintains an approved Leak Detection and Repair (LDAR) program for FG-2019, which contains the requirements listed in this condition.

VI. MONITORING/RECORDKEEPING

1. IN COMPLIANCE. All records and calculations are maintained in an acceptable manner and made available to AQD by the 15th day of the calendar month.
2a and b. IN COMPLIANCE. The facility calculates VOC emissions on a monthly and 12-month rolling time period basis. VOC emission calculations are based on throughput activity, transfer activity, and tank cleanout activity, as required.
3. IN COMPLIANCE. The facility maintains records of the amount of material received by tanker truck on a monthly and 12-month rolling time period basis.
4. IN COMPLIANCE. The facility maintains all monitoring data and actions taken under the MAP. These records were reviewed during the onsite inspection.
5. IN COMPLIANCE. The facility maintains records of all monitoring and corrective actions as specified in the LDAR program. These records were reviewed by AQD during the onsite inspection.
6. NOT EVALUATED. Based on previous inspections, the facility maintains records of all tank cleanouts, including identity of the tank, date(s) cleanout occurred, and composition/vapor pressure of the material in the

tank at time of cleanout. however, no tank cleanouts have been performed during this compliance period, so this condition was not evaluated during this inspection.

VII. REPORTING

1. IN COMPLIANCE. The facility submitted a MAP to the AQD District Supervisor on September 4, 2019, within 90 days of issuance of PTI No. 6-19. The MAP was reviewed and approved by AQD staff. A copy of the plan can be found in the facility file.
2. IN COMPLIANCE. The facility submitted an LDAR program to the AQD District Supervisor on September 4, 2019, within 90 days of issuance of PTI No. 6-19. The LDAR program was reviewed and approved by AQD staff. A copy of the plan can be found in the facility file.

FGFACILITY: The following conditions apply source-wide to all process equipment including equipment covered by other permits, grand-fathered equipment and exempt equipment.

I. EMISSION LIMITS

1. IN COMPLIANCE. No individual HAP exceeded the permit limit of 8.9 tons per 12-month rolling time period. The highest 12-month rolling total for any individual HAP during the compliance period was 0.64 tons of toluene in the 12-month rolling time period ending April 2020. The highest 12-month rolling total for any individual HAP at the time of inspection was 0.63 tons of toluene in the 12-month rolling time period ending August 2020.
2. IN COMPLIANCE. Aggregate HAP emissions did not exceed the permit limit of 22.4 tons per 12-month rolling time period. The highest 12-month rolling total HAP emissions during the compliance period was 1.6 tons in the 12-month rolling time period ending April 2020. The 12-month rolling total HAP emissions at the time of inspection was 1.57 tons in the 12-month rolling time period ending August 2020.

II. MATERIAL LIMITS

1. IN COMPLIANCE. The facility did not process more than 10 megagrams of benzene per 12-month rolling time period in FGFACILITY. The highest 12-month rolling total amount of benzene processed during the compliance period was 0.83 megagrams in the 12-month rolling time period ending December 2019. The 12-month rolling total benzene processed at the time of inspection was 0.30 megagrams in the 12-month time period ending August 2020.

VI. MONITORING/RECORDKEEPING

1. IN COMPLIANCE. All records and calculations are maintained in an acceptable manner and made available to AQD by the 15th day of the calendar month.
2a and b. IN COMPLIANCE. Individual and aggregate HAP emissions calculations maintained on a monthly and 12-month rolling time period basis.
2c. IN COMPLIANCE. HAP Emission calculations are based on actual throughput, composition/sample data of the waste processed, storage tank emission calculations, transfer line clearing activity, and tank cleanout activity.
3. IN COMPLIANCE. The facility monitors the total benzene processed in FGFACILITY on a monthly and 12-month rolling time period basis, in accordance with the Benzene Waste Monitoring Plan.
4. IN COMPLIANCE. The facility monitors emissions and operating and maintenance information in accordance with the National Emission Standards for Hazardous Air Pollutants as specified in 40 CFR Part 61, Subparts A and FF. The records were reviewed by AQD staff during the onsite inspection.
5. IN COMPLIANCE. The facility maintains records of the total benzene processed in FGFACILITY on a monthly and 12-month rolling time period basis.
6. IN COMPLIANCE. The facility maintains records identifying each waste stream subject for 40 CFR Part 61, Subpart FF. All benzene waste processed in FGFACILITY is controlled by the vapor balance system.
7. IN COMPLIANCE. The facility maintains records of emission information and operating and maintenance information in accordance with the requirements of 40 CFR Part 61, Subparts A and FF. This information was reviewed by AQD staff during the onsite inspection.

VII. REPORTING

1. NOT APPLICABLE. The total annual benzene throughput did not exceed 1 megagram for any 12-month rolling time period during the compliance period, so annual reporting is not required.
2. IN COMPLIANCE. The facility submitted a Benzene Waste Monitoring Plan to the AQD District Supervisor on September 4, 2019, within 90 days of issuance of PTI No. 6-19. The Benzene Waste Monitoring Plan was reviewed and approved by AQD staff. A copy of the plan can be found in the facility file.

IX. OTHER REQUIREMENTS

1. IN COMPLIANCE. Based on a review of processing and emissions records, the facility appears to be in compliance with the applicable provisions of 40 CFR Part 61, Subparts A and FF.

FINAL COMPLIANCE DETERMINATION:

At the time of inspection, Clean Earth was determined to be in substantial compliance with the conditions of PTI No. 6-19 and the applicable requirements of 40 CFR 61, Subpart FF and 40 CFR 60, Subpart Kb.

NAME Jonathan Lamb DATE 7/13/2021 SUPERVISOR Jeff Korniski

MICHIGAN DEPARTMENT OF ENVIRONMENT, GREAT LAKES, AND ENERGY
AIR QUALITY DIVISION

June 18, 2019

PERMIT TO INSTALL
6-19

ISSUED TO
Stericycle Environmental Solutions, Inc.

LOCATED AT
421 Lycaste Street
Detroit, Michigan

IN THE COUNTY OF
Wayne

STATE REGISTRATION NUMBER
N0731

The Air Quality Division has approved this Permit to Install, pursuant to the delegation of authority from the Michigan Department of Environment, Great Lakes, and Energy. This permit is hereby issued in accordance with and subject to Section 5505(1) of Article II, Chapter I, Part 55, Air Pollution Control, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended. Pursuant to Air Pollution Control Rule 336.1201(1), this permit constitutes the permittee's authority to install the identified emission unit(s) in accordance with all administrative rules of the Department and the attached conditions. Operation of the emission unit(s) identified in this Permit to Install is allowed pursuant to Rule 336.1201(6).

DATE OF RECEIPT OF ALL INFORMATION REQUIRED BY RULE 203: **June 5, 2019**	
DATE PERMIT TO INSTALL APPROVED: **June 18, 2019**	SIGNATURE:
DATE PERMIT VOIDED:	SIGNATURE:
DATE PERMIT REVOKED:	SIGNATURE:

PERMIT TO INSTALL

Table of Contents

COMMON ACRONYMS

AQD	Air Quality Division
BACT	Best Available Control Technology
CAA	Clean Air Act
CAM	Compliance Assurance Monitoring
CEMS	Continuous Emission Monitoring System
CFR	Code of Federal Regulations
COMS	Continuous Opacity Monitoring System
Department/department/EGLE	Michigan Department of Environment, Great Lakes, and Energy
EU	Emission Unit
FG	Flexible Group
GACS	Gallons of Applied Coating Solids
GC	General Condition
GHGs	Greenhouse Gases
HVLP	High Volume Low Pressure*
ID	Identification
IRSL	Initial Risk Screening Level
ITSL	Initial Threshold Screening Level
LAER	Lowest Achievable Emission Rate
MACT	Maximum Achievable Control Technology
MAERS	Michigan Air Emissions Reporting System
MAP	Malfunction Abatement Plan
MSDS	Material Safety Data Sheet
NA	Not Applicable
NAAQS	National Ambient Air Quality Standards
NESHAP	National Emission Standard for Hazardous Air Pollutants
NSPS	New Source Performance Standards
NSR	New Source Review
PS	Performance Specification
PSD	Prevention of Significant Deterioration
PTE	Permanent Total Enclosure
PTI	Permit to Install
RACT	Reasonable Available Control Technology
ROP	Renewable Operating Permit
SC	Special Condition
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SRN	State Registration Number
TBD	To Be Determined
TEQ	Toxicity Equivalence Quotient
USEPA/EPA	United States Environmental Protection Agency
VE	Visible Emissions

*For HVLP applicators, the pressure measured at the gun air cap shall not exceed 10 psig

POLLUTANT / MEASUREMENT ABBREVIATIONS

acfm	Actual cubic feet per minute
BTU	British Thermal Unit
°C	Degrees Celsius
CO	Carbon Monoxide
CO_2e	Carbon Dioxide Equivalent
dscf	Dry standard cubic foot
dscm	Dry standard cubic meter
°F	Degrees Fahrenheit
gr	Grains
HAP	Hazardous Air Pollutant
Hg	Mercury
hr	Hour
HP	Horsepower
H_2S	Hydrogen Sulfide
kW	Kilowatt
lb	Pound
m	Meter
mg	Milligram
mm	Millimeter
MM	Million
MW	Megawatts
NMOC	Non-Methane Organic Compounds
NO_x	Oxides of Nitrogen
ng	Nanogram
PM	Particulate Matter
PM10	Particulate Matter equal to or less than 10 microns in diameter
PM2.5	Particulate Matter equal to or less than 2.5 microns in diameter
pph	Pounds per hour
ppm	Parts per million
ppmv	Parts per million by volume
ppmw	Parts per million by weight
psia	Pounds per square inch absolute
psig	Pounds per square inch gauge
scf	Standard cubic feet
sec	Seconds
SO_2	Sulfur Dioxide
TAC	Toxic Air Contaminant
Temp	Temperature
THC	Total Hydrocarbons
tpy	Tons per year
µg	Microgram
µm	Micrometer or Micron
VOC	Volatile Organic Compounds
yr	Year

GENERAL CONDITIONS

1. The process or process equipment covered by this permit shall not be reconstructed, relocated, or modified, unless a Permit to Install authorizing such action is issued by the Department, except to the extent such action is exempt from the Permit to Install requirements by any applicable rule. **(R 336.1201(1))**

2. If the installation, construction, reconstruction, relocation, or modification of the equipment for which this permit has been approved has not commenced within 18 months, or has been interrupted for 18 months, this permit shall become void unless otherwise authorized by the Department. Furthermore, the permittee or the designated authorized agent shall notify the Department via the Supervisor, Permit Section, Air Quality Division, Michigan Department of Environment, Great Lakes, and Energy, P.O. Box 30260, Lansing, Michigan 48909-7760, if it is decided not to pursue the installation, construction, reconstruction, relocation, or modification of the equipment allowed by this Permit to Install. **(R 336.1201(4))**

3. If this Permit to Install is issued for a process or process equipment located at a stationary source that is not subject to the Renewable Operating Permit program requirements pursuant to Rule 210 (R 336.1210), operation of the process or process equipment is allowed by this permit if the equipment performs in accordance with the terms and conditions of this Permit to Install. **(R 336.1201(6)(b))**

4. The Department may, after notice and opportunity for a hearing, revoke this Permit to Install if evidence indicates the process or process equipment is not performing in accordance with the terms and conditions of this permit or is violating the Department's rules or the Clean Air Act. **(R 336.1201(8), Section 5510 of Act 451, PA 1994)**

5. The terms and conditions of this Permit to Install shall apply to any person or legal entity that now or hereafter owns or operates the process or process equipment at the location authorized by this Permit to Install. If the new owner or operator submits a written request to the Department pursuant to Rule 219 and the Department approves the request, this permit will be amended to reflect the change of ownership or operational control. The request must include all of the information required by subrules (1)(a), (b), and (c) of Rule 219 and shall be sent to the District Supervisor, Air Quality Division, Michigan Department of Environment, Great Lakes, and Energy. **(R 336.1219)**

6. Operation of this equipment shall not result in the emission of an air contaminant which causes injurious effects to human health or safety, animal life, plant life of significant economic value, or property, or which causes unreasonable interference with the comfortable enjoyment of life and property. **(R 336.1901)**

7. The permittee shall provide notice of an abnormal condition, start-up, shutdown, or malfunction that results in emissions of a hazardous or toxic air pollutant which continue for more than one hour in excess of any applicable standard or limitation, or emissions of any air contaminant continuing for more than two hours in excess of an applicable standard or limitation, as required in Rule 912, to the Department. The notice shall be provided not later than two business days after start-up, shutdown, or discovery of the abnormal condition or malfunction. Written reports, if required, must be filed with the Department within 10 days after the start-up or shutdown occurred, within 10 days after the abnormal conditions or malfunction has been corrected, or within 30 days of discovery of the abnormal condition or malfunction, whichever is first. The written reports shall include all of the information required in Rule 912(5). **(R 336.1912)**

8. Approval of this permit does not exempt the permittee from complying with any future applicable requirements which may be promulgated under Part 55 of 1994 PA 451, as amended or the Federal Clean Air Act.

9. Approval of this permit does not obviate the necessity of obtaining such permits or approvals from other units of government as required by law.

10. Operation of this equipment may be subject to other requirements of Part 55 of 1994 PA 451, as amended and the rules promulgated thereunder.

11. Except as provided in subrules (2) and (3) or unless the special conditions of the Permit to Install include an alternate opacity limit established pursuant to subrule (4) of Rule 301, the permittee shall not cause or permit to be discharged into the outer air from a process or process equipment a visible emission of density greater than the most stringent of the following. The grading of visible emissions shall be determined in accordance with Rule 303 (R 336.1303). **(R 336.1301)**
    a) A six-minute average of 20 percent opacity, except for one six-minute average per hour of not more than 27 percent opacity.
    b) A visible emission limit specified by an applicable federal new source performance standard.
    c) A visible emission limit specified as a condition of this Permit to Install.

12. Collected air contaminants shall be removed as necessary to maintain the equipment at the required operating efficiency. The collection and disposal of air contaminants shall be performed in a manner so as to minimize the introduction of contaminants to the outer air. Transport of collected air contaminants in Priority I and II areas requires the use of material handling methods specified in Rule 370(2). **(R 336.1370)**

13. The Department may require the permittee to conduct acceptable performance tests, at the permittee’s expense, in accordance with Rule 1001 and Rule 1003, under any of the conditions listed in Rule 1001. **(R 336.2001)**

EMISSION UNIT SPECIAL CONDITIONS

EMISSION UNIT SUMMARY TABLE

The descriptions provided below are for informational purposes and do not constitute enforceable conditions.

Emission Unit ID	Emission Unit Description (Including Process Equipment & Control Device(s))	Installation Date / Modification Date	Flexible Group ID
EU-TS1TransferPad	West tanker truck load/unloading pad with vapor balance system		FG-TruckTransfer, FG-2019
EU-TS2TransferPad	Northwest tanker truck load/unloading pad with vapor balance system		FG-TruckTransfer, FG-2019
EU-TS1Tank16	30,000 gallon waste fuel tank 16 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank17	30,000 gallon waste fuel tank 17 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank18	30,000 gallon waste fuel tank 18 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank19	30,000 gallon waste fuel tank 19 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank20	30,000 gallon waste fuel tank 20 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank21	30,000 gallon waste fuel tank 21 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank22	30,000 gallon waste fuel tank 22 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank23	30,000 gallon waste fuel tank 23 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank24	30,000 gallon waste fuel tank 24 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank25	30,000 gallon waste fuel tank 25 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank26	30,000 gallon waste fuel tank 26 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank27	30,000 gallon waste fuel tank 27 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank28	30,000 gallon waste fuel tank 28 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS1Tank29	30,000 gallon waste fuel tank 29 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019

Emission Unit ID	Emission Unit Description (Including Process Equipment & Control Device(s))	Installation Date / Modification Date	Flexible Group ID
EU-TS1Tank30	30,000 gallon waste fuel tank 30 located in the West Tank Farm (formerly PCPG Tank Farm)		FG-TS1BlendTanks, FG-2019
EU-TS2Tank35	30,000 gallon waste fuel tank 35 located in the Northwest Tank Farm (formerly SBS Tank Farm)		FG-TS2BlendTanks, FG-2019
EU-TS2Tank36	30,000 gallon waste fuel tank 36 located in the Northwest Tank Farm (formerly SBS Tank Farm)		FG-TS2BlendTanks, FG-2019
EU-TS2Tank37	30,000 gallon waste fuel tank 37 located in the Northwest Tank Farm (formerly SBS Tank Farm)		FG-TS2BlendTanks, FG-2019
EU-TS2Tank38	30,000 gallon waste fuel tank 38 located in the Northwest Tank Farm (formerly SBS Tank Farm)		FG-TS2BlendTanks, FG-2019
EU-TS2Tank39	30,000 gallon waste fuel tank 39 located in the Northwest Tank Farm (formerly SBS Tank Farm)		FG-TS2BlendTanks, FG-2019
EU-TS2Tank40	30,000 gallon waste fuel tank 40 located in the Northwest Tank Farm (formerly SBS Tank Farm)		FG-TS2BlendTanks, FG-2019
EU-TS3TANK61	8,000 gallon oil/oily water storage tank 61 in Tank System 3, equipped with vapor balance for all material transfers. This tank is not subject to the Resource Conservation and Recovery Act (RCRA).	5-6-2014	FG-TS3NONRCRATKS, FG-2019
EU-TS3TANK62	8,000 gallon oil/oily water storage tank 62 in Tank System 3, equipped with vapor balance for all material transfers. This tank is not subject to RCRA.	5-6-2014	FG-TS3NONRCRATKS, FG-2019
EU-TS3TANK63	8,000 gallon oil/oily water storage tank 63 in Tank System 3, equipped with vapor balance for all material transfers. This tank is not subject to RCRA.	5-6-2014	FG-TS3NONRCRATKS, FG-2019
EU-TS3TANK64	8,000 gallon oil/oily water storage tank 64 in Tank System 3, equipped with vapor balance for all material transfers. This tank is not subject to RCRA.	5-6-2014	FG-TS3NONRCRATKS, FG-2019
EU-TS3TANK65	8,000 gallon oil/oily water storage tank 65 in Tank System 3, equipped with vapor balance for all material transfers. This tank is not subject to RCRA.	5-6-2014	FG-TS3NONRCRATKS, FG-2019
EU-TS3TANK66	8,000 gallon oil/oily water storage tank 66 in Tank System 3, equipped with vapor balance for all material transfers. This tank is not subject to RCRA.	5-6-2014	FG-TS3NONRCRATKS, FG-2019
EU-TS3TANK67	8,000 gallon oil/oily water storage tank 67 in Tank System 3, equipped with vapor balance for all material transfers. This tank is not subject to RCRA.	5-6-2014	FG-TS3NONRCRATKS, FG-2019
EU-TS3TANK68	8,000 gallon oil/oily water storage tank 68 in Tank System 3, equipped with vapor balance for all material transfers. This tank is not subject to RCRA.	5-6-2014	FG-TS3NONRCRATKS, FG-2019

Emission Unit ID	Emission Unit Description (Including Process Equipment & Control Device(s))	Installation Date / Modification Date	Flexible Group ID
EU-TS3TANK69	13,277 gallon waste fuel storage and blending tank 69 in Tank System 3, equipped with vapor balance for all material transfers. This tank may also store alkaline wastes. This tank is subject to RCRA.	5-6-2014	FG-TS3RCRATANKS, FG-2019
EU-TS3TANK70	13,277 gallon waste fuel storage and blending tank 70 in Tank System 3, equipped with vapor balance for all material transfers. This tank may also store alkaline wastes. This tank is subject to RCRA.	5-6-2014	FG-TS3RCRATANKS, FG-2019
EU-TS3TANK71	10,201 gallon waste fuel storage and blending tank 71 in Tank System 3, equipped with vapor balance for all material transfers. This tank may also store alkaline wastes. This tank is subject to RCRA.	5-6-2014	FG-TS3RCRATANKS, FG-2019
EU-TS3TANK72	10,201 gallon waste fuel storage and blending tank 72 in Tank System 3, equipped with vapor balance for all material transfers. This tank may also store alkaline wastes. This tank is subject to RCRA.	5-6-2014	FG-TS3RCRATANKS, FG-2019

Changes to the equipment described in this table are subject to the requirements of R 336.1201, except as allowed by R 336.1278 to R 336.1291.

FLEXIBLE GROUP SPECIAL CONDITIONS

FLEXIBLE GROUP SUMMARY TABLE

The descriptions provided below are for informational purposes and do not constitute enforceable conditions.

Flexible Group ID	Flexible Group Description	Associated Emission Unit IDs
FG-BlendingTanks	Waste fuel storage tanks – all subject to 40 CFR Part 60 Subpart Kb and 40 CFR Part 61 Subpart FF. All material transfers are conducted using vapor balance.	EU-TS1Tank16, EU-TS1Tank17, EU-TS1Tank18, EU-TS1Tank19, EU-TS1Tank20, EU-TS1Tank21, EU-TS1Tank22, EU-TS1Tank23, EU-TS1Tank24, EU-TS1Tank25, EU-TS1Tank26, EU-TS1Tank27, EU-TS1Tank28, EU-TS1Tank29, EU-TS1Tank30, EU-TS2Tank35, EU-TS2Tank36, EU-TS2Tank37, EU-TS2Tank38, EU-TS2Tank39, EU-TS2Tank40
FG-TruckTransfer	Two tanker truck load/unloading pads, each with a vapor balance system.	EU-TS1TransferPad, EU-TS2TransferPad
FG-TS3NONRCRATKS	Eight 8,000 gallon oil/oily water storage tanks in Tank System 3. All material transfers are conducted using vapor balance. These tanks are not subject to RCRA.	EU-TS3TANK61, EU-TS3TANK62, EU-TS3TANK63, EU-TS3TANK64, EU-TS3TANK65, EU-TS3TANK66, EU-TS3TANK67, EU-TS3TANK68
FG-TS3RCRATANKS	Four waste fuel storage and blending tanks (two 13,277 gallon and two 10,201 gallon) in Tank System 3. All material transfers are conducted using vapor balance. These tanks may also store alkaline wastes. These tanks are subject to RCRA.	EU-TS3TANK69, EU-TS3TANK70, EU-TS3TANK71, EU-TS3TANK72
FG-2019	All storage and blending tanks and all transfer pads as of PTI No. 6-19.	EU-TS1Tank16, EU-TS1Tank17, EU-TS1Tank18, EU-TS1Tank19, EU-TS1Tank20, EU-TS1Tank21, EU-TS1Tank22, EU-TS1Tank23, EU-TS1Tank24, EU-TS1Tank25, EU-TS1Tank26, EU-TS1Tank27, EU-TS1Tank28, EU-TS1Tank29, EU-TS1Tank30, EU-TS2Tank35, EU-TS2Tank36, EU-TS2Tank37, EU-TS2Tank38, EU-TS2Tank39, EU-TS2Tank40, EU-TS3TANK61, EU-TS3TANK62, EU-TS3TANK63, EU-TS3TANK64, EU-TS3TANK65, EU-TS3TANK66, EU-TS3TANK67, EU-TS3TANK68, EU-TS3TANK69, EU-TS3TANK70, EU-TS3TANK71, EU-TS3TANK72, EU-TS1TransferPad, EU-TS2TransferPad

FG-BlendingTanks
FLEXIBLE GROUP CONDITIONS

DESCRIPTION

Waste fuel storage tanks – all subject to 40 CFR Part 60 Subpart Kb and 40 CFR Part 61 Subpart FF. All material transfers are conducted using vapor balance.

Emission Unit: EU-TS1Tank16, EU-TS1Tank17, EU-TS1Tank18, EU-TS1Tank19, EU-TS1Tank20, EU-TS1Tank21, EU-TS1Tank22, EU-TS1Tank23, EU-TS1Tank24, EU-TS1Tank25, EU-TS1Tank26, EU-TS1Tank27, EU-TS1Tank28, EU-TS1Tank29, EU-TS1Tank30, EU-TS2Tank35, EU-TS2Tank36, EU-TS2Tank37, EU-TS2Tank38, EU-TS2Tank39, EU-TS2Tank40

POLLUTION CONTROL EQUIPMENT

Vapor balance system connecting all the tanks
Conservation vent for each tank

I. EMISSION LIMIT(S)

NA

II. MATERIAL LIMIT(S)

1. Before beginning cleanout of any tank in FG-BlendingTanks, the permittee shall ensure that no single component of the material last stored in the tank exceeded 40 percent by weight of the material. Water is not subject to this requirement.[1] **(R 336.1225)**

III. PROCESS/OPERATIONAL RESTRICTION(S)

NA

IV. DESIGN/EQUIPMENT PARAMETER(S)

1. The permittee shall not load or unload any tank in FG-BlendingTanks unless the tank's conservation vent and the vapor balance system are installed, maintained, and operated in a satisfactory manner. **(R 336.1224, R 336.1225, R 336.1702(a), R 336.1910)**

2. The permittee shall equip and maintain FG-BlendingTanks with high level alarms and pressure/vacuum relief valves for each tank and with pumps with automatic cut-off systems. **(R 336.1224, R 336.1225, R 336.1702(a), R 336.1910)**

V. TESTING/SAMPLING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

NA

VI. MONITORING/RECORDKEEPING

Records shall be maintained on file for a period of five years, except as noted below. **(R 336.1201(3))**

1. The permittee shall perform inspections and monitor operating information for the tanks in FG-BlendingTanks in accordance with the federal Standards of Performance for New Stationary sources as specified in 40 CFR Part 60 Subparts A and Kb. **(40 CFR Part 60 Subparts A & Kb)**

2. The permittee shall monitor, in a satisfactory manner, the vapor pressure of the contents of each tank in FG-BlendingTanks at least once every six months. **(40 CFR 60.116b(f), 40 CFR Part 60 Subpart Kb)**

3. The permittee shall keep records of inspections and operating information for FG-BlendingTanks in accordance with the federal Standards of Performance for New Stationary sources as specified in 40 CFR Part 60 Subparts A and Kb. The permittee shall keep all records on file at the facility and make them available to the Department upon request. **(40 CFR Part 60 Subparts A & Kb)**

4. The permittee shall keep records of the dimensions of each tank and an analysis showing the capacity in accordance with the federal Standards of Performance for New Stationary Sources as specified in 40 CFR Part 60 Subparts A and Kb. The permittee shall keep this record on file at the facility for the life of the tank and make it available to the Department upon request. **(40 CFR Part 60 Subparts A & Kb)**

5. The permittee shall keep, in a satisfactory manner, records of the vapor pressure of the contents of each tank in FG-BlendingTanks, as required by FG-BlendingTanks SC VI.2. The permittee shall keep all vapor pressure records on file at the facility and make them available to the Department upon request. **(40 CFR 60.116b(f), 40 CFR Part 60 Subpart Kb)**

6. The permittee shall keep, in a satisfactory manner, monthly records of tank cleanouts for FG-BlendingTanks. The records shall identify which tanks were cleaned during the period, the date each tank was cleaned, and the composition of the material last stored in each tank before cleanout. The composition of the material last stored in a tank shall be determined no longer than one month before the cleanout occurs, unless the permittee can demonstrate to the satisfaction of the AQD District Supervisor that older data is adequate for demonstrating compliance with SC II.1 and for calculating emissions from tank cleanout. The permittee shall keep all records on file at the facility and make them available to the Department upon request.[1] **(R 336.1225)**

VII. REPORTING

NA

VIII. STACK/VENT RESTRICTION(S)

NA

IX. OTHER REQUIREMENT(S)

1. The permittee shall comply with all provisions of the federal Standards of Performance for New Stationary Sources as specified in 40 CFR Part 60 Subparts A and Kb, as they apply to each tank in FG-BlendingTanks. **(40 CFR Part 60 Subparts A & Kb)**

Footnotes:

[1] This condition is state only enforceable and was established pursuant to Rule 201(1)(b).

FG-TruckTransfer
FLEXIBLE GROUP CONDITIONS

DESCRIPTION

Two tanker truck load/unloading pads, each with a vapor balance system.

Emission Unit: EU-TS1TransferPad, EU-TS2TransferPad

POLLUTION CONTROL EQUIPMENT

Vapor balance system for each transfer pad.

I. EMISSION LIMIT(S)

NA

II. MATERIAL LIMIT(S)

1. The permittee shall not transfer more than 43,404,000 gallons of material through FG-TruckTransfer per year, based on a 12-month rolling time period as determined at the end of each calendar month. This restriction applies to the sum of the amount of material transferred to the facility through FG-TruckTransfer and the amount of material transferred from the facility through FG-TruckTransfer. **(R 336.1205, R 336.1224, R 336.1225, R 336.1702(a))**

III. PROCESS/OPERATIONAL RESTRICTION(S)

1. The permittee shall install, maintain and operate in a satisfactory manner, a vapor balance system for all organic liquid transfers involving FG-TruckTransfer. **(R 336.1225, R 336.1702(a), R 336.1910)**

2. The permittee shall implement and maintain an approved malfunction abatement plan (MAP) for the loading rack and vapor balance system. The MAP shall include the following:
   a) Recordkeeping provisions for part replacements, repairs and maintenance with respect to the loading control device.
   b) Procedures for maintaining and operating FG-TruckTransfer, the vapor balance system, and any monitoring equipment in a satisfactory manner during malfunction events.
   c) A program for corrective action for all malfunction events.
   d) Schedule of inspections for system integrity.

   If the malfunction abatement plan fails to address or inadequately addresses an event that meets the characteristics of a malfunction at the time the plan is initially developed, the owner or operator shall revise the malfunction abatement plan within 45 days after such an event occurs. **(R 336.1225, R 336.1702(a), R 336.1910, R 336.1911)**

3. No later than 90 days after issuance of PTI No. 6-19, the permittee shall revise the MAP required by SC III.2 to include provisions to ensure that the vapor balance system operates in compliance with SC IV.1 and submit the revised MAP to the AQD District Supervisor for approval. **(R 336.1702(a), R 336.1910, R 336.1911)**

IV. DESIGN/EQUIPMENT PARAMETER(S)

1. The permittee shall not load or unload any delivery vessel unless the vapor balance system is installed, maintained and operated in a satisfactory manner as follows:
   a) The vapor-tight collection line shall be connected to the delivery vessel before any organic compound is transferred.
   b) The vapor-tight collection line shall close upon disconnection so as to prevent release of vapor.

   c) Hatch and other openings on the delivery vessel shall be closed and vapor-tight to prevent emission of displaced vapor during transfer operations, except under emergency conditions.
   d) The liquid transfer line shall be equipped with a device, or a procedure shall be implemented, to prevent liquid drainage from the line when it is disconnected and not in use.

   The permittee shall develop written procedures for the operation of all the control measures described above, and such procedures shall be available in an accessible location near the transfer equipment. **(R 336.1702(a))**

V. TESTING/SAMPLING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

NA

VI. MONITORING/RECORDKEEPING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

1. The permittee shall keep, in a satisfactory manner, monthly records of the quantity of material, in gallons, transferred through FG-TruckTransfer, as required by FG-TruckTransfer SC II.1. The permittee shall keep all records on file at the facility and make them available to the Department upon request. **(R 336.1205, R 336.1224, R 336.1225, R 336.1702(a))**

2. The permittee shall make all required records available in a format acceptable to the AQD District Supervisor by the 15th day of the calendar month, for the previous calendar month, unless otherwise specified in any monitoring/recordkeeping special condition. **(R 336.1225, R 336.1702(a))**

3. The permittee shall keep records of the total amount of material transferred through FG-TruckTransfer of each specific product for each calendar month and 12-month rolling time period. The permittee shall keep all records on file at the facility and make them available to the Department upon request. **(R 336.1225, R 336.1702(a))**

4. The permittee shall keep records of the following:
   a) All monitoring data specified in the approved MAP.
   b) All actions taken under the approved MAP.

   The permittee shall keep all records on file at the facility, in a format acceptable to the AQD District Supervisor, and make them available to the Department upon request. **(R 336.1225, R 336.1910, R 336.1911)**

VII. REPORTING

NA

VIII. STACK/VENT RESTRICTION(S)

NA

IX. OTHER REQUIREMENT(S)

NA

Footnotes:

[1] This condition is state only enforceable and was established pursuant to Rule 201(1)(b).

FG-TS3NONRCRATKS
FLEXIBLE GROUP CONDITIONS

DESCRIPTION

Eight 8,000-gallon oil/oily water storage tanks in Tank System 3. All material transfers are conducted using vapor balance. These tanks are not subject to RCRA.

Emission Unit: EU-TS3TANK61, EU-TS3TANK62, EU-TS3TANK63, EU-TS3TANK64, EU-TS3TANK65, EU-TS3TANK66, EU-TS3TANK67, EU-TS3TANK68

POLLUTION CONTROL EQUIPMENT

All material transfers are conducted using vapor balance.

I. EMISSION LIMIT(S)

NA

II. MATERIAL LIMIT(S)

NA

III. PROCESS/OPERATIONAL RESTRICTION(S)

1. The permittee shall not provide heat to any tank located in FG-TS3NONRCRATKS. **(R 336.1225, R 336.1702)**

IV. DESIGN/EQUIPMENT PARAMETER(S)

1. The permittee shall not load or unload any tank in FG-TS3NONRCRATKS unless the conservation vents and vapor balance system are installed, maintained, and operated in a satisfactory manner. **(R 336.1225, R 336.1702(a), R 336.1910)**

2. The permittee shall equip and maintain each tank in FG-TS3NONRCRATKS with high level alarms and pumps with automatic cut-off systems. **(R 336.1225, R 336.1702(a), R 336.1910)**

V. TESTING/SAMPLING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

NA

VI. MONITORING/RECORDKEEPING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

1. All required calculations shall be completed in a format acceptable to the AQD District Supervisor and made available by the 15th day of the calendar month, for the previous calendar month, unless otherwise specified in any recordkeeping, reporting or notification special condition. **(R 336.1225, R 336.1702(a))**

2. For each load of material received for treatment in FG-TS3NONRCRATKS, on an as received basis, the permittee shall monitor and record, in a satisfactory manner, the following information. Material is determined to be “received for treatment in FG-TS3NONRCRATKS” at the time the material is either treated, blended, or transferred to equipment on site. **(R 336.1225, R 336.1702(a))**
    a) The identification of the waste generator
    b) The waste code
    c) The date, time, and amount of material received for treatment in FG-TS3NONRCRATKS

VII. REPORTING

NA

VIII. STACK/VENT RESTRICTION(S)

NA

IX. OTHER REQUIREMENT(S)

NA

Footnotes:

[1] This condition is state only enforceable and was established pursuant to Rule 201(1)(b).

FG-TS3RCRATANKS
FLEXIBLE GROUP CONDITIONS

DESCRIPTION

Four waste fuel storage and blending tanks (two 13,277 gallon and two 10,201 gallon) in Tank System 3. All material transfers are conducted using vapor balance. These tanks may also store alkaline wastes. These tanks are subject to RCRA.

Emission Unit: EU-TS3TANK69, EU-TS3TANK70, EU-TS3TANK71, EU-TS3TANK72

POLLUTION CONTROL EQUIPMENT

All material transfers are conducted using vapor balance.

I. EMISSION LIMIT(S)

NA

II. MATERIAL LIMIT(S)

Material	Limit	Time Period / Operating Scenario	Equipment	Monitoring / Testing Method	Underlying Applicable Requirements
1. Formaldehyde	0.06 weight %[1]	Instantaneous	FG-TS3RCRATANKS	SC VI.3	R 336.1225

III. PROCESS/OPERATIONAL RESTRICTION(S)

1. The permittee shall not provide heat to any tank located in FG-TS3RCRATANKS. **(R 336.1225, R 336.1702)**

IV. DESIGN/EQUIPMENT PARAMETER(S)

1. The permittee shall not load or unload any tank in FG-TS3RCRATANKS unless the conservation vents and vapor balance system are installed, maintained, and operated in a satisfactory manner. **(R 336.1225, R 336.1702(a), R 336.1910)**

2. The permittee shall equip and maintain each tank in FG-TS3RCRATANKS with high level alarms and pumps with automatic cut-off systems. **(R 336.1225, R 336.1702(a), R 336.1910)**

V. TESTING/SAMPLING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

NA

VI. MONITORING/RECORDKEEPING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

1. All required calculations shall be completed in a format acceptable to the AQD District Supervisor and made available by the 15th day of the calendar month, for the previous calendar month, unless otherwise specified in any recordkeeping, reporting or notification special condition. **(R 336.1225, R 336.1702(a))**

2. For each load of material received for treatment in FG-TS3RCRATANKS, on an as received basis, the permittee shall monitor and record, in a satisfactory manner, the following information. Material is determined to be “received for treatment in FG-TS3RCRATANKS” at the time the material is either treated, blended, or transferred to equipment on site. **(R 336.1225, R 336.1702(a))**

a) The identification of the waste generator.
b) The waste code.
c) The date, time, and amount of material received for treatment in FG-TS3RCRATANKS.

3. The permittee shall keep records of the formaldehyde concentration of each waste fuel received in FG-TS3RCRATANKS. All records shall be kept on file and made available to the Department upon request.[1] **(R 336.1225)**

VII. REPORTING

NA

VIII. STACK/VENT RESTRICTION(S)

NA

IX. OTHER REQUIREMENT(S)

NA

Footnotes:

[1] This condition is state only enforceable and was established pursuant to Rule 201(1)(b).

FG-2019
FLEXIBLE GROUP CONDITIONS

DESCRIPTION

All storage and blending tanks and all transfer pads as of PTI No. 6-19.

Emission Unit: EU-TS1Tank16, EU-TS1Tank17, EU-TS1Tank18, EU-TS1Tank19, EU-TS1Tank20, EU-TS1Tank21, EU-TS1Tank22, EU-TS1Tank23, EU-TS1Tank24, EU-TS1Tank25, EU-TS1Tank26, EU-TS1Tank27, EU-TS1Tank28, EU-TS1Tank29, EU-TS1Tank30, EU-TS2Tank35, EU-TS2Tank36, EU-TS2Tank37, EU-TS2Tank38, EU-TS2Tank39, EU-TS2Tank40, EU-TS3TANK61, EU-TS3TANK62, EU-TS3TANK63, EU-TS3TANK64, EU-TS3TANK65, EU-TS3TANK66, EU-TS3TANK67, EU-TS3TANK68, EU-TS3TANK69, EU-TS3TANK70, EU-TS3TANK71, EU-TS3TANK72, EU-TS1TransferPad, EU-TS2TransferPad

POLLUTION CONTROL EQUIPMENT

Vapor balance system connecting all the tanks
Vapor balance system for each transfer pad

I. EMISSION LIMIT(S)

Pollutant	Limit	Time Period / Operating Scenario	Equipment	Monitoring / Testing Method	Underlying Applicable Requirements
1. VOC	6.9 tpy	12-month rolling time period as determined at the end of each calendar month	FG-2019	SC VI.2	R 336.1205

II. MATERIAL LIMIT(S)

Material	Limit	Time Period / Operating Scenario	Equipment	Monitoring / Testing Method	Underlying Applicable Requirements
1. Material received by tanker truck	21,702,000 gallons per year	12-month rolling time period as determined at the end of each calendar month	FG-2019	SC VI.3	R 336.1205

III. PROCESS/OPERATIONAL RESTRICTION(S)

1. The permittee shall implement and maintain an approved malfunction abatement plan (MAP) for all vapor balance equipment in FG-2019. The MAP shall include the following:
   a) A complete preventative maintenance program
   b) Recordkeeping provisions for part replacements, repairs and maintenance with respect to the vapor balance equipment.
   c) Procedures for maintaining and operating the vapor balance equipment and any monitoring equipment in a satisfactory manner during malfunction events.
   d) A program for corrective action for all malfunction events.

   If the malfunction abatement plan fails to address or inadequately addresses an event that meets the characteristics of a malfunction at the time the plan is initially developed, the owner or operator shall, within 45 days after such an event occurs, revise the malfunction abatement plan and submit the revised MAP to the District Supervisor for review and approval. **(R 336.1205, R 336.1910, R 336.1911)**

2. The permittee shall implement and maintain a leak detection and repair (LDAR) program, approved by the AQD District Supervisor, for FG-2019. The LDAR program shall include the following elements, as a minimum:
   a) An inventory of components, connectors, and other equipment to be monitored.
   b) The monitored concentration constituting a leak.
   c) Monitoring of components, connectors, and other equipment monthly or more often, unless a modified schedule is approved by the AQD District Supervisor.
   d) Calibration of the monitoring instrument.
   e) Records of calibrations.
   f) Repair of all components, connectors, and other equipment with monitored values above the concentration specified to be a leak within 15 days of leak detection, except as allowed in the approved LDAR program.
   g) Records of monitoring results.
   h) Records of repairs.

   (R 336.1205, R 336.1910)

IV. DESIGN/EQUIPMENT PARAMETER(S)

NA

V. TESTING/SAMPLING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

NA

VI. MONITORING/RECORDKEEPING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

1. The permittee shall complete all required calculations and records in a format acceptable to the AQD District Supervisor by the 15th day of the calendar month, for the previous calendar month, unless otherwise specified in any monitoring/recordkeeping special condition. **(R 336.1205, R 336.1910)**

2. The permittee shall record the following information on a monthly basis for FG-2019:
   a) VOC emission calculations determining the monthly emission rate in tons per calendar month.
   b) VOC emission calculations determining the annual emission rate in tons per 12-month rolling time period as determined at the end of each calendar month.

   Emission calculations shall be based on throughput activity, transfer activity including transfer line clearing activity, and tank cleanout activity, or an alternate method acceptable to the AQD District Supervisor. The permittee shall keep the records on file at the facility, in a format acceptable to the AQD District Supervisor, and make them available to the Department upon request. **(R 336.1205)**

3. The permittee shall keep a record of the amount of material received by tanker truck for FG-2019 for each calendar month and for the 12-month rolling time period ending that month. The permittee shall keep the records on file at the facility, in a format acceptable to the AQD District Supervisor, and make them available to the Department upon request. **(R 336.1205)**

4. The permittee shall keep records of the following:
   a) All monitoring data specified in the approved MAP.
   b) All actions taken under the approved MAP.

   The permittee shall keep all records on file at the facility, in a format acceptable to the AQD District Supervisor, and make them available to the Department upon request. **(R 336.1205, R 336.1910, R 336.1911)**

5. The permittee shall keep all records specified in the approved LDAR program on file at the facility, in a format acceptable to the AQD District Supervisor, and make them available to the Department upon request. **(R 336.1205, R 336.1910)**

6. The permittee shall keep a record of the following information for cleanout activity for tanks in FG-2019:
   a) The identity of the tank cleaned out.
   b) The date cleanout occurred.
   c) The composition of the tank when cleanout occurred.

   The permittee shall keep all records on file at the facility, in a format acceptable to the AQD District Supervisor, and make them available to the Department upon request. **(R 336.1205)**

VII. REPORTING

1. No later than 90 days after issuance of PTI No. 6-19, the permittee shall submit an approvable MAP meeting the requirements of SC III.1 to the AQD District Supervisor for approval. **(R 336.1205, R 336.1910, R 336.1911)**

2. No later than 90 days after issuance of PTI No. 6-19, the permittee shall submit an approvable LDAR program meeting the requirements of SC III.2 to the AQD District Supervisor for approval. **(R 336.1205, R 336.1910)**

VIII. STACK/VENT RESTRICTION(S)

NA

IX. OTHER REQUIREMENT(S)

NA

Footnotes:

[1] This condition is state only enforceable and was established pursuant to Rule 201(1)(b).

FGFACILITY CONDITIONS

DESCRIPTION: The following conditions apply source-wide to all process equipment including equipment covered by other permits, grand-fathered equipment and exempt equipment.

POLLUTION CONTROL EQUIPMENT

Vapor balance system connecting all the tanks
Vapor balance system for each transfer pad

I. EMISSION LIMIT(S)

Pollutant	Limit	Time Period / Operating Scenario	Equipment	Monitoring / Testing Method	Underlying Applicable Requirements
1. Individual HAP	Less than 8.9 tpy	12-month rolling time period as determined at the end of each calendar month	FGFACILITY	SC VI.2	R 336.1205
2. Aggregate HAPs	Less than 22.4 tpy	12-month rolling time period as determined at the end of each calendar month	FGFACILITY	SC VI.2	R 336.1205

II. MATERIAL LIMIT(S)

1. The permittee shall not process more than 10 megagrams of benzene from facility waste in FGFACILITY per year, based on a 12-month rolling time period as determined at the end of each calendar month. **(40 CFR 61.342(a))**

III. PROCESS/OPERATIONAL RESTRICTION(S)

NA

IV. DESIGN/EQUIPMENT PARAMETER(S)

NA

V. TESTING/SAMPLING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

NA

VI. MONITORING/RECORDKEEPING

Records shall be maintained on file for a period of five years. **(R 336.1201(3))**

1. The permittee shall complete all required calculations and records in a format acceptable to the AQD District Supervisor by the 15th day of the calendar month, for the previous calendar month, unless otherwise specified in any monitoring/recordkeeping special condition. **(R 336.1205, 40 CFR 61.342(g), 40 CFR Part 61 Subparts A & FF)**

2. The permittee shall keep the following information on a calendar month basis for FGFACILITY:
   a) Individual and aggregate HAP emission calculations determining the monthly emission rate of each in tons per calendar month.
   b) Individual and aggregate HAP emission calculations determining the cumulative emission rate of each during the first 12-months and the annual emission rate of each thereafter, in tons per 12-month rolling time period as determined at the end of each calendar month.

c) Emission calculations shall be based on actual throughput, information on the waste processed and sampling data, storage tank emission calculations such as those in AP-42 Chapter 7.1, transfer line clearing activity, and tank cleanout activity, or an alternative approach acceptable to the AQD District Supervisor.

The permittee shall keep the records on file at the facility, in a format acceptable to the AQD District Supervisor, and make them available to the Department upon request. **(R 336.1205)**

3. The permittee shall monitor, in a satisfactory manner and in accordance with the Benzene Waste Monitoring Plan, the total benzene quantity from facility waste processed in FGFACILITY on a monthly and 12-month rolling time period basis. **(40 CFR 61.342(g), 40 CFR 61.355)**

4. The permittee shall monitor emissions and operating and maintenance information in accordance with the National Emission Standards for Hazardous Air Pollutants as specified in 40 CFR Part 61 Subparts A and FF. **(40 CFR Part 61 Subparts A & FF)**

5. The permittee shall keep, in a satisfactory manner, monthly and 12-month rolling time period records of the total benzene quantity from facility waste processed in FGFACILITY. The permittee shall keep all records on file at the facility and make them available to the Department upon request. **(40 CFR 61.342(g))**

6. The permittee shall maintain records that identify each waste stream at the facility subject to 40 CFR Part 61 Subpart FF, and indicate whether or not the waste stream is controlled for benzene emissions in accordance with 40 CFR Part 61 Subpart FF. In addition, the permittee shall maintain the following records:
   a) For each waste stream not controlled for benzene emissions in accordance with 40 CFR Part 61 Subpart FF, the records shall include all test results, measurements, calculations, and other documentation used to determine the following information for the waste stream: waste stream identification, water content, whether or not the waste stream is a process wastewater stream, annual waste quantity, range of benzene concentrations, annual average flow-weighted benzene concentration, and annual benzene quantity.

   (40 CFR 61.356(b)

7. The permittee shall keep records of emission information and operating and maintenance information to comply with the National Emission Standards for Hazardous Air Pollutants as specified in 40 CFR Part 61 Subparts A and FF, as these standards apply to FGFACILITY. The permittee shall keep all source emissions and operating and maintenance information on file at the facility and make the information available to the Department upon request. **(40 CFR Part 61 Subparts A & FF)**

VII. REPORTING

1. If the total annual benzene throughput from facility waste for FGFACILITY equals or exceeds 1 megagram during any 12-month rolling time period, the permittee shall submit annual reports to the AQD District Supervisor as required by 40 CFR 61.357. **(40 CFR 61.357)**

2. No later than 90 days after issuance of PTI No. 6-19, the permittee shall submit an update to the Benzene Waste Monitoring Plan to the AQD District Supervisor for approval. **(40 CFR 61.354, 40 CFR 61.355)**

VIII. STACK/VENT RESTRICTION(S)

NA

IX. OTHER REQUIREMENT(S)

1. The permittee shall comply with all provisions of the National Emission Standards for Hazardous Air Pollutants as specified in 40 CFR Part 61 Subparts A and FF, as they apply to FGFACILITY. **(40 CFR Part 61 Subparts A & FF)**

Footnotes:

[1] This condition is state only enforceable and was established pursuant to Rule 201(1)(b).

DEA REGISTRATION NUMBER	THIS REGISTRATION EXPIRES	FEE PAID
RN0589551	10-31-2022	$1850
SCHEDULES	BUSINESS ACTIVITY	ISSUE DATE
1,2,2N, 3,3N,4,5	REVERSE DISTRIB	09-07-2021

NORTRU LLC
421 LYCASTE ST
DETROIT, MI 482143434

CONTROLLED SUBSTANCE REGISTRATION CERTIFICATE
UNITED STATES DEPARTMENT OF JUSTICE
DRUG ENFORCEMENT ADMINISTRATION
WASHINGTON D.C. 20537

Sections 304 and 1008 (21 USC 824 and 958) of the Controlled Substances Act of 1970, as amended, provide that the Attorney General may revoke or suspend a registration to manufacture, distribute, dispense, import or export a controlled substance.

THIS CERTIFICATE IS NOT TRANSFERABLE ON CHANGE OF OWNERSHIP, CONTROL, LOCATION, OR BUSINESS ACTIVITY, AND IT IS NOT VALID AFTER THE EXPIRATION DATE.

CONTROLLED SUBSTANCE REGISTRATION CERTIFICATE
UNITED STATES DEPARTMENT OF JUSTICE
DRUG ENFORCEMENT ADMINISTRATION
WASHINGTON D.C. 20537

DEA REGISTRATION NUMBER	THIS REGISTRATION EXPIRES	FEE PAID
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421 LYCASTE ST
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Form DEA-223 (9/2016)

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Process:	Renew License process
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GLWA
Great Lakes Water Authority

Wastewater Operating Services
Industrial Waste Control
9300 W. Jefferson, Ste. 210
Detroit, Michigan 48209

CERTIFIED MAIL

January 29, 2020

Ms. Melanie Frohriep
Stericycle Environmental Solutions, Inc.
515 Lycaste
Detroit, MI 48214

Re: Special Discharge Permit No. SD3-94065
Site: Petro-Chem Processing LLC
421 Lycaste
Detroit, MI 48214

Dear Ms. Frohriep:

Enclosed is your Special Discharge Permit issued by the Great Lakes Water Authority (GLWA) to discharge storm water from tank containment areas from the above site into the Detroit sewer system. The GLWA based this permit on the data and other related information your company submitted to Industrial Waste Control Division.

Your permit contains specific discharge limitations, flow rate, self-monitoring and reporting requirements. The GLWA can rescind this permit at any time if the discharge shows noncompliance with the discharge limitations or if the GLWA determines that the effluent has an adverse effect on the Detroit Wastewater Treatment Plant. Failure to comply with these terms and conditions may result in the immediate permit revocation and appropriate enforcement action.

Should you have any questions, please contact Mr. Mahbubur Bhuiyan, P. E., of the Permits Section, at (313) 297 5839.

Sincerely,

JIBelen

Joe I. Belen, P.E.
Engineer
Industrial Waste Control Group

JB/MB

GLWA
Great Lakes Water Authority

Wastewater Operating Services
Industrial Waste Control
9300 W. Jefferson, Ste. 210
Detroit, Michigan 48209

SPECIAL DISCHARGE PERMIT NO.: SD3-94065

SECTION A: GENERAL INFORMATION

Facility I.D. No.:	94065
Company Name:	Petro-Chem Processing LLC
Facility Address:	421 Lycaste Detroit, MI 48214
Mailing Address:	515 Lycaste Detroit, MI 48214 Ms. Melanie Frohriep 313-557-1591

The Great Lakes Water Authority ("GLWA") hereby authorizes Petro-Chem Processing LLC to discharge stormwater from tank containment areas from the said site into the Detroit sewer system. The GLWA grants this permit in accordance with the company's application and in conformity with plans, specifications, and other substantial data submitted to the GLWA.

All parameters listed in the permit must be analyzed. If there is a need to extend the permit, the company must submit a written request for an extension to the GLWA at least ninety (90) days before the permit's expiration date.

Effective Date:	January 29, 2020
Expiration Date:	December 31, 2024

Authorized by:

JIBelen

Joe I. Belen, P.E.
Engineer
Industrial Waste Control Division

SECTION B: DISCHARGE LIMITATIONS AND MONITORING REQUIREMENT

1. Representative Sampling Location/Discharge Point:

Sampling box adjacent to RTO; 55' S. of north concrete curb; 42' W. of west concrete curb of truck staging area

Table I: The following parameters shall be analyzed and reported as per reporting requirements. (reported in mg/l unless otherwise indicated)

Parameter	Daily Max	Min Sampling Frequency **
Acidity/Alkalinity (pH)	5-11.5 SU	1 per 3 Months
Biochemical Oxygen Demand (BOD)	7500	1 per 3 Months
Arsenic (As)	1	1 per 3 Months
Cadmium (Cd)	1	1 per 3 Months
Chromium (Cr)	25	1 per 3 Months
Copper (Cu)	2.5	1 per 3 Months
Cyanide (Available) (AVCN)	1	1 per 3 Months
Fats, Oil or Grease (FOG)	1500	1 per 3 Months
Iron (Fe)	1000	1 per 3 Months
Lead (Pb)	1	1 per 3 Months
Mercury (Hg)	Non-detect	1 per 3 Months
Nickel (Ni)	5	1 per 3 Months
Phosphorus (P)	250	1 per 3 Months
Silver (Ag)	1	1 per 3 Months
Total PCB (PCB)	Non-detect	1 per 3 Months
Total Phenolic Compounds (4AAP)	1	1 per 3 Months
Total Suspended Solids (TSS)	7500	1 per 3 Months
Zinc (Zn)	7.3	1 per 3 Months
Total Toxic Organics (TTO)	*	1 per 3 Months
Per- and Poly- Fluoroalkyl Substances (PFAS)	*	1 per 3 Months

*See preceding pages for complete TTO and PFAS list and limitations/requirements

Limitations are based on grab samples. All parameters must be analyzed according to methods outlined by EPA in 40 CFR Part 136. The toxic organics must be analyzed with detection limit of 10 µg/l. The detection limit must be indicated in the wastewater analytical report. Matrix interference must be specified where applicable.

Table II: Monitoring Requirements for Total Toxic Organics (TTO)

Purgeable Compounds	Limit	Extractable Compounds	Limit
1,1,1-Trichloroethane	20 ppb	Alpha-BHC	20 ppb
1,1,2,2-Tetrachloroethane	20 ppb	Alpha-Endosulfan or (Endosulfan I)	20 ppb
1,1,2-Trichloroethane	20 ppb	Anthracene	20 ppb
1,1-Dichloroethane	20 ppb	Benzidine	20 ppb
1,1-Dichloroethylene	20 ppb	Benzo (a) Anthracene or (1,2-Benzanthracene)	20 ppb
1,2-Dichlorobenzene	20 ppb	Benzo (a) Pyrene or (3,4-Benzopyrene)	20 ppb
1,2-Dichloroethane	20 ppb	Benzo (b) Fluoranthene or (3,4-Benzofluoranthene)	20 ppb
1,2-Dichloropropane	20 ppb	Benzo (ghi) Perylene or (1,12-Benzoperylene)	20 ppb
1,3-Dichloropropylene or (1,3-Dichloropropene)	20 ppb	Benzo (k) Fluoranthene or (11,12-Benzofluoranthene)	20 ppb
1,2-Trans-Dichloroethylene or (Trans-1,2-Dichloroethene)	20 ppb	Beta-BHC	20 ppb
1,3-Dichlorobenzene	20 ppb	Beta-Endosulfan or (Endosulfan II)	20 ppb
1,4-Dichlorobenzene	20 ppb	Bis (2-Chloroethoxy) Methane	20 ppb
2-Chloroethylvinyl Ether	20 ppb	Bis (2-Chloroethyl) Ether	20 ppb
Acrolein	20 ppb	Bis (2-Chloroisopropyl) Ether	20 ppb
Acrylonitrile	20 ppb	Bis (2-Ethylhexyl) Phthalate	20 ppb
Benzene	20 ppb	Butyl benzyl phthalate or (Benzyl butyl phthalate)	20 ppb
Bromoform or (Tribromomethane)	20 ppb	Chlordane	20 ppb
Carbon Tetrachloride or (Tetrachloromethane)	20 ppb	Chrysene	20 ppb
Chlorobenzene	20 ppb	Delta-BHC	20 ppb
Chlorodibromomethane or (Dibromochloromethane)	20 ppb	Dibenzo (a,h) Anthracene or (1,2,5,6- Dibenzanthracene)	20 ppb
Chloroethane	20 ppb	Dieldrin	20 ppb
Chloroform or (Trichloromethane)	20 ppb	Diethyl Phthalate	20 ppb
Dichlorobromomethane or (Bromodichloromethane)	20 ppb	Dimethyl Phthalate	20 ppb
Ethylbenzene	20 ppb	Di-N-Butyl Phthalate	20 ppb
Methyl Bromide or (Bromomethane)	20 ppb	Di-N-Octyl Phthalate	20 ppb
Methyl Chloride or (Chloromethane)	20 ppb	Endosulfan sulfate	20 ppb
Methylene Chloride or (Dichloromethane)	20 ppb	Endrin	20 ppb
Tetrachloroethylene or (Tetrachloroethene)	20 ppb	Endrin Aldehyde	20 ppb
Toluene	20 ppb	Fluoranthene	20 ppb
Trichloroethylene or (Trichloroethene)	20 ppb	Fluorene	20 ppb
Vinyl Chloride or (Chloroethylene)	20 ppb	Gamma-BHC	20 ppb
Xylene	20 ppb	Heptachlor	20 ppb
Extractable Compounds	**Limit**	Heptachlor Epoxide or (BHC-Hexachlorocyclohexane)	20 ppb
1,2,4-Trichlorobenzene	20 ppb	Hexachlorobenzene	20 ppb
1,2-Diphenylhydrazine	20 ppb	Hexachlorobutadiene	20 ppb
2,3,7,8-Tetrachlorodibenzo-p-Dioxin	20 ppb	Hexachlorocyclopentadiene	20 ppb
2,4,6-Trichlorophenol	20 ppb	Hexachloroethane	20 ppb
2,4-Dichlorophenol	20 ppb	Indeno (1,2,3-cd) Pyrene or (2,3-o-Phenylene Pyrene)	20 ppb
2,4-Dimethylphenol	20 ppb	Isophorone	20 ppb
2,4-Dinitrophenol	20 ppb	Naphthalene	20 ppb
2,4-Dinitrotoluene	20 ppb	Nitrobenzene	20 ppb
2,6-Dinitrotoluene	20 ppb	N-Nitrosodimethylamine	20 ppb
2-Chloronapthalene	20 ppb	N-Nitrosodi-N-Propylamine	20 ppb
2-Chlorophenol	20 ppb	N-Nitrosodiphenylamine	20 ppb
2-Nitrophenol	20 ppb	PCB-1016 or (Arochlor 1016)	Non-detect◆
3,3-Dichlorobenzidine	20 ppb	PCB-1221 or (Arochlor 1221)	Non-detect◆
4,4-DDD or (p,p-TDE)	20 ppb	PCB-1232 or (Arochlor 1232)	Non-detect◆
4,4-DDE or (p,p-DDX)	20 ppb	PCB-1242 or (Arochlor 1242)	Non-detect◆
4,4-DDT	20 ppb	PCB-1248 or (Arochlor 1248)	Non-detect◆
4,6-Dinitro-o-Cresol	20 ppb	PCB-1254 or (Arochlor 1254)	Non-detect◆
4-Bromophenyl Phenyl Ether	20 ppb	PCB-1260 or (Arochlor 1260)	Non-detect◆
4-chloro-3-methyl phenol or (p-Chloro-m-Cresol)	20 ppb	Pentachlorophenol	20 ppb
4-Chlorophenyl Phenyl Ether	20 ppb	Phenanthrene	20 ppb
4-Nitrophenol	20 ppb	Phenol	20 ppb
Acenaphthene	20 ppb	Pyrene	20 ppb
Acenaphthylene	20 ppb	Toxaphene	20 ppb
Aldrin	20 ppb		

◆ Quantification level shall not exceed 0.2 ug/L based on U.S. EPA method 608

Table III: Monitoring Requirements For Per- and Poly- fluoroalkyl Substances (PFAS)

Parameter	Requirement / Limit	Min Sampling Frequency
Perfluorobutanoic acid (PFBA)	Report	1 per 3 Months
Perfluoropentanoic acid (PFPeA)	Report	1 per 3 Months
Perfluorohexanoic acid (PFHxA)	Report	1 per 3 Months
Perfluoroheptanoic acid (PFHpA)	Report	1 per 3 Months
Perfluorooctanoic acid (PFOA)	Report **	1 per 3 Months
Perfluorononanoic acid (PFNA)	Report	1 per 3 Months
Perfluorodecanoic acid (PFDA)	Report	1 per 3 Months
Perfluoroundecanoic acid (PFUnDA)	Report	1 per 3 Months
Perfluorododecanoic acid (PFDoDA)	Report	1 per 3 Months
Perfluorotridecanoic acid (PFTrDA)	Report	1 per 3 Months
Perfluorotetradecanoic acid (PFTeDA)	Report	1 per 3 Months
Perfluorobutane Sulfonic acid (PFBS)	Report	1 per 3 Months
Perfluoropentane Sulfonic acid (PFPeS)	Report	1 per 3 Months
Perfluorohexane Sulfonic acid (PFHxS)	Report	1 per 3 Months
Perfluoroheptane Sulfonic acid (PFHpS)	Report	1 per 3 Months
Perfluorooctane Sulfonic acid (PFOS)	Report **	1 per 3 Months
Perfluorononane Sulfonic acid (PFNS)	Report	1 per 3 Months
Perfluorodecane Sulfonic acid (PFDS)	Report	1 per 3 Months
Perfluorooctane sulfonamide (PFOSA)	Report	1 per 3 Months
4:2 Fluorotelomer sulfonic acid (4:2 FTSA)	Report	1 per 3 Months
6:2 Fluorotelomer sulfonic acid (6:2 FTSA)	Report	1 per 3 Months
8:2 Fluorotelomer sulfonic acid (8:2 FTSA)	Report	1 per 3 Months
N-Ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)	Report	1 per 3 Months
N-Methyl perfluorooctane sulfonamide (N-MeFOSA)	Report	1 per 3 Months

** - See Section E,2

Analytical Requirement: US EPA Method 537 (modified) or ASTM D7979

2. Permit Definition

Petro-Chem Processing LLC is in the business of waste management-fuel blending, solvent reclamination, storage and transfer. The facility was previously classified as an Significant Industrial User (SIU) and since it stopped discharging process wastewater; therefore, from March 2, 2010 the company is no longer an SIU. The company does not generate any process water. The only wastewater for discharge is the boiler blowdown and stormwater. The stormwater from tank containment areas is passed through filter and carbon pretreatment unit prior to discharge into the sewer system.

3. Discharge Flow Rate

The maximum discharge rate from containment site shall not exceed 10,000 gallons per day. Any plans to increase the flow rate must be approved in writing by the GLWA prior to implementation.

SECTION C: MONITORING REQUIREMENTS

1) Analytical Requirements
During the permit's time duration, the company shall monitor and analyze the discharge once every three (3) months.

2) The GLWA may collect independent samples for analysis, or may request "split" portion of the sample the company collected.

SECTION D: REPORTING REQUIREMENTS

1. Quarterly monitoring analytical data shall be submitted on or before 15th day of each quarter (April, July, October and January).

2. In addition to the laboratory analysis, each report shall include the following information:
   - i) Reporting period, date of sampling, sampling location and total flow to date
   - ii) Certification that the analyzed discharge is, or is not in compliance with the permit discharge limits
   - iii) Copy of the maintenance logbook. (Refer to Section E,9)
   - iv) Signature of the company's authorized representative

SECTION E: GENERAL CONDITIONS AND REQUIREMENTS

1. If the sampling performed indicates non-compliance of the permit limitations; the company must:
   - a) Cease the discharge to the Detroit sewer system,
   - b) Notify the Department within 24 hours of becoming aware of the violation, and
   - c) Arrange a meeting with the Industrial Waste Control Division to discuss corrective actions prior to resumption of discharge.

2. If analytical results for PFOS and/or PFOA show above the MDEQ's Water Quality Standards (11 ngms/l for PFOS and 420 ngms/l for PFOA), the company shall upgrade treatment system or install appropriate equivalent technology to remove PFOS and PFOA and maintain PFOS and PFOA concentrations below the Michigan Water Quality Standards

3. The company shall report all interruptions and shutdowns due to rainfall, mechanical breakdowns or other major causes within 24 hours of becoming aware of the event.

4. The company must comply with the General and Specific Pollutant Prohibitions described in the City of Detroit Ordinance 08-05.

5. No other discharge beyond those described and authorized by this permit shall occur without written approval from the GLWA.

6. Non-compliance with any term or condition of this permit shall constitute a violation of the GLWA's sewer use ordinance, and may result in immediate revocation of the permit and appropriate enforcement action.

7. The requirements and conditions established in this permit do not relieve the company of its obligation to comply with any applicable pretreatment regulations, standards, requirements, or laws that may become effective during the term of this permit.

8. The company shall take all necessary precautions to avoid the obstruction of the normal flow of traffic customary to the street(s).

9. The company must maintain a maintenance log. This log shall at least contain dated and timed records of all:

   a. Inspection visits
   b. Changes or replacements of the Activated Carbon Units
   c. Samples taken
   d. Breakdown of operations with:
      i) Reason for breakdown
      ii) Actions taken to prevent reoccurrence of breakdown

10. The company shall notify the GLWA in writing or by telephone at least twenty-four (24) hours prior to initial discharge.

11. The Special Discharge Permit shall not be reassigned or transferred without the written approval of the GLWA

12. The company will be billed for sewer charges based on the current sewer charge rate

13. In the event of slug loading or accidental discharge the Permittee shall telephone the GLWA at the Systems Control Center (313 267 6000) and inform the GLWA about the details of discharge within one (1) hour of becoming aware

14. Any violations of the permit parameter limitations and requirements shall be subjected to a penalty of $500.00 per violation per day.

DEPARTMENT OF LICENSING AND REGULATORY AFFAIRS
BUREAU OF PROFESSIONAL LICENSING
P.O. BOX 30670
LANSING, MI 48909

NORTRU LLC
421 LYCASTE
DETROIT, MI 48214

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P357824

GRETCHEN WHITMER
GOVERNOR

STATE OF MICHIGAN
DEPARTMENT OF LICENSING AND REGULATORY AFFAIRS
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P357043

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Section 2

Environmental Monitoring (B5)

FORM EQP 5111 ATTACHMENT TEMPLATE B5
ENVIRONMENTAL MONITORING PROGRAMS

This document is an attachment to the Michigan Department of Environment, Great Lakes, and Energy's (EGLE) *Form EQP 5111, Operating License Application Form for Hazardous Waste Treatment, Storage, and Disposal Facilities.* See the instructions for Form EQP 5111 for details on how to use this attachment. All references to Title 40 of the Code of Federal Regulations (40 CFR) citations specified herein are adopted by reference in R 299.11003.

The administrative rules promulgated pursuant to Part 111, Hazardous Waste Management, of Michigan's Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (Act 451), R 299.9611 establishes requirements for the environmental monitoring programs for hazardous waste management facilities. Owners and operators of hazardous waste treatment, storage, or disposal facilities must develop an environmental monitoring program capable of detecting a release of hazardous waste or hazardous waste constituents from the facility to groundwater, air, or soil.

This license application template addresses requirements for an environmental monitoring program for hazardous waste management units and the hazardous waste management facility for the Petro-Chem facility. The template includes either a monitoring program description or a demonstration for a waiver from the monitoring requirements in accordance with R 299.9611(3)(a) and (b) and R 299.9611(4) as indicated below:

Groundwater Monitoring Program *(Check as appropriate)*

☒ R 299.9612 compliance monitoring program and sampling and analysis plan for one or more units
☐ Waiver for one or more units

If appropriate, both boxes may be checked if different monitoring programs and waivers apply to the units at the facility.

Ambient Air Monitoring Program (Check as appropriate)

☒ Monitoring program and sampling and analysis plan

☒ Waiver

Annual Soil Monitoring Program (Check as appropriate)

☐ Monitoring program and sampling and analysis plan

☒ Waiver

Ensure that all samples collected for environmental monitoring are collected, transported, analyzed, stored, and disposed by trained and qualified individuals in accordance with the QA/QC Plan. The QA/QC Plan should at a minimum include the written procedures outlined in "Test

Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW-846, Third Edition, Chapter 1 (November 1986), and its Updates.

This form is organized as follows:

B5.A GROUNDWATER MONITORING PROGRAM

[R 299.9611(2)(b) and (3), R 299.9612, and R 299.9629 and 40 CFR, Part 264, Subpart F, except 40 CFR §§264.94(a)(2) and (3), (b), and (c), 264.100, and 264.101]

This section describes the facility's unit-specific groundwater monitoring program as outlined in Table B5.A.1. The basis for determining the groundwater monitoring program for each unit described below is provided in EGLE Form B3 and the 1996 Hydrogeological Report. EGLE form B3 is attached to this application in Volume II which was prepared in accordance with R 299.9506.

B5.A.1 Unit-Specific Groundwater Monitoring Program

Under the direction of the MDEQ/EGLE, the Petro-Chem facility will no longer conduct groundwater sampling in a detection monitoring program. MDEQ/EGLE has indicated that the facility will be required to conduct groundwater sampling through a Corrective Acton groundwater monitoring program.

The facility currently operates and maintains a groundwater monitoring system consisting of twelve monitoring wells labeled MW-1 through MW-12 as shown on Figure B5, attached as Volume IV, Section 2, Appendix B5.1 and provided in the 2021 Groundwater Monitoring report. The parameters and frequency of the sampling and analysis portion of the Groundwater Monitoring Program are provided in Volume IV, Section 2, EGLE Form B5. Section A.3(a).

The basis for determining the groundwater monitoring is also based on the 1996 hydrogeological report referenced in Volume II EGLE Form B3.

Table B5.A.1 Groundwater Monitoring Program

Unit	Name of Unit Subject to Monitoring[1]	Conditional Non-LDF Waiver[2]	No Migration Waiver[3]	Detection Monitoring[4]	Compliance Monitoring[5]	Corrective Action Monitoring[6]
1	**Entire Facility**	**Not Applicable**	**Not Applicable**	**Not Applicable**	**Not Applicable**	**Yes**

B5.A.2 Groundwater Monitoring Program Waiver
[R 299.9611(3)]

The Petro-Chem facility is not seeking a waiver of the groundwater monitoring requirements. Therefore, this section is not applicable.

B5.A.2(a) Other Units
[R 299.9611(3)(a)]

The Petro-Chem facility is not seeking a waiver of the groundwater monitoring requirements. Therefore, this section is not applicable.

B5.A.2(b) No Migration
[R 299.9611(3)(b)]

The Petro-Chem facility is not seeking a waiver of the groundwater monitoring requirements. Therefore, this section is not applicable.

B5.A.3 General Groundwater Monitoring Requirements
[R 299.9612 and 40 CFR §§264.97 and 264.91(b)]

The Petro-Chem facility will comply with the requirements for a groundwater monitoring program by implementing the program described in this section. This program was developed to satisfy the requirements of R 299.9612 and R 299.9629 and 40 CFR §§264.98 and 264.99, except 40 CFR §§264.94(a)(2) and (3) and 264.94(b) and (c). The basis for determining the groundwater monitoring program for each unit is provided in EGLE Form B3, the 1996 Hydrogeologic Report and the Corrective Measures Study, dated November 17, 2016.

The Facility samples and analyzes the groundwater collected from the monitoring wells in conformance with applicable MDEQ/EGLE procedures including scheduling, indicator parameters, and analytical procedures as specified in Section B5.A.3(a).

B5.A.3(a) Sampling and Analysis Plan
[R 299.9611(2)(a)]

A summary of the sampling and analysis plan for groundwater monitoring at the Petro-Chem facility is presented below. The sampling and analysis plan was prepared in accordance with the requirements specified in R 299.9611(2)(a). All sampling and analysis performed pursuant to this application will be consistent with the MDEQ/EGLE Environmental Resource Management Division's Quality Assurance Quality Control Manual for the Sampling and Analysis of Environmental Media Plan (QA/QC Plan). All samples for the purpose of environmental monitoring will be collected, transported, stored, and disposed by trained and qualified individuals.

Groundwater sampling will include collecting and analyzing groundwater samples from the twelve (12) existing groundwater monitoring wells. The samples will be collected utilizing low-flow sampling techniques.

The following procedures will be utilized during sampling activities:

- Measure static water levels (to the nearest 0.01-foot) in each of the monitoring wells utilizing a conductivity sensor well probe. Measurements will be collected from the top of the casing (fixed datum). The elevation of the static water level will be calculated by subtracting the distance from the fixed datum to the static water level from the elevation of the fixed datum.

  Decontamination of the measuring equipment will be conducted to prevent cross contamination between each monitoring well. Decontamination will include a solution of potable water and Alconox.

- Purge the monitoring wells using low-flow purging methods (e.g., using a Horiba D-25 purge pump). It is anticipated that low-flow purging flow rates will be on the order of 0.1 to 0.5 liters per minute (L/min).

- Collect groundwater samples using low-flow sampling methods after each wells indicator parameters (e.g., temperature, pH, and dissolved oxygen, etc.) stabilize during low-flow purging. Field-measured, secondary parameter (pH and Specific Conductance) data will be collected at this time.

Many of the monitoring wells do not yield sufficient groundwater to allow for the stabilization of indicator parameters. When this occurs, the monitoring well will be pumped dry and allowed to recover prior to sampling. Sampling will be conducted on the same day, if there is sufficient recovery; otherwise, the wells will be allowed to recover overnight prior to sampling. Decontamination of the low-flow sampling equipment will be conducted to prevent cross contamination between each monitoring well.

- Groundwater samples will be placed into 40-mL glass containers and field preserved with hydrochloric acid for VOC and gasoline range organics (GRO) analysis. Six containers will be filled for each monitoring well and will contain no headspace or air bubbles.

  Groundwater samples for SVOCs and petroleum distillates (i.e., diesel range organics [DRO]) analysis will be placed into two 1-L amber glass containers.

  Samples collected for analysis will be stored in the field on ice. Appropriate chain-of-custody (COC) documentation will be maintained for the samples. COC documentation will include the sample number, date and time of collection, location, number of containers, requested analyses, and sample handling sequence. Trip blanks will be prepared and follow the samples for appropriate QA/QC documentation. A (blind) duplicate sample and field or equipment blank will also be collected for analysis. A copy of the laboratory QA/QC package and the sampling SOPs are provided in Appendix B5.2.

- Analyze groundwater samples for VOCs, SVOCs and petroleum distillates in accordance with the protocols set forth EPA SW-846 - Test Methods for Evaluating Solid Waste and in accordance with Table 1 of Operation Memo GEN-8, Revision 8.

  Appropriate QA/QC documentation will be provided with each batch of samples. Quality control replicates, laboratory spikes, and control blanks will be analyzed according to standard protocols and in accordance with RRD Operational Memorandum No. 2, Attachments 4 (Sample Preservation, Sample Handling, and Holding Time Specifications) and 6 (Sampling Methods for Volatile Organic Compounds).

- Purge and sampling water collected from the wells will be containerized in a DOT-approved 55-gallon drum and stored onsite for proper disposal.

The sampling and analysis plan meets the requirements included in Waste and Hazardous Materials Division, Quality Assurance and Quality Control Manual for Sampling and Analysis of Environmental Media, Revision 4, dated September 15, 2009

B5.A.3(b) Description of Wells

[R 299.9612 and 40 CFR §264.97(a), (b), and (c)]

The monitoring well network was originally installed at the Facility in 1982; however, some wells have been damaged and relocated, and the well network has expanded. The current monitoring network is shown in Figure B4.2 in Volume IV, Section 1, Appendix 4.2, and consists of 12 wells, Monitoring Wells MW-1 through MW-12. Monitoring Well MW-4 has historically been considered the upgradient well with the remaining wells being compliance wells.

The two-inch-diameter monitoring wells range in depths from 11 to 14 feet below ground surface (bgs) and are constructed with galvanized well casing. The well screens are three feet in length and are stainless steel, with iron core. Two of the monitoring wells are constructed of PVC well casing with a 5-foot PVC well screen. A bentonite grout extends from the ground surface to the top of the well screen. A gravel pack is located beneath the bentonite grout to the final depths of the wells.

The monitoring wells have protective barriers, are clearly labeled, and are securely capped and locked when not in use.

The depth to groundwater is typically 5 to 11 feet bgs. Refer to Attachment B3 in Volume III the 1996 Hydrogeological Report and the 2021 annual ground water monitoring report for additional well information.

B5.A.3(c) Procedure for Establishing Background Quality

[R 299.9612 and 40 CFR §264.97(a)(1) and (g)]

Background has previously been established for the majority of primary parameters identified at concentrations exceeding method detection limits. However, additional primary parameters were added to the list of analytes in 2009. Therefore, background will be established for those parameters following the completion of six sampling events. Following six consecutive sampling events, the mean background values, variance, and standard deviations for each parameter will be calculated.

B5.A.3(d) Statistical Procedures

[R 299.9612 and 40 CFR §§264.97(h) and 264.97(i)(1), (5), and (6)]

Statistical analysis will be performed utilizing the Mann-Kendall non-parametric statistical test. The Mann-Kendall test is used to assess trends in groundwater concentration data. The test compares the most recent groundwater quality datum with the results of earlier rounds. If the most recent concentration is larger than earlier rounds, a score of +1 is assigned. If the most recent concentration is smaller than earlier rounds, a score of -1 is assigned. The total score for the series of data is the Mann-Kendall statistic. The statistic is compared to a critical value to determine if the trend is increasing, decreasing, or if no trend can be determined.

B5.A.4 Detection Monitoring Program

[R 299.9612 and 40 CFR §§264.91(a)(4) and 264.98]

Detection groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.4(a) Indicator Parameters, Waste Constituents, and Reaction Products

[R 299.9506(3)(a) and (f), R 299.9506(4)(a), and R 299.9612 and 40 CFR §264.98(a)]

Detection groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.4(b) Groundwater Monitoring System

[R 299.9612 and 40 CFR §§264.97(a)(2), (b), and (c) and 264.98(b)]

Detection groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.4(c) Background Concentration Values for Proposed Parameters

[R 299.9612 and 40 CFR §§264.98(c) and 264.97(g)(1) and (2)]

Detection groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.4(d) Proposed Sampling and Analysis Procedures

[R 299.9506(3)(e) and R 299.9612 and 40 CFR §§264.97(d), (e), and (f) and 264.98(d), (e), and (f)]

Detection groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.5 Compliance Monitoring Program

Compliance groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.5(a) Hazardous Constituents to be Monitored in Compliance Program

[R 299.9612 and 40 CFR §§264.99(a)(1) and 264.98(g)(3)]

Compliance groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.5(b) Concentration Limits

[R 299.9612 and 40 CFR §§264.99(a)(2) and (c)(3) and 264.97(g) and (h)]

Compliance groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.5(c) Concentration Limit Other than Background
[R 299.9612(d)]

Compliance groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.5(d) Groundwater Monitoring System
[R 299.9612 and 40 CFR §§264.95, 264.97(a)(2) and (c)]

Compliance groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.A.5(e) Sampling and Analysis Procedures
[R 299.9612 and 40 CFR, Sections 264.97(d), (e), and (f) and 264.99(c), (d), (e), (f), and (g)]

Compliance groundwater monitoring is not required at the Facility at this time, as MDEQ/EGLE will require that a corrective action groundwater monitoring program be commenced. Therefore, this section is not applicable.

B5.B AMBIENT AIR MONITORING PROGRAM
[R 299.9611(2)(c) and (4)]

B5.B.1 Sampling and Analysis Plan
[R 299.9611(2)(a)]

Petro-Chem monitors ambient air in accordance with the Hazardous Waste Facility Operating License issued by the Michigan Department of Environmental Quality. Around the perimeter of the facility, there are four locations, with one station having duplicate samplers for QA/QC. Organic samplers are located at each of the four monitoring locations and collect an 8-hour composite sample over a 24-hour period (1 minute on, two minutes off) every six days. Samples are analyzed for: Benzene, Carbon Tetrachloride, Chororform, Methylene Chloride, Tetrachloroethane, Trichloroethylene, Vinyl Chloride, 1,1,1-Trichlorethane, Toluene, and Xylene. The data collected is reported to the Michigan Department of Environmental Quality. The original monitoring plan indicated that once a record of compliance had been established, the facility would request a reduction in the sampling frequency or adjustment in the scope of the monitoring program. Based on analysis of the air monitoring results, the facility is requesting a waiver from the ambient air monitoring program. The formal request memo with supporting analysis is provided in Volume IV, Section 2, Appendix B5.0 Attachment 1.6. The data presented in Attachment 1.6 waiver memorandum supports the reduction of the monitoring locations to only one ambient monitoring location MS2 and analyzing for only TCE on a monthly frequency. In addition, after three months of operations occurring in the new container management building (CMB-2) that will capture and control the loading/unloading commingling emissions with an activated carbon system and if TCE is below the AQD ITSL, all air monitoring requirements should be waived. Until this waiver is approved, the facility will continue to perform the air monitoring as described below.

The current sampling and analysis plan for ambient air monitoring for the facility is summarized below. The sampling and analysis plan was prepared in accordance with the requirements specified in R 299.9611(2)(a). All sampling and analysis performed pursuant to this application will be consistent with the DEQ Environmental Resource Management Division's Quality Assurance Quality Control Manual for the Sampling and Analysis of Environmental Media Plan (QA/QC Plan). All samples for the purpose of environmental monitoring will be collected, transported, stored, and disposed by trained and qualified individuals in accordance with the QA/QC Plan.

The facility currently conducts ambient air monitoring to detect violations of the provisions of Part 55 of Act 451.

The facility completes ambient air monitoring following their Ambient Monitoring Network Plan originally developed in November 1999 and updated in September 2011. A copy of the Ambient Air Monitoring Program has been attached to this document as Volume IV, Section 2, Appendix B5.0, Attachment 1.0 Ambient Air Monitoring Program. The updated Ambient Monitoring Network Plan has been submitted separately from this form. The Ambient Monitoring Network Plan describes Petro-Chem's sampling methodology, sampling locations, sampling schedule, analysis conducted, QA/QC, recordkeeping documents, schedule of monitoring, data evaluation, inspection schedule and suitable response procedures if a non-compliance is detected.

Additionally, as required, the following are included in the Ambient Monitoring Network Plan. The sampling procedure is provided in Volume IV, Section 1, Appendix 5.0, Attachment 1.01. A summary of each of the sections follows:

(1) Sampling locations. Four monitoring locations have been selected and approved by the MDEQ/EGLE. They are located on the northern, eastern, southern and western edges of the property. In addition, the sampling is conducted 2 to 4 meters (6 to 13 feet) above ground level.

(2) Constituents to be monitored and frequency of monitoring. A table of the analytes tested and reported in the program has been provided in Volume IV, Section 2, Appendix B5.0 Attachment 1.3. An eight-hour composite sample is taken over a twenty-four hour period (one minute on and two minutes off) using Suma canasters. Compounds are sampled every 6 days. A letter to EGLE dated May 17, 2016 summarized a modification of the ambient air monitoring plan from using Method TO-17 to Method TO-15 (Suma Canister method). A copy of this letter is provided in Volume IV, Section 2, Appendix B5.0, Attachment 1.5.

(3) Procedures to maintain integrity of monitoring devices. Monitoring is conducted by Petro-Chem. The monitoring devices are serviced at regular intervals and calibrated prior to each sampling event. Devices may also be supplied by a third part (subcontractor). The subcontractor is responsible to maintain the integrity of their monitoring devices. Petro-Chem verifies that device integrity is intact by collecting a field blank and field duplicate. Additionally, laboratory QA/QC, including a laboratory spike, is completed in accordance

with EPA Method TO-15. A copy of TO-15 has been provided in Volume IV, Section 2, Appendix 5.0 Attachment 1.4.

(4) Sample collection and preservation. Sampling is performed in accordance to EPA Method TO-15, Method for the Determination of Volatile Organic Compounds in Ambient Air using Suma canisters.

(5) Analytical methods. Analysis is performed in accordance to EPA Method TO-15, Method for the Determination of Volatile Organic Compounds in Suma canisters.

(6) The procedure for sampling is attached in Volume IV, Section 1, Appendix 5.0, Attachment 1.01.

Revaluation: Laboratory data will be evaluated and reviewed for compliance with the proper QA/QC procedures. Including; (1) proper sample handling (strict chain-of-custody documentation), (2) field blank analysis and results, (3) field duplicate analysis and results to determine if results are within 25% of each other, and (4) laboratory spike data.

(7) Appropriate response procedures. Petro-Chem will review analytical data for compliance with ambient air monitoring limits. If analytical data results or current site conditions are found to poses a danger to human health or the environment, Petro-Chem will notify MDEQ/EGLE immediately.

The facility will notify MDEQ/EGLE of all other non-compliance issues within 30 days or during the normal monthly reporting period, whichever is sooner.

B5.C ANNUAL SOIL MONITORING PROGRAM

[R 299.9611(2)(d) and (4)]

B5.C.1 Sampling and Analysis Plan

[R 299.9611(2)(a)]

The facility requested and was granted a waiver under R299.9611(2)(d) from soil monitoring requirements as part of the previous permit. There have been no significant changes to the facility, in regard to engineering controls in place, facility procedures and geological conditions. The majority of the facility's footprint is concrete covered, including all loading and unloading areas. A gravel parking area is used as a staging area for vehicles, no transfer or long-term storage is utilized in this area. Soils under the facility are a mixture of fill with underlying layers of thick dense natural clays which provide a naturally low permeability barrier to fluid movement.

Refer to Attachment B3, Volume III of this application and the 1996 Hydrogeological Report for additional information regarding geology at the site.

Appendix B5.0

Ambient Air Monitoring Program

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October 19, 2011

Mr. Jeffrey Davis
PSC Environmental Services
Director, Program Compliance
3428 SW 15th Street
Deerfield Beach, Florida 33442

Bureau Veritas Project No. 11010-000175.00

Subject: Form EQP 5111 Attachment B4 – Environmental Assessment and the Ambient Monitoring Network Plan – UPDATE 2.0

Dear Mr. Davis:

Bureau Veritas North America, Inc. is pleased to present our second updated Form EQP 5111 Attachment B4 – Environmental Assessment document and Ambient Monitoring Network Plan for the Petro-Chem Processing Group of Nortru, LLC located in Detroit, Michigan.

We appreciate the opportunity to be of service. If you have any questions, please contact me at 248.344.3018 or by e-mail at michele.strickland@us.bureauveritas.com.

Sincerely,

Michele J Strickland

Michele J. Strickland
Project Manager
Health, Safety, and Environmental Services
Detroit Regional Office

Enclosure

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Ambient Monitoring Network Plan

Prepared for:

Petro-Chem Processing Group of Nortru, LLC

Site ID No. MID 980 615 298

421 Lycaste Street
Detroit, Michigan

Bureau Veritas Project Number: 11010-000175.00.002
October 2011

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SECTION ***PAGE***

1.0 INTRODUCTION

At the request of Petro-Chem Processing Group of Nortru, LLC. (PCPG), Bureau Veritas prepared this work plan to conduct an ambient air monitoring network for the PCPG plant located at 421 Lycaste in Detroit, Michigan. Four locations will be monitored for a select list of volatile organic compounds (VOCs) in the program. The network will be monitored continually in conjunction with the requirements of the Part B Hazardous Waste Operating License. PCPG will provide a written request for decreased monitoring requirements at a future date based on monitoring results.

The following sections detail PCPG's technical approach for conducting the requested ambient air monitoring.

2.0 AMBIENT AIR MONITORING

The following subsections detail the sampling methodology, sampling locations and frequency of sampling to be implemented in the monitoring network.

2.1 SAMPLING METHODOLOGY

Sampling will be performed in accordance to EPA Method TO-17, Method for the Determination of Volatile Organic Compounds in Ambient Air using Active Sampling onto sorbent tubes (make: Perkin Elmer glass sorbent tubes, model: Automatic Thermo Desorbers, Type: Carbopack C, Carbopack B, Carboxen 1000). A copy of this method in included in Appendix A.

Ambient air is drawn through a sorbent packing and certain VOCs are trapped on the adsorbent media while highly volatile organic compounds and most inorganic atmospheric constituents pass through the packing. The sorbent tubes are transferred to a laboratory for analysis.

Samples will be collected by drawing a known volume of air through the media using a calibrated flow pump. Precautions to minimize breakthrough and obtain a completeness of objective of 85% will be taken. Based on literature information, a combination tube and an air volume of approximately 4 liters will be used.

An eight-hour composite sample will be taken over a twenty-four hour period (one minute on, and two minutes off) using low flow sampling pumps.

A data sheet will be maintained an each sampling location that contains the following information:

- Sampling location;
- Sample collection start time;
- Flow rate calibration data;
- Flow rate;
- Cartridge number; and

- Serial number,

The following meteorological data will be obtained from Detroit City airport throughout the sampling effort:

- Ambient temperature;
- Wind Speed;
- Wind Direction;
- Barometric Pressure; and
- Relative humidity.

2.2 SAMPLE LOCATIONS

Four monitoring locations have been selected in accordance with 40 CFR 58 and "Design Criteria for Source Specific Non-Criteria Ambient Air Monitoring Networks for Act 64 Activities (November 9, 1987)". These four locations have been agreed to with the Michigan Department of Environmental Quality (MDEQ). A site diagram showing the locations of the ambient air sampling stations is provided in the attached Figure – Detroit Monitoring Stations. A description of each of these locations is as follows:

- Site #1 – Located at the northern extreme of the PCPG complex just inside the existing fence line;
- Site #2 – Located south of the laboratory at the eastern edge of the site;
- Site #3 – Located at the southern edge of the site, approximately one hundred feet west of the main processing building; and
- Site #4 – Located along the western edge of the site at St. Jean Street, approximately one hundred sixty feet north of Freud Street.

All sampling locations are within the PCPG fence line; however, they will be considered representative of ambient air in the proximity of the complex. In addition, sampling is conducted at 2 to 4 meters (6 to 13 feet) above ground level.

2.3 SAMPLING SCHEDULE

A sample will be collected from each location every sixth day.

Once a year of valid data is collected, PCPG will evaluate the results and a reduction in sampling may be requested. Note that MDEQ defines "valid data" as being 75% complete and having laboratory QA/QC data that is acceptable to MDEQ, Air Quality Division (AQD).

2.4 INSPECTION SCHEDULE

PCPG will inspect equipment associated with the ambient air monitoring procedures (e.g., pumps, tubing, sorbet tubes, etc.) on a regular basis and prior to sampling to ensure it is in good working order. All areas of the facility will be inspected in relation to the ambient air network every sixth day, during sampling.

In addition, air pumps are serviced at regular intervals and calibrated prior to each sampling event.

3.0 ANALYSIS

Analysis will be performed in accordance with EPA Method TO-17. The following subsections present a general description of the analytical methodology, the analyte list and associated detection limits, and project specific quality assurance/quality control requirements.

3.1 SAMPLING METHODOLOGY

The sorbent tube (make: Perkin Elmer glass sorbent tubes, model: Automatic Thermo Desorbers, Type: Carbopack C, Carbopack B, Carboxen 1000) is initially dry purged with dry, inert gas before analysis to remove water vapor and air. The tube then undergoes thermal desorption with analyte refocusing on a secondary trap. The trap next undergoes rapid desorption and injection/transfer of the target analytes into a gas chromatograph. Compounds are separated by high-resolution capillary gas chromatography. Specific analytes are quantified using mass spectrometry.

3.2 ANALYTES

The following table is a list of the analytes to be reported in the program along with the required detection limits:

COMPOUND	DETECTION LIMIT (µg/m^3)
Benzene	0.05
Carbon Tetrachloride	0.01
Chloroform	0.01
Methylene Chloride	0.03
Tetrachloroethene	0.05
Trichloroethene	0.02
Vinyl Chloride	0.01
1,1,1-Trichloroethane	1.5
Toluene	1.0
Xylene	1.0

3.3 QUALITY ASSURANCE/QUALITY CONTROL

Collection of an accurately known volume of air is critical to the accuracy of the results; therefore, flow rate calibrations will be made for each sampling train prior to, and after each sample collection. In addition, the following QA/QC samples will be collected:

- Field Blank – During each sampling event, one clean sorbent tube will accompany the samples to the field and back to the laboratory without being used for sampling; and

- Field Duplicate – At one location during each sampling event, a parallel sample will be drawn to insure the reproducibility of the sampling methods. Parallel samples should be within approximately 25% of one another. If not, subsequent sampling events should have modified flow rates and sampling intervals.

Laboratory QA/QC will be in accordance with EPA Method TO-17 that includes a laboratory spike.

In addition, PCPG has the air pumps services at regular intervals and calibrated before each sampling event.

4.0 DOCUMENTATION AND DATA EVALUATION

PCPG will receive and review analytical results from each sampling event from the third party laboratory.

Laboratory data will be reviewed for compliance with the proper QA/QC procedures. Including; (1) proper sample handling (strict chain-of-custody documentation), (2) field blank analysis and results, (3) field duplicate analysis and results to determine if results are within 25% of each other, and (4) laboratory spike data.

PCPG will monitor and record weather and site condition data as related to the ambient air sampling.

PCPG will continue to use the existing excel spreadsheets for data input and interpretation. Once the data has been input into the excel spreadsheet it will be reviewed for compliance with limits as specified by MDEQ.

Written reports will be submitted to MDEQ Air Monitoring Unit within thirty (30) days of the end of each month that the data was collected. Results will be submitted to MDEQ electronically via email.

Each report will be submitted in an agreed upon format and include the following information:

- Results of all samples collected;
- QA/QC data;
- Lab blank data;
- Field and field calibration data; and
- Meteorological data.

Meteorological data will be obtained from Detroit City Airport (located four miles north of the site) and will be considered representative of meteorological conditions at the site. If ambient air monitoring data indicate emission levels are of a magnitude to effect health and welfare of the community, a micro-meteorological station will be installed on site to more accurately access emissions.

5.0 RESPONSE PROCEDURES

PCPG will review analytical data for compliance with ambient air monitoring limits. If analytical data results or current site conditions are found to be a non-compliance that poses a danger to human health or the environment, PCPG will notify MDEQ immediately of the non-compliance.

PCPG will notify MDEQ of all other non-compliance issues within 30 days or during the normal monthly reporting period, which ever is sooner.

6.0 SCHEDULE

PCPG will continue sampling each of the four parameter locations every sixth day. Once a year of valid data is collected, PCPG will evaluate the results and a reduction in sampling may be requested.

APPENDIX A

EPA Method TO-17

EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-17

Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

January 1999

Method TO-17
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This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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DISCLAIMER

METHOD TO-17

Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes

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METHOD TO-17

Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes

1. Scope

1.1 This document describes a sorbent tube/thermal desorption/gas chromatographic-based monitoring method for volatile organic compounds (VOCs) in ambient air at 0.5 to 25 parts per billion (ppbv) concentration levels. Performance criteria are provided as part of the method in Section 14. EPA has previously published Compendium Method TO-1 describing the use of the porous polymer Tenax® GC for sampling nonpolar VOCs and Compendium Method TO-2 describing the use of carbon molecular sieve for highly volatile, nonpolar organics (1). Since these methods were developed, a new generation of thermal desorption systems as well as new types of solid adsorbents have become available commercially. These sorbents are used singly or in multisorbent packings. Tubes with more than one sorbent, packed in order of increasing sorbent strength are used to facilitate quantitative retention and desorption of VOCs over a wide volatility range. The higher molecular weight compounds are retained on the front, least retentive sorbent; the more volatile compounds are retained farther into the packing on a stronger adsorbent. The higher molecular weight compounds never encounter the stronger adsorbents, thereby improving the efficiency of the thermal desorption process.

1.2 A large amount of data on solid adsorbents is available through the efforts of the Health and Safety Laboratory, Health and Safety Executive (HSE), Sheffield, United Kingdon (UK). This group has provided written methods for use of solid adsorbent packings in monitoring workplace air. Some of their documents on the subject are referenced in Section 2.2. Also, a table of information on safe sampling volumes from their research is provided in Appendix 1.

1.3 EPA has developed data on the use of solid sorbents in multisorbent tubes for concentration of VOCs from the ambient air as part of its program for methods development of automated gas chromatographs. The experiments required to validate the use of these sorbent traps include capture and release efficiency studies for given sampling volumes. These studies establish the validity of using solid adsorbents for target sets of VOCs with minimal (at most one hour) storage time. Although questions related to handling, transport and storage of samples between the times of sampling and analysis are not addressed, these studies provide information on safe sampling volumes. Appendix 2 delineates the results of sampling a mixture of humidified zero air and the target VOCs specified in the Compendium Method TO-14 (2) using a specific multisorbent.

1.4 An EPA workshop was convened in November of 1995 to determine if a consensus could be reached on the use of solid sorbent tubes for ambient air analysis. The draft method available at the workshop has evolved through several reviews and modifications into the current document. The method is supported by data reported in the scientific literature as cited in the text, and by recent experimental tests performed as a consequence of the workshop (see Table 1).

1.5 The analytical approach using gas chromatography/mass spectroscopy (GC/MS) is identical to that mentioned in Compendium Method TO-15 and, as noted later, is adapted for this method once the sample has been thermally desorbed from the adsorption tube onto the focusing trap of the analytical system.

1.6 Performance criteria are given in Section 14 to allow acceptance of data obtained with any of the many variations of sampling and analytical approaches.

2. Summary of Method

2.1 The monitoring procedure involves pulling a volume of air through a sorbent packing to collect VOCs followed by a thermal desorption-capillary GC/MS analytical procedure.

2.2 Conventional detectors are considered alternatives for analysis subject to the performance criteria listed in Section 14 but are not covered specifically in this method text.

2.3 Key steps of this method are listed below.

2.3.1 Selection of a sorbent or sorbent mix tailored for a target compound list, data quality objectives and sampling environment.

2.3.2 Screening the sampling location for VOCs by taking single tube samples to allow estimates of the nature and amount of sample gases.

2.3.3 Initial sampling sequences with two tubes at nominally 1 and 4 liter total sample volumes (or appropriate proportional scaling of these volumes to fit the target list and monitoring objectives).

2.3.4 Analysis of the samples and comparison to performance criteria.

2.3.5 Acceptance or rejection of the data.

2.3.6 If rejection, then review of the experimental arrangement including repeat analysis or repeat analysis with backup tubes and/or other QC features.

[Note: EPA requires the use of distributed volume pairs (see Section14.4) for monitoring to insure high quality data. However, in situations where acceptable data have been routinely obtained through use of distributed volume pairs and the ambient air is considered well characterized, cost considerations may warrant single tube sampling. Any attendant risk to data quality objectives is the responsibility of the project's decision maker.]

2.4 Key steps in sample analysis are listed below.

2.4.1 Dry purge of the sorbent tube with dry, inert gas before analysis to remove water vapor and air. The sorbent tube can be held at temperatures above ambient for the dry purge.

2.4.2 Thermal desorption of the sorbent tube (primary desorption).

2.4.3 Analyte refocusing on a secondary trap.

2.4.4 Rapid desorption of the trap and injection/transfer of target analytes into the gas chromatograph (secondary desorption).

2.4.5 Separation of compounds by high resolution capillary gas chromatography (GC).

2.4.6 Measurement by mass spectrometry (MS) or conventional GC detectors (only the MS approach is explicitly referred to in Compendium Method TO-17; an FID/ECD detector combination or other GC detector can be used if Section 14 criteria are met. However, no explicit QA guidelines are given here for those alternatives).

2.5 The target compound list (TCL) is the same as listed in Compendium Method TO-15 (i.e., subsets of the 97 VOCs listed as hazardous pollutants in Title III of the Clean Air Act Amendments of 1990). Only a portion of these compounds has been monitored by the use of solid adsorbents. This method provides performance criteria to demonstrate acceptable performance of the method (or modifications of the method) for monitoring a given compound or set of compounds.

3. Significance

3.1 This method is an alternative to the canister-based sampling and analysis methods that are presented in Compendium Methods TO-14 and TO-15 and to the previous sorbent-based methods that were formalized as Compendium Methods TO-1 and TO-2. All of these methods are of the type that include sampling at one location, storage and transport of the sample, and analysis at another, typically more favorable site.

3.2 The collection of VOCs in ambient air samples by passage through solid sorbent packings is generally recognized to have a number of advantages for monitoring. These include the following:

- The small size and light weight of the sorbent packing and attendant equipment.
- The placement of the sorbent packing as the first element (with the possible exception of a filter or chemical scrubber for ozone) in the sampling train so as to reduce the possibility of contamination from upstream elements.
- The availability of a large selection of sorbents to match the target set of compounds including polar VOC.
- The commercial availability of thermal desorption systems to release the sample from the sorbent and into the analytical system.
- The possibility of water management using a combination of hydrophobic sorbents (to cause water breakthrough while sampling); dry gas purge of water from the sorbent after sampling; and splitting of the sample during analysis.
- The large amount of literature on the use of sorbent sampling and thermal desorption for monitoring of workplace air, particularly the literature from the Health and Safety Executive in the United Kingdom.

3.3 Accurate risk assessment of human and ecological exposure to toxic VOCs is an important goal of the U. S. Environmental Protection Agency (EPA) with increased emphasis on their role as endocrine disrupters. Accurate data is fundamental to reaching this goal. The portability and small size of typical sampling packages for sorbent-based sampling and the wide range of sorbent choices make this monitoring approach appealing for special monitoring studies of human exposure to toxic gases and to use in network monitoring to establish prevalence and trends of toxic gases. Microenvironmental and human subject studies are typical of applications for Compendium Method TO-17.

3.4 Sorbent-based monitoring can be combined with canister-based monitoring methods, on-site autoGC systems, open path instrumentation, and other specialized point monitoring instruments to address most monitoring needs for volatile organic gases. More than one of these approaches can be used simultaneously as a means to check and insure the quality of the data being produced.

3.5 In the form specified in Compendium Method TO-17, sorbent sampling incorporates the distributed volume pair approach that provides inherently defensible data to counter questions of sample integrity, operator performance, equipment malfunction during sampling, and any other characteristic of sample collection that is not linear with sampling volume.

3.6 In keeping with the consensus of EPA scientists and science advisors, the method is performance-based such that performance criteria are provided. Any modification of the sorbent approach to monitoring for VOCs can be used provided these criteria are met.

4. Applicable Documents

4.1 ASTM Standards

- Method D1356 *Definition of Terms Relating to Atmospheric Sampling and Analysis*
- Method E260 *Recommended Practice for General Gas Chromatography*
- Method E355 *Practice for Gas Chromatography Terms and Relationships*

4.2 EPA Documents

- *Technical Assistance Document for Sampling and Analysis Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Quality Assurance Handbook for Air Pollution Measurement Systems*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Methods TO-1 and TO-2*, U. S. Environmental Protection Agency, EPA 600/4-84-041, April 1984.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14, Second Supplement*, U. S. Environmental Protection Agency, EPA 600/4-89-018, March 1989.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-15*, U. S. Environmental Protection Agency, EPA 625/R-96-010b, January 1997.

4.3 Other Documents

- MDHS 3 - Generation of Test Atmospheres of Organic Vapors by the Syringe Injection Technique, *Methods for the Determination of Hazardous Substances (MDHS)*, Health and Safety Laboratory, Health and Safety Executive, Sheffield, UK.
- MDHS 4 - Generation of Test Atmospheres of Organic Vapors by the Permeation Tube Method, *Methods for the Determination of Hazardous Substances (MDHS)*, Health and Safety Laboratory, Health and Safety Executive, Sheffield, UK.
- MDHS 72 - Volatile Organic Compounds in Air, *Methods for the Determination of Hazardous Substances (MDHS)*, Health and Safety Laboratory, Health and Safety Executive, Sheffield, UK.
- TAD - *Technical Assistance Document (TAD) on the Use of Solid Sorbent-based Systems for Ambient Air Monitoring*, Perkin Elmer Corp., 50 Danbury Rd., Wilton, CT 06897, USA.

5. Definitions

[Note: Definitions used in this document and any user-prepared Standard Operating Procedures (SOPs) should be consistent with those used in ASTM D1356. All abbreviations and symbols are defined within this document at the point of first use.]

5.1 Thermal Desorption-the use of heat and a flow of inert (carrier) gas to extract volatiles from a solid or liquid matrix directly into the carrier gas and transfer them to downstream system elements such as the analytical column of a GC. No solvent is required.

5.2 Two-stage Thermal Desorption-the process of thermally desorbing analytes from a solid or liquid matrix, reconcentrating them on a focusing tube and then rapidly heating the tube to ?inject" the concentrated compounds into the GC system in a narrow band of vapor compatible with high resolution capillary gas chromatography.

5.3 Sorbent Tube (Also referred to as 'tube' and 'sample tube')-stainless steel, glass or glass lined (or fused silica lined) stainless steel tube, typically 1/4 inch (6 mm) O.D. and of various lengths, with the central portion packed with greater than 200 mg of solid adsorbent material, depending on density and packing bed length. Used to concentrate VOCs from air.

5.4 Focusing Tube-narrow (typically <3mm I.D.) tube containing a small bed of sorbent, which is maintained near or below ambient temperature and used to refocus analytes thermally desorbed from the sorbent tube. Once all the VOCs have been transferred from the sorbent tube to the focusing tube, the focusing tube is heated very rapidly to transfer the analytes into the capillary GC analytical column in a narrow band of vapor.

5.5 Cryogen (Also referred to as 'cryogenic fluid')-typically liquid nitrogen, liquid argon, or liquid carbon dioxide. In the present context, cryogens are used in some thermal desorption systems to cool the focusing tube.

5.6 High Resolution Capillary Column Chromatography-conventionally describes fused silica capillary columns with an internal diameter of 320 µm or below and with a stationary phase film thickness of 5 µm or less.

5.7 Breakthrough Volume (BV)-volume of air containing a constant concentration of analyte which may be passed through a sorbent tube before a detectable level (typically 5%) of the analyte concentration elutes from the nonsampling end. Alternatively, the volume sampled when the amount of analyte collected in a back-up sorbent tube reaches a certain percentage (typically 5%) of the total amount collected by both sorbent tubes. These methods do not give identical results. For purposes in the document the former definition will be used.

5.8 Retention Volume (RV)-the volume of carrier gas required to move an analyte vapor plug through the short packed column which is the sorbent tube. The volume is determined by measuring the carrier gas volume necessary to elute the vapor plug through the tube, normally measured at the peak response as the plug exits the tube. The retention volume of methane is subtracted to account for dead volume in the tube.

5.9 Safe Sampling Volume (SSV)-usually calculated by halving the retention volume (indirect method) or taking two-thirds of the breakthrough volume (direct method), although these two approaches do not necessarily give identical results. The latter definition is used in this document.

5.10 Sorbent Strength—term used to describe the affinity of sorbents for VOC analytes. A stronger sorbent is one which offers greater safe sampling volumes for most/all VOC analytes relative to another, weaker sorbent. Generally speaking, sorbent strength is related to surface area, though there are exceptions to this. The SSVs of most, if not all, VOCs will be greater on a sorbent with surface area ?10n” than on one with a surface area of ?n”. As a general rule, sorbents are described as ?weak” if their surface area is less than 50 m^{2}g^{-1} (includes Tenax®, Carbopack™/trap C, and Anasorb® GCB2), ?medium strength” if the surface area is in the range 100-500 m^{2}g^{-1} (includes Carbopack™/trap B, Anasorb® GCBI and all the Porapaks and Chromosorbs listed in Tables 1 and 2) and ?strong” if the surface area is around 1000 m^{2}g^{-1} (includes Spherocarb®, Carbosieve™ S-III, Carboxen™ 1000, and Anasorb® CMS series sorbents.)

5.11 Total Ion Chromatogram (TIC)-chromatogram produced from a mass spectrometer detector operating in full scan mode.

5.12 MS-SCAN-mode of operation of a GC mass spectrometer detector such that all mass ions over a given mass range are swept over a given period of time.

5.13 MS -SIM-mode of operation of a GC mass spectrometer detector such that only a single mass ion or a selected number of discrete mass ions are monitored.

5.14 Standard Sorbent (Sample) Tube-stainless steel, glass or glass lined (or fused silica lined) stainless steel tube, 1/4 inch (6 mm) O.D. and of various lengths, with the central portion packed with ≥200 mg of solid adsorbent material depending on sorbent density. Tubes should be individually numbered and show the direction of flow.

5.15 Time Weighted Average (TWA) Monitoring-if air is sampled over a fixed time period - typically 1,3, 8 or 24 hours, the time weighted average atmospheric concentration over the monitoring period may be calculated from the total mass of analyte retained and the specific air volume sampled. Constraints on breakthrough volumes make certain combinations of sampling time and flow rates mutually exclusive.

6. Overview of Methodology

[*Note: The following is intended to provide a simple and straightforward method description including the example of a specific sampling problem. Although specific equipment is listed, the document is intended only as an example and equipment mentioned in the text is usually only one of a number of equally suitable components that can be used. Hence trade names are not meant to imply exclusive endorsement for sampling and analysis using solid sorbents. Later sections in the text give guidance as to what considerations should be made for a number of VOC monitoring applications.*]

6.1 Selection of Tube and Sorbent

6.1.1 Select a tube and sorbent packing for the sampling application using guidance from Tables 1 and 2 on sorbent characteristics as well as guidance from Appendix 1 and Table 3 on safe sampling volumes and breakthrough characteristics of sorbents.

6.1.2 As an example, assume the TCL includes a subset of the compounds shown in Table 3. In this case, the multisorbent tube chosen consists of two sorbents packed in a 1/4 inch O.D., 3.5" long glass tube in the following order and amounts: 160 mg of Carbopack™ graphitized carbon black (60/80 mesh) and 70 mg of Carboxen™-1000 type carbon molecular sieve (60/80 mesh). This is an example of Tube Style 2 discussed Section 9.1.3.2.

6.1.3 Pack the tube with the adsorbent by using the guidance provided in Section 10.1 or buy a prepacked tube from a supplier. In the example, tubes were purchased from Supelco Inc., Supelco Park, Bellefonte, PA 16823-0048.

6.2 Conditioning the Tube

6.2.1 Condition newly packed tubes for at least 2 hours (30 mins for preconditioned, purchased tubes) at 350°C while passing at least 50 mL/min of pure helium carrier gas through them.

[Note: Other sorbents may require different conditioning temperatures - see Table 2 for guidance.]

Once conditioned, seal the tube with brass, 1/4 inch Swagelok® -type fittings and PTFE ferrules. Wrap the sealed tubes in uncoated aluminum foil and place the tubes in a clean, airtight, opaque container.

6.2.2 A package of clean sorbent material, e.g. activated charcoal or activated charcoal/silica gel mixture, may be added to the container to ensure clean storage conditions.

6.2.3 Store in a refrigerator (organic solvent-free) at 4°C if not to be used within a day. On second and subsequent uses, the tubes will generally not require further conditioning as above. However, tubes with an immediate prior use indicating high levels of pollutant trace gases should be reconditioned prior to continued usage.

6.3 Sampling Apparatus

6.3.1 Select a sampling apparatus with accommodations for two sampling tubes capable of independent control of sampling rate at a settable value in the range 10 to 200 mL/min. Laboratory and field blanks must also be included in the monitoring exercise.

6.3.2 Backup tubes may be required to determine the cause of any problem if performance criteria, outlined in Section 14, are not met.

6.4 Sampling Rates

6.4.1 Select sampling rates compatible with the collection of 1 and 4 liter total sample volume (or of proportionally lower/higher sampling volumes).

6.4.2 Air samples are collected over 1 hour with a sampling rate of 16.7 mL/min and 66.7 mL/min, respectively.

6.5 Preparing for Sample Collection

6.5.1 At the monitoring location, keep the tubes in their storage and transportation container to equilibrate with ambient temperature.

6.5.2 Using clean gloves, remove the sample tubes from the container, take off their caps and attach them to the sampling lines with non-outgassing flexible tubing. Uncap and immediately reseal the required number of field blank tubes.

6.5.3 Place the field blank tubes back in the storage container. If back-up tubes are being used, attach them to the sampling tubes using clean, metal Swagelok® type unions and combined PTFE ferrules.

6.6 Set the Flow Rates

6.6.1 Set the flow rates of the pump using a mass flow monitor.

6.6.2 The sampling train includes, from front to back, an in-line particulate filter (optional), an ozone scrubber (optional), a sampling tube, a back-up tube if any is being used, and a flow controller/pump combination.

6.6.3 Place the mass flow monitor in line after the tube. Turn the pump on and wait for one minute. Establish the approximate sampling flow rate using a dummy tube of identical construction and packing as the sampling tube to be used. Record on Field Test Data Sheet (FTDS), as illustrated in Figure 1.

6.6.4 Place the sampling tubes to be used on the sampling train and make final adjustments to the flow controller as quickly as possible to avoid significant errors in the sample volume.

6.6.5 Adjust the flow rate of one tube to sample at 16.7 mL/min. Repeat the procedure for the second tube and set the flow rate to 66.7 mL/min. Record on FTDS.

6.7 Sample and Recheck Flow Rates

6.7.1 Sample over the selected sampling period (i.e., 1-hour). Recheck all the sampling flow rates at the end of the monitoring exercise just before switching off each pump and record on FTDS.

6.7.2 Make notes of all relevant monitoring parameters including locations, tube identification numbers, pump flow rates, dates, times, sampled volumes, ambient conditions etc. on FTDS.

6.8 Reseal the Tubes

6.8.1 Immediately remove the sampling tubes with clean gloves, recap the tubes with Swagelok® fittings using PTFE ferrules, rewrap the tubes with uncoated Al foil, and place the tubes in a clean, opaque, airtight container.

6.8.2 If not to be analyzed during the same day, place the container in a clean, cool (<4°C), organic solvent-free environment and leave there until time for analysis.

6.9 Selection of Thermal Desorption System

6.9.1 Select a thermal desorption system using the guidance provided in Section 8.

6.9.2 Place the thermal unit in a ready operational status.

6.10 Dry Purge the Tubes and Prepare for Thermal Desorption

6.10.1 Remove the sampling tubes, any backup tubes being used, and blanks from the storage area and allow the tubes to come to room temperature. Using clean gloves, remove the Swagelok®-type fittings and dry purge the tubes with a forward (sampling direction) flow of, for example, 50 mL/min of dry helium for 4 minutes (see Section 7.2 concerning dry purging).

[Note: Do not dry purge the laboratory blanks.]

6.10.2 Reseal the tubes with Teflon® (or other) caps compatible with the thermal desorber operation. Place the sealed tubes on the thermal desorber (e.g., Perkin Elmer Model ATD 400 Automated System or equivalent). Other thermal desorbers may have different arrangements for automation. Alternatively, use equivalent manual desorption.

6.11 Check for System Integrity

6.11.1 Check the air tightness of the seals and the integrity of the flow path.
6.11.2 Guidance is provided in Section 11.2 of this document.

6.12 Repurge of Tube on the Thermal Desorber/Addition of Internal Standard

6.12.1 Because of tube handling after dry purge, it may be necessary to repurge each of the tubes with pure, dry helium (He) before analysis in order to eliminate any oxygen.
6.12.2 If the initial dry purge can be performed on the thermal desorber so as to prevent any further exposure of the sorbent to air, then this step is not necessary. Proceed with the addition of an internal standard to the sorbent tube or the focusing tube.

6.13 Thermally Desorb the Packing

6.13.1 Reverse the flow direction of He gas, set the flow rate to at least 30 mL/min, and heat the tube to 325°C (in this case) to achieve a transfer of VOCs onto a focusing tube at a temperature of 27°C. Thermal desorption continues until all target species are transferred to the focusing trap. The focusing trap is typically packed with 20 mg of Carbopack™ B (60/80 mesh) and 50 mg of a Carboxen™ 1000-type sorbent (60/80 mesh).

6.14 Trap Desorption and GC/MS Analysis

6.14.1 After each tube is desorbed, rapidly heat the focusing trap (to 325°C in this example) and apply a reverse flow of at least 3 mL/min of pure helium carrier gas. Sample splitting is necessary to accommodate the capillary column. Analytes are transferred to the column in a narrow band of vapor.
6.14.2 The GC run is initiated based on a time delay after the start of thermal desorption. The remaining part of the analytical cycle is described in Section 3 of Compendium Method TO-15.

6.15 Restoring the Tubes and Determine Compliance with Performance Standards

6.15.1 When tube analysis is completed, remove the tubes from the thermal desorber and, using clean gloves, replace the Teflon® caps with Swagelok fittings and PTFE ferrules, rewrap with aluminum foil, replace in the clean, airtight container, and re-store the tubes in a cool environment (<4°C) until the next use.

6.15.2 Using previously prepared identification and quantification subroutines, identify the target compounds and document the amount of each measured compound (refer to the Section 3 of Compendium Method TO-15). Compare the results of analysis for the distributed volume pair taken during each sampling run and use the comparison to determine whether or not the performance criteria for individual sampling events have been met. Also examine the results of any laboratory blanks, field blanks, and any backup tube being used. Accept or reject the data based on the performance criteria (see Section 14).

6.16 Record and Store Data

6.16.1 Accurately retrieve field data (including the tube identification number) from the FTDS. The data should include a sampling site identifier, time of sample initiation, duration of sampling, air pump identification, flow rate, and other information as appropriate.

6.16.2 Store GC/MS data in a permanent form both in hard copy in a notebook and in digital form on a disk. Also store the data sheet with the hard copy.

[Note: Sections 7 through 14 below elaborate on the method by providing important information and guidance appropriate to explain the method as outlined in Section 6 and also to generalize the method for many applications. Section 14 gives the performance criteria for the method.]

7. Interferences and Limitations

7.1 Interference from Sorbent Artifacts

7.1.1 Minimizing Artifact Interference.

7.1.1.1 Stringent tube conditioning (see Section 10.2.1) and careful tube capping and storage procedures (see Section 10.2.2) are essential for minimizing artifacts. System and sorbent tube conditioning must be carried out using more stringent conditions of temperature, gas flow and time than those required for sample analysis.

7.1.1.2 A reasonable objective is to **reduce artifacts to 10% or less of individual analyte masses** retained during sampling. A summary of VOC levels present in a range of different atmospheric environments and the masses of individual components collected from 1, 2 or 10 L samples of air in each case is presented in Table 4.

7.1.1.3 Given that most ambient air monitoring is carried out in areas of poor air quality, for example in urban, indoor and factory fenceline environments where VOC concentrations are typically above 1 ppb, Table 4 demonstrates that the mass of each analyte retained will, therefore, range from ~5 ng to ~10 μg in most monitoring situations. Even when monitoring 'ultraclean' environments, analyte masses retained will usually exceed 0.1 ng (3).

7.1.1.4 Typical artifact levels for 1/4 inch O.D. tubes of 3.5" length range from 0.01 ng and 0.1 ng for carbonaceous sorbents and Tenax® respectively. These levels compare well with the masses of analytes collected - even from sub-ppb atmospheric concentrations (see Table 4). Artifact levels are around 10 ng for Chromosorb® Century series and other porous polymer sorbents. However, these types of sorbents can still be used for air monitoring at low ppb levels if selective or mass spectrometer detectors are used or if the blank profile of the tube demonstrates that none of the sorbent artifacts interfere analytically with the compounds of interest.

7.1.1.5 Some varieties of charcoal contain metals which will catalyze the degradation of some organic analytes during thermal desorption at elevated temperatures thus producing artifacts and resulting in low analyte recoveries.

7.1.2 Artifacts from Long-term Storage of Blank Tubes.

7.1.2.1 Literature reports of the levels of artifacts on (a) Carbotrap/pack™ C, Carbotrap/pack™ B and Carbosieve™ SIII multi-bed tubes and (b) Tenax® GR tubes, by workers sealing the tubes using metal Swagelok®-type caps and PTFE ferrules with multi-tube, glass storage jars are reported to be between 0.01 ng [after 1-2 months (4)] and 0.1 ng [after 6 months (5)] for (a) and (b) respectively.

7.1.2.2 Artifact levels reported for other porous polymers are higher - for example 5 ng for Chromosorb 106 after 1 week (5). More information is given in the Technical Assistance Document (TAD) referred to in Section 4.3.

7.1.3 Artifacts Generated During Sampling and Sample Storage.

7.1.3.1 Benzaldehyde, phenol and acetophenone artifacts are reported to be formed via oxidation of the polymer Tenax® when sampling high concentration (100-500 ppb) ozone atmospheres (6).

7.1.3.2 Tenax® should thus be used with an ozone scrubber when sampling low levels (<10 ppb) of these analytes in areas with appreciable ozone concentrations. Carbotrap™/pack type sorbents have not been reported to produce this level of artifact formation. Once retained on a sorbent tube, chemically stable VOCs, loaded in laboratory conditions, have been shown to give good recoveries, even under high ozone concentrations for storage of a year or more (7-9).

7.2 Minimizing Interference from Water

7.2.1 Selection of Hydrophobic Sorbents

7.2.1.1 There are three preferred approaches to reducing water interference during air monitoring using sorbent tubes. The first is to minimize water collection by selecting, where possible, a hydrophobic sorbent for the sample tube.

7.2.1.2 This is possible for compounds ranging in volatility from n-C5 (see SSVs listed in Appendix 1). Tenax®, Carbotrap™ or one of the other hydrophobic sorbents listed in Table 2 should be used.

[<u>Note</u>: It is essential to ensure that the temperature of the sorbent tube is the same and certainly not lower than ambient temperature at the start of sampling or moisture will be retained via condensation, however hydrophobic the sorbent.]

7.2.2 Sample Splitting

7.2.2.1 If the sample loading is high, it is usually possible to eliminate sufficient water to prevent analytical interference by using sample splitting (10).

7.2.2.2 Sample may be split either (1) between the focusing trap and the capillary column (single splitting) during trap (secondary) desorption or (2) between both the tube and the focusing trap during primary (tube) desorption and between the focusing trap and the column during secondary (trap) desorption (see Section 8.2.3) (double splitting). It may, in fact, be necessary to split the sample in some cases to prevent overloading the analytical column or detector.

7.2.3 Dry Purge

7.2.3.1 The third water management method is to ?dry purge” either the sorbent tube itself or the focusing trap or both (11-13). Dry purging the sample tube or focusing trap simply involves passing a volume of pure, dry, inert gas through the tube from the sampling end, prior to analysis.

7.2.3.2 The tube can be heated while dry purging at slightly elevated temperatures (11). A trap packing combination and a near ambient trapping temperature must be chosen such that target analytes are quantitatively retained while water is purged to vent from either the tube or trap.

7.3 Atmospheric Pollutants not Suitable for Analysis by this Method

7.3.1 Inorganic gases not suitable for analysis by this method are oxides of carbon, nitrogen and sulfur, O_3 and other permanent gases. Exceptions include CS_2 and N_2O.

7.3.2 Other pollutants not suitable are particulate pollutants, (i.e., fumes, aerosols and dusts) and compounds too labile (reactive) for conventional GC analysis.

7.4 Detection Limits and Maximum Quantifiable Concentrations of Air Pollutants

7.4.1 Detection limits for atmospheric monitoring vary depending on several key factors. They are:

- Minimum artifact levels.
- GC detector selection.
- Volume of air sampled. The volume of air sampled is in turn dependent upon a series of variables including SSVs (see Section 10.8, Table 1 and Appendix 1), pump flow rate limitations and time-weighted-average monitoring time constraints.

7.4.2 Generally speaking, detection limits range from sub-part-per-trillion (sub-ppt) for halogenated species such as CCl_4 and the freons using an electron capture detector (ECD) to sub-ppb for volatile hydrocarbons in 1 L air samples using the GC/MS operated in the full SCAN mode.

7.4.3 Detection limits are greatly dependent upon the proper management of water for GC capillary analysis of volatile organics in air using sorbent technology (14).

7.5 Suitable Atmospheric Conditions

7.5.1 Temperature range.

7.5.1.1 The normal working range for sorbent packing is 0-40°C (8).

7.5.1.2 In general, an increase in temperature of 10ºC will reduce the breakthrough volume for sorbent packings by a factor of 2.

7.5.2 Humidity.

7.5.2.1 The capacity of the analytical instrumentation to accommodate the amount of water vapor collected on tubes is usually the limitation in obtaining successful results, particularly for GC/MS applications. This limitation can be extreme, requiring the use of a combination of water management procedures (see Section 7.2).

7.5.2.2 The safe sampling volumes of VOCs on hydrophobic adsorbents such as Tenax®, other porous polymers, Carbotrap™ and Carbopack™ are relatively unaffected by atmospheric humidity. Spherocarb® or carbonized molecular sieve type sorbents such as Carbosieve™ SIII and the Carboxens® are affected by high humidity, however, and SSVs should typically be reduced by a factor of 10 at 90-95% RH (8). Hydrophilic zeolite molecular sieves cannot be used at all at high humidity.

7.5.3 Wind speeds.

7.5.3.1 Air movement is not a factor indoors or outdoors at wind speeds below 10 miles per hour (<20 km per hour).

7.5.3.2 Above this speed, tubes should be orientated perpendicular to the prevailing wind direction and should be sheltered from the direct draft if wind speeds exceed 20 miles per hour (30-40 km per hour) (see Section 10.5).

7.5.4 High concentrations of particulates.

7.5.4.1 It may be necessary to connect a particulate filter (e.g., a 2 micron Teflon® filter or short clean tube containing a loose plug of clean glass wool) to the sampling end of the tube in areas of extremely high particulate concentrations.

7.5.4.2 Some compounds of interest may, however, be trapped on the Teflon® or on the glass wool. Particulates trapped on the sorbent tube have the potential to act as a source or sink for volatiles, and may remain on the tube through several cycles of sampling and desorption. Frequent replacement of the particulate filter is therefore recommended.

8. Apparatus Selection and Preparation

8.1 Sample Collection

8.1.1 Selection of Tube Dimensions and Materials.

8.1.1.1 The most extensively used sorbent tubes are 1/4 inch O.D. stainless steel or 6 mm O.D. stainless steel or glass. Different suppliers provide different size tubes and packing lengths; however, 3.5 inch long tubes with a 6 cm sorbent bed and 1/4 inch O.D. stainless steel (see Figure 2) were used to generate the SSV information presented in Appendix 1.

8.1.1.2 As an approximate measure, for sorbents contained in equal diameter tubes the breakthrough volume is proportional to the bed-length (weight) of sorbent. Therefore, doubling the bed-length would approximately double the SSV (15).

8.1.1.3 Stainless steel (304 or “GC” grade) is the most robust of the commonly available tube materials which include, in addition, glass, glass-lined, and fused silica lined tubing. Tube material must be chosen to be compatible with the specifics of storage and transport of the samples. For example, careful attention to packaging is required for glass tubes.

8.1.2 Tube Labeling.

8.1.2.1 Label sample tubes with a unique identification number and the direction of sampling flow. Stainless steel tubes are most conveniently labeled by engraving. Glass tubes are best labeled using a temperature resistant paint. If empty sample tubes are obtained without labels, it is important to label and condition them before they are packed with adsorbent.

8.1.2.2 Recondition prepacked, unlabeled tubes after the tube labeling process and record the blank chromatogram from each tube. Record in writing the details of the masses and/or bed lengths of sorbent(s) contained in each tube, the maximum allowable temperature for that tube and the date each tube was packed or repacked.

8.1.3 Blank and Sampled Tube Storage Apparatus.

8.1.3.1 Seal clean, blank sorbent tubes and sampled tubes using inert, Swagelok®-type fittings and PTFE ferrules. Wrap capped tubes individually in uncoated aluminum foil. Use clean, sealable glass jars or metal cans containing a small packet of activated charcoal or activated charcoal/silica gel for storage and transportation of multiple tubes. Store the multi-tube storage container in a clean environment at 4°C.

8.1.3.2 Keep the sample tubes inside the storage container during transportation and only remove them at the monitoring location after the tubes have reached ambient temperature. Store sampled tubes in a refrigerator at 4°C inside the multi-tube container until ready for analysis.

[Note: The atmosphere inside the refrigerator must be clean and free of organic solvents.]

8.1.4 Selection of Sampling Pumps.

8.1.4.1 The selected monitoring pump(s) should be capable of operating in the range 10 to 200 mL/min. Label the pumps with a unique identification number and operate them according to manufacturer's guidelines.

8.1.4.2 Constant mass flow type pumps are ideal for air monitoring as they deliver a constant flow rate for a wide range of tube impedances. They thus compensate for moderate impedance variations between the sorbent tubes in use. The pump should meet US criteria for intrinsic safety where applicable. Connect the pump to the non-sampling end of the sample tube by means of flexible, nonoutgassing tubing.

8.1.5 Parallel Sampling onto Multiple Tubes with a Single Pump.

8.1.5.1 Select a sample collection system for collecting samples onto 2 tubes in parallel.

8.1.5.2 If a single pump is used for both tubes, ensure that the flow rates will be controlled at a constant flow rate during sampling and that the two flow rates can be independently controlled and stabilized.

8.1.6 Apparatus for Calibrating the Pumped Air Flow.

8.1.6.1 Calibrate the pump with the type of sorbent tube to which it will be connected during the monitoring exercise. Use the actual sampling tube to fine tune the sampling flow rate at the start of sample collection.

8.1.6.2 Use a flow meter certified traceable to NIST standards.

8.1.7 Sorbent Tube Protection During Air Sample Collection.

8.1.7.1 Protect sorbent tubes from extreme weather conditions using shelters constructed of inert materials. The shelter must not impede the ingress of ambient air.

8.1.7.2 If the atmosphere under test contains significant levels of particulates - fume, dust or aerosol, connect a Teflon® 2-micron filter or a (metal, glass, glass-lined or fused silica lined stainless) tube containing a short plug of clean glass wool prior to the sampling end of the tube and using inert, Swagelok®-type fittings and PTFE ferrules for fitting connections.

8.2 Apparatus

8.2.1 Essential Sample Protection Features of the Thermal Desorption Apparatus.

8.2.1.1 As thermal desorption is generally a one shot process, (i.e., once the sample is desorbed it cannot readily be reinjected or retrieved), stringent sample protection measures and thorough preanalysis system checks must form an integral part of the thermal desorption-GC procedure and should be systematically carried out.

8.2.1.2 The sample integrity protection measures and preanalysis checks required include:

- **Sealed tubes**. Sample tubes awaiting analysis on an automated desorption system must be completely sealed before thermal desorption to prevent ingress of VOC contaminants from the laboratory air and to prevent losses of weakly retained analytes from the tube.
- **Inert and heated sample flow path**. To eliminate condensation, adsorption and degradation of analytes within the analytical system, the sample flow path of manual and automated thermal desorbers should be uniformly heated (minimum temperature range 50° - 150°C) between the sample tube and the GC analytical column. The components of the sample flow path should also, as far as possible, be constructed of inert materials, i.e., deactivated fused silica, glass lined tubing, glass, quartz and PTFE.
- **Tube leak testing**. This activity must not jeopardize sample integrity.
- **Leak testing of the sample flow path**. This activity must not jeopardize sample integrity.
- **System purge**. Stringent, near-ambient temperature carrier gas purge to remove oxygen.
- **Analytical system**. **?**Ready" status checks.

8.2.2 Thermal Desorption Apparatus.

8.2.2.1 Two-stage thermal desorption is used for the best high resolution capillary chromatography (i.e., analytes desorbed from the sorbent tube must be refocused before being rapidly transferred to the GC analytical column). One type of analyte refocusing device which has been successfully used is a small sorbent trap (17). One cryogen-free trap cooling option is to use a multistage Peltier electrical cooler (18,19).

8.2.2.2 Closed cycle coolers are also available for use. At its low temperature, the trap must provide quantitative analyte retention for target compounds as well as quantitative and rapid desorption of target analytes as high boiling as n-C_{12}. The peak widths produced must be compatible with high resolution capillary gas chromatography.

8.2.2.3 Typical key components and operational stages of a two-stage desorption system are presented in Figure 3(a) - (f) and a stepwise description of the thermal desorber operation is presented in Section 11.3.

8.2.3 Sample Splitting Apparatus.

8.2.3.1 Sample splitting is often required to reduce water vapor interference, for the analysis of relatively high concentration (>10 ppb level) air samples, when large volume air samples are collected, or when sensitive selective detectors are in use.

8.2.3.2 Sample splitting is one of the three key approaches to water management detailed in this method (see Section 7.2). Moisture management by sample splitting is applicable to relatively high concentrations ($\geq$10 ppb) or large volume air samples or to analyses employing extremely sensitive detectors - for example, using the ECD for low levels of tetrachloroethylene. In these cases the masses of analytes retained by the sorbent tube when monitoring such atmospheres is large enough to allow, or even require, the selection of a high split ratio (>10:1) during analysis to avoid overloading the analytical column or detector. The mass of water retained by the sorbent tube during sample collection may be sufficiently reduced by the split alone to eliminate the need for further water management steps.

8.2.4 The Thermal Desorber - GC Interface.

8.2.4.1 Heat the interface between the thermal desorber and the GC uniformly. Ensure that the interface line is leak tight and lined with an inert material such as deactivated fused silica.

8.2.4.2 Alternatively, thread the capillary column itself through the heated transfer line/interface and connected directly into the thermal desorber.

[Note: Use of a metal syringe-type needle or unheated length of fused silica pushed through the septum of a conventional GC injector is not recommended as a means of interfacing the thermal desorber to the chromatograph. Such connections result in cold spots, cause band broadening and are prone to leaks.]

8.2.5 GC/MS Analytical Components. This method uses the GC/MS description as given in Compendium Method TO-15, Section 7.

8.3 Tube Conditioning Apparatus

8.3.1 Tube Conditioning Mode

8.3.1.1 Condition freshly packed tubes using the analytical thermal desorption apparatus if it supports a dedicated ‘tube conditioning mode’ (i.e., a mode in which effluent from highly contaminated tubes is directed to vent without passing through key parts of the sample flow path such as the focusing trap).

8.3.2 Stand Alone System

8.3.2.1 If such a tube conditioning mode is not available, use separate stand-alone tube conditioning hardware.

8.3.2.2 The tube conditioning hardware must be leak-tight to prevent air ingress, allow precise and reproducible temperature selection (±5°C), offer a temperature range at least as great as that of the thermal desorber and support inert gas flows in the range of 50 to 100 mL/min.

[Note: Whether conditioning is carried out using a special mode on the thermal desorber or using separate hardware, pass effluent gases from freshly packed or highly contaminated tubes through a charcoal filter during the process to prevent desorbed VOCs polluting the laboratory atmosphere.]

9. Reagents and Materials

9.1 Sorbent Selection Guidelines

9.1.1 Selection of Sorbent Mesh Size.

9.1.1.1 Sieved sorbents of particle size in the range 20 to 80 mesh should be used for tube packing.

9.1.1.2 Specific surface area of different sorbents is provided in Table 2.

9.1.2 Sorbent Strength and Safe Sampling Volumes.

9.1.2.1 Many well-validated pumped and diffusive sorbent tube sampling/thermal desorption methods have been published at the relatively high atmospheric concentrations (i.e., mid-ppb to ppm) typical of workplace air and industrial/mobile source emissions (8, 20-30).

9.1.2.2 These methods show that SSVs are unaffected by analyte concentrations far in excess of the 25 ppb upper limit of this method. The effect of humidity on SSVs is discussed in Section 7.5 and Table 2.

9.1.2.3 Select a sorbent or series of sorbents of suitable strength for the analytes in question from the information given in Tables 1 and 2 and Appendices 1 and 2. Where a number of different sorbents fulfill the basic safe sampling volume criteria for the analytes in question, choose that (or those) which are hydrophobic and least susceptible to artifact formation. Keep the field sampling volumes to 80% or less of the SSV of the least well-retained analyte. Using one of the two procedures given in Section 10.8, check the safe sampling volumes for the most volatile analytes of interest on an annual basis or once every twenty uses of the sorbent tubes whichever occurs first.

9.1.3 Three General-Purpose 1/4 Inch or 6 mm O.D. Multi-Bed Tube Types.

[Note: The three general-purpose tubes presented in this section are packed with sorbents in the mesh size range of 20-80 mesh. The difference in internal diameter between standard glass and stainless steel tubes will result in different bed volumes (weights) for the same bed length.]

9.1.3.1 Tube Style 1 consists of 30 mm Tenax®GR plus 25 mm of Carbopack™ B separated by 3 mm of unsilanized, preconditioned glass or quartz wool. Suitable for compounds ranging in volatility from n-C_6 to n-C_{20} for air volumes of 2 L at any humidity. Air volumes may be extended to 5 L or more for compounds ranging in volatility from n-C_7.

9.1.3.2 Tube Style 2 consists of 35 mm Carbopack™ B plus 10 mm of Carbosieve™ SIII or Carboxen™ 1000 separated by glass/quartz wool as above. Suitable for compounds ranging in volatility from n-C_3 to n-C_{12} (such as ?Compendium Method TO-14 air toxics") for air volumes of 2 L at relative humidities below 65% and temperatures below 30°C. At humidities above 65% and ambient temperatures above 30°C, air volumes should be reduced to 0.5 L. Air volumes may be extended to 5 L or more for species ranging in volatility from n-C_4. A dry purge procedure or a large split ratio must be used during analysis when humid air has been sampled on these tubes.

9.1.3.3 Tube Style 3 consists of 13 mm Carbopack™ C, 25 mm Carbopack™ B plus 13 mm of Carbosieve™ SIII or Carboxen™ 1000 all separated by 3 mm plugs of glass/quartz wool as above. Suitable for compounds ranging in volatility from n-C_3 to n-C_{16} for air volumes of 2 L at relative humidities below 65 percent and temperatures below 30°C. At humidities above 65 percent and ambient temperatures above 30°C, air volumes should be reduced to 0.5 L. Air volumes may be extended to 5 L or more for compounds ranging in volatility from n-C_4. A dry purge procedure or a large split ratio must be used during analysis when humid air has been sampled on these tubes.

[Note: These multi-bed tubes are commercially available prepacked and preconditioned if required.]

[Note: These general purpose multi-bed tubes are only recommended for monitoring unknown atmospheres or wide volatility range sets of target analytes. Most routine monitoring of industrial air (for example at factory fencelines) only involves monitoring a few specific target analytes such as benzene, toluene, ethylbenzene, and xylenes (BTEX), carbon disulfide (CS_2) or 1,1,1-trichloroethane. Single-bed sorbent tubes selected from the options listed in Appendix 1 are typically used in these cases.]

[Note: In the interests of minimizing water retention it is advisable to stick to hydrophobic (i.e., weak and medium strength) sorbents whenever possible; this generally is the case when components more volatile than n-C_6 are not of interest.]

9.2 Gas Phase Standards

9.2.1 Standard Atmospheres.

9.2.1.1 Standard atmospheres must be stable at ambient pressure and accurate (±10%). Analyte concentrations and humidities should be similar to those in the typical test atmosphere. Standard atmospheres must be sampled onto conditioned sorbent tubes using the same pump flow rates as used for field sample collection.

9.2.1.2 If a suitable standard atmosphere is obtained commercially, manufacturer's recommendations concerning storage conditions and product lifetime should be rigidly observed.

9.2.2 Concentrated, Pressurized Gas Phase Standards.

9.2.2.1 Use accurate (± 5%), concentrated gas phase standards in pressurized cylinders such that a 0.5 - 5.0 mL gas sampling volume (GSV) loop contains approximately the same masses of analytes as will be collected from a typical air sample. Introduce the standard onto the sampling end of conditioned sorbent tubes using at least ten times the loop volume of pure helium carrier gas to completely sweep the standard from the GSV.

9.2.2.2 Manufacturer's guidelines concerning storage conditions and expected lifetime of the concentrated gas phase standard should be rigidly observed.

9.3 Liquid Standards

9.3.1 Solvent Selection.

9.3.1.1 If liquid standards are to be loaded onto sorbent tubes for calibration purposes, select a solvent for the standard that is pure (contaminants <10% of minimum analyte levels) and that, if possible, is considerably more volatile than the target analytes. This then allows the solvent to be purged and eliminated from the tube during the standard preparation process.

9.3.1.2 Methanol most commonly fills these criteria. If the target analyte range includes very volatile components, it will not be possible to do this. In these cases, select a pure solvent which is readily chromatographically resolved from the peaks/components of interest (ethyl acetate is commonly used) or use a gas phase standard. Test the purity of the solvent by comparing an analysis of the prepared standard with an analysis of pure solvent under identical chromatographic conditions.

9.3.2 Liquid Standard Concentrations.

9.3.2.1 Liquid standards should be prepared so that the range of analyte masses introduced onto the tubes is in the same order as the range of masses expected to be collected during sampling.

9.3.2.2 Concentrations of benzene in urban air may be expected to range from 0.5-25 ppb. Thus if 5 L air samples were to be collected at approximately 25°C, the masses of benzene collected would range from around 8 ng (0.5 ppb level) to around 400 ng (25 ppb level).

[Note: The above calculation was derived from Boyle's law (i.e., 1 mole of gas occupies around 25 L at 25°C and 760 mm Hg).

- *25 L of pure benzene vapor contains 78 g benzene*
- *5 L of pure benzene vapor contains 15.6 g benzene*
- *5 L of a 1 ppm benzene atmosphere contains 15.6 μg benzene*
- *5 L of a 100 ppb benzene atmosphere contains 1560 ng benzene*
- *5 L of a 1 ppb benzene atmosphere contains 15.6 ng benzene.]*

9.3.3 Loading Liquid Standards onto Sorbent Tubes.

9.3.3.1 Introduce 0.1 - 10 μL aliquots of the liquid standards onto the sampling end of conditioned sorbent tubes using a conventional 1/4 inch GC packed column injector and a 1, 5 or 10 μL syringe. The injector is typically unheated with a 100 mL/min flow of pure carrier gas. The solvent and analytes should completely vaporize and pass onto the sorbent bed in the vapor phase. It may be necessary to heat the injector slightly (typically to 50°C) for analytes less volatile than n-C_{12} to ensure that all the liquid vaporizes.

9.3.3.2 The sample tube should remain attached to the injector until the entire standard has been swept from the injector and onto the sorbent bed. If it has been possible to prepare the liquid standard in a solvent which will pass through the sorbent while analytes are quantitatively retained (for example, methanol on Tenax® or Carbopack™ B), the tube should not be disconnected from the injector until the solvent has been eliminated from the sorbent bed - this takes approximately 5 minutes under the conditions specified. Once the tube has been disconnected from the injector, it should be capped and placed in an appropriate storage container immediately.

[Note: In cases where it is possible to purge the solvent from the tube while quantitatively retaining the analytes, a 5-10 μL injection should be made as this can usually be introduced more accurately than smaller volumes. However, if the solvent is to be retained in the tube, the injection volume should be as small as possible (0.5 - 1.0 μL) to minimize solvent interference in the subsequent chromatogram.]

9.3.3.3 This method of introducing liquid standards onto sorbent tubes via a GC injector is considered the optimum approach to liquid standard introduction as components reach the sorbent bed in the vapor phase (i.e., in a way which most closely parallels the normal air sample collection process). Alternatively, liquid standards may be introduced directly onto the sorbent bed via the non-sampling end of the tube using a conventional GC syringe.

[Note: This approach is convenient and works well in most cases, but it may not be used for multi-bed tubes or for wide boiling range sets of analytes and does not allow solvent to be purged to vent.]

9.4 Gas Phase Internal Standards

9.4.1 The ideal internal standard components are:

- chemically similar to the target analytes
- extremely unlikely to occur naturally in the atmosphere under test
- readily resolved and distinguished analytically from the compounds of interest
- stable in the vapor phase at ambient temperature
- compatible with metal and glass surfaces under dry and humid conditions
- certified stable in a pressurized form for a long time period (i.e., up to 1 year).

9.4.2 Deuterated or fluorinated hydrocarbons usually meet all these criteria and make perfect internal standards for MS based systems. Typical compounds include deuterated toluene, perfluorobenzene and perfluorotoluene. Multiple internal standards should be used if the target analytes cover a very wide volatility range or several different classes of compound.

9.4.3 Obtain a pressurized cylinder containing accurate (±5%) concentrations of the internal standard components selected. Typically a 0.5 to 5.0 mL volume of this standard is automatically introduced onto the back of the sorbent tube or focusing trap after the tube has passed preliminary leak tests and before it is thermally desorbed. The concentration of the gas should be such that the mass of internal standard introduced from the GSV loop is approximately equivalent to the mass of analytes which will be sampled onto the tube during sample collection. For example, a 1 L air sample with average analyte concentrations in the order of 5 ppb, would require a 10 ppm internal standard, if only 0.5 mL of the standard is introduced in each case.

9.5 Commercial, Preloaded Standard Tubes

9.5.1 Certified, preloaded commercial standard tubes are available and should be used for auditing purposes wherever possible to establish analytical quality control (see Section 14). They may also be used for routine calibration. Suitable preloaded standards should be accurate within ±5% for each analyte at the microgram level and ±10% at the nanogram level.

9.5.2 The following information should be supplied with each preloaded standard tube:

- A chromatogram of the blank tube before the standard was loaded with associated analytical conditions and date.
- Date of standard loading
- List of standard components, approximate masses and associated confidence levels
- Example analysis of an identical standard with associated analytical conditions (these should be the same as for the blank tube)
- A brief description of the method used for standard preparation
- Expiration date

9.6 Carrier Gases

Inert, 99.999% or higher purity helium should be used as carrier gas. Oxygen and organic filters should be installed on the carrier gas lines supplying the analytical system. These filters should be replaced regularly according to the manufacturer's instructions.

10. Guidance on Sampling and Related Procedures

10.1 Packing Sorbent Tubes

10.1.1 Commercial Tubes

10.1.1.1 Sorbent tubes are commercially available either prepacked and preconditioned or empty.

10.1.1.2 When electing to purchase empty tubes and pack/condition them as required, careful attention must be paid to the appropriate manufacturer's instructions.

10.1.2 Tube Parameters

10.1.2.1 Key parameters to consider include:

- **Sorbent bed positioning within the tube**. The sampling surface of the sorbent bed is usually positioned at least 15 mm from the sampling end of the tube to minimize sampling errors due to diffusive ingress. The position of the sorbent bed must also be entirely within that section of the tube which is surrounded by the thermal desorption oven during tube desorption.
- **Sorbent bed length**. The sorbent bed must not extend outside that portion of the tube which is directly heated by the thermal desorption oven.
- **Sorbent mesh size**. 20 to 80 mesh size sorbent is recommended to prevent excessive pressure drop across the tube which may cause pump failure. It is always recommended that sorbents be sieved to remove **?**fines" (undersized particles) before use.
- **Use of appropriate sorbent bed retaining hardware inside the tube**. Usually 100 mesh stainless steel gauzes and retaining springs are used in stainless steel tubes and unsilanized, preconditioned glass or quartz wool in glass tubes.
- **Correct conditioning procedures**. See Table 2 and Section 10.2.
- **Bed separation**. If a single tube is to be packed with two or three different sorbents, these must be kept in discreet beds separated by ~3 mm length plugs of unsilanized, preconditioned glass or quartz wool or glass fiber disks and arranged in order of increasing sorbent strength from the sampling end of the tube. Do not use sorbents of widely different maximum temperatures in one tube or it will be difficult to condition the more stable sorbents without exceeding the maximum recommended temperature of the less stable sorbents.

[Note: Silanized glass or quartz wool may be used for labile species such as sulfur or nitrogen containing compounds but should not be taken to temperatures above 250°C.]

- **Compression of bed**. The sorbent bed must not be compressed while packing the tube. Compression of the sorbent can lead to excessive tube impedance and may produce **?**fines".

10.1.2.2 Tubes packed with porous polymer sorbents (Chromosorbs®, Porapaks® and Tenax®) should be repacked after 100 thermal cycles or if the performance criteria cannot be met. Tubes packed with carbonaceous sorbents such as Spherocarb®, Carbotrap™, Carbopack™, Carbosieve™ SIII and Carboxens® should be repacked every 200 thermal cycles or if the safe sampling volume validation procedure fails.

10.2 Conditioning and Storage of Blank Sorbent Tubes

10.2.1 Sorbent Tube Conditioning.

10.2.1.1 The success of sorbent tube sampling for ppb and sub-ppb level air monitoring is largely dependent on artifact levels being at significantly lower levels (<10%) than the masses of analytes collected during air monitoring. A summary of recommended conditioning parameters for various individual sorbents and multibed tubes is given in Table 2. 1/4 inch O.D. sorbent tubes may be adequately conditioned using elevated temperatures and a flow of ultra-pure inert gas. Washing or any other preconditioning of the bulk sorbent is not usually necessary. Appropriate, dedicated tube conditioning hardware should be used for tube conditioning unless the thermal desorption system offers a separate tube conditioning mode.

10.2.1.2 The tube conditioning temperatures and gas flows recommended in Table 2 should be applied for at least 2 hours when a tube is packed with fresh adsorbent or when its history is unknown.

Sorbent tubes which are:

- desorbed to completion during routine analysis (as is normally the case)
- stored correctly (see Section 10.2.2)
- re-issued for air sampling within 1 month (1 week for Chromosorb®, Tenax® and Porapak® porous polymers)
- and are to be used for atmospheres with analytes at the 10 ppb level or above

do not usually require any reconditioning at all before use. However, tubes to be used for monitoring at lower levels should be both reconditioned for 10-15 minutes using the appropriate recommended conditioning parameters and put through a ?dummy" analysis using the appropriate analytical conditions to obtain blank profiles of each tube before they are issued for sampling.

10.2.1.3 Analytical system conditioning procedures are supplied by system manufacturers. Generally speaking, both system and sorbent tube conditioning processes must be carried out using more stringent conditions of temperature, gas flow and time than those required for sample analysis - within the maximum temperature constraints of all the materials and equipment involved.

10.2.2 Capping and Storage of Blank Tubes.

10.2.2.1 Blank tubes should be capped with ungreased, Swagelok®-type, metal screw-caps and combined PTFE ferrules. The screw caps should be tightened by hand and then an extra 1/4 turn with a wrench. If uncoated aluminum foil is required, tubes should be wrapped individually.

10.2.2.2 Batches of blank, sealed tubes should be stored and transported inside a suitable multi-tube container.

10.3 Record Keeping Procedures for Sorbent Tubes

Sample tubes should be indelibly labeled with a unique identification number as described in Section 8.1.2. Details of the masses and/or bed lengths of sorbent(s) contained in each tube, the maximum allowable temperature for that tube and the date each tube was packed should be permanently recorded. A record should also be made each time a tube is used and each time the safe sampling volume of that tube is retested so that its history can be monitored. If a tube is repacked at any stage, the records should be amended accordingly.

10.4 Pump Calibration and Tube Connection

10.4.1 Tube Deployment

10.4.1.1 Once at ambient temperature, remove the tubes from the storage container, uncap and connect them to the monitoring pumps as quickly as possible using clean, non-outgassing flexible tubing. Multi-bed sorbent tubes must be orientated so that the air sample passes through the series of sorbents in order of increasing sorbent strength (i.e., weaker sorbent first). This prevents contamination of the stronger adsorbent with less volatile components.

10.4.1.2 In all cases the sampling end of the tube must be clearly identified and recorded.

10.4.1.3 A typical sampling configuration for a distributed volume pair of sampling tubes is shown in Figure 4.

10.4.2 Pump Calibration

10.4.2.1 Pumps should be calibrated according to the manufacturer’s instructions, preferably at the monitoring location immediately before sampling begins or, alternatively, in a clean environment before the tubes and pumps are transported to the monitoring site. The apparatus required is described in Section 8.1.6. Details of the pump flow rate delivered with a given identified tube and the flow rate, stroke rate or pressure selected on the pump itself should be recorded together with the date.

10.4.2.2 The pump flow rate should be retested at the end of each sampling period to make sure that a constant pump rate was maintained throughout the sample collection period. The flow rate measured at the end of sampling should agree within 10% with that measured at the start of the sampling period for the sample to be considered valid and the average value should be used.

10.5 Locating and Protecting the Sample Tube

The sampling points of individual sorbent tubes or sequential tube samplers should not be unduly influenced by nearby emission sources unless the emission source itself is specifically being monitored. Common sense generally determines the appropriate placement. Field notes on the relative location of known emission sources should be part of the permanent record and identified on the FTDS. Some shelter or protection from high winds (see Section 8.1.7) other extreme weather conditions and high levels of particulates is required for the sample tube if it is to be left unattended during the monitoring period.

10.6 Selection of Pump Flow Rates and Air Sample Volumes

10.6.1 Flow Rate Selection

10.6.1.1 For 1/4 inch O.D. tubes, 50 mL/min is the theoretical optimum flow rate (31). However, negligible variation in retention volume will in fact be observed for pump flow rates varying from 5 to 200 mL/min. Pump flow rates above 10 mL/min are generally used in order to minimize errors due to ingress of VOCs via diffusion. Flow rates in excess of 200 mL/min are not recommended for standard 1/4-inch sample tubes unless for short term (e.g. 10 minute) monitoring (21).

[Note: High sampling flow rates can be used longer term for high boiling materials such as low level, vapor phase polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in air.]

10.6.1.2 One and four liter air sample volumes are recommended for this method if consistent with anticipated safe sampling volumes. Adjustments of the flow rates to accommodate low safe sampling volumes should be made by proportionally reducing both rates with the qualification that the lower flow rate result is no less than 300 mL total volume. The 300 mL sample gives adequate detection limits (<0.5 ppb per analyte) with full scan mass spectrometry detection for ambient air applications (see Table 4). Sensitivity is generally enhanced at least ten-fold if conventional GC detectors or selected ion monitoring are applied. However; the pump flow rate, sampling time and consequently air volume selected may be varied to suit the requirements of each individual air monitoring exercise.

10.6.1.3 Typical example pump flow rates include:

- 16 mL/min to collect 1 L air samples in 1 hour
- 67 mL/min to collect 4 L air samples in 1 hour
- 10 mL/min to collect 1800 mL air samples over 3 hours
- 40 mL/min to collect 7200 mL air samples over 3 hours

10.6.2 Pump Flow Rate Selection

10.6.2.1 The pump flow rate used is dependent upon:

- **Safe sampling volume constraints**. The flow rate must be adjusted (within the allowed range) to ensure that, for the chosen sample collection time, SSVs are not exceeded for any target analyte
- **Time weighted average monitoring requirements**. If long-term - 3, 8 or even 24 hour - time weighted average data are required, the pump flow rate must be adjusted to ensure SSVs are not exceeded during the sample collection period.
- **GC detection limits**. Within the constraints of safe sampling volumes and pump flow rate limits, air volumes selected for trace level (ambient) air monitoring, should be maximized such that the largest possible analyte masses are collected.

10.6.2.2 Typical VOC concentrations and the associated analyte masses retained from a range of different air sample volumes in various atmospheres are presented in Table 4.

10.7 Sampling Procedure Verification - Use of Blanks, Distributed Volume Pairs, Back-Up Tubes, and Distributed Volume Sets

10.7.1 Field and Laboratory Blanks

10.7.1.1 Laboratory blanks must be identically packed tubes, from the same batch, with similar history and conditioned at the same time as the tubes used for sample collection. At least two are required per monitoring exercise. They must be stored in the laboratory in clean controlled conditions (<4°C) throughout the monitoring program and analyzed at the same time as the samples-- one at the beginning and one at the end of the sequence of runs.

10.7.1.2 Field blanks are the same as laboratory blanks except that they are transported to and from the monitoring site, are uncapped and immediately resealed at the monitoring site, but do not actually have air pumped through them. One field blank tube is taken for every ten sampled tubes on a monitoring exercise and no less than two field blanks should be collected, however small the monitoring study. The field blanks should be distributed evenly throughout the set of sampled tubes to be analyzed. Guidance on acceptable performance criteria for blanks is given in Section 13.

10.7.2 Distributed Volume Pairs

10.7.2.1 When monitoring for specific analytes using a validated sorbent tube but in an uncharacterized atmosphere, it is advisable to collect distributed volume tube pairs - e.g. 1 and 4 L samples - in parallel at every monitoring location as described in Section 6. If single tube sampling is used to reduce analysis costs, a reduction in the quality assurance associated with this method has to be assumed.

10.7.2.2 Back-up tubes (identical to those used for sample collection) should be used to investigate situations in which distributed volume pairs do not agree within acceptable tolerance. To use back-up tubes, a second identical sampling tube is placed in series with a primary (front) tube. The purpose of the backup tube is to capture compounds that pass through the primary tube because of breakthrough. Analysis of the backup tube may indicate unexpected breakthrough or give evidence of channeling of sample through the tube because of loose packing.

10.7.2.3 A significant volume of literature exists on the use of distributed volume sets to determine the occurrence of nonlinearities when different sample volumes are taken from the same sample air mix. Ideally, the quantity of material collected scales linearly with sample volume. If this is not the case, then one of a number of problems has occurred. The 4-tube distributed volume developed by Walling, Bumgardner, and co-workers (32,33) is a method by which sample collection problems can be investigated.

10.8 Determining and Validating Safe Sampling Volumes (SSV)

10.8.1 Field Test Method for Tube Breakthrough.

10.8.1.1 If SSV information is not readily available for the analytes under test on the sorbent tube selected, or if the safe sampling volumes need validating - the following field experiment may be used. Link at least 12 of the sorbent tubes under test together in series to give 6 pairs of tubes. Use inert, preferably Swagelok®-type 1/4-inch metal unions with PTFE fittings. The sampling end of the back up tube should be connected to the exit end of the front tube in each of the pairs. The tube pairs are then connected to calibrated monitoring pumps and used to simultaneously sample at least 3 different air volumes at pump flow rates between 10 and 200 mL/min with 2 replicates at each air sample volume.

10.8.1.2 The experiment should be carried out in the atmosphere to be monitored and, if possible, under worst-case conditions (i.e., highest natural humidity and highest typical VOC concentrations). The sampling points of all the tube pairs should be placed close together to ensure that, as far as possible, tubes are all sampling the same atmosphere. The sampling location selected should be well ventilated. Both the front and back-up tubes of each tube pair should subsequently be analyzed using thermal desorption - capillary GC.

10.8.1.3 If more than 5% of one or more of the target analytes is observed on any of the back-up tubes, breakthrough is shown to have occurred at that sample volume. For practical purposes, the BV for a given sorbent/analyte combination is usually considered to be the sample volume at which there is 5% breakthrough of that analyte onto the back-up tube. The SSV for that analyte/sorbent combination is then taken as two thirds (~66%) of the BV.

10.8.2 Chromatographic Test of Tube Retention Volume for Individual Analytes

10.8.2.1 Inject 0.5 mg of each analyte into a stoppered ~1L volume glass flask fitted with a septum. Check that all the analyte has evaporated.

10.8.2.2 Connect the sample tube under test to a 1/4 inch injection port inside a GC oven. Use 530 μm, uncoated fused silica capillary tubing, or other appropriate narrow bore tubing, to connect the other end of the sample tube to a FID detector. Use 1/4 inch fittings with graphite ferrules to connect to the sample tube itself.

10.8.2.3 Set a nitrogen carrier gas flow of 50 mL/min through the tube.

10.8.2.4 Inject a 0.1 mL sample of the vapor phase standard onto the tube using a gas syringe. Adjust the GC oven temperature so that the analyte peak elutes on the FID between 1 and 20 minutes.

10.8.2.5 Repeat the experiment 4 or 5 times using different GC oven temperatures. Try to ensure that at each of the GC temperatures selected, the peak elutes within 1-20 minutes.

[Note: Use the time from injection to peak crest as the retention time. This may have to be measured manually, depending on the type of integrator available.]

10.8.2.6 Inject a sample of methane to measure the delay time of the system and subtract this from the analyte retention times determined.

10.8.2.7 Use the flow of nitrogen carrier gas and corrected retention times to calculate the analyte retention volumes at different sorbent temperatures.

10.8.2.8 A graph of $\log_{10}$ retention volume vs. 1/temp(K) should produce a straight line plot which can be readily extrapolated to ambient temperatures. Use this plot to obtain the retention volume.

A SSV for the analyte on that sorbent tube is then derived by halving the calculated retention volume at ambient temperature. When required, this experiment should be carried out for the least well retained compound(s) of interest.

10.9 Resealing Sorbent Tubes After Sample Collection

Sampled tubes should be recapped with the metal, Swagelok®-type caps and combined PTFE ferrules, rewrapped in the aluminum foil (if appropriate) and replaced in the storage container immediately after sampling. They should not be removed from the sampling container until they are in the laboratory and about to be analyzed.

10.10 Sample Storage

Samples should be refrigerated at <4°C in a clean environment during storage and analyzed within 30 days of sample collection (within one week for limonene, carene, *bis*-chloromethyl ether and labile sulfur or nitrogen-containing volatiles). Samples taken on tubes containing multiple sorbent beds should be analyzed as soon as possible after sampling unless it is know in advance that storage will not cause significant sample recovery errors (see also Section 7.1.3 concerning artifacts).

11. Analytical Procedure

11.1 Preparation for Sample Analysis

Follow the description given in Compendium Method TO-15 for set up of the GC/MS analytical system including column selection, MS tune requirements, calibration protocols, etc.

11.2 Predesorption System Checks and Procedures

The following sample and system integrity checks and procedures must be carried out manually or automatically before thermal desorption:

- **Dry purge**. Dry purge the batch of sampled, back-up and field blank tubes (do not purge lab blanks).
- **Cap**. Cap tubes with PTFE ‘analytical’ caps and place on instrument carousel.
- **Leak test the tubes**. Each tube must be stringently leak tested at the GC carrier gas pressure, without heat or gas flow applied, before analysis. Tubes which fail the leak test should not be analyzed, but should be resealed and stored intact. On automated systems, the instrument should continue to leak test and analyze subsequent tubes after a given tube has failed. Automated systems should also store a record of which tubes in a sequence have failed the leak test in battery-protected system memory until the error is acknowledged by an operator. These measures prevent sample losses and help ensure data quality.

- **Leak test the sample flow path**. All parts of the sample flow path should be stringently leak tested before each analysis without heat or gas flow applied to the sample tube. An automatic sequence of tube desorptions and GC analyses should be halted if any leak is detected in the main sample flow path.
- **Purge air**. Purge air from the tube and sample flow path at ambient temperature using carrier gas immediately before tube desorption. It helps to dry the sample and prevents analyte and sorbent oxidation thus minimizing artifact formation, ensuring data quality and extending tube lifetimes. The focusing trap should be in-line throughout the carrier gas purge to retain any ultra-volatile analytes "desorbed" from the tube prematurely.
- **Check GC/MS analytical system ready status**. The "ready" status of the GC, detector(s), data processor and all parts of the analytical system should be automatically checked by the thermal desorption device before each tube desorption. It should not be possible to desorb a tube into the analytical system if it is not ready to accept and analyze samples.
- **Internal standard**. Introduce a gas phase internal standard onto the sorbent tube or focusing trap before primary (tube) desorption, as an additional check of system integrity (optional).

A series of schematics illustrating these steps is presented in Figure 3, Steps (a) through (f).

11.3 Analytical Procedure

11.3.1 Steps Required for Reliable Thermal Desorption.

11.3.1.1 A stepwise summary of the complete thermal desorption procedure is as follows:

- Predesorption system checks (see Section 11.2).
- Introduction of a fixed volume gas phase internal standard (optional) [see Figure 3, Step (d)].
- Desorption of the sorbent tube (typically 200-300°C for 5-15 minutes with a carrier gas flow of 30-100 mL/min - see Table 2) and refocusing of the target analytes on a focusing trap held at near- ambient or subambient temperatures [see Figure 3, Step (e)].

[Note: Analytes should be desorbed from the tube in ?backflush" mode, i.e., with the gas flow in the reverse direction to that of the air flow during sampling].

- Splitting the sample as it is transferred from the tube to the focusing trap (Optional). This is only required to prevent column or detector overload due to excess water accumulation or during the analysis of high concentration/large volume air samples or when using ultra-sensitive detectors such as the ECD [see Figure 3, Step (e)].
- Rapid desorption of the focusing trap (typically 40 deg/sec. to a top temperature of 250-350°C, with a ?hold" time of 1-15 mins at the top temperature and an inert/carrier gas flow of 3-100 mL/min) and transfer of the analytes into the analytical column [see Figure 3, Step (f)].

[Note: Components should normally be desorbed from the focusing trap in ?backflush" mode, i.e., with the gas flow through the 'cold' trap in the reverse direction to that used during analyte focusing.]

- Splitting the sample as VOCs are transferred from the focusing trap to the analytical column. (Optional). This is only required to prevent column or detector overload due to excess water accumulation or during the analysis of high concentration/large volume air samples or when using ultra-sensitive detectors such as the ECD [See Figure 3, Step (f)].
- Desorbing the focusing trap initiates the GC run. [See Figure 3, Step (f)].

- All volatiles should be stripped from the sorbent tubes during the thermal desorption process leaving them clean and ready for reuse. The tubes should be resealed to ensure they are kept clean and ready for immediate reuse while the sequence of tube desorptions and analyses is completed.

11.3.2 GC/MS Analytical Procedure

11.3.2.1 Once the GC run has been initiated by desorption of the focusing trap, the chromatographic procedure continues as described in Compendium Method TO-15.

11.3.2.2 The precision of the analytical system should be tested using six standard tubes all loaded with a mid-concentration-range standard. This procedure should be carried out whenever the thermal desorption - GC/MS analytical method is changed and should be repeated once every tenth series of samples run with an analytical method or once every three months, whichever happens first. The report produced from the most recent precision test should be included with the final batch report generated for each series of samples.

12. Calibration of Response

Descriptions of how to load tubes from standard atmospheres, concentrated gas phase standards or liquid standards are given in Sections 9.2 and 9.3. Once the tubes are desorbed to the focusing trap and into the analytical GC/MS system the calibration procedure becomes identical to that presented in Section 3 of Compendium Method TO-15. The guidance given in Section 3 of Compendium Method TO-15 concerning multi-level calibration procedures and calibration frequencies should be followed for this Compendium method. It is also advisable to analyze a single level calibrant (i.e. tubes loaded with analyte masses in the mid-range of those expected to be collected during sampling) approximately every tenth sample during an analytical sequence, as a check on system performance. All samples processed that exceed the calibration range will require data qualifiers to be attached to the analytical results.

13. Quality Assurance

13.1 Validating the Sample Collection Procedure

13.1.1 Blanks.

13.1.1.1 Artifact levels on laboratory and field blanks should be at the low or sub-nanogram level for carbonaceous sorbents and Tenax® and at the double digit ng level for Porapaks®, Chromosorb® Century series sorbents and other porous polymers as described in Section 7.1. If artifact levels are considerably above this, careful attention must be paid to the tube conditioning and storage procedures described in Sections 10.2.1 and 10.2.2. Artifact peaks which are 10% or more of the area of average component peaks should be marked as artifacts in the final data reports. When monitoring unknown atmospheres, special care must be taken to distinguish between sorbent artifacts and analytes, using the MS to identify components which are significant in both blank and sampled tubes.

13.1.1.2 If the same profile/pattern of VOCs is observed on the field blanks as on the sampled tubes and if the level of these components is 5% or more of the sampled volatiles, careful attention must be paid to the method of sealing the tubes and other storage procedures in future studies. If the profile of volatiles on the field blanks matches that of the sampled tubes and if the areas of the peaks on the field blank are 10% or more of sampled tube levels, the sampled tube data are invalidated.

13.1.2 Routine Checking of Sorbent Tube Safe Sampling Volumes.

13.1.2.1 The SSVs of sorbent tubes should be retested annually or once every 20 uses (whichever happens first) using one of the procedures described in Section 10.8.

13.1.2.2 If the SSV of a tube (i.e., half the RV or two thirds of the BV) falls below the normal air sample collection volume for the analytes in question, the tube should be repacked with fresh adsorbent and reconditioned.

13.2 Performance Criteria for the Monitoring Pump

Records of the pump flow rate delivered against the pump flow rate, stroke rate or pressure selected on a pump should be reviewed at least once per three months. If the performance of any pump has been found to have changed significantly over that time; for example if completely different pump settings are required to deliver the same pump flow rate, the pump should be serviced by the manufacturer or their approved agent.

Sampling pump errors can normally be presumed to be in the order of 5% (8). If the pump sampling flow rate measured at the end of sample collection varies more than 10% from that measured at the beginning of sample collection, then that sample is invalidated.

14. Performance Criteria for the Solid Adsorbent Sampling of Ambient Air

14.1 Introduction

There are four performance criteria which must be met for a system to qualify under Compendium Method TO-17. These criteria closely parallel those of Compendium Method TO-15, *"The Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)"*. These criteria are:

- A method detection limit $\leq$0.5 ppb.
- Duplicate (analytical) precision within 20% on synthetic samples of a given target gas or vapor in a typical target gas or vapor mix in humidified zero air.
- Agreement within 25% for distributed volume pairs of tubes taken in each sampling set.
- Audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppb). Either mass spectrometry as emphasized here, or specific detectors can be used for analysis. Details for the determination of each of the criteria follow.

14.2 Method Detection Limit

The procedure chosen to define the method detection limit is that given in the Code of Federal Regulations (40CFR136 Appendix B). The method detection limit is defined for each system by making seven replicate measurements of a concentration of the compound of interest near the expected detection limit (within a factor of five), computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (the Student's t value for 99 percent confidence for seven values).

14.3 Analytical Precision of Duplicate Pairs

The measure of analytical precision used for this method is the absolute value of the relative difference between two identical samples (same flow rate over the same time period from with a common inlet to the sample volume). The analytical precision is expressed as a percentage as follows:

$$\text{Analytical Precision} = \left(\frac{[|X1 - X2|]}{X}\right) 100$$

where:

X1 = A measurement value taken from one of the two tubes using in sampling.
X2 = A measurement value taken from the second of two tubes using in sampling.
X = Average of X1 and X2.

The analytical precision is a measure of the precision achievable for the entire sampling and analysis procedure including the sampling and thermal desorption process mentioned above and the analytical procedure that is same as the TO-15 analytical finish, although specific detector systems can also be used.

14.4 Precision for the Distributed Volume Pair

The measure of precision used for this method is the absolute value of the relative difference between the distributed volume pair expressed as a percentage as follows:

$$\text{percent difference} = \left(\frac{[|X1 - X2|]}{X}\right) 100$$

where:

X1 = One measurement value (e.g., for a defined sample volume of 1 L).
X2 = Duplicate measurement value (e.g., for a defined sample volume of 4 L taken over the same time period as the first sample).
X = Average of the two values.

There are several factors that may affect the precision of the measurement as defined above. In fact any factor that is nonlinear with sample volume may be significant enough to violate the constraint placed on distributed volume pair precision. These factors include artifact formation, compound reactions on the sorbent, breakthrough of target compounds, etc.

14.5 Audit Accuracy

A measure of audit accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the relative difference between the measurement result and the nominal concentration of the audit compound:

$$\text{Audit Accuracy, \%} = \left[\frac{(\text{Spiked Value} - \text{Observed Value})}{(\text{Spiked Value})}\right] \text{x } 100$$

The choice of audit standard is left to the analyst.

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TABLE 1. GUIDELINES FOR SORBENT SELECTION

Sample Tube Sorbent	Approx. Analyte Volatility Range	Max. Temp., (°C)	Specific Surface Area, (m^2/g)	Example Analytes
CarbotrapC® CarbopackC® Anasorb® GCB2	n-C_8 to n-C_{20}	>400	12	Alkyl benzenes and aliphatics ranging in volatility from n-C to n-C .
Tenax® TA	bp 100°C to 400°C n-C_7 to n-C_{26}	350	35	Aromatics except benzene, Apolar components (bp>100°C) and less volatile polar components (bp>150°C).
Tenax GR	bp 100°C to 450°C n-C_7 to n-C_{30}	350	35	Alkyl benzenes, vapor phase PAHs and PCBs and as above for Tenax TA.
Carbotrap® CarbopackB® Anasorb® GCB1	(n-C_4) n-C_5 to n-C_{14}	>400	100	Wide range of VOCs inc., ketones, alcohols, and aldehydes (bp>75°C) and all apolar compounds within the volatility range specified. Plus perfluorocarbon tracer gases.
Chromosorb® 102	bp 50°C - 200°C	250	350	Suits a wide range of VOCs incl. oxygenated compounds and haloforms less volatile than methylene chloride.
Chromosorb 106	bp 50°C - 200°C	250	750	Suits a wide range of VOCs incl. hydrocarbons from n-C to n-C . Also good for volatile oxygenated compounds
Porapak Q	bp 50°C - 200°C n-C_5 to n-C_{12}	250	550	Suits a wide range of VOCs including oxygenated compounds.
Porapak N	bp 50°C - 150°C n-C_5 to n-C_8	180	300	Specifically selected for volatile nitriles; acrylonitrile, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from EtOH, MEK, etc.
Spherocarb*	-30°C - 150°C C_3 to n-C_8	>400	1,200	Good for very volatile compounds such as VCM, ethylene oxide, CS and CH Cl . Also good for volatile polars e.g. MeOH, EtOH and acetone.
Carbosieve SIII*® Carboxen 1000*® Anasorb® CMS*	-60°C to 80°C	400	800	Good for ultra volatile compounds such as C C hydrocarbons, volatile haloforms and freons.
Zeolite Molecular Sieve 13X**	-60°C to 80°C	350		Used specifically for 1,3- butadiene and nitrous oxide.
Coconut Charcoal* (Coconut charcoal is rarely used)	-80°C to 50°C	>400	>1,000	Rarely used for thermal desorption because metal content may catalyze analyte degradation. Petroleum charcoal and Anasorb® 747 are used with thermal desportion in the EPA's volatile organic sampling train (VOST), Methods 0030 and 0031.

* These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high (>90%) relative humidity.

** Significantly hydrophilic. Do not use in high humidity atmospheres unless silicone membrane caps can be fitted for diffusive monitoring purposes.

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TABLE 2. GUIDELINES FOR SORBENT USE

Sample Tube Sorbent	Maximum Temp., (°C)	Hydro-phobic (?)	Temp. and Gas Flow for Conditioning	Temp. and Min. Gas Flow for Desorption	Recommended Focusing Trap Packing
CarbotrapC® CarbopackC® Anasorb® GCB2	>400	Yes	350°C and 100 mL/min	325°C and 30 mL/min	Tenax® or Carbopack C®
Tenax® TA	350	Yes	330°C and 100 mL/min	300°C and 30 mL/min	Tenax®
Tenax GR	350	Yes	330°C and 100 mL/min	300°C and 30 mL/min	Tenax®
Carbotrap® CarbopackB® Anasorb® GCB1	>400	Yes	350°C and 100 mL/min	325°C and 30 mL/min	Tenax or Carbopack B®
Chromosorb® 102	250	Yes	250°C and 100 mL/min	225°C and 30 mL/min	Dual-bed CB plus CMS trap or Chrom. 102
Chromosorb 106	250	Yes	250°C and 100 mL/min	250°C and 30 mL/min	Dual-bed CB plus CMS trap or Chrom. 106
Porapak Q	250	Yes	250°C and 100 mL/min	225°C and 30 mL/min	Dual-bed CB plus CMS trap or Porapak Q
Porapak N	180	Yes	180°C and 100 mL/min	180°C and 30 mL/min	Dual-bed CB plus CMS trap or Porapak N
Spherocarb*	>400	No	400°C and 100 mL/min	390°C and 30 mL/min	Dual-bed CB plus CMS trap or Spherocarb
CMS such as CSIII*® Carboxen 1000*® Anasorb® CMS*	400	No	350°C and 100 mL/min	325°C and 30 mL/min	Dual-bed CB plus CMS trap or CMS alone
Zeolite Molecular Sieve 13X**	350	No	330°C and 100 mL/min	300°C and 30 mL/min	Dual-bed CB plus CMS trap or CMS alone
Tenax / CB : comb. Tube Type 1 (see Sect. 9.1.3)	350	Yes	330°C and 100 mL/min	300°C and 30 mL/min	Tenax
Carb B / CMS* comb. Tube Type 2 (see Sect. 9.1.3)	400	No	350°C and 100 mL/min	325°C and 30 mL/min	Dual-bed CB plus CMS trap
Carb. 300 type*, comb. Tube Type 3 (see Sect. 9.1.3)	400	No	350°C and 100 mL/min	325°C and 30 mL/min	Dual-bed CB plus CMS trap

* These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high (>90%) relative humidity.

** Significantly hydrophilic. Do not use in high humidity atmospheres unless silicone membrane caps can be fitted for diffusive monitoring purposes.

CB is short for Carbopack B and CMS is short for carbonized molecular sieve.

CarbotrapC™, CarbopackC™, CarbopackB™, Carboxen™ and Carbosieve SIII™ are all trademarks of Supelco, Inc., USA; Tenax® is a trademark of Enka Research Institute; Chromosorb® is a trademark of Manville Corp.; Anasorb® is a trademark of SKC, Inc.; Porapak® is a trademark of Waters Corporation.

TABLE 3 - LIST OF COMPOUNDS WITH BREAKTHROUGH VOLUMES >5L USING THE AIR TOXICS TUBE STYLE 2 LISTED IN SECTIONS 6.1.2 AND 9.1.3 OF COMPENDIUM METHOD TO-17

*[Note: The following list of compounds was determined to have breakthrough volumes of greater than 5 liters of trace levels in humidified zero air for humidities of 20%, 65% and 90% RH at 25°C. The tests were performed immediately prior to the publication of this document at the Research Triangle Institute, Research Triangle Park, NC as a result of activities leading up to the publication of this document. Compounds with an * were not tested at 90% RH.]*

Halocarbon 114
1,3,5-Trimethylbenzene
Halocarbon 11
1,2,4-Trimethylbenzene
Halocarbon 113
Dichlorobenzenes
1,1-Dichloroethene
1,2,4-Trichlorobenzene
Methylene Chloride
Hexachloro-1,3,-butadiene
1,1 Dichloroethane
*1,3 Butadiene
cis-1,2-Dichloroethene
*Acetonitrile
Chloroform
*Acetone
1,1,1-Trichloroethane
*2-Propanol
Carbon tetrachloride
*Acrylonitrile
Benzene
*Isoprene
1,2-Dichloroethane
*Methyl Acetate
Trichloroethene
*Methyl tert-Butyl Ether
1,2-Dichloropropane
*Methyl Ethyl Ketone
cis-1,3-Dichloropropene
*Ethyl Acrylate
Toluene
*Methyl Acrylate
Trans-1,3-Dichloropropene
*Methyl Isobutyl Ketone
*Furfural
Tetrachloroethene
1,2-Dibromoethane
Chlorobenzene
Ethylbenzene
m-Xylene
p-Xylene
o-Xylene
1,1,2,2-Tetrachloroethane

TABLE 4. MASS OF AN ANALYTE 'X' COLLECTED FROM 1, 2 OR 10 L AIR SAMPLES AT DIFFERENT ATMOSPHERIC CONCENTRATIONS
(ASSUMING 'X' HAS A MOLAR WEIGHT OF 100 g)

Sample type	Typical concentration	Mass collected in 1 L sample volume	Mass collected in 2 L sample volume	Mass collected in 10 L sample volume
Fenceline/severe urban area	10-250 ppb	40-1,000 ng	80 ng-2 μg	0.4-10μg
Indoor air sampling	1-100 ppb	4-400 ng	8-800 ng	40 ng-4μg
Avg. exposure to benzene	~3 ppb	11 ng	22 ng	110 ng
Normal urban area	1-10 ppb	4-40 ng	8-80 ng	40-400 ng
Normal rural area	0.1-1 ppb	0.4-4 ng	0.8-8 ng	4-40 ng
Forested area	0.25-2.5 ppb	1-10 ng	2-20 ng	10-100 ng
Mt. Everest/K2 site	0.025-7.5 ppb	0.1-30 ng	0.2-60 ng	1-300 ng
Arctic on an ultraclean day	15-50 ppt	60-200 pg	0.12-0.4 ng	0.6-2 ng

COMPENDIUM METHOD TO-17
FIELD TEST DATA SHEET (FTDS)

I. GENERAL INFORMATION

PROJECT:__________________________ DATE(S) SAMPLED:________________________
SITE:________________________________ TIME PERIOD SAMPLED:__________________
LOCATION:_________________________ OPERATOR:______________________________
INSTRUMENT MODEL NO.:_________ CALIBRATED BY:__________________________
PUMP SERIAL NO.:_________________ RAIN: ____YES _____NO

ADSORBENT CARTRIDGE INFORMATION:

	Tube 1	Tube 2
Type:	__________	__________
Adsorbent:	__________	__________
Serial No.:	__________	__________
Sample No.:	__________	__________

II. SAMPLING DATA

Tube Identification	Sampling Location	Ambient Temp., °F	Ambient Pressure, in Hg	Flow Rate (Q), mL/min		Sampling Period		Total Sampling Time, min.	Total Sample Volume, L
				Tube 1	Tube 2	Start	Stop		

III. FIELD AUDIT

	Tube 1	Tube 2
Audit Flow Check Within 10% of Set Point (Y/N)?	_ pre-	_ pre-
	__________ post-	__________ post-

CHECKED BY:____
DATE:____

Figure 1. Compendium Method TO-17 Field Test Data Sheet.

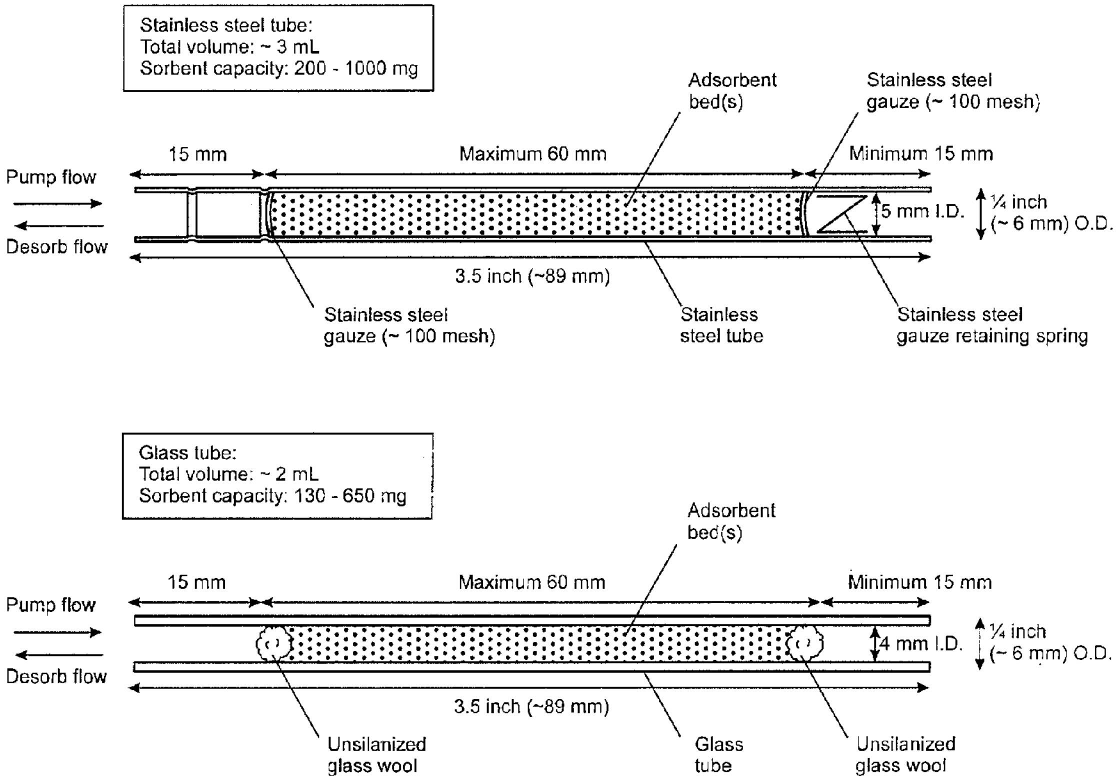
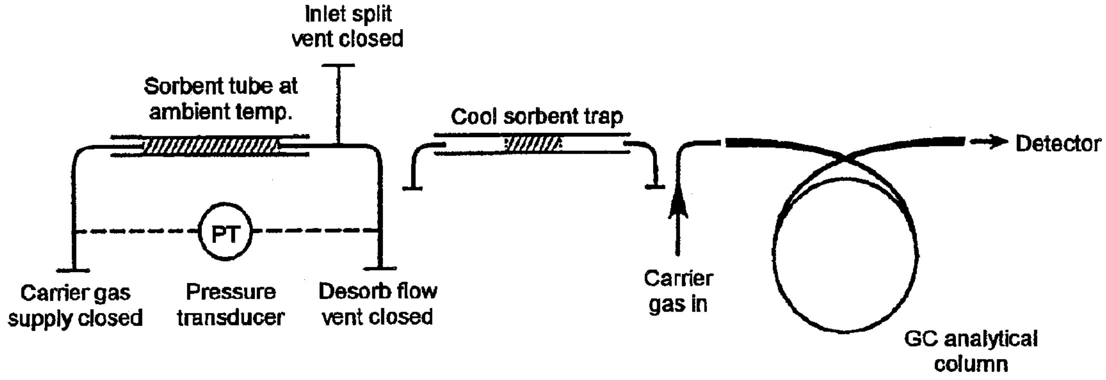
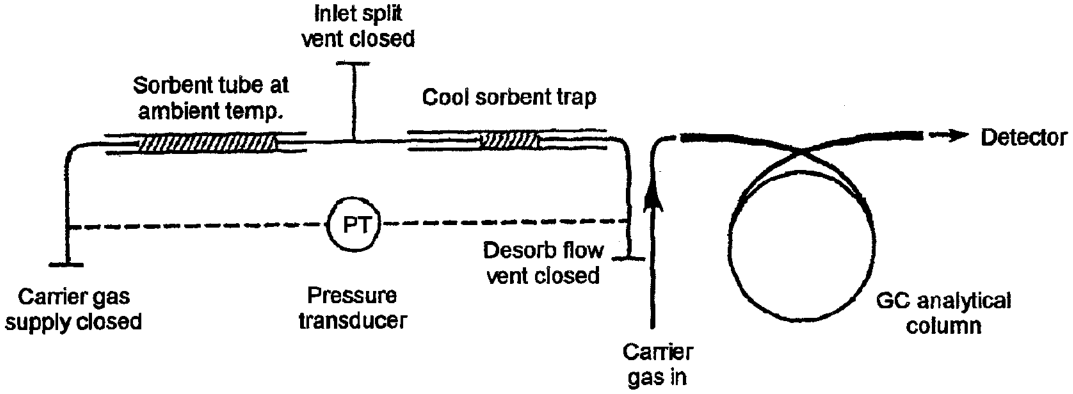


Figure 2. Example of construction of commercially available adsorbent tubes.

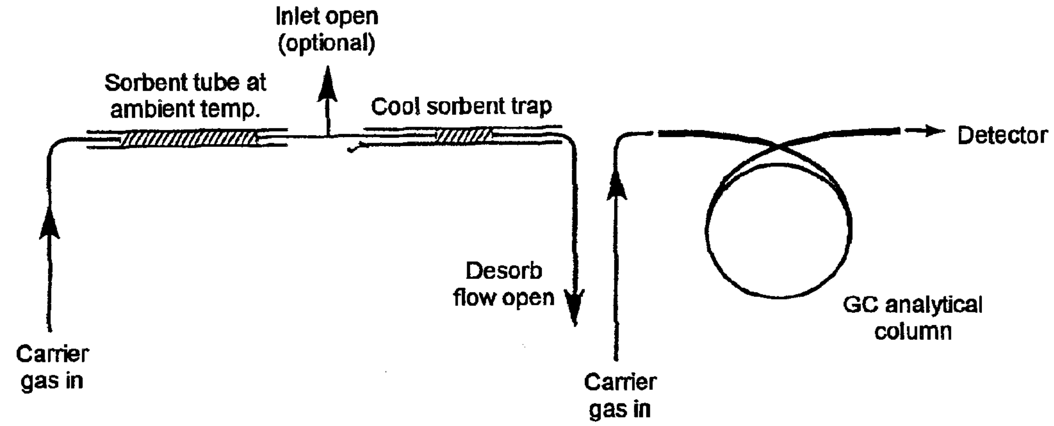


(a) Tube leak check.

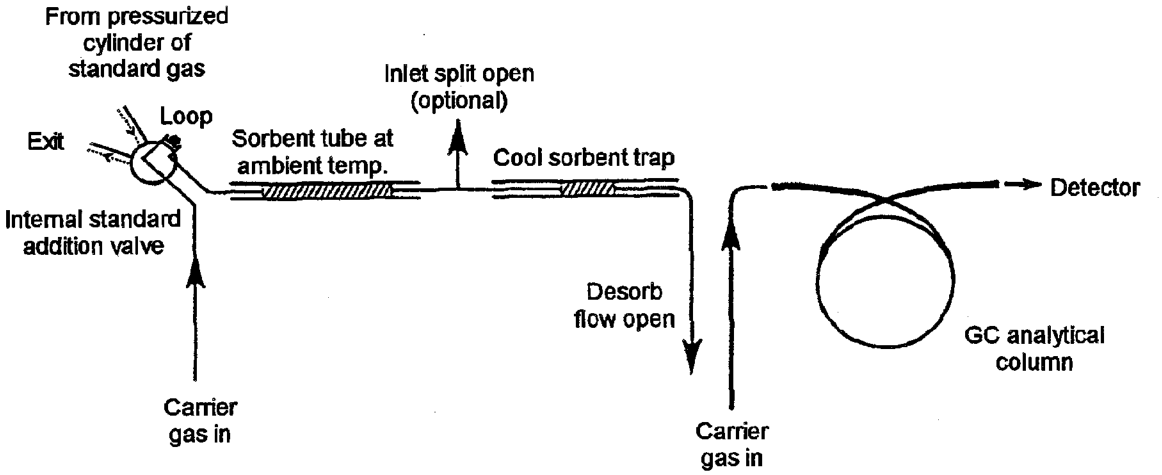


(b) Leak check sample flow path.

Figure 3. Sequence of operations to thermally desorb the sample from the sorbent tube and transfer to the gas chromatograph: (a) tube leak test and (b) leak check flow path.

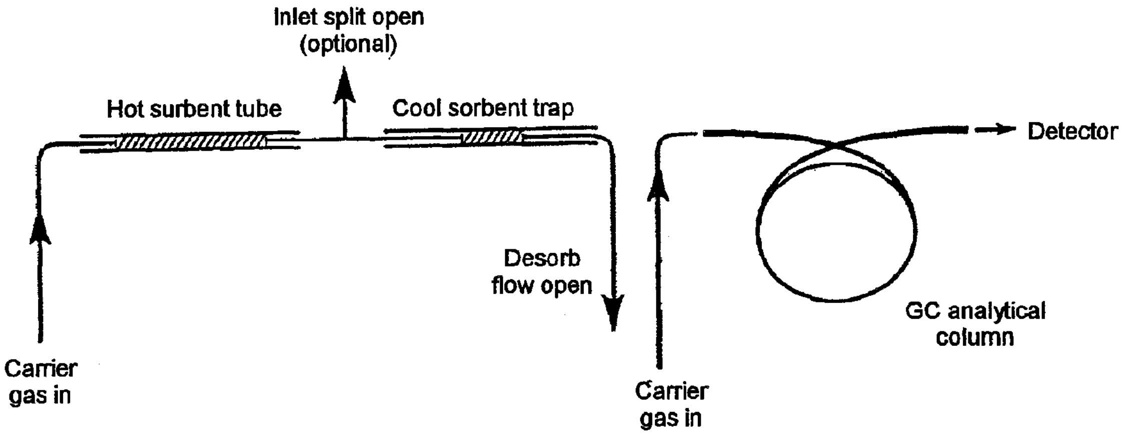


(c) Purge to remove air.

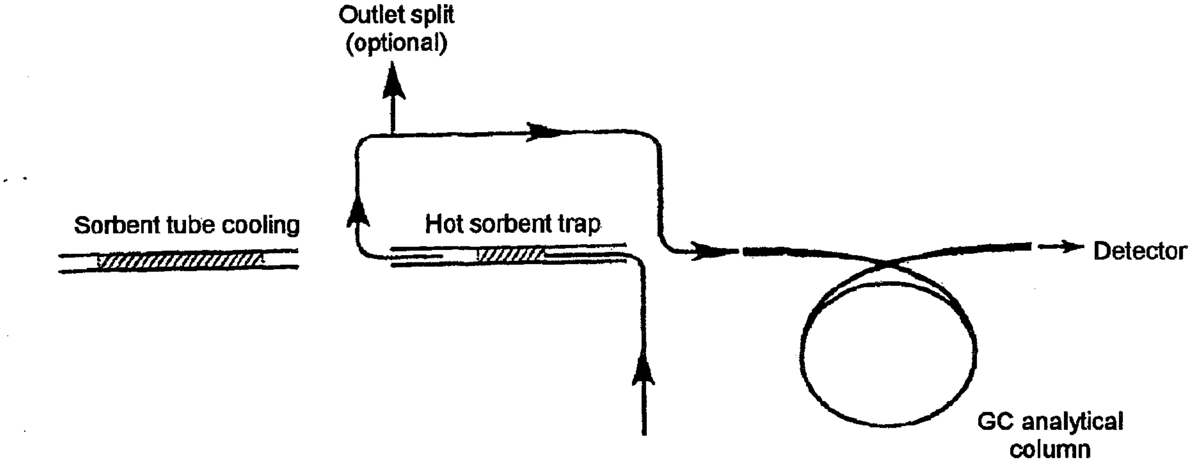


(d) Gas phase internal standard addition to sample tube.

Figure 3 (cont). Sequence of operations to thermally desorb the sample from the sorbent tube and transfer to the gas chromatograph: (c) purge to remove air and (d) gas phase internal standard addition to sample tube.



(e) Primary (tube) desorption.



(f) Secondary (trap) desorption.

Figure 3 (cont). Sequence of operations to thermally desorb the sample from the sorbent tube and transfer to the gas chromatograph: (e) primary (tube) desorption and (f) secondary (trap) desorption.

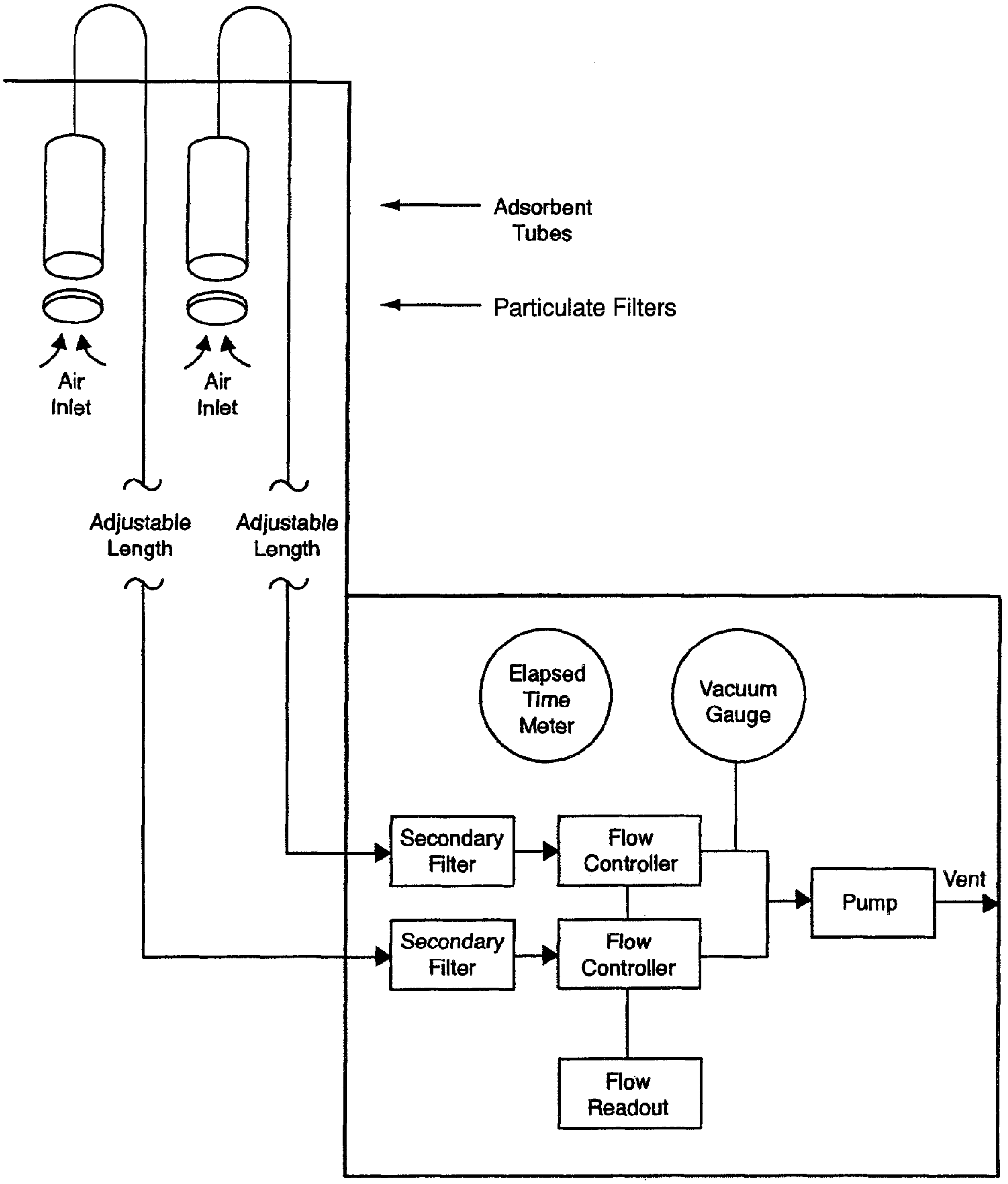


Figure 4. Example of distributive air volume using adsorbent tube technology.

APPENDIX 1.

The following list includes safe sampling volume data generated by the UK Health and Safety Executive (4) on single sorbent bed 1/4 inch O.D. stainless steel tubes and compatible with a thermal desorption - capillary GC analytical procedure. It is provided as a resource to readers only. The recommendation for Tube Style 2 is based on the specific tube referenced in Section 6.1.2 and Table 3. Where tubes are not listed with safe sample volumes they have not been tested and their inclusion represents a suggestion only. Application to air sampling is subject to criteria listed in Section 14 of Compendium Method TO-17.

[Note: Combination tubes 1, 2, and 3 referenced in this Appendix are those adsorbent tubes described in Section 9.1.3.]

Compound	Suitable sorbents and SSV's where available

Hydrocarbons

This procedure is suitable for all aliphatic, aromatic and cyclic hydrocarbons less volatile than ethane and more volatile than n-C20. These include:

Compound	Suitable sorbents and SSV's where available
n-Butane	CS III, C 1000, Combination Tubes 2 or 3 or Spherocarb (SSV 820L).
n-Pentane	CS III, C 1000, Spherocarb (SSV 30,000L), Combination Tubes 2 or 3 or Chromosorb 106 (SSV 5.5L).
n-Hexane	Carbopack™ B, Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 30L).
Benzene	Carbopack™ B, Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 26L) or Tenax (SSV 6L).
n-Heptane	Carbopack™ B, Tenax (SSV 17L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 160L).
Toluene	Carbopack™ B, Tenax (SSV 38L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 80L).
n-Octane	Carbopack™ B, Tenax (SSV 700L) Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 1000L).
Ethylbenzene	Carbopack™ B, Tenax (SSV 180L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 360L).
all Xylenes	Carbopack™ B, Tenax (SSV 300L), Combination Tubes 1, 2, 3 or Chromosorb 106 (SSV 770L).
n-Nonane	Carbopack™ C/B, Tenax (SSV 700L), Combination Tubes 1, 2 or 3 or Chromosorb 106 (SSV 7000L).
Styrene	Carbopack™ C/B, Tenax (SSV 300L) or Combination Tubes 1, 2 or 3.
Isopropylbenzene	Carbopack™ C/B, Tenax (SSV 480L) or Combination Tubes 1, 2 or 3.
n-Propylbenzene	Carbopack™ C/B, Tenax (SSV 850L) or Combination Tubes 1, 2 or 3.
1-Methyl-3-ethylbenzene	Carbopack™ C/B, Tenax (SSV 1000L) or Combination Tubes 1, 2 or 3.
1-Methyl-4-ethylbenzene	Carbopack™ C/B, Tenax (SSV 1000L) or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
1,3,5-Trimethylbenzene	Carbopack™ C/B, Tenax (SSV 1800L), Combination Tubes 1, 2 or 3 or Chromosorb 106 (SSV 2800).
Methylstyrene	Carbopack™ C/B, Tenax (SSV 1200L) or Combination Tubes 1, 2 or 3.
Methyl-2-ethylbenzene	Carbopack™ C/B, Tenax (SSV 1000L) or Combination Tubes 1, 2 or 3.
1,2,4-Trimethylbenzene	Carbopack™ C/B, Tenax (SSV 1800L) or Combination Tubes 1, 2 or 3.
n-Decane	Carbopack™ C/B, Tenax (SSV 2100L), Combination Tubes 1, 2 or 3 or Chromosorb 106 (SSV 37,000L).
1,2,3-Trimethylbenzene	Carbopack™ C/B, Tenax (SSV 1800L) or Combination Tubes 1, 2 or 3.
n-Undecane	Carbopack™ C/B, Tenax (SSV 12,000L) or Combination Tubes 1, 2 or 3.
n-Dodecane	Carbopack™ C, Tenax (SSV 63,000L) or Combination Tubes 1 or 3.

Halogenated Hydrocarbons including PCBs

This procedure is suitable for all aliphatic, aromatic and cyclic halogenated hydrocarbons more volatile than n-C20. Examples include:

Compound	Suitable sorbents and SSV's where available
Dichloromethane	CS III, C 1000, Spherocarb (SSV 200L) or Combination Tubes 2 or 3.
1,2-Dichloroethane	CS III, C 1000, Spherocarb, Chrom. 106 (SSV 17L), Carbopack™ B, Tenax (SSV 5.4L) or Combination Tubes 1, 2 or 3.
1,1,1-Trichloroethane	Spherocarb (SSV 8,000L), Chrom. 106 (SSV 8L), Carbopack™ B, or Combination Tubes 1, 2 or 3.
Carbontetrachloride	Chrom. 106 (SSV 22L), Carbopack™ B, Tenax (SSV 6.2L) or Combination Tubes 1, 2 or 3.
Trichloroethylene	Chrom. 106, Carbopack™ B, Tenax (SSV 5.6L) or Combination Tubes 1, 2 or 3.
1,1,2-Trichloroethane	Chrom. 106, Carbopack™ B, Tenax (SSV 34L) or Combination Tubes 1, 2 or 3.
Tetrachloroethylene	Chrom. 106, Carbopack™ B, Tenax (SSV 48L) or Combination Tubes 1, 2 or 3.
Chlorobenzene	Chrom. 106, Carbopack™ B, Tenax (SSV 26L) or Combination Tubes 1, 2 or 3.
1,1,1,2-Tetrachloroethane	Chrom. 106, Carbopack™ B, Tenax (SSV 78L) or Combination Tubes 1, 2 or 3.
1,1,2,2-Tetrachloroethane	Chrom. 106, Carbopack™ B, Tenax (SSV 170L) or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available

Alcohols

This procedure is suitable for alcohols more volatile than n-C20 and sufficiently stable to be analyzed by conventional GC techniques. Examples include:

Methanol	CSIII, C1000, Spherocarb (SSV 130L) or Combination Tubes 2 or 3.
Ethanol	CSIII, C1000, Spherocarb (SSV 3500L) or Combination Tubes 2 or 3.
n-Propanol	Porapak N (SSV 20L), Chrom 106 (SSV 8L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Isopropanol	Chrom 106 (SSV 44L), Carbopack™ B or Combination Tubes 1, 2 or 3.
n-Butanol	Chrom 106 (SSV 50L), Carbopack™ B, Porapak N (SSV 5L), Tenax (SSV 5L) or Combination Tubes 1, 2 or 3.
iso-Butanol	Chrom 106 (SSV 30L), Carbopack™ B, Tenax (SSV 2.8L) or Combination Tubes 1, 2 or 3.
Octanol	Tenax (SSV 1400L), Carbopack™ C or Combination Tubes 1 or 3.

Esters and Gycol Ethers

This procedure is suitable for all esters and glycol ethers more volatile than n-C20 and sufficiently stable to be analyzed by conventional GC techniques. Examples include:

Methylacetate	Chromosorb 106 (SSV 2.6L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Ethylacetate	Chromosorb 106 (SSV 20L), Carbopack™ B, Tenax (SSV 3.6L) or Combination Tubes 1, 2 or 3.
Propylacetate	Chromosorb 106 (SSV 150L), Carbopack™ B, Tenax (SSV 18L) or Combination Tubes 1, 2 or 3.
Isopropylacetate	Chromosorb 106 (SSV 75L), Carbopack™ B, Tenax (SSV 6L) or Combination Tubes 1, 2 or 3.
Butylacetate	Chromosorb 106 (SSV 730L), Carbopack™ B, Tenax (SSV 85L) or Combination Tubes 1, 2 or 3.
Isobutylacetate	Chromosorb 106 (SSV 440L), Carbopack™ B, Tenax (SSV 130L) or Combination Tubes 1, 2 or 3.
Methyl-t-butyl ether	Chromosorb 106 (SSV >6L), Carbopack™ B or Combination Tubes 1, 2 or 3.
t-Butylacetate	Chromosorb 106 (SSV 160L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Methylacrylate	Chromosorb 106, Carbopack™ B, Tenax (SSV 6.5L) or Combination Tubes 1, 2 or 3.

Compound	Suitable sorbents and SSV's where available
Ethylacrylate	Chromosorb 106, Carbopack™ B, Tenax (SSV 60L) or Combination Tubes 1, 2 or 3.
Methylmethacrylate	Chromosorb 106, Carbopack™ B, Tenax (SSV 27L) or Combination Tubes 1, 2 or 3.
Methoxyethanol	Chromosorb 106 (SSV 5L), Carbopack™ B, Tenax (SSV 3L) or Combination Tubes 1, 2 or 3.
Ethoxyethanol	Chromosorb 106 (SSV 75L), Carbopack™ B, Tenax (SSV 5L) or Combination Tubes 1, 2 or 3.
Butoxyethanol	Chromosorb 106, Carbopack™ B, Tenax (SSV 35L) or Combination Tubes 1, 2 or 3.
Methoxypropanol	Chromosorb 106, Carbopack™ B, Tenax (SSV 13L) or Combination Tubes 1, 2 or 3.
Methoxyethylacetate	Chromosorb 106 (SSV 860L), Carbopack™ B, Tenax (SSV 8L) or Combination Tubes 1, 2 or 3.
Ethoxyethylacetate	Chromosorb 106 (SSV 4000L), Carbopack™ B, Tenax (SSV 15L) or Combination Tubes 1, 2 or 3.
Butoxyethylacetate	Chromosorb 106, Carbopack™ B, Tenax (SSV 150L) or Combination Tubes 1, 2 or 3.

Aldehydes and Ketones

This procedure is suitable for all aldehydes and ketones more volatile than n-C20 and sufficiently stable to be analyzed using conventional GC techniques. Examples include:

Acetone	CSIII, C1000, Spherocarb, Chrom 106 (SSV 1.5L) or Combination Tubes 2 or 3.
Methylethylketone (2-butanone)	Chromosorb 106 (SSV 10L), Tenax (SSV 3.2L), Porapak N (SSV 50L) Carbopack™ B or Combination Tubes 1, 2 or 3.
n-Butanal	Chromosorb 106, Carbopack™ B, Porapak N (SSV 50L) or Combination Tubes 1, 2 or 3.
Methylisobutylketone	Chromosorb 106 (SSV 250L), Tenax (SSV 26L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Cyclohexanone	Chromosorb 106, Tenax (SSV 170L), Carbopack™ B or Combination Tubes 1, 2 or 3.
3,5,5-Trimethylcyclohex-2-enone	Tenax (SSV 5600L), Carbopack™ B or Combination Tubes 1 or 3.
Furfural	Tenax (SSV 300L), Carbopack™ B or Combination Tubes 1, 2 or 3.

Miscellaneous VOCs

This procedure is suitable for the analysis of most VOCs in air. It is generally compatible with all organics less volatile than ethane, more volatile than n-C20 and sufficiently stable to be analyzed using conventional GC techniques. Examples include:

Compound	Suitable sorbents and SSV's where available
Acetonitrile	Porapak N (SSV 3.5L), CSIII, C1000 or Combination Tubes 2 or 3.
Acrylonitrile	Porapak N (SSV 8L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Propionitrile	Porapak N (SSV 11L), Carbopack™ B or Combination Tubes 1, 2 or 3.
Maleic anhydride[a]	Tenax (SSV 88L), Chrom. 106, Carbopack™ B or Combination Tubes 1, 2 or 3.
Pyridine	Tenax (SSV 8L), Porapak N (SSV 200L) Chrom. 106, Carbopack™ B or Combination Tubes 1, 2 or 3.
Aniline	Tenax (SSV 220L), Chrom. 106, Carbopack™ B or Combination Tubes 1, 2 or 3.
Nitrobenzene	Tenax (SSV 14,000L) Carbopack™ C or Combination Tubes 1 or 3.
Acetic acid	Porapak N (SSV 50L), Carbotrap™ B or Combination Tubes 1, 2 or 3.
Phenol	Tenax (SSV 240L) or combination tube 1.

APPENDIX 2.

LINEARITY TESTING OF ONE SORBENT TUBE/FOCUSING TUBE COMBINATION

Introduction

Automated gas chromatographs such as those used at network monitoring stations for hourly updates of volatile organic compounds (VOCs) have a solid adsorbent concentrator for the VOCs. This unit is comparable to the sorbent tubes being discussed in this document. The table below shows the results of sampling a synthetic mixture of the Compendium Method TO-14 target list in humidified zero air (approximately 70% RH at 25°C). Sampling occurred for 6, 12, and 24 min at a rate of 80 mL/min giving a total sampling volume of 480, 960, and 1920 mL. These results are similar to the determination of safe sampling volume and the amount of material collected should be related linearly to the sample period. The results indicate that breakthrough has not occurred to any appreciable extent at a sampling volume of approximately 2 L for the stated experimental conditions. The response measured is the response of chlorine from an atomic emission detector after chromatographic separation. The sorbent tube mix was Carbotrap™ C/Carbotrap™ B/Carboxen™ 1000 and the focusing tube mix was Tenax-TA/Silica Gel/Ambersorb XE-340/Charcoal. The primary tube was 6 mm O.D. with 4 mm I.D., 110 mm in length. The focusing tube was 6 mm O.D., 0.9 mm I.D., 185 mm in length. The packing lengths for the sorbent tube per sorbent type were: 1.27 cm, 2.86 cm, and 3.18 cm, respectively. The packing lengths for the focusing tube per sorbent type were: 5.08 cm, 2.54 cm, and 1.27 cm.

Linearity test

[Note: Actual sampling volumes were 490, 980, and 1960 instead of 1/2,1, and 2L as listed for convenience in the table below. The response is obtained as chlorine response on an atomic emission detector. Compounds corresponding to the numbered compounds in the table are identified on the following page.]

Cpd.	1/2 L	1 L	2 L	2L/1L	2L/(1/2L)	1L/(1/2L)	% Diff (2L/0.5L) vs. 4
1	1255.4	2402.9	5337.2	2.22	4.25	1.91	-6.28
2	711.82	1802.2	3087	1.71	4.34	2.53	-8.42
3	2079.4	4853	9386	1.93	4.51	2.33	-12.85
4	978.14	2381.3	4680.1	1.97	4.78	2.43	-19.62
6	1155.7	2357.1	4725.2	2.00	4.09	2.04	-2.22
7	3072.8	6764.4	13662	2.02	4.45	2.20	-11.15
8	2337.3	4356.1	8697.2	2.00	3.72	1.86	6.97
9	3041.7	5986.6	11525	1.93	3.79	1.97	5.28
10	1061.7	2183.6	4296.5	1.97	4.05	2.06	-1.17
11	3800.5	7726.7	15182	1.96	3.99	2.03	0.13
12	2386.9	4877.5	9669	1.98	4.05	2.04	-1.27
13	2455.4	5063.5	9986.6	1.97	4.07	2.06	-1.68
14	3972.6	8118.4	15985	1.97	4.02	2.04	-0.60
15	2430.9	4947.9	9756.1	1.97	4.01	2.04	-0.33
16	6155.4	9247.4	16942	1.83	2.75	1.50	31.19

Cpd.	1/2 L	1 L	2 L	2L/1L	2L/(1/2L)	1L/(1/2L)	% Diff (2L/0.5L) vs. 4
18	4270.4	9233.8	18721	2.03	4.38	2.16	-9.60
19	2494.8	5115.2	10087	1.97	4.04	2.05	-1.08
20	4023.9	8379.4	16672	1.99	4.14	2.08	-3.58
21	1086.8	2295.4	4611.7	2.01	4.24	2.11	-6.08
22	793.33	1670.1	3375.2	2.02	4.25	2.11	-6.36
23	3708.2	7679	15165	1.97	4.09	2.07	-2.24
26	5094	10582	21139	2.00	4.15	2.08	-3.74
27	1265.1	2615.1	5136.9	1.96	4.06	2.07	-1.51
31	4434.9	9176.4	17975	1.96	4.05	2.07	-1.33
36	2320.7	5015.7	9827.3	1.96	4.23	2.16	-5.87
37	441.17	953.09	1894	1.99	4.29	2.16	-7.33
38	1410.7	3015	5895.2	1.96	4.18	2.14	-4.47
39	2338.7	4974.8	9858.8	1.98	4.22	2.13	-5.39
40	2640.9	6269.4	12495	1.99	4.73	2.37	-18.28
41	6796.5	14938	29274	1.96	4.31	2.20	-7.68

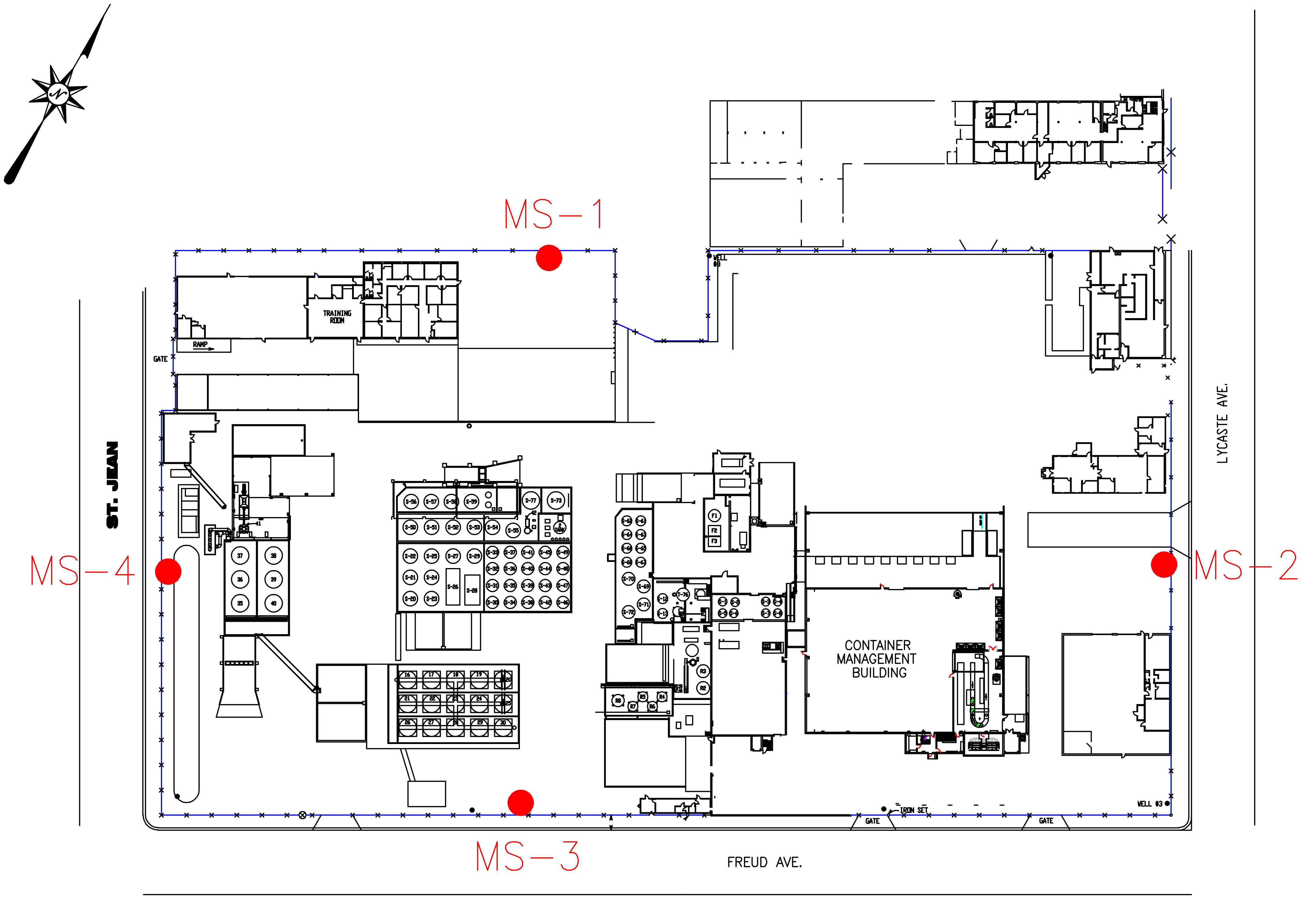
There are no values presented in the above table for hydrocarbons and brominated hydrocarbons (compounds numbered 5, 17, 24, 25, 28, 29, 30, 32, 33, 34, and 35) which do not respond to the chlorine detector used to collect this data.

Compendium Method TO-14
Target Compound List (TCL)

1. Dichlorodifluoromethane
2. Methyl Chloride
3. 1,2-dichloro-1,1,2,2-tetrafluoroethane
4. Vinyl Chloride
5. Methyl Bromide
6. Ethyl Chloride
7. Trichlorofluoromethane
8. 1,1-dichloroethene
9. Dichloromethane
10. 3-chloropropene
11. 1,1,2-trichloro-1,2,2-trifluoroethane
12. 1,1-dichloroethane
13. Cis-1,2-dichloroethene
14. Trichloromethane
15. 1,2-dichloroethane
16. 1,1,1-trichloroethane
17. Benzene
18. Carbon Tetrachloride
19. 1,2-dichloropropane
20. Trichloroethene
21. Cis-1,3-dichloropropene
22. Trans-1,3-dichloropropene
23. 1,1,2-trichloroethane
24. Toluene
25. 1,2-dibromoethane
26. Tetrachloroethene
27. Chlorobenzene
28. Ethylbenzene
29. m,p-xylene
30. Styrene
31. 1,1,2,2-tetrachloroethane
32. o-xylene
33. 4-ethyltoluene
34. 1,3,5-trimethylbenzene
35. 1,2,4-trimethylbenzene
36. m-dichlorobenzene
37. Benzyl Chloride
38. p-dichlorobenzene
39. o-dichlorobenzene
40. 1,2,4-trichlorobenzene
41. Hexachlorobutadiene

FIGURE

Detroit Monitoring Stations



LEGEND

● MONITORING STATION

MS-3 MONITORING STATION NUMBER

PSC

09/26/11

DETROIT MONITORING STATIONS

DRAWN BY: LEWIS KRYK

098

Volatile Organic Compounds in Air by EPA TO-15 (GC/MS)

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1. Scope and Application

1.1 This SOP describes the analytical procedure for the analysis of volatile organic compounds (VOCs) captured in whole air samples.

1.2 This procedure may be employed for the analysis of canister, Bottle-Vac™ or Tedlar® Bag samples.

1.3 This SOP is to be used by all personnel conducting this analysis at Fibertec, Inc., Holt, MI.

1.4 Analyses using this SOP are reported as using method EPA TO-15.

1.5 The target compounds and reporting limits evaluated by this SOP are found in Table 1 and may vary depending on client requirements, sample dilutions, sample size, MDL study results, etc. Other volatile compounds may be detected and tentatively identified by comparing their mass spectrum to a NIST spectral library. Their concentrations may be estimated.

Note: Only analytes listed in the referenced method or listed on the Ohio certificate of accreditation may be reported for Ohio VAP.

2. Summary of Method

2.1 A measured amount of the air sample and internal standard are transferred by the autosampler onto the concentrator traps. Trap 1 has been cooled below the freezing point of water. As the target analytes are flushed onto Trap 2, Trap 1 is then heated to just above the freezing point of water to recover any target analytes that may have condensed in Trap 1. The trapped analytes are desorbed to Trap 2, leaving most of the moisture behind on Trap 1. Trap 2 is heated, and the sample is desorbed to the cryofocuser which has been cooled to below -150°C. The cryofocuser is then heated to deliver the compounds to the capillary column for analysis by Gas Chromatography/Mass Spectroscopy.

3. Deviations from Method

3.1 Per EPA TO-15 all canisters are to be leak-tested by pressurizing them to approximately 30 psig with zero air. In this SOP, the canisters or Bottle-Vacs™ are evacuated to at least -28" Hg once cleaned and allowed to sit at least 12 hours. The vacuum pressure is checked before a canister or Bottle-Vac™ is used, and if the vacuum loses ≥ 1" Hg vacuum, it is not used. This allows the canisters and Bottle-Vacs™ to be prepared for the field in a single automated step using the cleaning oven rather than pressurizing and then evacuating. It is also representative of the conditions that supplies are subject to under storage in the laboratory and heading to the field for client sampling. Additionally, Bottle-Vacs™ have a pressure tolerance of about 5 psig.

3.2 Per EPA TO-15, the canister(s) must be evacuated to <0.05 mm Hg for at least 1 hour during the cleaning process and remain in this state until the canister is requested by a client. 0.05 mm Hg is approximately two orders of magnitude lower than commercially available gauges. This SOP uses the procedure outlined in Section 3.1.

3.3 In this SOP the internal standards are used at 6.25 ppbv (nominal value) instead of 10 ppbv per EPA TO-15. This keeps the internal standard working concentration consistent with the other working standards, and the injection volume (100cc) is as recommended by the manufacturer. Certified values are used for all internal standards, surrogates, and target analytes.

3.4 Per TO-15 audit standards must be used to determine audit accuracy. These are normally done using performance evaluation (PE) samples. However, PE samples are cost-prohibitive for TO-15 compounds. In lieu of a PE, second source standards (LCS/LCD) are analyzed and evaluated with each batch using a certified standard blend for this purpose.

3.5 Per EPA TO-15, the relative retention time (RRT) for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound. This SOP requires targets to be within 0.20 min of the CCV level standard of the calibration.

3.6 Per EPA TO-15, the RT of the internal standards in the method blank and samples must be within 0.33 minutes of the average RT in the calibration. This SOP requires internal standards to be within 0.20 min of the CCV level standard of the calibration.

3.7 Per EPA TO-15 the method blank must be less than 3x the MDL. This SOP requires the method blank to be less than the reporting limit.

3.8 Per EPA TO-15, the internal standard areas in the initial calibration, blank, and samples must be within 40% of the mean area response over the initial calibration range for each standard. This SOP requires that: 1.) the internal standard areas in each initial calibration standard, the ICV, and in the daily CCV are within 40% of the IS areas in the CCV-level calibration standard; 2.) the internal standards for data following the calibration in the same 24 hour BFB tune window are within 40% of the IS areas in the ICV; 3.) the internal standard areas in subsequent QC and samples are within 40% of the daily CCV. These criteria are based on the capabilities of manufacturer software.

3.9 Per EPA TO-15, the sample injection volume must remain constant. In this SOP, the sample volume may vary to reduce system exposure to contamination or for calibration. The prep factor accounts for the different amount of sample (see Section 15). The maximum sample volume used is the nominal volume of 400cc.

3.10 Per EPA TO-15, the primary ions listed in the method must be used for quantitation unless sample matrix interferences are present. In this SOP, a secondary ion is used for certain compounds in the initial calibration when bias may be introduced from other compounds.

4. Definitions

4.1 *Precision*

4.1.1 Replicate - two sample containers filled from the same environmental air mass over the same time period.

4.1.2 Duplicate - the analysis of two samples taken from the same air canister.

4.2 Refer to the Fibertec Quality Assurance Manual (QAM) for further definitions.

5. Interferences

5.1 Interferences in canister samples may result from improper use or contamination of: (1) the canisters due to poor manufacturing practices; (2) the canister cleaning apparatus; or (3) the sampling or analytical system. Refer to V-162 - *Canister and Bottle-Vac™ Preparation and Maintenance.*

5.2 The analytical system must be demonstrated to be free of contamination by running a blank before samples in each batch. See Section 16 for corrective actions if the system becomes contaminated.

6. Safety

6.1 Exercise general laboratory safety practices to ensure eye, skin, and respiratory protection at all times. At a minimum safety glasses must be worn at all times when performing this analysis.

6.2 High pressure gases require special handling and the use of eye protection while in use.

6.3 Gas cylinders must be secured to stationary objects while in use, transported using an approved gas cart, and must not be moved without the cap fastened. See the *Chemical Hygiene Plan* for more information.

6.4 Liquid nitrogen is extremely cold and can cause frostbite and damage to the skin and eyes. Avoid contact and splashes to the face. Safety glasses and gloves appropriate for handling extreme temperatures must be worn when working with liquid nitrogen.

6.5 The gas from cylinders and liquid nitrogen tanks can displace air in a closed environment, potentially causing asphyxiation. Care must be taken to prevent leaks and ensure proper ventilation.

6.6 All personnel working in the laboratory are required to follow the laboratory *Chemical Hygiene Plan*.

6.7 Avoid direct contact with samples. Limited information about sample characteristics is known and samples may be hazardous.

6.8 Safety Data Sheets for purchased chemicals are available in the Administrative Office.

7. Equipment and Supplies

7.1 Equipment is controlled, calibrated and checked per SOP G-350 - *Equipment Control.*

7.2 Specific vendors, part numbers, and settings are subject to change. Equivalents may be used provided that they meet any specific criteria listed below or criteria listed in SOP G-350.

7.3 GC/MS system with Autosampler and Preconcentrator.

7.3.1 Entech 7016D Autosampler with at least 16 sample ports, capable of interfacing up to 16 canisters, Bottle-Vacs, or Tedlar® bags with the GC/MS; or

7.3.2 Entech 7500A Autosampling System-Autosampler with 13 Bottle-Vac™ ports and 8 air canister/Tedlar® bag ports.

7.3.3 Preconcentrator, Entech 7200.

7.3.4 Gas Chromatograph / Mass Spectrometer (GC/MS), Agilent 6890N GC, Agilent 5975 MS, capable of the following settings:

7.3.4.1 Temperature program: 35 °C for 6 minutes; 10 °C per minute to 110 °C, hold 0 minutes; 15 °C per minute to 240 °C, hold for 9.83 minutes. Total run time 35.5 minutes.

7.3.4.2 MS transfer line at 240 °C. Inlet at 220 °C, splitless, purge flow 100 mL/min.

7.3.4.3 MS scan 35 to 265AMU with a 2.5 minute solvent delay.

7.3.4.4 70V Nominal energy.

7.3.4.4.1 Capillary Column – Restek RTX-1MS 1 µm film, 0.32 mm X 60 m, at 1.5 mL/minute.

7.3.5 Data System, compatible with the GC/MS instruments, Agilent (or HP) Chemstation, and Entech concentrator software on a current Windows operating system.

7.4 Digital pressure gauge, Omega model number PX603. Calibration certified annually by the vendor.

7.5 Tedlar® bags, 1L, SKC Outside, Catalog #232-01.

7.6 Bottle-Vac™, 32 oz./1L, Entech (must be certified clean and leak tested per SOP V-162 before use).

7.7 Sample flow controller to fit on the Bottle-Vac™ or canister, Entech (must be certified clean, leak tested, and the flow adjusted per SOP V-162 before use).

7.8 Canisters, various sizes up to 15 L, Restek (must be certified cleaned and leak tested per SOP V-162 before use).

7.9 Nitrogen humidification chamber.

8. Reagents and Standards

8.1 Specific vendors, part numbers, and spiking solutions are subject to change. Equivalents may be used provided that they meet the specified grade criteria.

8.2 All laboratory prepared reagents and standards must be entered into the LIMS or on the forms indicated. All purchased reagents and chemicals are entered into the LIMS per SOP G-304 - *Purchasing*.

8.3 All chemicals, reagents, and standards are stored at room temperature. Purchased items have an expiration date determined by the manufacturer unless otherwise indicated.

8.4 ***Reagents***

8.4.1 Liquid nitrogen (N_2), industrial grade, Airgas

8.4.2 Helium, ultra high purity, Airgas

8.4.3 Nitrogen, ultra high purity, Airgas

8.4.4 Organic-free reagent water - produced by passing the general deionized reagent water through an additional purification system containing an activated carbon filter bed (organic removal cartridge (DO813) purchased from Barnstead International) located in the Volatiles laboratory.

8.5 ***Stock Standard Blends***--Nominally 100 ppbv in nitrogen. Certified concentrations are listed on the manufacturer's certificate of analysis or on the Fibertec Certificate of Analysis, V-405, for recertified standards. See SOP G-225 – *Re-establishing Standard or Reagent Certification.*

8.5.1 Internal Standard/Surrogate Stock Blend, Bromochloromethane (BCM), 1,4-Difluorobenzene (1,4-DFB), Chlorobenzene-d5 (CB-d5), 4-Bromofluorobenzene (BFB), certified, Linde Gases. Expires one year after certification.

8.5.2 Calibration Standard Stock Blend, see Table 1 for target list. Certified, Linde Environmental Gases.

8.5.2.1 Expires one year after certification.

8.5.2.2 The standard may be recertified in the laboratory against a manufacturer certified, NIST traceable standard, per G-225 - *Re-establishing Certification* and spreadsheet V-405. Once re-certified, this standard becomes the LCS/ICV Standard Stock Blend.

8.5.3 LCS/ICV Standard Stock Blend, see Table 1 for target list. Linde Environmental Gases.

8.5.3.1 Must be a different blend lot number than the calibration blend used.

8.5.3.2 Expires one year after certification.

8.5.3.2.1 If at least 750 psig remains, the standard may be recertified by the manufacturer. This standard becomes the Calibration Standard Stock Blend.

8.5.3.2.2 Alternatively, the standard may be recertified in the laboratory against a manufacturer certified, NIST traceable standard, per G-225 - *Re-establishing Certification* and spreadsheet V-405. Once re-certified, this standard remains a LCS/ICV Standard Stock Blend.

8.6 ***Calibration Standard, LCS/ICV, and Internal Standard/Surrogate Standard Working Blends*** (nominally 25 ppbv in nitrogen)

8.6.1 Dilute the Calibration, LCS/ICV, and Internal Standard / Surrogate Stock Standard Blends as follows.

8.6.1.1 Measure the original vacuum status of a clean, evacuated 6 or 15-liter canister. Record on the field tag.

8.6.1.2 Purge the delivery line and regulator from the Stock Standard Blend tank to eliminate any dead-volume.

8.6.1.3 Attach the line to the clean canister, and slowly open the valve until a slight hissing can be heard.

8.6.1.4 Observe the change in pressure on the gauge attached to the canister to a pressure of about -10" Hg. Shut off the valves and remove the line.

8.6.1.5 Attach the vacuum gauge, and observe and record the vacuum status. This will differ slightly from the volume indicated by the gauge on the can. Always use the volume indicated by the separate vacuum gauge. The gauges on the cans are less accurate and have insufficient resolution.

8.6.1.6 Pressurize with humid nitrogen to approximately 25 to 30 psig. Record the final pressure. The resulting concentration will be nominally 25 ppbv. The actual concentration is determined by multiplying the certified value of the standard blend by the dilution factor determined by the calculation in Section 15.2.5. Let any diluted standard equilibrate at least three hours before use or further dilutions

8.6.1.7 Using the first dilution, prepare further dilutions at 2.5 and 0.25 ppbv. For example a 2.5 standard can be made by starting at a pressure of -28" Hg and adding an aliquot of the 25 ppbv standard to a pressure of -21.2" Hg and pressurizing to a level of 18.7 psig. Let any standard dilution equilibrate at least three hours before use or further dilutions.

8.6.1.8 For each of the above dilutions, record the initial and final pressures on the canister tag as well as the date prepared, expiration date, can identification number and analyst initials. File old canister tags for prepared standards in the Volatiles laboratory. Also enter the standard prep into LIMS.

8.6.1.9 Working standards expire 30 days after preparation of the 25 ppbv standard.

9. Sample Collection, Preservation, Shipment, and Storage

9.1 Canisters and Bottle-Vacs™ are prepared according to V-162.

9.2 Samples must be collected in accordance with EPA TO-15.

9.3 Canister and Bottle-Vac™ samples are stored at room temperature and must be analyzed within 30 days of sampling.

9.4 Tedlar® bag samples are stored at room temperature and must be analyzed within 72 hours of sampling. The hold time may be extended up to 30 days from sampling if the sample is transferred to a Canister or Bottle-Vac™ within 72 hours of sampling.

10. Quality Control

10.1 The following spiking concentrations are subject to change based on instrument conditions, statistical analyses (control charts) and client requirements.

10.2 The following quality control (QC) standards are analyzed according to Section 14.

10.3 *Method Blank*

10.3.1 Analyze one for each batch of 20 samples or less.

10.3.2 The MB consists of a clean canister or Bottle-Vac™, prepared as in SOP V-162. Inject at least the maximum volume to be used for client samples in the corresponding analytical sequence.

10.4 *LCS and LCD (nominally 12.5 ppbv)*

10.4.1 Analyze one LCS and LCD for every batch of 20 samples or less.

Note: Do <u>not</u> report an LCD for Ohio VAP samples.

10.4.2 Prepare as in section 8.6

10.5 *Replicates and Duplicates*

10.5.1 Prepare and analyze one replicate or duplicate for each batch of 20 samples or less.

10.5.2 When the client supplies replicate samples, replicate precision is evaluated.

10.5.3 When a client replicate sample is not provided, duplicate precision is evaluated.

10.6 *Internal Standards / Surrogate Standards (nominally 6.25 ppbv)*

10.6.1 Internal standard and surrogate standard compounds are added to each sample, blank, and all QC standards as they are drawn into the concentrator. See Table 1 for list of analytes and the internal standards used to control each.

10.6.2 Prepare as in Section 8.6.

11. Initial Demonstration of Performance

11.1 Each analyst must complete an initial demonstration of capability (IDOC) prior to reporting any data using this SOP.

11.1.1 Four LCSs are prepared and analyzed according to the procedure in Section 14. The analyst may complete a preparation DOC separate from an analysis DOC, provided that both are documented.

11.1.2 The average recovery of the four injections must be within laboratory established control limits for the LCS. If laboratory established limits are not available, the average must be 70-130%. The RSD between the four LCS recoveries must be ≤ 20%.

11.2 Continuing demonstrations of capability are completed according to SOP G-380 - *Employee Training*.

12. Limit of Detection

12.1 Record LOQ and MDL preparation information on form V-537—*Airs MDL/LOQ Preparation*.

12.2 LOQ and MDL studies must be performed annually according to G-200-*Detection, Quantitation, and Reporting Limits*.

12.2.1 The calculated MDL must be ≤ 0.5 ppbv.

12.2.2 If the calculated MDL is >0.5 ppbv but lower than the LOQ, and corrective action is not sufficient, the MDL may be considered for approval by the Technical Director.

12.3 Spike values entered into the LOQ and MDL reports for the certified concentrations of spikes used must be verified by peer review.

13. Calibration and Standardization

13.1 *Air and Water Check*

13.1.1 The air and water check demonstrates that there are no leaks in the system. It must be performed before tuning and calibration when maintenance is performed in which the vacuum is broken or if the system has been idle for a significant amount of time.

13.1.2 Using the system software, initiate the air and water check. The software program will introduce perfluorotributylamine (PFTBA) to the MS and compare the ions 18 and 28 to 69. If 18 and 28 are each below 10% of the abundance of 69, the system is considered to be air-tight.

13.1.3 If there is a leak in the analytical system, take corrective action (see Section 16) before proceeding with tuning and calibration.

13.2 *MS Tune*

13.2.1. Set the GC oven to 150°C and allow it to equilibrate. Settings may need to be changed if the GC run program is changed. Using the system software, initiate the Autotune. The instrument will release perfluorotributylamine (PFTBA), autotune and generate a tune report indicating the mass ratios and instrument settings. See instrument manuals for more specific tuning instructions as necessary.

13.3 *MS Tune Verification*

13.3.1 After tuning, the mass calibration and resolution of the GC/MS system is verified by the analysis of 4-bromofluorobenzene (BFB), which is contained in the Internal Standard/Surrogate Standard. The BFB is also analyzed at the beginning of each 24 hour period during which samples or standards will be analyzed. The 24 hour time period begins at the timestamp of the BFB injection recorded by the GC/MS software and ends 24 hours later.

13.3.2 Analysis is performed by injecting ≤ 50 ng of BFB into the GC/MS. See Section 14 for instrument setup to inject the internal/surrogate standard or manufacturer instructions for the GC/MS.

13.3.3 A background-corrected mass spectrum of BFB is obtained by the vendor supplied software.

13.3.3.1 The tune may be obtained using the software Autofind function or it may be manually evaluated. To manually evaluate the tune, average the top three scans of the BFB peak (apex plus one scan on either side), and subtract one scan from the baseline occurring just before the beginning of the peak (within 20 scans).

13.3.4 The tune criteria in Table 3 must be met in order to proceed with calibration.

13.3.5 If any of the criteria are not met, manually tune the instrument according to manufacturer's instructions, and reanalyze the BFB. Corrective actions as described in Section 16 may be necessary.

13.3.5.1 NOTE: All subsequent standards, samples, and blanks must use the same mass spectrometer settings as those used for the BFB tune at the start of the 24 hour period.

13.4 *Calibration*

13.4.1 Each instrument is calibrated when a significant change in instrument response is observed (e.g., CCV and/or LCS recoveries become consistently high or low and other corrective action measures are unsuccessful, or when significant maintenance is performed (see SOP G-350) and also when a new calibration standard is used for the first time.

13.4.2 When a new calibration standard is received at the lab, use the Certificate of Analysis to enter the certified concentrations of each analyte into the Volatiles Cal Table Spreadsheet (V-404). This spreadsheet will calculate the concentrations to be entered for each calibration level, the IS level, Sample ISTD Concentration, and the N7 field of the Chemstation software.

13.4.2.1 Print the Cal Table Spreadsheet, and use it to enter the certified concentrations of each analyte into the Chemstation calibration table. Also enter the internal standard concentration into the Sample ISTD Concentration field and the concentrations of the CCV level into the N7 field of the calibration table. The value in N7 is extracted by LIMS for the CCV report. File the spreadsheet with the current calibration data.

13.4.2.2 All Chemstation standard entries entries must be peer-reviewed before sample analysis when use of a new stock standard is implemented. Generate the Chemstation Entry Verification Spreadsheet (V-403) for each instrument to determine whether any entry errors have been made in the Calibration Table or N7. Refer directly to the Certificate of Analysis if any corrections are needed. A copy of the reviewed spreadsheet is signed, dated, and stored with the Certificate of Analysis. The Sample ISTD field must be manually reviewed.

13.4.3 Prepare calibration working standards as outlined in Section 8.6. Analyze the Calibration Working Standards at the levels listed in Table 4. Concentrations are based on a trapped sample size of 400cc.

13.4.3.1 NOTE: The concentrations of analytes in the calibration may vary based on system sensitivity. However, the calibration must contain at least 5 non-zero calibration standards, one of which must be at the same level as the CCV. The lowest calibration standard must be at or below the reporting limit, and all calibration criteria in Section 13 and QC criteria in Section 16 must be met for each analyte reported.

13.4.4 Analyze the calibration standards per Section 14.

13.4.5 At least ten scans should be collected for each analyte peak in the mid-level standard. If not, the acquisition method may need to be updated.

13.4.6 Review the autosampler report for each injection to ensure the correct volume was sampled. If the internal standard or calibration standard volume was not within 10% of expected, inspect the system for errors. Reanalyze the calibration standard if time remains in the tune window.

13.4.7 When the calibration is complete, the software will determine the average response factor and %RSD. (See section 15 for calculations.)

13.4.8 The average response factor for each analyte in the calibration must be less than 30% RSD. Up to 2 compounds may be ≥ 30% but must be ≤ 40%.

13.4.9 Internal standard responses in each calibration standard must be 60-140% of the CCV level calibration standard. Their retention times (RT) must be within 0.2 minutes of their RT in the CCV level calibration standard.

13.4.10 All calibration levels must be analyzed within the same 24 hour tune window. If there is technical justification to reprep and/or reanalyze a calibration level, the injection must take place within the same 24 hour window.

13.4.11 If any of the criteria for calibration are not met take corrective action before proceeding with sample analysis.

13.4.11.1 If the samples are not being reported for any of the failing analyte(s), the calibration may be used for the passing analytes. Place an "x" before the compound name in the calibration to prevent the parameter from being recognized by LIMS and accidentally reported. Corrective action must be taken as soon as practical for the failing analytes.

13.5 ***Initial Calibration Verification (12.5 ppbv nominal value)***

13.5.1 The ICV must be analyzed immediately after calibration under a passing BFB tune evaluation.

13.5.2 The ICV is prepared as in Section 8.6.

13.5.3 Evaluate the ICV using the LIMS LCS report in Data Bridge. This report will calculate the percent recovery of each target analyte and surrogate in the ICV.

13.5.4 The percent recovery for all analytes and the surrogate must be ≤ 30%.

13.5.5 If an analyte does not meet criteria for the ICV and the client will accept qualified data (due to time constraints, lack of sufficient sample, etc.), the data may be reported with the appropriate flag in lieu of reanalysis. However, corrective action must be taken as soon as practical thereafter.

13.5.6 Initial calibrations must be peer reviewed and documented on form V-529—*Volatiles Calibration Checklist, TO-15.* Calibration raw data is stored in the laboratory.

13.5.7 If time remains within the 24 hour BFB window used for an Initial Calibration (ICAL), client samples may be analyzed following a successful ICV, LCD, and MB. The ICV is evaluated as the LCS in this situation.

13.6 *Continuing Calibration Verification (12.5 ppbv nominal value)*

13.6.1 A CCV and MB must be analyzed before samples are analyzed at the start of every 24 hour tune window.

13.6.2 The CCV is prepared as in Section 8.6.

13.6.3 Use the LIMS report in Data Bridge to evaluate the CCV. Criteria for all compounds is ≤±30% difference (%D).

13.6.4 The method blank is a 400cc injection from a clean canister or Bottle-Vac.

13.6.5 All analytes in the blank must have concentrations less than the respective routine reporting limits.

13.6.6 If an MB and/or CCV do not meet criteria and the client will accept qualified data (due to time constraints, lack of sufficient sample, etc.), the data may be reported with the appropriate flag in lieu of reanalysis. However, corrective action must be taken as soon as practical thereafter.

13.6.6.1 If a compound fails the CCV high, samples which are found to be non-detect for that compound may be reported without qualification.

13.6.7 Internal Standards/Surrogate Standards (6.25 ppbv nominal value)

13.6.7.1 Every calibration verification standard is injected with 100cc of internal standard / surrogate working blend, prepared as in Section 8.6.

13.6.7.2 The internal standard corresponding to each compound is listed in Table 1.

13.6.7.3 The internal standard responses of the ICV and CCV must be 60 - 140% of the area response of the internal standards in the CCV level of the most recent calibration. The retention time must be within 0.2 minutes of the CCV level of the calibration.

13.6.7.4 The internal standard responses of the MB must be 60 - 140% of the area response of the internal standards in the CCV (or ICV if in the same tune window as an ICAL). The retention time must be within 0.2 minutes of the

CCV level standard of the calibration.

13.6.7.5 If internal standard criteria are not met, take corrective action, and reanalyze as appropriate.

14. Procedure

14.1 *Instrument set up*

14.1.1 Set up the instrument according to Section 7 and Table 2.

14.1.2 Prior to analysis, or if the system has been idle, bake the system for about 30 minutes with the GC split valve open and the GC oven set to 220°C to remove excess moisture.

14.1.3 The system may be cleaned and/or conditioned by running standards or instrument blanks. These injections must be clearly named as "rinses," conditioning," or as appropriate, to indicate their purpose.

14.1.4 Conditioning injections run in an analytical sequence with client samples must not be quantified under a calibrated method.

14.2 *Sample Preparation*

14.2.1 When the canister or Bottle-Vacs™ are received at the lab, allow their temperature to equilibrate to ambient.

14.2.2 Check that the client descriptor on the container matches the description information on the log-in sample ID sticker. If it does not, inform the Sample Custodian for correction.

14.2.3 Attach the digital gauge to the valve to check the vacuum status. Record the observed vacuum on the canister tag (see Figure 1 for example of a canister tag), and determine if the sample is intact or may have leaked during transportation.

14.2.3.1 If the container was under vacuum at the end of sampling, and the observed vacuum is zero, there is a leak in the canister or Bottle-Vac™. Notify the Client Services Manager before proceeding, and flag any data generated.

14.2.4 Sample can be drawn by the autosampler from canisters or Bottle-Vacs™ with pressures greater than -10" Hg. Samples at greater vacuum may need to be pressurized before analysis.

14.2.5 If a sample does require pressurization before analysis, record the initial vacuum/pressure on the field tag, add humidified UHP nitrogen, and record the final vacuum/pressure on the field tag. Allow at least 3 hours rest time for the gases to equilibrate before analysis.

14.2.5.1 Pressurize canister samples to a final pressure of between 3 and 28 psig with nitrogen (depends on the reporting limits). Pressurize Bottle-Vac™ samples to a final pressure of between 3 and 7 psig with nitrogen. Note: Bottle-Vacs™ are not to exceed pressures recommended by the manufacturer.

14.2.5.2 Record the vacuum/pressures for all samples on Worksheet V-534, and calculate the dilution factor in LIMS using the Summa Canister Worksheet.

14.2.6 Tedlar® bag samples do not require preparation.

14.3 *Sample Analysis*

14.3.1 Load each standard, blank, or sample on the autosampler. Note their positions.

14.3.2 Set up the Entech software.

14.3.2.1 Set the schedule to trap: 100cc internal standard/surrogate standard for all injections; 200cc for the CCV, LCS, and LCD standards; 400cc for the Method Blank; and no more than 400cc for client samples.

14.3.2.2 If an elevated reporting limit is acceptable or the samples are expected to be highly contaminated, a smaller sample volume may be trapped.

14.3.2.2.1 Instrument VK has an option to trap 1cc of sample using a separate sample loop. This loop is currently used only for screening purposes. Refer to volume correction factor in Section 15.2.14 when using this loop.

14.3.3 Save, and start the Entech sequence.

14.3.4 Program the Chemstation software to collect GC/MS data.

14.3.4.1 Modify the GC/MS sequence to include the CCV followed by LCS/LCD, MB, and then samples to analyze.

14.3.4.2 Include the LIMS sample number, canister number, and dilution factor.

14.3.5 Start the Chemstation sequence.

14.4 *Sample Dilutions*

14.4.1 If the instrument response raw result is greater than the highest concentration of the calibration, the sample must be diluted prior to final reporting or the data qualified. Alternatively, a smaller volume of the sample may be trapped. Dilutions should be targeted to keep the largest peak within the top half of the calibration range.

14.4.2 Sampling smaller aliquots of a sample, transferring part of a sample to a new canister and pressurizing, venting and repressurizing a sample, and a combination of any or all of these methods are acceptable methods of diluting a sample. Sample pressures are recorded before and after any changes to the sample container. The final dilution factor is calculated by multiplying all of the intermediate dilution factors.

14.4.3 To dilute a Bottle-Vac™ or canister sample, first measure the pressure in the sample container, and record it on the field tag. Using the quick connects in the cleaning oven or prep station, pressurize the sample with humidified nitrogen. Bottle-Vac™ samples may be pressurized to ~7 psig, and canisters may be pressurized up to ~30 psig. Record the new pressure on the field tag and on V-534. Allow the sample to equilibrate for at least three hours.

14.4.4 For greater dilutions an aliquot of the pressurized sample is transferred to a clean canister at full vacuum (about -29.9"

Hg).

14.4.4.1 Using laboratory nitrogen, clear out the transfer line designated for dilutions. Transfer approximately 2 psi of sample from the pressurized sample container to the new canister, and record the new vacuum on the field tag. Pressurize the canister to ~20-30 psig, and record the final pressure on the tag. Allow the sample to equilibrate for at least three hours. Repeat this step for greater serial dilutions, if necessary.

14.4.5 Dilution factors are calculated using equations in 15.2 and may be calculated using the Summa Canister Dilution Calculator in Prep Master. Document dilutions on worksheet V-534—*Volatiles TO-15 Dilution Bench Sheet.*

15. Data Analysis and Calculations

15.1 *Data Analysis*

15.1.1 Verify that the sequence in the autosampler matches the Chemstation and autosampler sequences.

15.1.2 Check the autosampler report for each injection to verify the volume of sample and internal standard drawn. Volumes drawn must be within 10% of the scheduled volume. Reanalyze samples with IS volumes outside of this criteria. Edit the sample pull volume in Prep Master and Chemstation for sample volumes outside of criteria.

15.1.3 Internal standards for all samples and QC must be within 0.2 minutes of the RT of the CCV level standard in the initial calibration.

15.1.4 Internal standards in QC and samples following the CCV must be within 40% of the area response of the daily CCV.

15.1.5 Evaluate each retention time window to verify the absence or presence of any peaks. The retention time window for each calibrated analyte in a sample is automatically adjusted by the software proportional to any shift observed in the associated internal standard.

15.1.5.1 Identification of target compounds is determined by using the Agilent Q-Edit function of the Chemstation software. Evaluate the sample by recognizing a peak within 0.2 minutes of the expected retention time as compared to the CCV level standard of the initial calibration.

15.1.5.2 Any shift in the target analyte retention time, which may be due to the sample matrix, should be comparable to the shift of the associated internal standards. Carefully evaluate each compound for correct identification. If the analyst is not sure that the peak was correctly identified, consult another analyst or the Group Leader. The sample may require dilution and reanalysis.

15.1.6 Examine the peaks generated for the confirming (secondary) ion(s).

15.1.6.1 The confirming ions should maximize within one scan of the primary ion. Occasionally analytes may have confirming ions maximizing more than one scan away from the primary ion due to matrix interference or low analyte concentration. In these cases the identified targets must be critically evaluated by the analyst and peer reviewer. If necessary, the results may be qualified or reported as "non-detect" with raised reporting limits, depending on client requirements. Unless specified, Fibertec will qualify results rather than raise reporting limits.

15.1.7 The relative intensities of the confirming ions must be within 30% of their expected ion ratio. All ions must be reviewed for possible background contamination or presence of co-eluting compounds. At low concentrations, ions expected at low ratios (~10% of the primary ion or less), may be absent due to instrument sensitivity.

15.1.7.1 If any confirming ion that was expected > 10% of the primary ion is missing, the peak may be interference. The analyte result must be qualified, deleted, or the reporting limit raised to a value above the quantitated concentration if the peak is suspected to be interference.

15.1.7.2 If the expected ion ratios have not been populated in the Chemstation Q-edit feature, the analyst should refer to the CCV, mid-point of the calibration, or a NIST library search to verify ion ratios.

15.1.8 If the data is still questionable, (i.e., the criteria above are not met, the analytes appear to be co-eluting, etc.), confirm the presence or absence of the analyte with another trained analyst, Group Leader, or Supervisor. A library search may also be performed. If the other analyst has a differing opinion or the library search does not confirm the analyte, consult with a third experienced analyst. If two analysts are unable to reach a conclusive decision, qualify the data with the appropriate flag indicating that the identification of the compound is questionable.

15.1.8.1 In general it is best to favor false-positives with appropriate qualification than to delete a possible target analyte.

15.1.9 In the event that manual integration is required, follow SOP G-200 - *Chromatographic Manual Integration Procedure.* Label the target compound which was manually integrated with the appropriate manual integration code. Manual integration codes are: 'B' for Baseline, 'CE' for Co-Eluting Analytes, 'MP' for Missed Peak, 'T' for Tailing, 'WP' for Wrong Peak, and 'AE' for Analyst Error. If changes need to be made while editing, make the changes to the chromatogram or quant file, save the changes, and print out the corrected data file. Initial and date the corrected data file. Keep both the original raw data and the reviewed corrected data together so there is proper documentation of the changes made.

15.2 ***Calculations***

15.2.1 Relative Response Factor

$$RRF = \frac{A_X C_{IS}}{A_{IS} C_X}$$

RRF = Relative Response Factor

A_x = Area of the primary ion for the compound to be measured, counts

A_{IS} = Area of the primary ion for the internal standard, counts

C_x = Concentration of the compound in the calibration standard, ppbv

C_{IS} = Concentration of the internal standard, ppbv

15.2.2 Mean Relative Response Factor

$$\overline{RRF} = \sum_{i=1}^{n} \frac{RRF_i}{n}$$

$\overline{\text{RRF}}$ = Mean of initial relative response factors (per compound)
RRF_i = RRF of the compound at concentration i
n = Number of concentration values

15.2.3 Standard Deviation of Response Factor

$$SD_{RRF} = \sqrt{\sum_{i=1}^{n} \frac{\left(RRF_i - \overline{RRF}\right)^2}{n-1}}$$

SD_{RRF} = Standard deviation of initial response factors (per compound)
RRF_i = Relative response factor at concentration level i
$\overline{\text{RRF}}$ = Mean of initial relative response factors (per compound)

15.2.4 Percent Relative Standard Deviation

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

%RSD = Percent Relative Standard Deviation of Response Factors
SD_{RRF} = Standard deviation of initial response factors (per compound)
$\overline{RRF}$ = Mean of initial relative response factors

15.2.5 Sample Dilution Factor (if initially under vacuum)

$$DF = \frac{(RP - SP) \times \left(\frac{14.7}{29.9}\right)}{FP + 14.7} \quad \text{~OR~} \quad FP = \frac{(RP - SP) \times \left(\frac{14.7}{29.9}\right)}{DF} - 14.7$$

DF = dilution factor
RP = pressure when received at the lab or after adding an aliquot of standard or sample, in. Hg
SP = starting pressure when container was sent to the field, in. Hg
FP = final pressure in psig after adding humidified nitrogen

15.2.6 Sample Dilution Factor, (if container under positive pressure)

$$DF = \frac{P_i + 14.7}{P_f + 14.7}$$

DF = Dilution Factor
P_i = initial pressure (psig)
P_f = final pressure (psig)

15.2.7 The total dilution factor is the product of the multiplication of all dilution factors.

$$DF_{total} = DF_1 \times DF_2 \cdots$$

15.2.8 Raw Concentration

$$C_{raw} = \frac{A_x \times C_{is}}{A_{is} \times \overline{RRF}}$$

C_{raw} = Raw compound concentration, ppbv
A_x = Area of the characteristic ion for the compound to be measured, counts
A_{is} = Area of the characteristic ion for the specific internal standard, counts
C_{is} = Concentration of the internal standard spiking mixture, ppbv
$\overline{RRF}$ = Average relative response factor from the initial calibration

15.2.9 Final Concentration

$$C_{reported} = \frac{C_{raw}}{(DF_{total}) \times \left(\frac{V_x}{400cc} \right)}$$

$C_{reported}$ = Final Concentration (ppbv)
C_{raw} = Raw Concentration (ppbv)
V_x = Volume of sample trapped (mL)
400cc = Nominal Calibration Injection Volume

Note: V_x / 400cc = prep factor

15.2.10 Converting from ppbv to µg/m³

$$\mu g / m^3 = \frac{(MW) \times (PPBv)}{MV}$$

MW = molecular weight (g/mole)
MV = molar volume (24.46 L/mole at 25 ºC)

15.2.11 % Difference

$$\%D = \frac{RRF_c - \overline{RRF}}{\overline{RRF}}$$

% D = % Difference
RRF_c = RRF of the compound in the continuing calibration standard.
$\overline{RRF}$ = average relative response factor of the compound in the most recent calibration.

15.2.12 Relative Percent Difference

$$\%RPD = \frac{|X_a - X_b|}{(X_a + X_b)/2} \times 100\%$$

%RPD = Relative Percent Difference
X_a = First Analyte concentration
X_b= Second Analyte concentration

15.2.13 Percent recovery = (analytical result / true or assigned value) x 100

15.2.14 Correction Factor for 1cc Concentrator Loop, with temperatures in °K:

$$Volume = 1cc \times \frac{(Re\ servoirTemp\ )/(\ RoomTemp\ )}{(\ RotaryValuePlateTemp\ )/(\ LoomTemp\ )}$$

16. Method Performance, Data Review, and Acceptance Criteria

16.1 *Method Performance and Acceptance Criteria*

16.1.1 The following criteria are subject to change based on analyte recoveries or client requested limits.

16.1.2 All method blank concentrations must be less than the reporting limit.

16.1.3 The LCS percent recoveries must fall within the control chart upper and lower control limits which are calculated annually according to G-306 – *Control Charting.* If control limits are not available, the recoveries must be within 70 - 130% of the target values.

16.1.4 The RPD between the LCS and LCD must be ≤ 20%.

16.1.4.1 If any parameters fail the LCS high or low, qualify all samples in the analytical batch for which that parameter is reported. If the %RPD between the LCS and LCD fails, all samples in the batch for which that parameter is reported are qualified, regardless of whether the failed analytes were detected. Only the failed parameter(s) are qualified.

16.1.5 For all injections, the internal standard retention times must be within 0.2 minutes of their RTs in the CCV-level calibration standard of the current calibration.

16.1.5.1 Internal standard retention times may shift due to matrix interferences. If all internal standard retention times shift and are still within the expected retention time window, the data are reported without qualification. If an internal standard retention time is not within the retention time window, the internal standard is manually identified, and all target compounds associated with that internal standard must be carefully verified before reporting. The sample may need to be reanalyzed at a dilution for the compounds associated with internals which do not pass criteria.

16.1.6 The area responses of the internal standards in the ICAL, ICV, and CCV must be ± 40% of the area response of the IS in the CCV-level standard of the initial calibration. Internal standards in subsequent QC and samples must be ± 40% of the areas in the daily CCV or the ICV if in the same tune window as an initial calibration.

16.1.7 The surrogate standard in client samples must be within the % recovery criteria established annually from laboratory data according to G-306 – *Control Charting*.

16.1.7.1 If a surrogate fails criteria, reanalyze the sample. A dilution may be necessary due to the sample matrix. If the second analysis still fails surrogate criteria, the sample may be qualified with a surrogate failure due to matrix and reported. If the surrogate passes in the second analysis at the same dilution, the failure was instrument-related. Report the passing data.

16.1.7.1.1 Reanalysis may not be necessary if the surrogate failure is due to matrix interference.

16.1.7.2 If any surrogate fails high or low, then the entire sample must be qualified as "potentially biased high," or as "potentially biased low," respectively.

16.1.8 If any of the above criteria are not met, take corrective action (see below) and/or reanalyze samples as appropriate.

16.1.8.1 If the client will accept qualified data (due to time constraints, lack of sufficient sample, etc.), the data may be reported with the appropriate flag(s) in lieu of reprep / reanalysis. However, corrective action must be taken as soon as practical. Refer to SOP G-364 - *Data Review and Results Validation* for data qualification. A partial summary of qualification necessary due to failed criteria is found in Table 5.

16.1.9 Replicate and Duplicate Precision

16.1.9.1 Use Form V-408 to calculate the relative percent difference between replicate or duplicate injections. The RPD must be ≤ 25%.

16.1.9.2 If the LCS/LCD RPD is within criteria, and the replicate / duplicate RPD is not within criteria, qualify the parent sample if no assignable laboratory cause is found.

16.1.9.3 If an assignable laboratory cause is found, reanalyze both the parent sample and / or the duplicate / replicate, as appropriate.

16.2 *Corrective Actions*

16.2.1 Corrective actions must be documented. They may be documented on the raw data and/or in the LIMS equipment maintenance log. Entries in the equipment maintenance log may be copied and included with the raw data.

16.2.2 The following are some suggested corrective actions. See also the manufacturer's operating manual (Section 18) for additional information.

16.2.2.1 Standards Failing Low

16.2.2.1.1 Check the concentrator QC reports for the appropriate flows and for the volumes of standard and internal standards trapped.

16.2.2.1.2 Condition the system with high level standards or multiple mid-level standards. Conditioning injections must be run under an uncalibrated method if client samples are to be analyzed in the same sequence.

16.2.2.1.3 Compare the internal standard responses to previous passing batches. A significant increase in IS response may cause target analytes to fail low.

16.2.2.1.4 Check the pressure of the standard canister. Standards with insufficient pressure need to be reprepared.

16.2.2.1.5 Check for leaks in the system. Tighten fittings as needed or vent the instrument and / or clean and reseat the main o-ring seal on the mass spec.

16.2.2.1.6 Retune the instrument.

16.2.2.1.7 Recalibrate.

16.2.2.2 Standards Failing High

16.2.2.2.1 Check the concentrator QC reports for the appropriate flows and volumes of standard and internal standard trapped.

16.2.2.2.2 Rinse and/or bake the system.

16.2.2.2.3 Determine if the system is contaminated by analyzing a blank.

16.2.2.2.4 Compare the internal standard responses to previous passing batches. A significant decrease in IS response may cause target analytes to fail high. Reprep the IS if necessary.

16.2.2.2.5 Retune the instrument.

16.2.2.2.6 Recalibrate.

16.2.2.3 Chlorobenzene-d5(I) area counts bouncing more than the other internal standards.

16.2.2.3.1 Filament is going bad.

16.2.2.4 Inconsistency from injection to injection, with responses bouncing high and low, for some or all compounds.

16.2.2.4.1 Filament is going bad.

16.2.2.5 Repeated, frequent, or unpredictable QC failures at similar retention time.

16.2.2.5.1 Run "low scan," to collect data on a standard down to 10AMU in order to determine the location and width of the first water peak in the chromatogram. Compare to previous low scans to determine if there has been any drastic change.

16.2.2.5.2 The water front may be focused by changing the Rotary Plate temperature or the M1—M2 transfer temperature, according to manufacturer directions.

16.2.2.6 Blank Failing High

16.2.2.6.1 Change the canister used for the MB. Rising levels of common laboratory contaminants in the blank may indicate that the volume of the blank is running low.

16.2.2.6.2 Run multiple rinses and/or bake the system to remove carry-over.

16.2.2.6.3 Trim the column.

16.2.2.6.4 Flush the sample transfer lines.

16.2.2.6.5 Replace the trap.

16.2.2.7 Internal Standard Failing

16.2.2.7.1 Check the concentrator QC reports for the appropriate flows and volumes trapped.

16.2.2.7.2 If the internal standard is failing criteria or has had a significant change in response, check the autosampler valve that controls the IS introduction.

16.2.2.7.3 Change the IS canister. When the pressure drops, this can sometimes affect recovery.

16.2.2.7.4 Bake the system with the GC oven set to 220 °C to get excess moisture out. Ensure that the GC split valve is open on the autosampler.

16.2.2.7.5 Remake the internal standard.

16.2.2.7.6 Check the tune in the Manual Tune page in Chemstation. The first internal standard is very sensitive to shifts in the tune.

16.2.2.8 Tune Failing

16.2.2.8.1 Evaluate the concentrator QC report for the correct injection volume.

16.2.2.8.2 Check the IS canister for adequate pressure and volume.

16.2.2.8.3 Bake the system with the GC oven set to 220 °C to get excess moisture out. Ensure that the vent valve is open on the autosampler.

16.2.2.8.4 Inject a higher volume of the internal standard/surrogate mix in a blank to increase the amount of BFB from ~18 ng to up to 50 ng.

16.2.2.8.5 Retune the instrument. If retuning does not change the BFB evaluation, clean the source.

16.2.2.9 Excessive Siloxanes

16.2.2.9.1 Traps may be over heating. Check autosampler report for set and actual temperatures.

16.2.2.10 Autosampler Stuck in "Cooling" Phase

16.2.2.10.1 Nitrogen may have run out.

16.2.2.10.2 Pressure builder on bulk nitrogen may not be turned on. The upper gauge on the bulk tank should read between ~20 and 50psi.

16.2.2.11 Dichlorodifluoromethane and/or propylene smearing or disappearing.

16.2.2.11.1 Check to see if the M3 cryo valve is opening twice, once during cooling and once during the transfer from M2 to M3. It should open only once. Opening twice is indicative of temperature control problems that may be caused by thermocouples or insulation.

16.2.2.12 Erratic Results

16.2.2.12.1 Bake the system.

16.2.2.12.2 Reboot the system. Diminished propylene peak at the start of a calibration standard can be an indicator that the system is "out of sync."

16.2.2.12.3 Condition the column.

16.2.2.12.4 Ensure valves for gas cylinders, standards, and samples are open.

16.2.2.12.5 Determine whether a highly contaminated sample analyzed previously is contributing contamination.

16.2.2.12.6 Replace the O-rings on the 7500A autosampler.

16.2.2.12.7 Replace any other seals on the autosampler.

16.2.2.12.8 Change the autosampler lines.

16.2.2.12.9 Remake calibration working standards and/or recalibrate.

16.2.2.12.10 Clean the source on the MS.

16.2.2.13 Software freezing, crashing, or generally slow.

16.2.2.13.1 Clear the primary QA/QC report database by saving the files to a secondary file named with the current date.

16.3 ***Data Review & Validation***

16.3.1 Primary Analyst Data Review

16.3.1.1 Print and save the sequence.

16.3.1.2 Review the data (reports generated in Section 15.1) against the method performance criteria in section 16.1, and take corrective action if necessary.

16.3.1.3 Review the autosampler report for each injection to ensure the correct volume was trapped. If the QC volume was not within 10% of expected, inspect the system for errors and reanalyze the samples associated with the batch.

16.3.1.3.1 Review the data according to the process in SOP G-364 - *Data Review and Results Validation* and document on a Volatiles Data Checklist as described in SOP G-364.

16.3.1.4 If all data is acceptable and ready for reporting, transfer the batch to the LIMS.

16.3.1.5 From the Fibertec 2.0 Page in LIMS, collect and upload the data.

16.3.1.6 From the Volatiles Data Bridge page in LIMS, click on Review and Post Results. Choose the appropriate instrument and batch number.

16.3.1.7 Click on a sample result.

16.3.1.8 The LIMS will multiply the result by any prep factor (resulting from volume injected) and dilution factors entered into the LIMS.

16.3.1.9 Then click Update Results to upload the data.

16.3.1.10 When all data are updated, print the Data Summary Report (DSR). This report includes the final result, dilution, batch number, analysis date and analyst initials for each sample.

16.3.1.11 Write any qualifying flags on the appropriate DSR, and record in LIMS Results Entry.

16.3.1.12 Print the internal standards summary data sheet for each analytical sequence batch from LIMS. Print the surrogate report, the CCV evaluation form, the LCS/LCD/MB evaluation form, and the tune report from the LIMS.

16.3.1.13 Place all printed reports, V-408 for duplicate/replicate precision, printed data and the completed Volatiles TO-15 Data Checklist, V-519, into a folder for peer review.

16.3.2 Peer Review

16.3.2.1 The reports in the folder are then reviewed by a second person trained in the procedure or a lab manager according to the process in SOP G-364 and the review documented using the Volatiles Data Checklist (V-514).

16.3.2.2 If all data is acceptable, the DSRs are initialed and dated by the reviewer and the data is validated in the LIMS. It is then submitted to the administrative department for final review and inclusion into the final report.

16.3.2.3 If any data needs correction, the folder is returned to the analyst for correction.

17. Pollution Prevention and Waste Management

17.1 Laboratory hazardous wastes are managed, accumulated and stored in accordance with all federal and state laws and regulations as outlined in the laboratory *Chemical Hygiene Plan.*

18. References

18.1 Compendium Method TO-15 - Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography / Mass Spectrometery (GC/MS), Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Ed., January, 1999, Center for Environmental Research Information, Office of Research and Development, US Environmental Protection Agency, Cincinnati, OH

18.2 CLP, Analytical Method for Determination of VOC in Air Collected in Canisters, June 1990 (used for reference only)

18.3 CLP, Exhibit D Analytical Method for the Analysis of VOC in Air Collected in Specially-Prepared Canisters and Analyzed by GC/MS, June 2008 (used for reference only)

18.4 HP 6890 Gas Chromatograph Operating Manual, part number G1530-90450, Agilent Technologies, Santa Clara, CA

18.5 Agilent 5975 Mass Selective Detector Manual, CD Version E.02.02.1431, Agilent Technologies, Santa Clara, CA

18.6 Tedlar® is a registered trademark of E. I. du Pont de Nemours and Company, Wilmington, DE

18.7 Bottle-Vac™ is a trademark of Entech Instruments, Inc., Simi Valley, CA

19. Changes from the Last Revision

19.1 Incorporated Notes to File.

19.2 Changed nominal volume to 400cc from 100cc.

19.3 Included extension of Tedlar hold time when sample is transferred to a Canister or Bottle-Vac™.

20. Tables

20.1 Table 1. Analyte List and Routine Reporting Limits

Compound	CAS #	MW	1° Ion	2° Ion	Indoor Air RL (ppbv)	Sub Slab RL (ppbv)
Bromochloromethane(I)	74-97-5	128	49	130	NA	NA
Dichlorodifluoromethane	75-71-8	121	85	87	3.00	6
Chloromethane	74-87-3	50	50	52	6.00	6
Vinyl Chloride	75-01-4	63	62	64	0.90	6
1,3-Butadiene	106-99-0	54	39	54	0.08	0.3
Bromomethane	74-83-9	95	94	96	0.90	6
Chloroethane	75-00-3	65	64	66	1.50	6
Trichlorofluoromethane	75-69-4	136	101	103	1.50	6
Isopropanol	67-63-0	60	45	43	6.00	12
Acetone	67-64-1	58	58	43	15.00	24
1,1-Dichloroethene	75-35-4	97	61	96	1.50	6
Methylene Chloride	75-09-2	85	84	49	6.00	12
1,1,2-Trichlorotrifluoroethane	76-13-1	187	151	101	3.00	6
Carbon Disulfide	75-15-0	76	76	78	6.00	12
trans-1,2-Dichloroethene	156-60-5	97	61	96	1.50	6
MTBE	1634-04-4	88	73.1	41.1	1.50	6
1,1-Dichloroethane	75-34-3	99	63	65	1.50	6
Vinyl Acetate	108-05-4	86	43	86	3.00	12
n-Hexane	110-54-3	86	57	41	3.00	12
2-Butanone	78-93-3	72	72	43	3.00	12
cis-1,2-Dichloroethene	156-59-2	97	61	96	1.50	6
Chloroform	67-66-3	119	83	85	0.12	1.2
Ethyl Acetate	141-78-6	88	43	73	3.00	12
Tetrahydrofuran	109-99-9	72	42	72	1.50	12
1,2-Dichloroethane	107-06-2	99	62	64	0.12	1.2
1,4-Difluorobenzene(I)	540-36-3	114	114	63	NA	NA
1,1,1-Trichloroethane	71-55-6	133	97	99	1.50	6
Cyclohexane	110-82-7	84	56	84	3.00	12
Carbon Tetrachloride	56-23-5	154	117	119	0.12	1.2
Benzene	71-43-2	78	78	77	0.90	6
n-Heptane	142-82-5	100	43	41	3.00	12
1,2-Dichloropropane	78-87-5	113	62	63	0.30	6
Trichloroethene	79-01-6	130	132	95	0.03	0.3
Bromodichloromethane	75-27-4	164	83	85	0.12	1.2

Compound	CAS #	MW	1° Ion	2° Ion	Indoor Air RL (ppbv)	Sub Slab RL (ppbv)
1,4-Dioxane	123-91-1	88	88	58	1.50	6
cis-1,3-Dichloropropene	542-75-6	111	75	39	0.90	6
4-Methyl-2-pentanone	108-10-1	100	58	43	3.00	12
trans-1,3-Dichloropropene	10061-02-6	111	75	39	0.90	6
Chlorobenzene-d5(I)	3114-55-4	112	112	77	NA	NA
1,1,2-Trichloroethane	79-00-5	133	97	83	0.12	1.2
Toluene	108-88-3	92	91	92	1.50	6
2-Hexanone	591-78-6	100	43	58	3.00	12
Dibromochloromethane	124-48-1	208	129	208	0.08	0.48
Ethylene Dibromide	106-93-4	186	107	109	0.03	0.12
Tetrachloroethene	127-18-4	166	166	164	0.90	6
Chlorobenzene	108-90-7	113	112	77	3.00	6
Ethylbenzene	100-41-4	106	91	106	1.50	12
m&p-Xylene	1330-20-7	106	91	106	3.00	12
Bromoform	75-25-2	253	173	171	1.50	6
Styrene	100-42-5	104	104	78	3.00	12
1,1,2,2-Tetrachloroethane	79-34-5	168	83	85	0.03	0.48
o-Xylene	95-47-6	106	91	106	3.00	12
4-Bromofluorobenzene(S)	460-00-4	174	174	95	NA	NA
1,3,5-Trimethylbenzene	108-67-8	120	105	120	0.90	6
1,2,4-Trimethylbenzene	95-63-6	120	105	120	0.90	6
1,3-Dichlorobenzene	541-73-1	147	146	148	0.30	6
Benzyl Chloride	100-44-7	127	91	126	1.50	6
1,4-Dichlorobenzene	106-46-7	147	146	148	0.30	6
1,2-Dichlorobenzene	95-50-1	147	146	148	1.50	6
1,2,4-Trichlorobenzene	120-82-1	182	180	182	3.00	12
Naphthalene	91-20-3	128	128.1	127.1	1.50	5.7
Hexachlorobutadiene	87-68-3	258	225	223	0.08	0.48
2-Methylnaphthalene	91-57-6	142	142.1	141.1	6.00	24

I = Internal Standard (compounds are listed under the internal standard used for quantitation)

S = Surrogate

20.2 Table 2: Concentrator and Autosampler Settings

Trap Temperatures
(All Temperatures In °C)

	Trap Temp	M1 PreHeat	M1→M2	M3 Precool	M2 Preheat	M2→M3	Inject	System Bake
Module 1 Trap	-45	5	5	---	---	---	---	150
Module 1 Bulkhead	30	---	60	---	---	---	---	150
Module 2	-50	---	-50	---	-50	230	---	210
Module 2 Bulkhead	30	---	---	---	80	---	---	150
Module 3	---	---	---	-190	---	-165	80	---

Temperatures (°C)	
Sample Transfer Line	80
GC Transfer Line	120
Rotary Valve Plate	90
7650/7500 Inlet Temp	50
7650/7500/7410 Oven	50

Flow Volume (CC)	
Helium Trap Flush	75
M1→M2 Volume	100

Flow Volume (CC)	
Helium Trap Flush	75
M1→M2 Volume	100

Flow Rate (CC/min)	
ISTD Trapping	25
Cal STD Trappinig	100
Sample Trapping	100
Helium Flush	100
M1→M2 Transfer	20

Event Time (Min)	
Sample Preheat	0
M3 Focusing	3
Inject Time	1
System Bake	15
Post Injection Delay	24
M3 Bake Time (Step 3)	6
Step 15 M3 (Cool Delay)	0.3

Prepurge Time (Sec)	
Internal Standard	10
Calibration Standard	10
Sample	10
He Sweep/Prg Gas	10
M3 focusing Enabled	

20.3 Table 3: BFB Tune Criteria

Mass	***Ion Abundance Criteria[1]***
50	8 to 40.0 Percent of m/e **95**
75	30.0 to 66.0 Percent of m/e **95**
95	Base Peak, 100 Relative Percent
96	5.0 to 9.0 Percent of m/e **95** (See note)
173	Less than 2.0 percent of m/e **174**
174	50.0 to 120.0 Percent of m/e **95**
175	4.0 to 9.0 Percent of m/e **174**
176	93.0 to 101.0 Percent of m/e **174**
177	5.0 to 9.0 Percent of m/e **176**

[1] All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

20.4 Table 4: Calibration Preparation

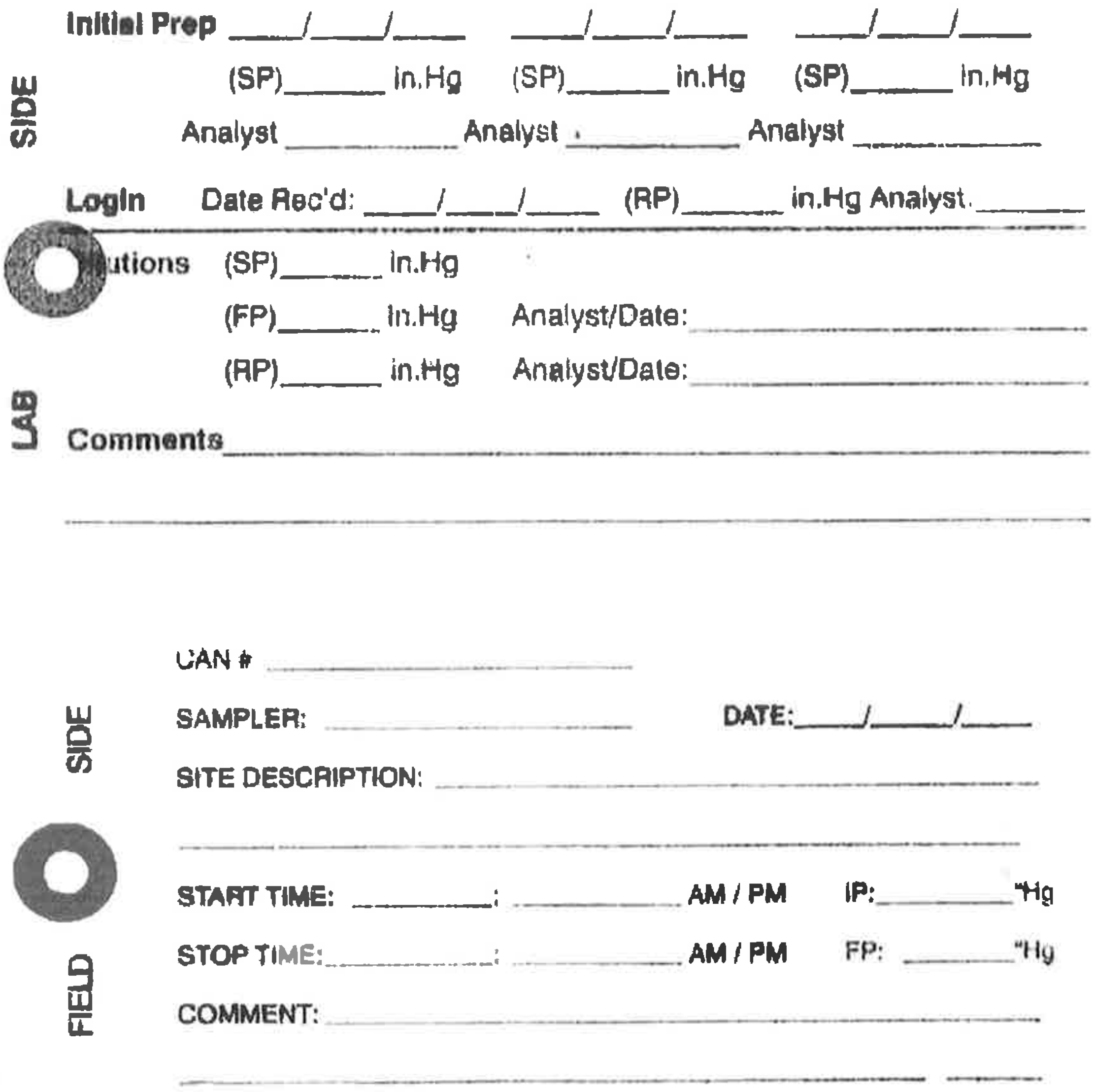
Calibration Level (ppbv)	25 ppbv Intermediate Standard	2.5 ppbv Intermediate Standard	0.25 ppbv Intermediate Standard	Internal & Surrogate Standard (25 ppbv Intermediate Standard, 6.25ppbv final)
0.025	---	---	40	100
0.0625	---	---	100	100
0.1	---	---	160	100
0.25	---	---	400	100
0.75	---	120	---	100
1.25	---	200	---	100
2.5	---	400	---	100
5	---	800	---	100
12.5	200	---	---	100
25	400	---	---	100
37.5	600	---	---	100
50	800	---	---	100

20.5 Table 5: Data Qualification Summary

Qualify All Samples	**Qualify Failed Sample**	**Qualify Parent Sample**
CCV+ All Failed Parameters w/Hits	Surrogate+ or - All Parameters	DUP RPD+ All Failed Parameters
CCV- All Failed Parameters		REP RPD+ All Failed Parameters
ICV+ or ICV- All Failed Parameters		
LCS+ or LCS- All Failed Parameters		
LCDRPD+ All Failed Parameters		
B+ All Failed Parameters (Blank >RL; Sample Detect or Non-Detect)		

Worksheets

20.6 Figure 1: Canister tags / field tags



LAB SIDE

Initial Prep ____/____/____ ____/____/____ ____/____/____

(SP)______ in.Hg (SP)______ in.Hg (SP)______ in.Hg

Analyst __________ Analyst __________ Analyst __________

Login Date Rec'd: ____/____/____ (RP)______ in.Hg Analyst ______

utions (SP)______ in.Hg

(FP)______ in.Hg Analyst/Date: ________________

(RP)______ in.Hg Analyst/Date: ________________

Comments ________________________________

FIELD SIDE

CAN # ________________

SAMPLER: ________________ **DATE:**____/____/____

SITE DESCRIPTION: ________________

START TIME: ________: ________ **AM / PM** **IP:**________"Hg

STOP TIME:________: ________ **AM / PM** **FP:** ________"Hg

COMMENT: ________________

Standard Operating Procedure No. 110

RECORDS, REPORTS, FIELD REPORTING, DOCUMENTATION, AND RECORD RETENTION

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 110 describes the guidelines for reporting significant events, procedures, observations, and data acquisition during field operations as described in the Work Plan or other specifications. The purpose of field reporting and documentation protocol is to reconstruct events and to provide testimony during legal proceedings.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. All field activities, data, and other significant occurrences at the site during field operations shall be documented in a bound field logbook with numbered pages or on a field report form. Subcontractors will provide similar documentation to the project manager or site manager.

B. Field measurements should be recorded on standard forms to facilitate the collection of field data during field operations.

C. The information in the logbook or standard data forms can be transcribed or duplicated. However, the bound logbook record will take official precedence over transcribed or duplicate records, if the same data (whether conflicting or agreeing) is contained in both.

D. The field logbook (and/or field report form) shall contain the following documentation:

   1. Facility name and address
   2. Date
   3. Brief description of daily field activities
   4. Names of project team members and subcontractors

5. Weather conditions
6. Planned levels of personnel protection
7. Time and description of field activities
8. Instrument calibration results and maintenance procedures
9. Field instrument measurements and results
10. Decontamination of personnel and equipment
11. Sample locations
12. Sample methods
13. Analytical parameters and sample containers
14. Time of sample collection
15. Sketch of sample location
16. Sample packaging and shipping
17. Visitors and deliveries
18. Exposure incidents and accidents (see Site Health and Safety Plan for requirements)
19. Field audits and corrective action

E. Documentation should be consistent with the requirements of the SOPs and Quality Assurance Project Plan (QAPP) for collecting samples, calibrating equipment, preserving samples, packaging samples, and tracking sample shipments. In the event this or other SOPs differ, the requirements of the QAPP will take precedence.

F. All entries in the field logbook (or field report form) should be legible and recorded in permanent ink. Each page of the logbook should be signed and dated. All field documents should be protected against contamination (soiling and smudging) to the extent possible.

G. Photocopies of all field forms should be made daily and maintained in a duplicate file onsite. Copies should be stamped, clearly marking the copy as a copy.

H. Records and documents received by/or originated at the site shall be maintained in an orderly fashion. This information shall be available for audit reviews by appropriate Bureau Veritas and outside parties.

I. At the termination of the contract, or at designated periods during the project, records and documents shall be disposed, filed, or distributed in accordance with applicable codes and/or contract requirements unless otherwise stipulated by code or contract. Site records, logbooks, and field reports will be maintained by Bureau Veritas for a minimum of 7 years after the completion of the Work Plan.

2.2 FIELD DOCUMENTS AND THEIR USE

2.2.1 Field Logbook

A. Field logbooks (or field report forms) will provide the documentation of all field activities performed by field personnel and subcontractors. Each entry should be recorded legibly and in permanent ink. The entries should contain accurate and complete field documentation of the specific field activities. The logbook (or field report form) should contain only facts and observations that pertain to the field activities and objectives of the Work Plan. Each page should be numbered, dated, and signed by all personnel making entries on that page. Under no circumstances will pages be removed from the logbook or report form.

B. General information that should be documented in the field logbook(s)/report form includes, but is not limited to, the following:

1. Project name and number.
2. Facility name, address, contact person(s), and telephone number, if available.
3. Directions to the site/facility.

C. Specific information that should be documented in the field logbook/report form includes, but is not limited to:

1. Brief description of planned field activities.
2. Name of project team members and subcontractors onsite.
3. Weather conditions.
4. Detailed description of health and safety related activities at the site, including use of personal protective equipment and air monitoring data.

5. Notation of time and chronological summary of field activities and events.

6. Calibration results and maintenance procedures for field instruments used.

7. Field measurements.

8. Sample collection information including sample number, location, descriptions, field measurements, analytical parameters, and sample containers, as described for specific activities presented in the SOPs for sampling and chain of custody procedures.

9. Identification of major equipment used onsite.

10. Documentation of personnel and equipment decontamination.

11. Photograph information and descriptions.

12. Signatures of individuals making entries.

D. Project field logbooks/report forms should generally not contain personnel records or data not relevant to the work being performed at the site.

2.2.2 Field Data Collection Forms

2.2.2.1 Groundwater Sampling Forms

A. Documentation of well purging activities prior to groundwater sampling may be kept on forms as a comprehensive means to record well purging activities.

B. The forms used should reflect the site-specific data required in the Work Plan or the SOP addressing that specific activity.

C. The information recorded on this form should be briefly described in the field logbook by the field team leader.

D. The well development/groundwater sampling form is referenced in SOP No. 410 for groundwater sampling, and should be used when appropriate.

E. The form should contain information and data including project name and number; rig-up and down time; well headspace reading; name of driller and geologist/hydrogeologist; development or purge method; fluid level measurements; depth to sediment and well casing; standing water volume; volume and number of well volumes removed; and water quality parameter measurements.

2.2.2.2 Water/Product Level Measurements

A. Documentation of water/product level measurements may be kept on forms as a comprehensive means to record fluid level measurements in wells.

B. The forms used should reflect the site-specific data required in the Work Plan or the SOP addressing that specific activity.

C. The information recorded on this form should be briefly described in the field logbook by the field team leader.

D. The water/product level form is referenced in SOP No. 220 and should be used when appropriate.

E. The form should contain information and data including the measurement location; measuring device; measurement point elevation; depth to water and product; elevation of water and product; and any comments.

2.2.4 Chain of Custody Forms

A. A chain of custody form shall accompany each batch of samples transported from the site. Forms will contain the minimum information specified in SOP No. 912.

B. If samples within a given shipment are to be separated at some point before their final disposition, then separate chain of custody forms will be provided for each separate group of samples.

2.2.5 Visitor’s Log

A. Names of people visiting the site, arrival and departure times and dates, and nature of their activities will be documented in the field logbook. It should be noted by the site manager whether the visitor remained in the clean zone of the site or not. Visitors will not be allowed in the work areas unless they have completed Health and Safety training and have reviewed the SHSP. All visitors that enter the work zone should have the appropriate personal protective equipment.

B. Unauthorized persons will not be permitted onsite during any field activities. Unauthorized visitors should be reported to the site manager or senior site authority for proper action.

2.2.6 Daily Field Report

A summary of daily field activities should be kept to report the progress of field operations for that day. Information that should be summarized includes, but is not limited to, the following:

1. Summary of all field activities.
2. Sampling locations worked.
3. Number of samples taken at each sample location.
4. Identification of problems, downtime, and corrective action taken.
5. Summary of weather and weather impacts.
6. Personnel and visitors recorded onsite that day.
7. Change in the work scope or methodology initiated in the field.
8. Changes or additional work or specification initiated by the client.

2.2.7 Daily Sheets

Daily sheets should include the following information:

A. List of equipment used and supplies purchased should be recorded in the daily equipment sheets.

B. Bureau Veritas and subcontractor man hours and travel expenses should be recorded in the daily personnel sheets.

2.2.8 Daily Health and Safety Sign-In Forms and Report

A. The daily health and safety report should include the levels of protection used by field personnel during field operations. This report should also include any exposure incidents, accidents, and any corrective action performed to prevent future incidents.

B. The daily sign-in form should be signed by all field personnel participating in the daily health and safety meetings.

2.2.9 Photographs

A. During field activities, photographs should be taken to document significant events that occur during field operations. The photograph should include the subject’s relation to site facilities.

B. Photographs may be used during site investigations to identify topographic features and to document site facilities.

C. Information concerning each photograph must be entered into the logbook immediately after the photograph has been taken, including the photograph and roll number, a description of the object being photographed, time, and geographic direction in which the photograph was taken.

D. Photographs of the sampling location should be taken after each sampling event in relation to site features.

E. Photo documentation sheets should be attached (by stapling) to the Daily Field report form or stored in a photo file if logbooks are used. The negatives should be stored in a sealed envelope by day and site. The envelope should be marked with site location data, date, and times. Photo negative envelopes should be stored in a photo file in the project file.

2.2.10 Other Field Documentation

Other field documentation may be generated at the site for purposes of quality assurance. These include audit reports and corrective action notices. These are discussed in the QAPP.

2.3 DOCUMENT CONTROL SYSTEM

2.3.1 Project Files

A. Project files should be maintained onsite including all current project plans, field documentation, and field communications/correspondence records.

B. A filing system should be used for maintaining project documents in a complete, organized manner. Should the project result in legal action, the status of these records should be easily attainable.

C. Each file entry should be designated by an appropriate project and task number.

D. Sign-out sheets should be used to have access to these files. An authorized access list should be posted near the document files and used to ensure that unauthorized personnel will not be able to check out files without the consent of the site manger or higher authority.

2.3.2 Serialization

A. Chain of custody forms, custody seals, and other data records may be serialized before being used in the field. Serialization will assist in controlling and tracing documents until they are placed into the project file.

B. Serialization may be accomplished using an inked stamp or adhesive label used to record the serial number used for this purpose. It is not recommended to hand write a serial number on a document without the use of a stamp or label indicating it as such in order to avoid confusion.

Standard Operating Procedure No. 120

BOREHOLE LOGGING AND MATERIAL CLASSIFICATION

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 120 describes the guidelines for logging and classifying soil samples and rock cores during drilling and sampling operations as described in the Work Plan, or as otherwise specified, for the purpose of characterizing subsurface geologic conditions at the sampling site.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Geologic logging and/or material classification will be conducted for all subsurface and surface soil sampling and rock coring activities based on the following:

1. Visual observation of recovered samples.
2. Examination of drill cuttings.
3. Driller's observations of drilling rig behavior between sample intervals and during coring.
4. Identification of the location of groundwater.
5. Results of downhole tests (e.g., Standard Penetration Test).

B. Geologic logging and material classification shall be conducted only by a qualified geologist or a hydrogeologist or by a trained logging technician under the supervision of a geologist or a hydrogeologist.

C. Subsurface soil sampling and rock coring will be conducted in accordance with the guidelines specified in SOP No. 200.

D. Borehole materials may contain hazardous constituents, and the logging personnel should use caution when extruding and examining samples to prevent exposure. Air monitoring, use of personal protective equipment, and other safety practices while logging will be in accordance with the approved Site Health and Safety Plan (SHSP).

E. Tools and equipment used while logging boreholes shall be decontaminated between boring locations and prior to each sampling event in accordance with the requirements of the QAPP and SOP No. 500.

F. Field data and observations associated with borehole logging shall be documented during logging and for all drilling and sampling activities in accordance with SOP No. 110, if not otherwise specified herein. All field drilling activities should be recorded in a field logbook; boring log forms (Attachment 1) should be used to allow for added detail and organization of field data.

2.2 LOGGING EQUIPMENT AND SUPPLIES

The geologist/hydrogeologist should maintain a collection of logging equipment and supplies needed for sample handling and logging. The equipment and supplies generally used, but not limited to, are listed below.

- Soil Sampling and Logging Equipment and Supplies:
    - Stainless-steel butcher knife
    - Aluminum foil
    - Paper towels
    - Slim stainless-steel spatulas or icing spreaders
    - Ruler, tape measure (in 0.01-inch increments)
    - Color chart
    - Appropriate sample containers and lids
    - Hand penetrometer
    - Photo ionization detector (PID)
    - Logbook and field document forms (as required)
- Rock Coring and Logging Equipment and Supplies:
    - Tape measure (in 0.01-inch increments)
    - Comparative charts for grain size, sphericity, and percentages of silt, clay, and sand
    - Hand lens
    - Pens (indelible ink)
    - Core box(es)

- Other Supplies:
  - Camera
  - 5-gallon plastic buckets and wire brushes
  - Decontamination fluids and supplies
  - Vinyl surgical gloves
  - Plastic bags
  - Distilled water
  - Personal protective equipment, if necessary

2.3 LOGGING AND DOCUMENTATION

A. The geologist/hydrogeologist shall record all pertinent drilling information on the boring log forms (Attachment 1). The following technical information shall be recorded, as a minimum:

1. Project name and number.
2. Location (well or boring number) or other sample station identification, including a rough sketch.
3. Name of geologist or hydrogeologist overseeing the drilling operation.
4. Approximate ground elevation based on topographic map information.
5. Well installation or boring date.
6. Drilling contractor, type of rig, personnel, and equipment.
7. Drilling method and fluid used.
8. Drilling fluid gain or loss.
9. Depth of fluid losses.
10. Problems with drilling rig.
11. Water levels encountered during drilling.
12. Presence and depth of petroleum product.
13. Casing type and diameter.
14. Screen type and diameter.
15. Rock and/or soil classification and lithology.
16. Lithologic changes and boundaries.
17. USCS classification.

18. Number of blows per foot.
19. PID readings (ppm).
20. Soil sample information (number, type, depth, recovery).

B. Additionally, when rock coring is performed, the following information shall be recorded:

1. Top and bottom of cored interval.
2. Core length.
3. Coring rate in minutes per foot.
4. Percentage of sample recovered.
5. Core breakage due to discontinuities (natural fractures vs. coring-induced breaks).
6. Total core breakage.
7. Number of breaks per foot.
8. Type of core (NX, BX, AQ).
9. Rock Quality Designation (RQD).

C. The geologic boring log forms should also include a complete visual lithological description of the soil/rock, description of any tests conducted in the borehole, and/or placement and construction details of wells.

2.4 SOIL SAMPLE CLASSIFICATION AND DESCRIPTIONS

2.4.1 Description of Hierarchy

The required order of terms is as follows:

1. Primary soil type followed by gradation modifier, if appropriate.
2. Secondary and tertiary (if needed) soil type modified by "slightly" or "very," if appropriate.
3. Color, if appropriate.
4. Texture.
5. Consistency, relative density, or the degree of cementation.
6. Structure.
7. Moisture content.

8. Trace components, sorting, and condition of sample.
9. Contamination, odor, if encountered.

2.4.2 Soil Types

Soil description and classification shall be in accordance with the Unified Soils Classification System (ASTM D2488-84). The order and presentation of the terms is as follows:

1. Major soil component of that portion of the soil which is the predominant grain size constituent. Nouns are used and are unabbreviated and capitalized (i.e., CLAY, SILT, SAND, or GRAVEL); "TOPSOIL" is an adequate single term for the naturally occurring organic soil found at the ground surface.

2. Secondary and tertiary (if needed) component greater than 20 percent of total, if present adjective used (i.e., clayey, silty, sandy, or gravelly).

2.4.3 Color

The color descriptions should be consistent with the Geological Society of America (GSA) Rock Color Chart. Numerical Munsell notation is acceptable, but a written description is preferred. The major color is listed first with any accessory colors thereafter (e.g., clay, yellow brown with occasional light-green mottles). If secondary or tertiary descriptors are used, the color designation follows each descriptor.

2.4.4 Consistency and Relative Density

The relative density of cohesionless soils and the consistency of cohesive soils should be included in visual classifications. Attachment 2 can be used in describing the consistency of cohesive soils, and Attachment 3 can be used in describing the relative density of cohesionless soils.

2.4.5 Miscellaneous Descriptions

A. *Structure* – Some soils possess structural features (e.g., fissures, slickensides, or lenses) and, if so, are described.

B. *Moisture Content* – Criteria for describing the moisture content of cohesive soils are described in Attachment 4.

C. *Accessories or Inclusions* – Elements such as rock fragments, fine roots, or nodules are included in the soil description following all other modifiers for the major components of the soil matrix. Any mineralogical or other significant components are described here.

D. *Contamination* – If monitoring or visual observations indicate the presence of contamination, it should be noted in detail.

E. *Descriptors* – To provide consistency in logging soils, a summary of descriptor guidelines is provided in Attachment 5.

F. *Measurement* – All lengths and measurements are recorded in feet and tenths of feet.

2.5 ROCK CLASSIFICATION

2.5.1 Lithology and Texture

A. The geologist/hydrogeologist should describe the lithology of the rock and its mineral composition. The geological name, such as granite, basalt, or sandstone, usually describes the rock's origin.

B. The stratigraphic unit should be identified and assigned the local geological name, if appropriate. Stratigraphic age or period should be identified, if possible.

C. Modifiers should be included to describe rock texture, including grain size, sorting, packing, cementation, etc. (i.e., interlocking, cemented, or laminated-foliated).

2.5.2 Color

The color descriptions should be consistent with the GSA Rock Color Chart. Numerical Munsell notation is acceptable. The major color is listed first with any accessory colors thereafter (e.g., shale, bluish-gray with occasional light-green laminae). If secondary or tertiary descriptors are used, the color designation follows each descriptor.

2.5.3 Hardness

Terms used to describe hardness are described below. One common method to determine hardness is the Mohs Scale of Hardness defined as follows:

Descriptive Term	**Defining Characteristics**

Descriptive Term	Defining Characteristics
Very Hard	Cannot be scratched with knife. Does not leave a groove on the rock surface when scratched.
Hard	Difficult to scratch with knife. Leaves a faint groove with sharp edges.
Medium	Can be scratched with knife. Leaves a well-defined groove with sharp edges.
Soft	Easily scratches with knife. Leaves a deep groove with broken edges.
Very Soft	Can be scratched with fingernail.

2.5.4 Weathering

Terms used to describe weathering are described below:

Descriptive Term	Defining Characteristics
Fresh	Rock is unstained. May be fractured, but discontinuities are not stained.
Slightly	Rock is unstained. Discontinuities show some staining on the surface, but discoloration does not penetrate rock mass.
Moderate	Discontinuous surfaces are stained. Discoloration may extend into rock mass along discontinuous surfaces.
High	Individual rock fragments are thoroughly stained and can be crushed with pressure of a hammer. Discontinuous surfaces are thoroughly stained and may crumble.
Severe	Rock appears to consist of gravel-sized fragments in a “soil” matrix. Individual fragments are thoroughly discolored and can be broken with fingers.

2.5.5 Rock Matrix Descriptions

A. Grain size is a term that describes the fabric of the rock matrix. It is usually described as fine-grained, medium-grained, or coarse-grained. The modified Wentworth scale should be used.

B. A description of bedding (after Ingram, 1954) or fracture joint spacing should be provided according to the following:

Spacing	**Bedding**	**Joints/Fractures**
<1 inch	Very thin	Very close
1 inch - 4 inches	Thin	Close
4 inches - 1 foot	Medium	Moderately close
1 foot - 4.5 feet	Thick	Wide
>4.5 feet	Very thick	Very wide

C. Discontinuity descriptions are terms that describe number, depth, and type of natural discontinuities. They also describe density, orientation, staining, planarity, alteration, joint or fracture fillings, and structural features.

2.6 ROCK CORE HANDLING

A. Core samples must be placed into core boxes in the sequence of recovery, with the top of the core placed in the upper left corner of the box. At the bottom of each core run, spacer blocks must be placed to separate the runs. The spacer should be indelibly labeled with the drilling depth to the bottom of the core run; regardless of how much core was actually recovered from the run. Figure 120-1 shows the proper storage and labeling methods.

B. Spacer blocks should be placed in the core box and labeled appropriately to indicate zones of core loss, if known. Where core samples are removed for laboratory testing, blocks equal in length to the core removed are placed in the box. If wooden core boxes are used, spacer blocks should be nailed securely in place.

C. The core boxes for each boring should be consecutively numbered from the top of the boring to the bottom. Core from only one boring should be placed in a core box.

D. The core boxes containing recovered rock cores should be photographed.

E. One core box should be photographed at a time. The box lid is framed in the picture to include information printed on the inside of the lid. Be sure to include a legible scale in the picture. Photographs are taken in the field most easily and efficiently with natural light and while the core is fresh.

F. When transporting a boxed core, the box should be moved only if the lid is closed and secured with tape or nails.

ATTACHMENT 1

BORING LOG FORM

Bureau Veritas Boring Log

Boring Location Map	**Project No.**	Soil Boring	Start Date
	Boring Depth ft	Monitoring Well	Finish Date
	Geologist or Consultant		

Boring Location Description	Client Name and Address	Site Name and Address

R (%)	ft	N	Color	Moisture	Description	PID	Comment
	0						
	1						
	2						
	3						
	4						
	5						
	6						
	7						
	8						
	9						
	10						

Drilling Contractor		Filter Pack Top	feet BGS	Well Type	☐Flush ☐Stick-up
		Filter Pack Bottom	feet BGS	Top of Cement	feet BGS
Drilling Method		Top of Screen	feet BGS	Bottom Cement	feet BGS
		Bottom of Screen	feet BGS	Bentonite Grout	feet
Sampling Method		Well Material		Pack Material	

Project No.	Soil Boring	Monitoring Well	**Bureau Veritas Boring Log**

R (%)	ft	N	Color	Moisture	Description	PID	Comment
	11						
	12						
	13						
	14						
	15						
	16						
	17						
	18						
	19						
	20						
	21						
	22						
	23						
	24						
	25						
	26						
	27						

ATTACHMENT 2

FIELD CLASSIFICATION OF SOILS

CONSISTENCY OF COHESIVE SOILS

Consistency	Rule-of-Thumb	Blows * per Foot
Very Soft	Core (height = twice diameter) sags under own weight	0 - 1
Soft	Can be easily pinched in two between thumb and forefinger	2 - 4
Firm (medium stiff)	Can be imprinted easily with fingers	5 - 8
Stiff	Can be imprinted with considerable pressure from fingers	9 - 15
Very Stiff	Barely can be imprinted by pressure from fingers	16 - 30
Hard	Can not be imprinted by fingers	>30

* Blows as measured with 2-inch OD, $1^3/8$-inch ID sampler driven 1 foot by 140-pound hammer falling 30 inches. See Standard Method for Penetration Test and Split-Barrel Sampling of Soils, ASTM D 1586-84. The resistances measured with a 2-inch ID, 2½-inch OD sampler driven with a 300-pound hammer falling 18 inches, as specified by some building codes, are roughly equivalent to those measured by the standard test. The consistency shown is not applicable if the blow counts are increased by the presence of rock fragments, chert, pebbles, etc.

ATTACHMENT 3

RELATIVE DENSITY OF COHESIONLESS SOILS

RELATIVE DENSITY OF COHESIONLESS SOILS

Term	Rule-of-Thumb	Blows per Foot *
Very Loose	Easily penetrated with a ½-inch diameter steel rod pushed by hand	0 - 4
Loose	Easily penetrated with a ½-inch diameter steel rod pushed by hand	5 - 10
Medium Dense	Easily penetrated with a ½-inch diameter rod driven with a 5-pound hammer	11 - 30
Dense	Penetrated a foot with ½-inch diameter steel rod driven with a 5-pound hammer	31 - 50
Very Dense	Penetrated only a few inches with ½-inch steel rod driven with a 5-pound hammer	>50

* Blows as measured with 2-inch OD, $1^{3}/8$-inch ID sampler driven 1 foot by 140-pound hammer falling 30 inches. See Standard Method for Penetration Test and Split-Barrel Sampling of Soils, ASTM D 1586-84. The resistances measured with a 2-inch ID, 2½-inch OD sampler driven with a 300-pound hammer falling 18 inches, as specified by some building codes, are roughly equivalent to those measured by the standard test. The consistency shown is not applicable if the blow counts are increased by the presence of rock fragments, chert, pebbles, etc.

ATTACHMENT 4

CRITERIA FOR ESTIMATING MOISTURE CONTENT OF SOILS

CRITERIA FOR ESTIMATING MOISTURE CONTENT OF SOILS

Term	**Relative Moisture**	
	Cohesive Soil	**Cohesionless Soil**
Dry	Powdery	Not moist to the touch
Damp	Moisture content below plastic limit	Feels moist to touch, but cannot be molded
Moist	Moisture content above plastic limit, but below liquid limit	Feels moist to touch and can be molded
Wet	Moisture content above liquid limit	Free water drips from the sample

ATTACHMENT 5

STANDARD SOIL DESCRIPTORS

STANDARD SOIL DESCRIPTORS

Grain Size Terminology		
Boulders		12-inch diameter or more
Cobbles		3- to 12-inch diameter
Gravel	Coarse	0.75 inch to 3 inches
	Fine	0.19 inch to 0.75 inch
Sand	Very Coarse	1 mm to 2 mm
	Coarse	0.5 mm to 1 mm
	Medium	0.25 mm to 0.5 mm
	Fine	0.06 mm to 0.25 mm
Silt		0.004 mm to 0.06 mm
Clay		0.004 mm or less

Consistency	
Very Soft	<2 blows/foot
Soft	2 to 4 blows/foot
Medium Stiff	5 to 8 blows/foot
Stiff	9 to 14 blows/foot
Very Stiff	15 to 30 blows/foot
Hard	>30 blows/foot

Density	
Very Loose	<2 blows/foot
Loose	2 to 10 blows/foot
Medium Dense	11 to 30 blows/foot
Dense	31 to 50 blows/foot
Very Dense	>50 blows/foot

STANDARD SOIL DESCRIPTORS

Estimated Plasticity, Silt/Clay Content		
Thread Diameter (inches)	**PI**	**Identification**
1/4	0	Silt
1/8	5 - 10	Clayey Silt
1/16	10 - 20	Clay and Silt
1/32	20 - 40	Silty Clay
1/64	40	Clay

Relative Proportions of Component	
Descriptive Term	**Percent**
Trace	1 - 10
Little	11 - 20
Some	21 - 35
And	36 - 50

Order and Punctuation	
1	Primary Soil Type
2	Secondary Soil Type
3	Tertiary Soil Type
4	Color
5	Consistency, Density (following each Soil Type)
6	Structure
7	Moisture Content
8	Trace Components, Sorting

Standard Operating Procedure No. 200

SOIL SAMPLING AND ROCK CORING

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 200 describes the guidelines for obtaining surface and subsurface soil and rock samples as stated in the Work Plan or as otherwise specified. Soil sampling and rock coring is conducted to evaluate surface and subsurface conditions.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Boreholes or test pits are drilled or excavated to provide stratigraphic, hydrogeologic, and geotechnical information on subsurface conditions, and to obtain representative disturbed or undisturbed samples for identification and laboratory testing. Boreholes are drilled to provide holes for geophysical logging, downhole hydraulic testing, and to install groundwater monitoring wells or other types of wells.

B. Prior to drilling or excavating test pits, the following steps must be taken:

   1. Obtain permits from the appropriate state agency or agencies, if required. If there is a fee for permits, subcontractors usually include this as part of their fee.

   2. Notify (verbally or in writing) the appropriate state (and sometimes federal) authorities in advance of the date that drilling or excavating is scheduled to begin.

   3. Check for buried and overhead utilities at all planned drilling/excavating locations. For reasons of safety and liability, no hole should be advanced if this step has not been completed.

C. Conduct sampling in accordance with the Site Health and Safety Plan (SHSP), adhering to all of its provisions for protection of the field crew.

D. Dispose of all cuttings and discharge water in accordance with regulations. Permits may be required.

E. A qualified field geologist or hydrogeologist must be present (onsite) during drilling or excavating.

2.2 SOIL SAMPLING EQUIPMENT AND METHODS

2.2.1 Manual Sampling Methods

A. In general, hand sampling using manually operated equipment is a quick and inexpensive sampling technique for shallow depths when precise data or high quality control is generally not required. The most common hand-operated samplers are hand augers, plugs, tubes, split-barrel or fixed piston samplers that are pushed or driven by hand. Hand augers are easily used at depths less than 10 feet. Pushed samplers can be used to obtain samples within about 3 feet of the surface or, with appropriate extensions, ahead of an augured hole.

B. The most commonly used manually operated hand augers include the ship, closed-spiral, and open-spiral augers. In operation, a hand auger is attached to the bottom of a length of pipe that has a crossarm at the top. The hole is drilled by turning this crossarm at the same time the operator presses the auger into the ground. As the auger is advanced and becomes filled with soil, it is taken from the hole, and the soil is removed. Additional lengths of pipe are added as required.

C. Care must be taken to prevent (to the extent possible) mixing of the soil from upper portions of the hole with lower samples. This is most likely to be a problem when augers are used to advance a hole and obtain samples from soil cuttings.

D. Because of the unpredictable disposal methods that have been used at many uncontrolled waste sites, sampling devices must never be forced into an abruptly hard material. The stiffness may be a natural lithology change, a rock ledge or cobble, or a buried drum. If resistance is encountered while auguring or pushing a sampler, the procedure must be stopped. The depth at which resistance was met should be entered into the field logbook or the appropriate field activity form.

2.2.2 Split-Spoon Sampler

A. The split-spoon type sampler is a thick-walled steel tube that is split lengthwise. A cutting shoe is attached to the lower end of the barrel; the upper end contains a check valve and is connected to the drilling rods. When a boring is advanced to the point that a sample is to be taken, drill tools are removed, and the sampler is lowered into the hole attached to the bottom of the drill rods.

B. The sampler should be driven 18 inches into the ground or until refusal occurs in accordance with a standard penetration test (ASTM D 1586) that provides a measure of strength and density. The effort taken to drive the sampler the last 12 inches is recorded at 6-inch intervals, and the sampler is removed from the boring. The density of the sampled material is obtained by counting the blows per foot as the split-spoon sampler is driven by a 140-lb hammer falling 30 inches. Only disturbed samples are obtained using this procedure.

C. The standard size split-spoon sampler is 2-inch outside diameter (OD), 1$^3/_8$-inch inside diameter (ID), and 24 inches long. When soil samples are taken for chemical analysis, a 2- or 2½-inch ID sampler should be used to provide a larger volume of material, but cannot be used to calculate strength or density properties by using the stated ASTM test method.

D. Upon retrieval, rinse or wipe excess soil or drilling fluid from the sampler's exterior, remove the cutting shoe, and break open the two halves of the sampler. Describe the sample in accordance with SOP No. 120. Collect samples for geotechnical and/or chemical analysis and decontaminate the sampler tube. The split-spoon sampler should be decontaminated between sample intervals in accordance with SOP No. 500.

E. Liner tubes or sleeves may be incorporated in certain samplers to contain samples temporarily. The liner tubes may be constructed from brass, plastic, or other inert materials used to store and transport the samples. If a sample is to be stored in the liner tube, the tube ends should first be covered with Teflon film, followed by a plastic slip cap. On each sample end, the Teflon film should be trimmed, and the cap sealed with vinyl tape to the liner tube. The sample liner should be labeled with depth, date, sample number, project number, top and bottom, and boring/well number. If the sampler is not to be stored in the liner, it can be transferred from the sampler to the appropriate sample container using either the liner tube or a stainless steel or plastic spoon or spatula.

F. When taking samples for geotechnical analyses, the disturbed soil samples removed from the sampler are placed in a sealable glass jar and labeled to indicate the project name and number, boring number, sample number, and depths at top and bottom of the sample interval.

This information is marked on the jar lid using a permanent marker. Other information required by the field engineer or geologist should be recorded in the field logbook.

2.2.3 Continuous Core Barrel Sampler (CME-Type)

A. A continuous core barrel sampler (CME-Type) is 5 feet long and fits inside the lead auger of the hollow-stem auger column. The sampler retrieves a 5-foot section of partially disturbed soil samples.

B. The sampler assembly consists of either a split barrel or solid barrel that can be used with or without liners. The split-barrel sampler is most commonly used because it is easier to access and remove the core samples.

C. The sampler is attached to the drill rod and is locked in-place inside the auger column. The open end of the sampler extends a short distance ahead of the cutting head of the lead auger.

D. The hollow-stem auger column is advanced 5 feet while the soil enters the non-rotating core sampling barrel. The barrel is then retrieved with the drill rod, and the core is extruded from the sampler.

E. The core barrel sampler takes the place of the pilot bit, thereby reducing sampling time. The sampler is most efficient in clays, silts, and fine sand.

2.2.4 Direct-Push Sampler (Geoprobe^{TM})

A. A direct-push sampler is a 2 or 4-feet long, hollow steel barrel that houses an acetate liner. One end of the barrel is closed and attached to length steel rods. The remaining end of the barrel remains open to accept soil.

B. The open end of the sampler is hydraulically driven into the ground, while the soil enters the barrel and liner. The barrel is then retrieved and the liner, containing the soil, is removed.

2.2.5 Thin-Walled (Shelby) Tube Samplers

A. Thin-walled samplers, such as a Shelby tube, should be used to collect relatively undisturbed samples of soil from borings. The samplers are constructed of steel tubing about 1 to 3 mm thick, depending upon its diameter. The lower end has a tapered cutting edge. The upper end is fastened to a sample head adapter with a check valve to help hold the sample in the tube when the tube is being withdrawn from the ground. Thin-walled tube samples are obtained by any one of several methods including pushed-tube, Pitcher sampler, Denison sampler, and piston sampler methods.

B. In obtaining pushed-tube samples, the tube is advanced by hydraulically pushing it in one continuous movement with the drill rig. At the end of the designated push interval and before lifting the sample, the tube is twisted to break the bottom of the sample.

C. One of two methods may be employed for handling the sample once it is retrieved from the boring:

   1. Extruding the sample from the sample tube in the field using an extruding device on the drilling rig, subsequently handling and containerizing specimen at the drilling site.

   2. Leaving the sample in the sampling tube, preparing it for transportation, with subsequent extrusion and handling elsewhere. In this case, the Shelby tube should be labeled with date, depth, sample number, project number, boring/well number, and top and bottom.

D. A hydraulic extruder should be used in all cases to minimize disturbance. To extrude the sample from the tube, connect the tube to the extruding device in the appropriate fashion for that type extruder. Some extruding devices push the sample in the same direction that the sample entered the tube, pushing out the top, while others push it out the bottom. It does not matter for environmental sampling, but the orientation of the sample should be known and kept clear by the sampling personnel.

E. Catch the sample on a split section of PVC pipe lined with polyethylene sheeting or aluminum foil. Do not use waxed paper. Carefully pour off drilling fluids and rake away cuttings or slough material at the top end of the sample, leaving only the true sample interval. Transfer the sample to a cutting board by lifting with the poly/sheeting or aluminum foil. Measure the length of the sample.

F. Log and describe sampled material in accordance with the geological logging and classification procedures specified in SOP No. 120.

G. Samples for geotechnical testing should be handled and packaged in accordance with standard practices for geotechnical investigations.

However, samples should be identified as potentially containing hazardous or toxic chemicals.

H. Shelby tubes should not be reused for subsequent sampling intervals. Be sure to bring a sufficient number of decontaminated sampling tubes to the sampling location and protect them from being contaminated before use.

2.2.6 Rotasonic Sampling

A. Rotasonic sampling utilizes a 10-foot long core barrel to retrieve a solid length of soil. The sampler consists of a hollow barrel that is used without liners.

B. The core barrel is attached to the drill rods and vibrated into the ground. A larger diameter secondary casing is driven around the outside of the core barrel. The core barrel is then retrieved with the sample.

C. The soil sample is gravity fed (assisted by vibrating the core barrel) into plastic sample bags with a diameter similar to the core barrel.

D. If the sample is locked in the core barrel (cohesive silts and clays), sample removal is assisted by introducing water pressure into the top of the core barrel.

2.2.7 Cuttings or Wash Samples

A. Drill cuttings or wash samples may be taken as the boring is advanced. A stainless steel or plastic scoop can be used to obtain a sample from the cuttings pile. The shovel used by drilling personnel to move cuttings should be stainless steel.

B. Prepare boring logs and describe the cuttings or wash samples according to the geological logging and classification procedures specified in SOP No. 120.

2.2.8 Test Pit Excavation and Sampling

A. Test pits, including trenches, consist of open shallow excavations to determine the subsurface conditions for engineering and geological purposes. Test pits at hazardous waste sites are typically conducted for waste characterization and waste source identification.

B. Test pits are excavated manually or by machine including backhoes, bulldozers, and trackhoes.

C. Test pit excavations must be in accordance with OSHA regulations, 29 CFR 1926, 29 CFR 1910.120, and 29 CFR 1910.134. All excavations deeper than 4 feet must be stabilized before personnel can enter the test pit or trench. Test pit or trenches deeper than 4 feet are considered confined spaces. Confined space entry forms should be completed and approved by the Site Health and Safety Officer. Continuous air monitoring of the work area is required.

D. Test pits are typically less than 15 feet below the ground surface. If data is required to characterize the soil at depths greater than 15 feet, the data should be obtained from soil borings.

E. Test pit locations should be documented in reference to at least two permanent landmarks on a scaled map. The dimensions and a rough sketch of the test pit should be recorded in the field activity log and field logbook.

F. Photographs of specific geologic features or contamination zones should be taken for documentation purposes. A scale should be placed near the test pit and incorporated in the photograph. The photograph, film roll number, direction, description, date of activity, and location of the trench activity should be recorded in the field logbook.

G. Soil samples can be collected from the backhoe/trackhoe bucket or directly from the wall or base of the test pit, depending on the depth of the pit. Disturbed samples are collected using a stainless steel scoop, shovel, or trowel. Undisturbed samples are typically collected using a hand auger and/or other coring tool. Soil sampling must be in accordance with all applicable health and safety regulations.

2.2.9 Surface Soil Sampling

Surface soil samples are collected to determine the surface soil conditions and characterize the waste source. Surface soil samples are generally collected at depths of less than 1 to 3 feet below the ground surface.

A. Before sample collection, remove all surface materials (i.e., excess gravel, vegetation, etc.) from the sample location.

B. Soil samples may be collected using a stainless steel scoop, trowel, or hand auger.

C. The sample location should be marked with a wooden stake and measured in reference to two permanent landmarks. The sample appearance, depth, and location should be recorded in the field logbook and/or appropriate field activity form.

D. Sampling should be conducted in accordance with the SHSP.

2.3 ROCK CORING EQUIPMENT AND METHODS

A. Rock coring will be initiated at the completion of surficial material sampling after properly seating the drilling stem into/onto the upper bedrock surface.

B. NX core barrel samplers may be used to collect core samples of consolidated and semi-consolidated rock. A 5-foot-long core sample can be obtained with this sampler.

C. A minimum of two 5-foot core samples or one 10-foot core sample can be obtained through dual-wall string using AQ coring equipment. AQ coring equipment has an outside diameter of 1.89 inches and yields a core with an outside diameter of 1.06 inches.

D. 10-foot core samples can be obtained through Rotasonic coring equipment. Rotasonic coring equipment has an outside diameter of 5 inches and yields a core with an outside diameter of 4.25 inches.

E. The supervising geologist will log the specific depth of each coring interval and will determine rock type, rock quality, and any notable structural features (open fissures, zones of weathering, zones of mineralization, lamination/layering, discontinuities, etc.).

F. All rock cores will be placed in the core boxes, photographed, and stored in a secured area in accordance with SOP No. 120.

2.4 SAMPLING AND SPECIMEN PREPARATION

A. Select representative sections of the specimen for chemical and/or geotechnical analysis. Based on analytical requirement and contract laboratory specifications, chemical analysis samples should be placed in appropriate sample containers. Samples for analytical procedures requiring zero headspace should be collected first. For geotechnical analysis of cohesive samples, cut minimally disturbed sections of the specimen and place it in the appropriate sample container.

B. Selected samples should represent the entire specimen or sampling interval.

C. Samples should be preserved and holding times should be observed according to analytical requirements and laboratory specifications, or as outlined in SOP No. 910.

D. If replicate or split samples are required, adjust the sections so that the additional samples are essentially identical.

E. Samples collected during rock coring samples should be logged and stored according to the procedures outlined in SOP No. 120.

F. Samples should be prepared for shipment in accordance with the specified procedures as described in SOP Nos. 911 and 912.

3.0 SUPPORTING MATERIALS

In addition to materials provided by a subcontractor, the geologist/engineer should have the following:

- Sample bottles/containers and labels
- Sample cutting/extracting equipment (scoops, trowels, shovels, hand augers)
- Boring logs and/or material sampling forms
- Field logbook
- Chain of custody forms
- Depth and length measurement devices
- Stakes and fluorescent flagging tape
- Decontamination materials
- Coolers and ice packs
- Personal protective equipment
- Camera
- Core boxes

4.0 DOCUMENTATION

A. Record sample information, labeling, and custody control in accordance with requirements specified in SOP Nos. 910 and 912.

B. Specific procedures for describing the samples and logging subsurface soil samples are presented in SOP No. 120. The material sampling form should be used to document soil sampling activities other than drilling. Briefly describe all soil sampling activities in the field logbook as specified in SOP No. 110.

Standard Operating Procedure No. 220

GROUNDWATER AND LNAPL LEVEL MEASUREMENTS

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 220 describes the guidelines for determining groundwater and LNAPL levels in monitoring wells, observation wells, and recovery wells as required in the Work Plan or as otherwise specified. The purpose of measuring groundwater and LNAPL levels will be to determine the depth of groundwater and/or LNAPL, hydraulic gradients, LNAPL thickness, and standing water volume in wells.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Water level and LNAPL (if present) measurements should be obtained at wells designated in the Work Plan. Water and LNAPL levels should be measured in reference to a common elevation or datum, preferably to a USGS benchmark located at the site. Water and LNAPL depths should be measured from a reference point marked on the top of the casing, which is, in turn, referenced to a permanent benchmark.

B. Water and product level measurement devices shall be decontaminated as per SOP No. 500 or as specified in the Work Plan before and after measuring at each location.

C. Personnel obtaining water and product level measurements could be subject to exposure from contamination and should follow the Site Health and Safety Plan (SHSP) regarding this activity. Care shall be exercised to avoid direct skin contact while measuring water level and product depth. All equipment should be decontaminated before and after each measurement.

D. Water and product level measurements should be recorded in the field logbook and/or the field activity form. The water/product level measurements form is provided in Attachment 1.

3.0 DISCRETE WATER LEVEL MEASUREMENT METHODS AND PROCEDURES

3.1 METHODS

A. Discrete water level measurements should be made by determining the depth to the water surface from the top of the well casing at the fixed reference point. The fixed reference point is established by permanently marking a point on the northern outer edge (lip) of the well casing. Caution should be exercised so that filings do not fall into the well.

B. The depth to water can be determined using a steel add-on tape or electronic water level indicator. The steel add-on tape consists of a measuring tape that has 1-foot increments and a 1-foot section at the end of the tape with 0.01-foot increments. The end of the tape is coated with chalk and lowered into the well. The water depth is read from the saturated mark on the chalked tape and added to the depth interval measured at the top of the well casing.

Electronic water level indicators are conducting probes that activate an alarm and a light when they intersect the water. The sounder wire is marked in 0.01-foot intervals to indicate depth. All sounders are equipped with weights to maintain line tension for accurate readings.

C. Discrete water levels are typically required from a series of wells when data for preparing groundwater contour maps are needed. However, discrete water levels may also be required when monitoring the changes in water level during aquifer testing if aquifer response is sufficiently slow. Continuous water level measurements are discussed in Section 5.0.

3.2 PROCEDURES

3.2.1 Electronic Water Level Indicator

A. Lower the sounder wire until it just makes contact with the water in the well and the indicator light goes on or the alarm is sounded. Record the position of the wire relative to the reference point at the top of the well casing. Record the actual water level reading to the nearest 0.01-foot. Repeat to confirm depth.

B. Withdraw the sounder from the well.

C. Record the water depth in the field logbook and/or the field activity form.

D. Decontaminate the sounder wire and electrode in accordance with SOP No. 500.

4.0 DISCRETE LNAPL LEVEL MEASUREMENT METHODS AND PROCEDURES

4.1 METHODS

A. Discrete LNAPL or product level measurements should be made by determining the depth to the product and water surface from the top of the well casing at the fixed reference point. The fixed reference point is established by permanently marking a point on the northern outer edge (lip) of the well casing. Caution should be exercised so that filings do not fall into the well.

B. The depth of the product and water level should be obtained using an electronic oil/water interface probe. An oil/water interface probe has a multi-conducting probe that activates different signals, typically pulsating beeps and continuous alarms, when they intersect the product and water, respectively. The sounder wire is marked in 0.01-foot increments to indicate depth. The interface probe is equipped with a weight to maintain line tension and obtain accurate readings.

4.2 PROCEDURES

A. Check the interface probe battery by pressing the test button to ensure the device is operating properly before and after taking the level measurement. Daily battery checks should also be made and documented in the logbook.

B. Lower the interface probe until it makes contact with the product in the well and the product indicator light goes on or the pulsating alarm is sounded. Record the position of the wire relative to the reference point to the nearest 0.01-foot. Repeat to confirm the depth of the product.

C. Continue to lower the interface probe, through the product layer, until it makes contact with the water level in the well and the water indicator light goes on or the continuous alarm is sounded. Record the position of the wire to the reference point to the nearest 0.01-foot. Repeat to confirm the depth of the water.

D. Withdraw the probe from the well.

E. Record the product and water depth in the field logbook and/or the field activity form.

F. Decontaminate the sounder wire and probe in accordance with the guidelines in SOP No. 500.

5.0 <u>CONTINUOUS WATER LEVEL MEASUREMENT METHODS AND PROCEDURES</u>

5.1 PRESSURE TRANSDUCER METHOD

Continuous water level measurements are made by determining the height of the water column above a pressure transducer and electronically recording fluctuations in this height with a data logger. The continuous recording of height of water above the transducer is used for aquifer testing where rapid changes in water level are anticipated.

5.2 PROCEDURES

A. Enter the program into a data logger that has fully charged batteries. Alkaline batteries are preferred. During use, the battery voltage should not drop below the minimum voltage specified by the manufacturer; damage to the data logger and loss of recorded data could result.

B. Select a pressure transducer for use in a given well that is compatible with both water quality and anticipated pressure sensitivity range (i.e., 5 psi, 30 psi, etc.). The pressure range selected is dictated by the anticipated range in the water column above the transducer and by the desired precision in measurement.

C. Hook up the transducers to the data logger in the field following manufacturer’s instructions. Typically, four to eight input channels are available on the system. Other factors affecting the sampling configuration include cable length; distance between monitored wells; terrain; local human activities (traffic, plant operations); and the ability to secure the system from weather and vandals.

D. Attach the transducer cable to the data logger and calibrate in air according to manufacturer’s instructions. If multiple data loggers are used, internal clock synchronization should also be performed.

E. Measure water level and depth to the bottom of the well before lowering the transducer into the well. Water levels are measured with an electrical water level indicator; total depth of the well is measured with a device compatible with well depth.

F. Secure a sanitary fitting (commonly a gasket adapted to the cable diameter) at the surface of the well. Lower transducer into the well through the sanitary fitting to a depth between the water level and the bottom of the well. The transducer must be kept submerged during the period of measurement. Take care to keep the piezometric crystal at the tip of the transducer out of any fine sediment that has accumulated in the bottom of the well. On some transducers, the crystal is protected from sediment intrusion. Measure water level again; record the time indicated on the data logger digital display and water level. From these readings (and other periodic manual water level measurements), the water levels can be converted to elevations.

G. Transfer data stored in the data logger periodically to a portable computer. The frequency of data transfer depends on available memory and conditions encountered in the field. Data may be transferred as frequently as daily. If the data logger has a wrap-around memory, the information should be transferred so that records are not recorded over.

ATTACHMENT 1

WATER LEVEL MONITORING FORM

Depth to Groundwater

Client ____________________ Site Name ____________________ Date ____________________, 2010

Project No. ____________________ Location ____________________ Method of Measurement Water level indicator

Monitoring Well	Time	Measuring Point	Elevation of Reference (feet)†	Depth to Groundwater (feet)	Groundwater Elevation (feet)†	Notes

† Vertical datum ☐ Mean sea level ☐ Arbitrary datum set at ___________feet located at ____________________

Standard Operating Procedure No. 320

FIELD MEASUREMENTS

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 320 guidance for measurement of specific field parameters as described in the Work Plan or as otherwise specified. Water quality measurements are required during well development and groundwater sampling. Vapor headspace measurements are performed during screening of the soil samples.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Field methods to be used include measurements of the following:

1. Temperature, pH, and specific conductance
2. Dissolved oxygen
3. Vapor headspace measurement

B. The site geologist or hydrogeologist is responsible for implementing the correct sampling techniques and for recording the field data and observations in the field logbook and/or field activity form.

C. Field measurement devices shall be calibrated in accordance with the manufacturer's procedures or as specified in SOP No. 930.

D. All field equipment shall be decontaminated after use in the field. Specific decontamination procedures are described in SOP No. 500.

2.2 PROCEDURES

2.2.1 Temperature / pH / Specific Conductance

Temperature, pH, and conductivity meters shall be calibrated in accordance with the manufacturer's instructions and SOP No. 930. Measurements shall be reported to the nearest 0.1° C for temperature, and to the nearest 0.01 unit for pH. Conductance shall be reported to the nearest ten units for readings under 1,000 mhos/cm and to the nearest 100 units for readings over 1,000 mhos/cm. All calibration and measurements shall be recorded in the field logbook and/or field activity form.

2.2.2 Dissolved Oxygen

Dissolved oxygen (DO) content of water samples shall be measured using a membrane electrode meter. The meter shall be calibrated in accordance with the manufacturer’s instructions and SOP No. 930. DO content shall be reported to the nearest 0.1 mg/L. All calibrations and measurements shall be recorded in the field logbook and/or field activity form.

2.2.3 Vapor Headspace Measurement

A flame ionization detector (FID) or a photoionization detector (PID) will be used during field screening and headspace analysis of soil samples. The FID or PID should be calibrated in accordance with the manufacturer’s instructions and guidelines in SOP No. 930. Vapor concentration measurements shall be reported to the nearest 1.0-ppm. Vapor headspace analysis procedures are provided in SOP No. 330. All calibrations and measurements shall be recorded in the field logbook and/or field activity form.

Standard Operating Procedure No. 330

VAPOR HEADSPACE SCREENING

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 330 discusses the guidelines for conducting vapor headspace screening as described in the Work Plan or as otherwise specified. Through vapor headspace screening, organic vapor concentrations will be measured in all collected soil samples and will be used as criteria for selecting a soil sample for chemical analysis.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Headspace screening or analysis involves measuring the near-equilibrium vapor concentration with an unknown concentration of volatile organic compounds (VOCs) in a soil sample.

B. The method involves placing a portion of a soil sample in a sealable plastic bas, sealing the bag, and allowing the test bag to equilibrate at room temperature for a predetermined length of time. The test bag is then punctured using the probe tip of an organic vapor detector (i.e., PID or FID) and the maximum vapor concentration is recorded.

C. The method provides a quick and inexpensive way of determining the relative degree of contamination in a soil sample and providing criteria with which to select a sample for laboratory analysis. The method can be used to determine the relative horizontal and vertical extent of soil contamination.

D. Organic vapor detection equipment should be calibrated before testing in accordance with the procedures provided in SOP No. 930.

2.2 SCREENING PROCEDURES

A. Soil samples collected from split-spoon samplers should be placed in the test bag immediately after opening. Soil samples collected from the surface, an excavation, or a soil pile should be obtained from a freshly exposed area and immediately placed in the test bag.

B. Place approximately 4 ounces of sample into a one-quart test bag.

C. Quickly seal the test bag. Write the sample location, sample number, and depth interval on the bag using a permanent marker or grease pencil. Allow the test bag to set for a minimum of 15 minutes at room temperature.

D. Puncture the test bag with the organic vapor detector probe tip. Be careful not to insert the probe tip into the soil sample.

E. Measure and record the maximum reading displayed by the organic vapor detector. Record the reading on the field activity form and/or field logbook. Erratic meter response may occur due to the presence of high vapor concentrations or excessive water vapor. If this occurs, the data should be disregarded.

F. Discard the soil sample and test bag in a 55-gallon drum for subsequent disposal as specified in the Work Plan.

G. The vapor headspace analysis should be performed the same day as the sample was collected.

2.3 EQUIPMENT AND MATERIALS

The equipment and materials required to conduct headspace screening are listed as follows:

- FID or PID with calibration kit
- Sealable plastic bag
- Permanent marker or grease pencil
- Field logbook

3.0 DOCUMENTATION

All headspace results should be recorded on the appropriate field activity reports and/or in the field logbook. Any conditions that may interfere with the headspace results (i.e., weather, water vapor, etc.) should also be noted.

Standard Operating Procedure No. 410

GROUNDWATER SAMPLING

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 410 describes the guidelines for obtaining groundwater samples from monitoring wells, recovery wells, or observation wells as described in the Work Plan or as otherwise specified for the purpose of determining groundwater quality.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Decontaminate all sampling instruments as specified in the SAP and in accordance with SOP No. 500.

B. Provide sufficient quantity and type of sample containers at the groundwater sampling location. Sample bottle sizes, preservation techniques, quantity, and other specifics are outlined in the Quality Assurance Project Plan (QAPP). Sample Classification, storage, packaging, and shipment will be conducted in accordance with SOP No. 911.

C. Field measurements including pH, temperature, and specific conductance of each well volume will be performed before sampling. Field measurements are discussed in detail in Section 3.4 of the SAP and SOP No. 320.

D. The first water sample collected will be for volatile organic analysis (VOC). The sample vials should be filled with as little agitation as possible as it passes from the sampling device to the sample bottle. There should be no air bubbles present in a VOC sample vial. Other sample bottles can then be filled and preserved as specified in the SAP and QAPP.

E. Trip blank samples supplied by the laboratory, along with the sample bottles, will be used as discussed in SOP No. 920 and the QAPP.

2.2 FIELD MEASUREMENTS

2.2.1 General

A. Measure and record depth to water in wells and calculate standing water volume in the well.

B. Record physical characteristics of the water sample in the field logbook and/or field activity forms. The physical characteristics include color, general turbidity, odor, viscosity, and other observations.

C. Measure and record water quality parameters of the water sample in the field logbook and/or field activity forms. The water quality parameters include:

   1. pH
   2. Temperature
   3. Specific conductance

D. Temperature, specific conductance and pH measurements are used to determine when the purging process is completed and representative groundwater from the aquifer is present in the well.

E. Due to the nature of most field measurement devices, it is difficult or impossible to decontaminate them thoroughly and so they should not enter the well directly. Therefore, samples for field measurements should be taken from the purged water. Care should be taken not to contaminate the field measurement equipment with material that cannot be safely rinsed off.

F. Field instruments should be calibrated before sampling. Calibration procedures for field instruments should be followed in accordance with SOP No. 930.

2.2.2 Field Measurement Procedures

The following field measurements should be performed and noted in the bound field logbook and/or field activity form:

A. Physical Measurements

   1. Well number and location

   2. Diameter and construction material of the well casing.

   3. Total depth of well from the top of casing (TOC), surveyor's mark, if present.

4. Depth from top of casing to water (DTW).
5. Calculate the linear feet of water in the well/borehole by subtracting depth to water from total depth of well/borehole. The capacity of various well casing/borehole diameters are as follows:

Casing or Borehole Diameter	**Gallons / Linear Feet**
2”	0.16
4”	0.66
6”	1.47
8”	2.61
12”	5.81

Now calculate the standing water volume (V) present in the well casing and filter pack as follows:

$V = nA (B-C) + CD$

where,

n = porosity of the filter pack (usually 0.25)
A = height (in feet) of the saturated filter pack
B = volume of water in the borehole (gallons)
C = volume of water in the well casing (gallons)
D = height (in feet) of the standing water column in the well

B. Water Quality Parameters

In addition to the physical measurements described above and other information that may identify the well, record the following water quality parameters for each well volume removed before sampling:

1. pH
2. Temperature
3. Specific conductance

2.3 WELL PURGING AND EVACUATION PROCEDURES

2.3.1 General

A. In order to obtain a representative groundwater sample, the water that has stagnated and/or thermally stratified in the well casing should be purged or evacuated. This evacuation procedure allows fresh or formation groundwater to enter the well. A minimum of three well volumes should be evacuated or until the water quality parameters stabilize in high-yield wells. In wells with very low recoveries, the well may be evacuated to near dryness and allowed to recover before sampling.

B. Criteria for parameter stabilization include:

   1. pH, ± 0.1 unit
   2. Temperature, ± 0.5 C
   3. Conductivity, ± 15%

C. All newly constructed wells should be allowed to stabilize for a minimum of 48-72 hours before sampling. Additionally, once a well is evacuated, it should be sampled within 2 hours. If an evacuated well is allowed to sit longer than the prescribed 2 hours, it should be re-evacuated as the water contained in the well casing may no longer be representative of aquifer conditions.

2.3.2 Evacuation by Pumping

A. Extreme caution should be exercised to ensure that this evacuation procedure does not cause cross-contamination from one well to the next. Therefore, dedicated tubing and pumps are preferred. If it is not practical to dedicate a pump to a specific well, it is permissible to decontaminate this equipment. The pump may be reused to sample monitoring wells installed at the same waste handling unit. Equipment should be decontaminated in accordance with SOP No. 500. Tubing should always be dedicated and never used for more than one well. Wash and rinse the pump and collect a sample of the rinse water as a field blank to ensure the integrity of the sample.

B. During evacuation, set the pump intake not greater than 6 feet below the dynamic water level in the well. This requires that the evacuation device may have to be lowered as purging continues.

C. During pumping, intermittently collect pump discharge in a container of known volume for a period of not less than 2 minutes to verify the pump flow rate and to check the purged volume.

D. Measure the temperature, conductivity, and pH after each required well casing volume and intermittently thereafter until field measurements are consistent within a 10 percent variance.

E. Collect purged well water in drums, buckets, or suitably sized containers for subsequent disposal as specified in the Work Plan.

2.3.3 Evacuation by Bailing

A. Hand bailing should be utilized when static water levels are greater than 25 feet or if no submersible pump is available. However, care should be exercised to prevent introduction of contaminants into the well and causing excessive aeration of the water sample.

B. For dedicated bailers, wash and rinse the bailer before purging if contaminants, foreign matter, or rust are present. For non-dedicated bailers used at more than one well, decontaminate the bailer in accordance with SOP No. 500.

C. Evacuate a minimum of three well volumes by repetitive bailing and until water quality parameters stabilize.

D. Collect purge water in 55-gallon drums or as specified in the Work Plan.

2.4 SAMPLING EQUIPMENT

Equipment to be used for groundwater sampling generally falls into two categories: those used to evacuate the well casing and those used to collect a discrete sample for analysis. In some instances, the device used for evacuation may also be used for sample collection. In many instances, however, characteristics exhibited by the evacuation device may preclude its use for sample collection. Types of equipment available for evacuation and/or sampling include the following:

1. Bottom fill bailers
    a. Single check valve (bottom)
    b. Double check valve (top and bottom)
    c. Polyethylene, polypropylene, PVC, or Viton® construction
    d. Teflon construction
    e. Stainless steel construction
    f. Stainless steel construction with Teflon check valve(s)
2. Suction lift pumps/centrifugal pumps
3. Portable submersible pumps
4. Bladder (gas squeeze) pumps
5. Continuous organics sampling system in conjunction with peristaltic pump

Hand bailers come in a variety of sizes and volumes to accommodate most well casing diameters. The preferable materials of construction are, in order of decreasing preference, Teflon, stainless steel, polypropylene, polyethylene, Viton®, PVC (low plasticizer content).

In addition to an evacuation and sampling device, other pieces of equipment and supplies necessary for sampling include:

1. Steel tape and chalk or electronic water level indicator
2. Sample containers
3. Preservatives, as needed
4. Ice or ice packs
5. Field instrumentation, as needed
6. Trip blanks
7. Bound field logbook
8. Sample analysis request forms
9. Chain of custody forms and custody seals
10. Sample labels, indelible
11. Appropriate personal protective equipment
12. Appropriate hand tools
13. Keys to locked wells, if needed
14. Water filtration device and disposable filters, if necessary

Field equipment for sampling, evacuation, and field measurements should be as specified in the SAP.

2.5 SAMPLING METHODS

2.5.1 Bottom-fill Bailer

A. After evacuation of the required volume of water from the well, proceed with sampling as soon as possible after evacuation, preferably immediately. In most cases, the time lapse between evacuation and sampling should not exceed 2 hours.

B. The type of bailer used for sampling will depend on the required quality of gathered information.

C. The bailer and any other equipment entering the well should be properly decontaminated and handled with new surgical gloves to preclude any potential contamination sources. Nothing entering the well should be allowed to contact the ground or any other potentially contaminated surfaces (i.e., gasoline pumps). If this should occur, that item should not be placed in the well or used for sampling. It is always a good practice to have an extra clean bailer on hand in the case of an emergency. Plastic sheeting should also be placed around the well to preclude any contact of equipment with the ground surface.

D. Lower the bailer by hand using either a stainless steel cable or a new length of nylon rope. Hand bailers should be lowered into the well using caution not to aerate the well water to be sampled. Lower the bailer to the well screen interval and pull up the rope. Retrieve the bailer and slowly transfer the sample to the appropriate sample containers, filling VOC vials first. If onsite filtration is required, extra quantities of sample should be collected.

2.5.2 Suction Lift Pumps/Centrifugal Pumps

A. Suction lift pumps (i.e., diaphragm, peristaltic, and centrifugal) are pumps used at the ground surface with polyethylene tubing inserted into the well. They are used to evacuate the well before sampling. The tubing should be new and dedicated to a particular monitoring well, and equipped with a valve that will prevent the aerated water from falling back into the well. The pump casing should be rinsed with tap water, then distilled water, between sampling points.

B. The limitation posed by this type of pump is its suction capability. Generally, the groundwater level should be less than 25 feet below the ground surface.

C. Due to the nature of these pumps, as well as their effect upon samples for chemical analysis, these devices should be used only for well evacuation and not groundwater sampling unless otherwise specified in the SAP.

2.5.3 Portable Submersible Pumps

When the groundwater level is greater than 25 feet, the use of suction lift pumps is prohibited, and another evacuation device should be used. If the diameter of the well casing allows, a portable submersible pump can be used. Due to the nature of these pumps, as well as their effect upon samples for chemical analysis, these devices should be used only for monitoring well evacuation and not groundwater sampling unless otherwise specified in the RP&S.

2.5.4 Bladder Pumps (Gas Squeeze Pumps)

A. A bladder pump consists of a stainless steel housing that encloses a flexible membrane. Below the bladder, a screen is attached to filter any material that may clog the check valves located above and below the bladder. The pump works as follows. Water enters the membrane through the lower check valve. Compressed gas is injected into the cavity between the housing and bladder. The water moves through the upper check valve and into the discharge line. This upper check valve prevents back flow into the bladder.

B. The bladder pump is used much like the portable submersible pump, except that no electrical lines are lowered down the well. The source of gas for the bladder is either bottled air or an onsite air compressor. Disadvantages include the large gas volumes needed, potential bladder rupture, and difficulty in cleaning the unit.

2.5.5 Potable Well Sampling Procedure

A. The first step in sampling a potable well, whether it be a homeowner's well or a municipal production well, is to obtain as much information as possible from the homeowner or water superintendent. This should include: depth of the well, formation in which it is completed, screen depth and length, diameter of casing, and when and who installed it. Caution should be used in applying this information unless confirmation can be obtained (i.e., drilling logs).

B. With this information, determine the number of gallons to be evacuated. If no information is available, evacuate for a minimum of 15 minutes. This evacuation is best accomplished from an outside faucet with a hose run away from the home. In this manner, overloading of the homeowner's septic system will be minimized.

C. An inspection of the system should be performed to locate the well, pump, storage tanks, and any treatment systems that may be present. The sample access point should be chosen as close to the well head as possible, before the storage tank or any treatment devices. Collect that sample at the first tap or spigot and note in the field logbook where the sample was collected, and any systems (storage and/or treatment) between the well head and sample collection point. For long-term monitoring projects, a specific tap or faucet could be designated as the sample access point and used for the duration of the project.

3.0 SAMPLE HANDLING

A. Groundwater samples should be placed in appropriate sample containers and preserved in accordance with SOP No. 910 and the QAPP.

B. Groundwater samples should be classified, stored, packaged, and shipped in accordance with SOP No. 911 and the QAPP.

C. Sample control and chain of custody protocol should be in accordance with SOP No. 912 and the QAPP.

4.0 DOCUMENTATION

The location of the well, physical characteristics, well evacuation volume, and water quality parameter measurements should be recorded on the groundwater data form (see Attachment 1) and/or the field logbook. Documentation procedures should be in accordance with SOP No. 110.

ATTACHMENT 1

GROUNDWATER DATA FORM

Well Number:_________

Well Development and Purging Data

Page _____ **of** _____

Project Name: ____________________________________

Project Manager:____

Client Company:___________________________________

Project No.:_______________________

Site Name:____

Site Address:____

Development Criteria

_______ 3 to 5 Casing Volumes of Water Removal
_______ Stabilization of Indicator Parameters
_______ Other___________________________

Methods of Development

Pump
_______ Centrifugal
_______ Submersible
_______ Peristaltic

Bailer
_______ Bottom Valve
_______ Double Check Valve
_______ Stainless-stell Kemmerer

Water Volume Calculation (2" = 0.1632; 4" = 0.6528)

Initial Depth of Well (feet):_________
Initial Depth to Water (feet):___________
Height of Water Column in Well (feet):_________
Diameter (inches): Well_______ Gravel Pack_______

Item	Water Volume in Well		Gallons - Removed
	Cubic Feet	Gallons	
Well Casing			
Gravel Pack			
Drilling Fluids			
Total			

Instruments

_______ Temperature Meter
_______ Conductivity Meter
_______ DO Meter
_______ pH Meter
_______ ORP Meter
_______ Turbidity Meter

Water Disposal:___________________________

Water Removal Data

Data	Time	Development Method		Removal Rate	Intake Depth	Ending Water Depth (feet)	Water Volume Removed (gallons)		Product Volume Removed (gallons)		Temp (◦C)	Conductivity (mS/cm) (ppm)	Dissolved Oxygen (mg/L)	pH	ORP (mV)	Turbidity (<10 NTUs)	Comments
		Pump	Bailer				Increment	Cumulative	Increment	Cumulative							
																	Start Purging
																	Collect Sample

Circle the date and time that the development criteria are met

Comments:____

Developer's Signature:____ Date:___________ Reviewer:__________________ Date:___________

Standard Operating Procedure No. 500

EQUIPMENT DECONTAMINATION

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 500 describes the guidelines for decontamination of personnel and equipment during hazardous waste investigation field activities as specified in the Work Plan or as otherwise specified.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. A decontamination plan should be developed and sufficiently scoped to address all the expected types and levels of contaminants at the site and the methods used to investigate them. Until proven otherwise, the decontamination plan should assume that all personnel and equipment exiting the area of potential contamination are contaminated and, therefore, comprehensive decontamination procedures must be implemented. Procedures for decontamination of equipment, as well as personal protective clothing and safety equipment, are included in the Site Health and Safety Plan (SHSP).

B. Personnel involved in decontamination efforts will be equipped with the same protective equipment as those conducting onsite investigations until a lower level of risk can be confirmed.

C. Procedures for decontamination of field personnel should be specifically addressed in the SHSP. These procedures should be followed and incorporated with the equipment decontamination procedures contained in the SAP to minimize exposure and cross-contamination potential.

D. Decontamination activities should be documented to verify that proper procedures are followed. Documentation shall be in accordance with the requirements specified in SOP No. 110, the Work Plan, and/or Quality Assurance Project Plan (QAPP).

E. The methods described in this SOP are considered sufficient for most hazardous waste investigations. However, more intensive site-specific procedures may be required under highly toxic or other “non-routine” conditions. In these cases, advice of in-house or consulting industrial hygienists and/or organic chemists may be of assistance in determining specific procedures necessary for decontamination.

F. Decontamination procedures may be subject to federal, state, local, and/or the client’s regulations. All regulatory requirements must be satisfied, but the procedures adopted should be no less rigorous than those presented in this SOP.

G. Climatic conditions anticipated during the decontamination activities may play a significant factor in the procedures selected. Special facilities may be needed to compensate for weather conditions, such as temporary heated structures for winter work and windscreens for dust prevention. It may be necessary to establish special work conditions during periods of high heat stress.

2.2 SITE FACILITIES AND SUPPLIES

2.2.1 Site Selection

A. The equipment decontamination facility should be in an area where contaminants can be controlled and at the boundary of a “clean” zone. The location should also be selected to prevent equipment from being exposed to additional or other contamination. On large projects, a formal “Contamination Reduction Zone” should be established in which all decontamination efforts will be conducted. This area should be conspicuously marked as “off-limits” to all personnel not involved with the decontamination process.

B. Due to the volume of wastewater generated the equipment decontamination area should be located where decontamination fluids can be easily discharged into adequate storage containers, followed by characterization and proper disposal.

C. The decontamination area should have adequate storage area for storing unused drums, used drums containing spent decontamination fluids and waste, and trash containers, until such time that they can be relocated or disposed offsite.

2.2.2 Decontamination Pad

A. Some sites under investigation may have an existing decontamination area. If an area has previously been constructed, it should be evaluated for logistics capabilities such as water supply, electrical power, by-product handling capabilities, and cleanliness. If the existing area can be used or modified for use, the savings in costs and level of effort may be significant.

B. On small projects where only hand sampling or other small equipment is being used, several small washtubs (filled with detergent and potable water) may be sufficient for decontamination.

2.2.3 Water Supply

A. Large volumes of water, often exceeding 1,000 gallons per day, may be required for cleaning, especially for drill rigs and other large equipment. The water used for equipment decontamination must be clean, potable water; municipal water supplies are generally adequate.

B. Stainless steel tank trucks or aluminum (if stainless steel is not available) can be used for onsite storage of the water supply. These tankers can be transported easily and are not excessively expensive. Typically, a week's supply of water can be stored onsite.

C. Water may also be stored in open-top watertight tanks or roll-off boxes located in the clean zone on the site. However, open-top tanks or box containers should not be used if airborne contaminants are present, unless a liner is used to cover the container. Containers should be steam-cleaned and acid-washed before use. Only containers used to store fresh water or inert materials should be used. Never use containers previously used to store petroleum products or organic chemicals.

2.2.4 Cleaning Equipment and Supplies

A. A portable steam cleaner or high-pressure hot water washer is normally required to clean contaminated heavy machinery (e.g., drill rig, backhoe, etc.) as well as materials and associated tools. Most washers and steam cleaners are commercially available for both portable generators or supplied AC power. Site logistical considerations may control the type of equipment required.

B. Typical steam cleaners/washers operate on relatively low water consumption rates (2 to 6 gpm) and can be used in conjunction with other cleaning fluids mixed with the water. High-pressure steam is preferred to high-pressure water because of steam's greater ability to volatilize organics and to remove oil and grease from equipment.

C. Units tend to malfunction easily and are susceptible to frequent maintenance and repair (especially under frequent use or use below freezing conditions). If possible, a second or back-up unit should be available onsite or arranged for with a nearby vendor.

D. On some small projects, garden sprayers may be used for final rinsing or cleaning. Typically, these sprayers are limited to use with small hand tools or sampling equipment. They also tend to break down and malfunction quickly.

E. Miscellaneous items required for decontamination efforts include some of the following:

- Potable water supply
- Decontamination solution
    - Potable water
    - Distilled water
    - Mild detergent (such as Alconox)
    - Isopropanol
- Brushes to remove heavy mud, dust, etc.
- Buckets
- Steam cleaner or high-pressure, hot water washer
- Racks normally metal (not wood) to hold miscellaneous equipment such as drill rods, sampling tools, etc.
- Utility pump to collect spent fluids for containerizing
- Drums to store contaminated materials (personal protective equipment, etc.)
- Tables (not wood) to hold small items after/during cleaning
- Plastic sheeting to wrap decontaminated equipment, tools, etc., after cleaning

2.3 EQUIPMENT AND VEHICLE DECONTAMINATION PROCEDURES

A. The following procedures are presented as a function of the level of contaminant concentration and are intended as general guidelines. Appropriate site procedures should be established based on the individual site characteristics and type of investigation prescribed.

1. Low to Moderate Contaminant Concentration:
    a. Steam or water rinse with potable water to remove mud or dirt
    b. Steam or hot water wash with a mixture of detergent and potable water
    c. Steam or hot water rinse with clean, potable water
    d. Air dry

2. High Contaminant Concentration:
    a. Steam rinse with potable water to remove mud or dirt.
    b. Steam wash with a mixture of detergent and potable water or other type of decontamination solution.
    c. Steam rinse with clean, potable water.
    d. Air dry.

B. During decontamination of drilling equipment and accessories, clean hollow-stem auger flights, drill rods, and drill bits (particularly roller bits), as well as all couplings and threads. Generally, decontamination can be limited to the back portion of the drill rig and those parts that come in direct contact with samples or casing, or drilling equipment placed into or over the borehole.

C. Some items of drilling equipment cannot typically be decontaminated; these include wood materials (planks, etc.), porous hoses, engine air filters, etc. These items should not be removed from the site until ready to dispose of in an appropriate manner.

Other drilling equipment (especially rotary drill rigs) that requires extensive decontamination are water or grout pumps. Flushing may be sufficient to clean them. However, if high concentration of constituents or visible product is known to exist, then disassembly and thorough cleaning of internal parts is required before removal of the equipment from the site.

D. The mud pumps, kelly, swivel, and suction hoses on rotary drill rigs should be cleaned by circulating a minimum of 1,000 gallons of clean water and cleaning solution through the system followed by a minimum of

200 gallons of clean water through the system, and finally rinsing with 50 gallons of clean water without recirculating the fluid.

2.4 SAMPLING EQUIPMENT DECONTAMINATION PROCEDURES

A. All sampling equipment that may contribute to the contamination of a sample must be thoroughly decontaminated before its initial use, unless specific documentation exists that the sampling equipment has been decontaminated.

B. Generally, sampling equipment can be cleaned by hand. The following procedure is given as a typical sequence that should be modified based on site conditions.

C. Split-spoon and Shelby-tube samplers, bailers, and other sampling equipment that can be cleaned by hand shall be decontaminated as follows:

1. Wash and scrub with detergent (non-ionic)
2. Tap water rinse
3. Air dry

Rotasonic sample core barrels will be decontaminated by flushing the interior of the barrel with tap water in between samples collected from the sample boring, and high-pressure steam washing the core barrel between boring locations.

D. Steel tapes, water probes, transducers, thermometers, and water quality meters shall be rinsed in distilled water or cleaned in a detergent solution and rinsed in distilled water after each use.

E. All pumps will be cleaned in water/detergent solution and flushed with clean water after each use.

F. Use of high-pressure steam or hot water washing may be substituted for hand scrubbing if it effectively removes contaminants and soil and can be done safely without burning or contaminating the personnel. Special racks should be used to hold equipment while high-pressure washing. High-pressure washing should not be conducted on delicate equipment.

G. More “complicated” samplers require more “complicated” decontamination procedures. Piston and other samplers with numerous internal parts should be avoided, if possible, on sites requiring extensive decontamination procedures.

2.5 WELL MATERIALS DECONTAMINATION PROCEDURES

Well-casing, whether constructed of PVC, stainless steel, or other materials will be cleaned with a steam cleaner or high-pressure hot-water washer before it is installed. All well construction materials will be handled while wearing latex gloves.

2.6 DISPOSAL PRACTICES

2.6.1 General Disposal Requirements

A. Proper disposal of decontamination, sampling, and drilling byproducts shall be conducted to prevent the spread of contaminants offsite and to protect individuals who may encounter the potentially hazardous materials.

B. Disposal practices shall be in accordance with the procedures specified in the Work Plan. In general, sampling, drilling, and decontamination byproducts should be collected and disposed in a manner consistent with the accepted disposal practices for the type and concentration of wastes that may be contained in the byproducts.

C. Contaminated equipment or solutions will not be discarded in any manner that may lead to contamination of the environment by the migration of hazardous constituents from the site by air, surface, or subsurface transport mechanisms.

2.6.2 Onsite Disposal

A. Certain materials that are not contaminated or contain very low levels of contamination may be disposed of onsite. Such materials may include drill cuttings, wash water, drilling fluids, and water removed in developing or flushing wells. The low level of contamination in these materials should be confirmed before onsite disposal.

B. On controlled, secured facilities, most contaminated materials may remain on the site, provided they do not pose a threat of contamination of personnel or areas to be sampled.

2.6.3 Offsite Disposal

A. Materials that cannot be disposed of onsite will require that specific procedures be developed to provide for offsite disposal. Storage areas and/or tanks will be provided to hold the material onsite before disposal. Offsite disposal may be appropriate at various locations depending upon the nature of the waste. Prior to transporting the storage containers offsite, steps should be taken to ensure that the containers are properly sealed and labeled.

B. Consideration should be given to use of sanitary and storm sewer systems, sanitary landfills, and licensed hazardous waste disposal facilities. Offsite disposal of wastes must comply with local, state, and federal laws and regulations. The Work Plan should identify the waste disposal options appropriate for offsite disposal of various classes of waste materials.

Standard Operating Procedure No. 910

SAMPLE CONTAINERS, PRESERVATION, AND HOLDING TIMES

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 910 describes the guidelines for preparation of sample containers, preservation of samples, and sample holding times as required in the Work Plan or as otherwise specified. This sampling protocol will be implemented to maintain the quality and integrity of the samples to be analyzed.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Sample containers and preservation methods should be selected and used to ensure the accuracy and validity of chemical and physical analyses. Materials or procedures that might cause overt disturbance, contamination, oxidation or other chemical decomposition or reaction of the sample should be avoided. This SOP addresses only containers and preservation of chemical analytical samples.

B. Sample preservation methods should adequately meet the requirements established in the Work Plan or QAPP.

C. Use of containers and preservation procedures should be consistent with the analytical procedures used by the analytical laboratory.

D. Preservation is generally limited to pH control, addition of chemicals, and refrigeration. These techniques are intended to retard biological action, retard hydrolysis of chemical compounds, keep metals in solution, and reduce volatility of constituents.

E. Hazardous samples (those that contain medium or high concentrations of contaminants) should not be prepared with any chemical preservative or cooled, except as specifically required for samples of known contaminant type.

F. Refrigeration to maintain the sample temperature near 4° C is the minimum amount of preservation that should be performed for environmental samples. Samples should not be frozen, and dry ice should not be used as the cooling agent (due to shipping restrictions). Chemical preservatives may be added to sample bottles in advance, either by the testing laboratory or by field personnel. The recommended preservatives for various constituents are presented in the QAPP.

G. Certain constituents may deteriorate within a given time span regardless of preservation. Based on the best available data, recommended maximum holding times for many constituents have been determined and are listed in the QAPP.

H. If, under any circumstances, the proper preservation technique is not used or if the recommended holding time is exceeded, the data as finally reported by the laboratory must indicate the particular variance.

I. Volumes of sample required for analysis vary widely depending on type of chemical analysis. The volumes required for a particular analysis are listed in the QAPP.

J. Sample bottle lids should be hand-tightened. The lids should not be taped as some tapes may contain chemicals that could contaminate the sample.

2.2 CONTAINER TYPES

A. Containers in which samples of soil or water are collected should be constructed of materials that remain inert with respect to the suspected contaminants. Amber glass and linear polyethylene (LPE) containers are recommended. They should have screw-type lids to assure adequate sealing of the bottles. Teflon inserts should be placed inside the lids of glass containers to prevent sample reaction to the lid and improve the quality of the seal.

B. The volumes of the containers used in sample collection are dependent upon the analytical requirements.

C. Sample containers should generally be supplied by the laboratory contracted to perform the analyses. In these cases, sample bottles should be cleaned by the laboratory before shipment to the field. If this procedure has been followed, each bottle should be clearly labeled as to the type of sample it should contain (e.g., metals, TOC, etc.).

2.3 CONTAINER AND PRESERVATION REQUIREMENTS FOR ENVIRONMENTAL SAMPLES

2.3.1 Water Samples

Organics

A. Water samples for organic analyses should be collected in glass bottles equipped with Teflon-lined screw caps. Water supply and other samples also suspected of containing residual chlorine should have 0.008 percent $Na_2S_2O_3$ (sodium thiosulfate) added. These water samples should be preserved by cooling with ice below 4° C and other preservatives as specified by the contracted laboratory.

B. Regulatory or other considerations may require that trip blanks be collected for volatile organic compounds (VOCs). Trip blank samples for VOC analysis should be collected in 40 ml glass vials (purge vials), preserved with hydrochloric acid (HCl), equipped with Teflon-backed, silicon septum screw caps and filled to the top with no visible air bubbles.

Metals

C. Water samples for metals analysis should be collected in one-liter high-density polyethylene bottles with solid polyethylene or polyethylene-lined caps. Bakelite caps should be avoided. The bottles are cleaned with dilute nitric acid and washed well with distilled or deionized water. The samples should be preserved with nitric acid to below pH 2. Nitric acid concentration should not exceed 0.15 percent if the sample is to be shipped via air cargo.

2.3.2 Soil or Sediment Samples

Soil or sediment samples should be collected in wide-mouth glass jars equipped with Teflon-lined screw caps. Samples should be preserved by cooling with ice or refrigeration at 4° C.

If Method 5035 preservation techniques are to be used for the collection of soil samples for VOC analysis, each sample will be placed in 2-40 mL vials preserved with sodium bisulfate (low level analysis), or 1-40 mL vial preserved with methanol (high level analysis), and 1-4 oz. jar. In order to minimize the physical disruption of the sample, disposable plastic syringes are used to collect soil from the most undisturbed soil (typically the center of the soil core) and placed it into the sample vials.

2.4 PRESERVATION PROCEDURES FOR UN-ANALYZED HAZARDOUS SAMPLES

2.4.1 Liquids and Solids, Excluding Samples from Closed Containers

Both liquid and solid samples should be placed in glass jars with Teflon-lined screw cap lids. Eight-fluid-ounce wide-mouth round jars of clear glass are recommended. These bottles can be centrifuged to facilitate phase separation in the laboratory before analysis. These samples are not treated with chemical preservatives or cooled.

2.4.2 Liquids and Solids from Closed Containers

Samples from closed containers must, unless clear evidence to the contrary is present, be handled as if Poison A is present. Such samples should be placed in 40 ml or similar glass bottles with Teflon-lined caps. The sample container must be small enough to fit through the valve hole of a DOT specification metal cylinder for packaging and shipping in accordance with DOT regulations. These samples are not treated with chemical preservatives or cooled.

2.5 SAMPLE HOLDING TIME

Liquid and soil samples should be submitted to the laboratory within the required holding time as specified in the QAPP. Failure to analyze the samples within the specified holding time will compromise the integrity and validity of the analytical data.

Standard Operating Procedure No. 911

SAMPLE CLASSIFICATION, STORAGE, PACKAGING, AND SHIPMENT

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 911 describes the guidelines for sample classification, storage, packaging, and shipment as described in the Work Plan or as otherwise specified to ensure proper handling of samples.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Classification of samples shall be made based on the suspected level of contaminant concentration. This will determine subsequent packaging and labeling requirements, shipping procedures, and laboratory handling of samples.

B. Contamination concentrations must be assessed early in the planning stage of an investigation because of their effect upon field operation.

C. Sample classification must be considered in the development of the Site Health and Safety Plan (SHSP). The procedures and materials used for sample packaging must adequately protect the sample container from accidental breakage and should be sufficient to prevent any leaks or spills.

D. Sample labels for proper sample identification should be in accordance with the QAPP. The correct labels must be applied to sample containers and shipping containers to conform to U.S. Department of Transportation (DOT) shipping regulations.

E. Samples classified as hazardous can be shipped only by means specified in the DOT regulations and as discussed herein.

2.1.1 Sample Classification

2.1.2 Environmental Samples

A. Environmental samples are those that contain less than 10 ppm of any one contaminant. Samples collected offsite are considered “environmental” unless information to the contrary exists. Onsite samples may be classed as “environmental” by the Consultant Site Manager or Contractor based on knowledge of the site and nature of the sample.

B. Initially, concentrations of constituents are estimated based on knowledge of contaminant sources and the contaminant transport mechanisms, and their effects on contaminant concentrations. It is, therefore, necessary to be conservative in the estimate of contaminant concentration. Sample classification can be downgraded for subsequent samples if data exist to support that decision.

2.1.3 Hazardous Samples

A. Two categories of hazardous samples are defined as follows:

1. Medium concentration - samples expected to contain greater than 10 ppm and up to 15 percent (150,000 ppm) concentration of any one contaminant.

2. High concentration - samples expected to contain greater than 15 percent of any one contaminant.

B. “Hazardous Samples” include soil or water samples that may be highly contaminated; product, sludge, or waste pile samples of concentrated wastes; and any sample from a closed drum or container.

2.2 SAMPLE STORAGE

A. Samples should be stored in a manner consistent with the requirement for sample preservation to maintain the quality of the sample. Samples preserved by cooling should be stored in such a way as to maintain the acceptable range of temperature for the duration of the holding time.

B. Samples should not be stored onsite for extended periods and should be protected from environmental extremes. Shipment to the laboratory should be completed as soon as possible and well within the specified holding times for each particular analysis (refer to the QAPP) to allow analysis within the holding time limits.

C. If temporary storage is necessary, samples should remain in an area that has been designated as the “sample storage area,” which must be locked and secured to maintain sample integrity and chain-of-custody requirements. Separate containers must be used to store or transport low, medium, and high concentration samples.

D. Samples shall not be stored in refrigerators or other areas where food or drink may also be stored, and vice versa.

2.3 ENVIRONMENTAL SAMPLE PACKAGING

2.3.1 Regulatory Considerations

A. DOT regulations do not consider environmental samples hazardous. In addition, DOT has stated that dilute solutions of chemical preservatives are not subject to Hazardous Materials Regulations as long as the concentrations do not exceed specified values listed in Table 911-1.

B. In accordance with 49 CFR 173.24(a), the following is required for all packages:

"Each package used for shipping hazardous materials . . . shall be so designed and constructed, and its contents so limited, that under conditions normally incident to transportation:

(1) there will be no significant release of the hazardous materials to the environment;

(2) the effectiveness of the packaging will not be substantially reduced; and

(3) there will be no mixture of gases or vapors in the package which could, through any credible spontaneous increase of heat or pressure, or through an explosion, significantly reduce the effectiveness of the packaging."

C. In accordance with 94 CFR 173.6(a), the following is required for all shipment by air:

"Each package . . . shall be so designed and constructed, and its contents so limited, that under conditions normally incident to transportation;

(1) there will be no significant release of . . . materials to the environment.

(2) Inner containers that are breakable (such as earthenware, glass, or brittle plastic) must be packaged to prevent breakage and leakage under conditions normally incident to transportation. Those completed packagings must be capable of withstanding a 4-foot drop on solid concrete in the position most likely to cause

damage. Cushioning and absorbent materials must not react dangerously with the contents . . .

(3) For any packaging with a capacity of 110 gallons or less containing liquids, sufficient outage (ullage) must be provided to prevent liquid contents from completely filling the packaging at 130º F. The primary packaging (which may include composite packaging), for which retention of the liquid is the basic function, must be capable of withstanding, without leakage, an internal absolute pressure of not less than 26 pounds per square inch or no less than the sum of the absolute vapor pressure of the contents at 130º F (55º C) and the atmospheric pressure at sea level, whichever is greater.

(4) Stoppers, corks, or other such friction-type closures must be held securely, tightly, and effectively in place with wire, tape, or other positive means. Each screw-type closure on any inside plastic packaging must be secured to prevent the closure from loosening due to vibration or substantial changes in temperature . . .”

2.3.2 Shipping Containers

A. All sample containers should be placed inside a strong shipping container capable of withstanding a 4-foot drop on solid concrete in the position most likely to cause damage. A metal or plastic picnic cooler (ice chest) with a hard plastic liner withstands this test. The drainage hole at the bottom of the cooler must be taped shut so that the contents from the broken containers or water from ice bags will not escape. The shipping container should be taped shut to form an adequate seal around the lid to prevent any leakage in the event that the cooler is turned over.

B. The shipping container should be marked “THIS END UP” with arrows indicating the proper upward position of the container affixed to all four sides. To prevent cross-contamination, the shipping container must be adequately cleaned between shipments.

2.3.3 Ice

Ice should be placed into 1-gallon size plastic bags (minimum 2-ml thick) and sealed tightly. The amount of ice used will depend on the available space in the cooler, but 10 pounds per 20 quarts of cooler volume would be the minimum to assure sufficient cooling. Dry ice (CO_2) generally should not be used.

2.3.4 Glass Containers

The lid of the container should be tightened to assure an adequate seal. The container may be placed into a clear plastic bag that has a minimum thickness of 2-ml (many 1-quart and 1-gallon size zip-lock bags are suitable) and this bag sealed. They should be wrapped and cushioned in an inert packing material such as bubble wrap or shredded paper.

2.3.5 Plastic Containers

Plastic containers do not require individual cushioning material, but should be packed to prevent movement during transport. Caps should be tightly screwed on. These bottles may also be placed into a 2-ml thick plastic bag and the bag sealed.

2.4 HAZARDOUS SAMPLE PACKAGING

2.4.1 Regulatory Considerations

A. Hazardous samples are classified as ORM-E (Other Regulated Material - Series E) substances by the DOT. They are treated as a flammable liquid or solid and must be packaged accordingly to conform to DOT requirements.

B. If a sample is known to contain a material identified in the DOT Hazardous Materials Table (49 CFR 172.101), packaging and shipment should conform to the specific requirements for that substance.

C. If the nature of the sample is unknown, the materials should be prepared for shipment in accordance with DOT regulations for packaging and labeling the ORM-E hazard class.

2.4.2 Shipping Containers for Unanalyzed Waste Excluding Closed Container Samples

A. The procedures in this section should be applied to unanalyzed waste samples except those that come from closed containers whose contents are presumed to warrant a more careful packaging as described in Section 2.4.3.

B. Each sample container, properly labeled with sample information, should be placed into a 4-ml minimum thickness polyethylene bag (one sample per bag) and the bag sealed tightly with tape. This sealed container is placed into a metal can or overpack (such as a 1-gallon paint can) with incombustible, absorbent cushioning material, such as bubble wrap. Only one bag should be placed inside each can. The can lid should be closed tightly and sealed using tape or clips.

C. Each metal can must bear the following labels and markings:

1. Testing laboratory name and address and a return address.

2. "Flammable Liquid, N.O.S." marking. The abbreviation "N.O.S." means "Not Otherwise Specified."

3. "This End Up" arrows.

D. The following labels must be placed next to one another and near the "Flammable Liquid, N.O.S." marking:

1. "Cargo Aircraft Only"

2. "Flammable Liquid" or "Flammable Solid" and "Dangerous When Wet"

E. More than one can may be placed in a shipping container surrounded with incombustible packaging material for stability. The outside of the shipping container must bear the following markings and labels:

1. All of the labels described above for the sample cans; and

2. "Laboratory Samples," and

3. "This End Up" on the container top with upward pointing arrows on all four sides.

F. Using the word "flammable" does not convey the certain knowledge that a sample is, in fact, flammable or how flammable, but is intended to prescribe the class of packaging in order to comply with DOT regulations.

2.4.3 Shipping Containers for Unanalyzed Waste from Closed Containers

A. The Project Manager should make a judgment as to the hazard class of all samples from closed containers based upon available data. The following procedures provide typical worst-case methods for packaging materials classed by the DOT as "Poison A"; this type of "reasonable doubt" practice is provided for in the regulation (49 CFR 172.402 h).

B. Unless reliable data exclude the possibility of the presence of "Poison A" substances (as defined in 49 CFR 163.326), sample containers of unanalyzed waste from tanks or drums (solid, liquid or gas) must be packaged in a DOT Spec. 3A1800 or 3AA1800 metal compressed gas cylinder.

C. The sample container is first labeled with required sample information. Then, using a string of flexible wire attached to the neck of the sample container, it is lowered into a metal cylinder partially filled with incombustible, absorbent, packaging material. Allow enough cushioning material between the bottom and sides of the sample container and metal cylinder to prevent breakage. After the sample container is completely covered with cushioning material, the string or wire is dropped into the cylinder. The cylinder valve assembly and protector are replaced.

D. The following markings must be placed on the tag wired to the cylinder valve protector or a label affixed to the cylinder itself:

1. "Poisonous Liquid, N.O.S."
2. Laboratory name and address and return address

E. The following label must be placed on the cylinder, regardless of the location of all other markings:

- "Poisonous Gas" (the "Poisonous Liquid" label is not acceptable here, even if the sample is a liquid).

F. One or more cylinders may be placed into the same shipping container. The shipping container must bear the following markings:

1. All of the labels described above for the metal cylinders, and

2. "Laboratory Sample" and "Inside Packages Comply with Prescribed Specifications" should be marked on top of the container.

3. "This Side Up" marking should be placed on the top of the container with upward pointing arrows on all four sides.

2.5 SHIPPING OF SAMPLES

2.5.1 Environmental Samples

Environmental samples may be shipped to the testing laboratory by commercial common carrier, bus, rental vehicle, or air cargo service. Samples should be received by the laboratory within 24 hours after sampling or sooner, if necessary, to allow initiation of analyses within prescribed holding times.

2.5.2 Hazardous Samples

A. Hazardous samples, excluding those from closed containers, may be shipped by common carrier, air cargo, or other more protective means suitable for closed container shipments as described below.

B. Carrier-provided bills of lading and certification for restricted articles will be completed and signed. Standard industry forms will be used if carrier does not provide them. One form may be used for multiple shipping containers. The following information should be entered on the shipping papers:

1. "Flammable Liquid (or Solid), N.O.S."
2. "Net Weight" by item or "Net Volume" by item
3. "Cargo Aircraft Only"
4. "Limited Quantity"
5. "Laboratory Samples"

C. Shipping containers with unanalyzed wastes from drums or tanks should be entered as "Poisonous Liquid, N.O.S." on the first line above.

D. Unanalyzed samples taken from closed containers may not be transported by commercial air cargo or common carrier aircraft or by rental, non-government aircraft. Federal regulations require shipment by common, public, or commercial "ground" carrier, or governmental aircraft.

Standard Operating Procedure No. 912

SAMPLE CONTROL AND CUSTODY PROCEDURES

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 912 describes the guidelines for controlling sample identification and chain of custody in order to maintain the quality and integrity of samples during collection, transportation, and storage for analysis as described in the Work Plan or as otherwise specified.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Sample control and custody shall be followed, without exception, by all persons involved in sampling and documentation activities as specified in the Work Plan and/or QAPP.

B. Samples may be defined as any physical evidence collected for environmental measuring and monitoring.

C. Sample identification documentation must be prepared to maintain sample identification and chain of custody. The following are examples of sample identification documentation:

1. Sample identification labels
2. Chain of custody records
3. Custody seals (if required in QAPP)
4. Field logbook

The above documentation items are discussed in the QAPP. Other documentation items including sample traffic reports, receipts for sample forms, analytical request forms, and shipment records may also be required for CLP laboratories.

2.2 SAMPLE IDENTIFICATION LABELS

2.2.1 Label Forms

A. Sample labels shall be provided to the sample personnel by the site manager in a form appropriate for the sampling activity. Labels may be pre-printed with spaces for the appropriate sample identification and information requirements, or may be blank with lines provided for uniform recording. The label shall be of the type material that ink will write, but not be so overly absorbent that ink will run. Labels should be self-adhesive on glass and polyethylene containers. An example of a sample label is shown in Figure 912-1.

B. The following sample information should be entered on each sample label and tabulated in the field logbook.

1. Project identification number or code.
2. Date and time of the sample collection.
3. Sample station identification (boring number, well number, etc.).
4. Sample identification number or code that uniquely identifies the sample's location (including area location and depth), whether it is a replicate or blank (see exception below**).
5. Preservative(s) used.
6. Analysis code, indicating which general group of analyses is intended for that particular container of sample.
7. Serial number (if required).
8. Comments or notations to inform the laboratory of any special circumstances or warnings. Also, indicate if sample is a "grab" or "composite" sample.
9. Internal temperature of shipping container when sample(s) is (are) placed in container.
10. Sampling personnel initials.

** Exception: If the quality assurance samples (replicates, blanks, etc.) are to be kept anonymous to the laboratory, then all samples should be identified by a code or numeric system that does not reference the sample as such.

2.2.2 Labeling Procedure

A. Following collection of the sample and placement into the appropriate container, wipe excess soil, waste, or water from the container. Affix adhesive label or tag to container.

B. Complete label information as prescribed above, using indelible ink. If a mistake is made, neatly mark through the mistake and write in the correction, initialing the correction. If the label is too smudged or damaged to neatly correct, void it by writing "VOID" across it and initial it, then affix a new label onto the container, partially covering the voided label.

C. Cover the label with clear plastic adhesive tape to protect the label and prevent it from being subsequently written upon.

D. Serialized sample labels, if used, require additional procedures and restrictions not provided in this SOP.

E. For custody control, a sample label should be considered to be in an individual's possession until it is filled out, attached to the sample, and transferred to another individual along with the corresponding chain of custody form.

2.3 CHAIN OF CUSTODY RECORD

2.3.1 Definition of Custody

A. A sample is under custody if one or more of the following criteria are met:

1. The sample is in sampler's possession.

2. It is in the sampler's view after being in possession.

3. It was in the sampler's possession and then was locked up to prevent tampering.

4. It is in a designated secure area.

B. Because samples collected during an investigation could be used as evidence in litigation, possession of the samples must be traceable from the time each sample is collected until the sample is introduced as evidence in legal proceedings. To document sample possession, chain of custody procedures and documentation are discussed below.

2.3.2 Chain of Custody Documentation and Forms

A. Chain of custody documents are initiated by the sampling personnel in the field with the notation of sampling data and sample identification during the sampling activity. Generally, these data are collected in the field logbook in a tabulated form along with the description of the sample and sampling procedure and includes the following:

1. Project number
2. Sample station identification
3. Sample identification
4. Data and time sample was taken
5. Sample type
6. Number and type of container used
7. Whether sample was grab or composite
8. Preservation method used
9. Analysis requested
10. Name of sampling personnel involved

B. Each sample sent offsite would be recorded on a chain of custody form by the sampler or a field sample custodian at the site. The form should be filled out after returning the sample from the sampling locations and after decontamination. An example chain of custody form is provided in Figure 912-2 and the QAPP.

C. The chain of custody form should be completed by the sampler or by the field sample custodian on behalf of the sampler. The information indicated on the chain of custody form should be reconciled with that in the field logbook used by the sampler personnel. The chain of custody form should be signed by the sampling personnel.

2.3.3 Custody Seals

A. When samples are shipped to the laboratory, they must be placed in containers sealed with tape, with custody seals affixed to the storage containers. Some custody seals are serially numbered. These numbers must appear in a cross-reference matrix of the field document and on the chain of custody report. Other types of custody seals include unnumbered seals and evidence tape.

B. When samples are shipped, two or more seals are to be placed on each shipping container (such as a cooler), with at least one at the back, located in a manner that would indicate if the container were opened in transit. Wide, clear tape should be placed over the seals to ensure that seals are not accidentally broken during shipment. Nylon packing tape may be used providing that it does not completely cover the custody seal. Completely covering the seal with this type of tape may allow the label to be peeled off. Alternatively, evidence tape may be substituted for custody seals.

C. If samples are subject to interim storage before shipment, custody seals or evidence tape may be placed over the lid of the jar or across the opening of the storage box. Custody during shipment should be the same as described above. Evidence tape may also be used to seal the plastic bags or metal cans used to contain samples in the cooler or shipping container. Sealing individual sample containers assures that sample integrity will not be compromised if the outer container seals are accidentally broken.

2.3.4 Field Custody Procedures

A. Only enough of the sample should be collected to provide a good representation of the medium being sampled. To the extent possible, the quantity and types of samples and the sample locations should be determined before the actual fieldwork. As few people as possible should handle the samples.

B. Field samplers are personally responsible for the care and custody of the samples collected by their teams until the samples are transferred or dispatched properly. A person should be designated to receive the samples from the field samplers after decontamination; this person maintains custody until the samples are dispatched.

C. The site manager should determine whether proper custody procedures were followed during the fieldwork and should decide if additional samples are required to make up for any deficiencies.

D. Samples shall be accompanied by a chain of custody form or record. When transferring samples, the individuals relinquishing and receiving them should sign, date, and note the time on the form. This form documents sample custody transfer from the sampler, often through another person, to the analyst at the laboratory.

E. Samples are packaged properly for shipment and dispatched to the appropriate laboratory for analysis, with a separate chain of custody record accompanying each shipment. Shipping containers are sealed with tape, and custody seals are affixed to the storage containers for shipment to the laboratory. The method for shipment, courier name(s), and other pertinent information such as the laboratory name and contact should be entered in the “Remarks” section of the chain of custody record.

F. When samples are split with an owner, operator, or government agency, the event is noted in the "Remarks" section of the chain of custody record. The note indicates with whom the samples are being split. The person relinquishing the samples to the facility or agency requests the signature of the receiving party on a receipt-for-samples form, thereby acknowledging receipt of the samples. If a representative is unavailable or refuses to sign, this situation is noted in the "Remarks" section of the chain of custody record. The samples shall be secured if no one is present to receive them.

G. All shipments are accompanied by a record identifying their contents. The original form accompanies the shipment; the copies are retained by the sampler.

H. If nonhazardous samples are sent by mail, the package is registered, and the return receipt is requested. (NOTE: Hazardous materials shall not be sent by mail.) If samples are sent by common carrier, a bill of lading is used. Airfreight shipments should be sent prepaid. Freight bills, postal service receipts, and bills of lading should be retained as part of the permanent documentation of the chain of custody records.

2.4 FIELD LOGBOOK

A. A bound field logbook must be maintained by the sampling team leader to provide daily records of significant events, observations, and measurements during field investigations as specified in SOP No. 110. All entries are to be signed and dated. Observations or measurements taken in an area where contamination of the field notebooks may occur may be recorded in separate bound and numbered logbooks before being transferred to the project logbook. The original records are retained, and the delayed entry is noted as such.

B. Field logbooks are intended to provide sufficient data and observations to enable participants to reconstruct events that occurred during projects and to refresh the memory of the field personnel if called upon to give testimony during legal proceedings. In a legal proceeding, notes, if referred to, are subject to cross-examination and are admissible as evidence. The field notebook entries should be factual, detailed, and objective.

2.4.1 Corrections to Documentation

A. Unless restricted by weather conditions, all original data recorded in field logbooks and on sample identification labels, chain of custody forms, and custody seals forms are written in waterproof ink. Accountable serialized documents are not to be destroyed or thrown away, even if they are illegible or contain inaccuracies that require a replacement document.

B. If an error is made on an accountable document assigned to one person, that individual may make corrections simply by crossing out the error and entering the correct information. The erroneous information should not be obliterated. Any error discovered on an accountable document should be corrected by the person who made the entry. All corrections must be initialed and dated.

C. For all photographs taken, a photographic log should be kept; the log records date, time, subject, frame, roll number, and photographer. The photographer should review the photographs or slides when they return from developing and compare them to the log to ensure that the log and photographs match.

FIGURES

FIGURE 912-1

SAMPLE LABEL

Client

Sample ID

Location

Site

Preservatives

Depth

Time

Date

Analysis

Project No.

Bureau Veritas North America, Inc.
22345 Roethel Drive, Novi, MI 48375
248-344-1770

FIGURE 912-2

CHAIN OF CUSTODY RECORD

BUREAU VERITAS 1828

BUREAU
VERITAS

Bureau Veritas North America, Inc.

INTERDEPARTMENTAL INTERNAL CHAIN-OF-CUSTODY

Page ____ of ____

IMPORTANT

Date Results Requested: ____________

Rush Charges Authorized? ☐ Yes ☐ No

For Bureau Veritas Use Only
Project No.

INTERNAL DEPARTMENTAL INFORMATION

Consultant's Name ____________
Consultant's Office Location ____________
Internal Project No. _ _ _ _ _ • _ _ _ _ _ _ • _ _ • _ _ _

OUTSIDE CLIENT INFORMATION

Vision Client Code:
Company Name:
Client Name:
Mailing Address: **Telephone No.:**
City, State, Zip:

PRICING INFORMATION

☐ **Fee Schedule Price**

☐ **Discount Price off list** ____________

☐ **Special Price Attached**

Send Report to:
☐ Client ☐ Internal Office

Send Via:
☐ Reg. Mail ☐ Overnight Mail
☐ Email
☐ Fax Fax # ____________

Special Instructions:

Soil Samples Only: Which state are these from? ____________

ANALYSIS REQUESTED
(Enter an 'X' in the box below to indicate request. Enter a 'P' if Preservative added.*)

CLIENT SAMPLE IDENTIFICATION	DATE SAMPLED	TIME SAMPLED	MATRIX/ MEDIA	AIR VOLUME (specify units)	Number of Containers											FOR LAB USE ONLY

CHAIN OF CUSTODY

Collected by: (print)	Collector's Signature		
Relinquished by:	Date/Time	Received by:	Date/Time
Relinquished by:	Date/Time	Received by:	Date/Time
Authorized by:	Date	Sample Condition Upon Receipt: ☐ Acceptable ☐ Other (explain)	

(Client Signature **MUST** Accompany Request)

Please return completed form and samples to one of the Bureau Veritas North America, Inc. locations below:

Detroit Lab: (800) 806-5887 – Industrial Hygiene / Environmental / Mold
Atlanta Lab: (800) 252-9919 – Asbestos / Specialty Microscopy
Lake Zurich Lab: (888) 576-7522 – Pharmaceutical Actives

Distribution:
White & Yellow: Lab
Pink: Consultant

Standard Operating Procedure No. 920

FIELD QUALITY ASSURANCE SAMPLES

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 920 describes the guidelines and typical frequencies for preparing and submitting quality assurance (QA) samples for chemical analyses along with site media to support the validity of chemical data generated for the sampling event as described in the Work Plan or otherwise specified.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS AND CONSIDERATIONS

A. QA samples should be included within each separate sampling event as a means of evaluating the validity of chemical data. The use of QA samples should provide sufficient evidence to conclude that media samples are representative of the in situ state of the media and that chemicals found within them are not overtly affected by chemicals from outside sources or cross-contamination.

B. Field QA samples may include one or more of the following types:

1. Replicates (Duplicates)
2. Equipment Blanks
3. Field Blanks
4. Trip Blanks

C. Media for QA sampling should be of similar physical condition as the site media being sampled (i.e., soil, liquid, vapor), so that the QA sample is likely to be contaminated the same way and by the same degree as would the site media being sampled.

D. All QA samples may be submitted to the laboratory “blind,” when possible, in cases where data results and validity are critical. Accordingly, sample identification should be used that does not designate the QA samples as being different from the actual site media samples collected. This is generally not to be performed unless specifically stated in the Work Plan.

2.2 REPLICATE SAMPLES

2.2.1 Replicate Purpose Types

A. Replicate samples provide duplicate or additional specimens or aliquot from the same sample by dividing the original sample at some point in the measurement process. Field replicates are split in the field for potential repeat testing of essentially the same sample at a given laboratory, or they may be split and tested at different laboratories.

B. Replicates may be discrete or composite; however, each replicate must be prepared the same way. Replicates from discrete samples must come from the same sample; that is, they must be divided from a portion of the sample taken from the same interval at the same time. For example, discrete replicates would be

   1. For solid sample media, the replicates could be divided from the same sampler device at a particular depth taken at the same location and time.

   2. For groundwater, the replicates would be divided from the contents of the same bailer full of water. Replicates from composite samples should be taken only after these samples have been thoroughly blended to insure uniformity.

2.2.2 Replicate Preparation and Sampling

A. Replicate (duplicate) soil samples or other solid matrices for volatile and semi-volatile organic compounds (VOCs and SVOCs) obtained with discrete samplers should be prepared as follows:

   1. Select the vertical interval of the cylindrical soil core to be replicated.

   2. Split the section in half along the length of the core, then split each half in half along its length into quarters.

   3. Combine diametrically opposite quarters from the core sections to create two duplicate samples.

B. Replicate (duplicate) soil samples or other solid matrices for other compounds (Metals, PCBs, etc.) obtained with discrete samplers should be prepared as follows:

    1. Put the soil core into a clean stainless steel mixing bowl and homogenize the media by mixing with a decontaminated implement until its appearance is consistent.

    2. The samples should them be collected alternately filling the investigative and duplicate sample containers from the homogenized sample media.

C. Typically, a composite replicate from each coring or sampling interval will be required to obtain the necessary volume of soil material to fill each sample aliquot for required analysis. In this case, select additional vertical core sections along the entire length of the core as is both available and representative, then repeat the process described in A above. For instance, if the available total core length from a particular sampling interval is 18 inches long, perhaps select the top and bottom 6-inch-long section to replicate. The remaining middle section could be used for additional chemical analysis, discrete replication, or for geotechnical testing. In this example, equivalent proportions from both the top and bottom sections would be included in each sample aliquot.

D. For aqueous matrices, the replicates should be prepared as follows:

    1. Obtain aqueous sample from well, surface body, or container, and pour contents of the sampler into a single collection container. For samples to be analyzed for volatile organic compounds (VOCs), alternate filling vials for regular and replicate samples from the sampling device to prevent agitation.

    2. If one sampler volume is not adequate for all required specimens and replicates, then a composite of more than one sampler volume should be made.

    3. The collection container should have only limited air space available to limit volatilization during blending. The agitation while decanting the sample into the collection container should be adequate to mix the sample from one or more samplers.

    4. Decant equivalent amounts from the collection container into appropriate jars to create replicates.

E. Replicates may be spiked in the laboratory to determine the extent of matrix bias or interference on analyte recovery and sample-to-sample precision.

F. The frequency required for obtaining replicates of site media samples may be conducted, as specified. Generally, duplicates should be taken at least once per analytical batch or once per 10 samples per matrix, whichever is more frequent.

2.3 EQUIPMENT BLANKS

2.3.1 Equipment Blank Purpose

A. Equipment or rinsate blanks are artificially prepared matrix-similar samples used to evaluate whether field equipment has been adequately decontaminated so as not to yield a false-positive concentration of contaminants.

B. Positive results from blanks should not be used to correct results from site media samples, but rather to identify a problem and warrant action to correct the source of cross-contamination.

2.3.2 Aqueous Equipment Blank Preparation and Sampling

A. For aqueous equipment blanks, two methods are available as follows:

1. Prepared container
2. Rinsate sample

For the prepared container equipment blank, a pint jar is filled to near-full with deionized water. For the rinsate sample, deionized water over equipment components that were exposed to the sample, then collected in a sample jar.

B. Transport prepared container of aqueous equipment blank to field in sample shuttle. Stir small sampling tools and probes of field instruments that come into direct contact with site media in the water in the container. Handle and preserve blank as for the media being sampled.

C. For rinsate samples, hold samplers and tools over a cleaned sample container. Using a squirt bottle, rinse the equipment with distilled water sufficiently to collect sample quantity for the analysis. For larger specimen quantity requirements, pour additional distilled water from a supply container over the equipment into a collection container, then decant into the appropriate sample containers. Equipment or rinsate samples should be handled and preserved similar to the site media samples.

2.4 FIELD BLANKS

2.4.1 Field Blank Purpose and Preparation

A. Field blanks are matrix-similar samples, artificially prepared, used to evaluate background or ambient conditions and handling procedures that may affect the results of site media samples.

B. Positive results from field blanks should not be used to correct results from site media samples, but rather should be used to identify potential sources of false positive results due to ambient conditions or handling procedures in the field.

C. Field blanks should be prepared identically as for equipment blanks previously described, except that no rinsate samples would be prepared.

2.4.2 Field Blank Sampling

A. Field blanks should be sampled by opening the sample container of material during the entire time that a site medium sample is exposed to ambient conditions.

B. The field blank should remain open in the general area of the sample handling activity, but in such a place that it is not subject to airborne or other undesirable contamination to which a site-medium sample would not also be subject.

C. Close the field blank container at the completion of the sampling interval activity and handle and preserve as for any other site medium.

2.5 TRIP BLANKS

2.5.1 Trip Blank Purpose and Preparation

A. Trip blanks are media-similar shapes, prepared in the analytical laboratory, shipped with the cleaned sample containers (usually provided by the laboratory), carried through the field sampling activity, and returned to the laboratory, having never been opened.

B. Trip blanks should be used by the laboratory to evaluate whether (1) the laboratory is contributing cross-contamination to tested samples either via the sample containers it provides or via laboratory contaminants during the testing or (2) contaminants are falsely introduced into site-media during handling at the laboratory or during shipping due to contaminants being on the outside of the sample container.

C. Positive results should not be used to correct results of analysis on site media samples, but rather should be used to identify sources of false positive results due to inadequate procedures and to enact corrective action.

D. Trip blanks should ideally be prepared using materials similar to the site media; however, typically deionized water or water identified as Type II reagent grade will be used.

2.5.2 Trip Blank Sampling

A. Place trip blank into field sample shuttle (cooler) along with sample containers for site media. Sample shuttle should remain shut except to take out or place in a sample container from that time until it is returned to the site sample dispensing area.

B. At a selected sampling interval or location, take out the trip blank along with sample containers for the sampling interval or location. Do not open the trip blank container.

C. Sample site media as per the Work Plan. Label and handle the trip blank as for any other sample at that location.

Standard Operating Procedure No. 930

CONTROL, CALIBRATION AND MAINTENANCE OF MEASUREMENT AND TEST EQUIPMENT

1.0 PURPOSE OF PROCEDURE

Standard Operating Procedure (SOP) No. 930 describes the guidelines for controls, calibration, and maintenance of measurement and test equipment to be used for obtaining samples for chemical analyses for measuring field parameters, and for testing various parameter/characteristics. The purpose of this SOP is to ensure the validity of field measurement data generated during field activities as required in the Work Plan or as otherwise specified.

2.0 EXECUTION

2.1 GENERAL REQUIREMENTS

A. Measuring devices must be calibrated before initial use and re-calibrated once daily at a minimum or as recommended in the manufacturer's instructions. Daily calibrations will be recorded on the daily field notes or logbook.

B. Instrument operators must be thoroughly familiar with the operation of measuring instruments. Users should complete the appropriate training and be certified, if required, before using the instrument in the field.

C. Manufacturer's instructions should be followed for correct methods of operation for various measuring devices.

D. All equipment/instrumentation will be uniquely and permanently identified (model/serial number, equipment inventory number, etc.). Maintenance / calibration instructions and permanent individual record books will be provided with each instrument or equipment. Manufacturers' recommended maintenance/calibration records will be kept with the equipment/instrument record book(s). (Note: Actual location of these maintenance/calibration records may vary; however, location must be stipulated by vendor, subcontractor, etc., before work. Records must also be available to Bureau Veritas staff upon request.)

E. If the calibration/maintenance frequency differs from that recommended by the manufacturer or applicable codes/specifications, the applicable code/specification frequency shall apply (or both may be used). The frequency or calibration may be shortened if equipment is subject to severe conditions or there is reason to believe the equipment is not functioning properly.

F. Equipment logs shall record the date equipment is entered to the project and withdrawn from the project.

G. The site manager will obtain, identify, and control all equipment/instruments to be used during the projects. Subcontractors will coordinate their equipment items/uses with the site manager in accordance with this SOP.

2.2 Photovac 2020 PID

2.2.1 Startup/Shutdown Procedures

A. Startup procedures for the Photovac 2020 are as follows:

1. Turn the unit on by pressing the on/off button. Let the PID run for approximately 5-10 minutes before calibrating. If “Lbat” appears on the LCD screen, the battery must be charged before using.

2. Check instrument with an organic point source, such as “magic marker,” before survey to verify instrument function.

B. Shutdown procedures for the HNU are listed below:

1. Turn the PID off by pressing and holding the on/off button for a few seconds.

2. Plug the instrument charger into the unit and the wall while recharging the battery.

2.2.2 Maintenance and Calibration Schedule

A. The following maintenance and calibration schedule represents the minimum requirements for operation of the Photovac tool.

Function	Frequency
Perform routine calibration	Prior to each use; at least once daily
Initiate factory checkout and calibration	Yearly or when malfunctioning or after changing UV light source
Wipe down readout unit	After each use
Replace Teflon filter	Every month or as use and site conditions dictate
Recharge battery	After each use

B. Instruments should be thoroughly checked before their first use.

2.2.3 Calibration Procedures (with Regulator)

The calibration of the analyzer can be rapidly checked by the use of a standard calibration gas cylinder containing isobutylene with a regulator. After calibration in the factory, the Photovac 2020 can be re-calibrated in the field as follows:

1. Make sure the sample probe is connected to the 2020 inlet. Ensure that the sample probe is free of any contamination, as this will effect the calibration. Press the ENTER key. Select “Set,” “Cal,” and then “Mem.”

2. Select “Chng” and then “User.” Enter a name for the calibration memory. Press the ENTER key and enter a response factor (RF). The RF for isobutylene gas is 1.0. The concentration detected by the 2020 will be multiplied by the RF before it is displayed and logged.

3. Press the ENTER key and enter an alarm level for STEL, TWA, and PEAK.

4. Press ENTER and expose the 2020 to a supply of zero air.

5. Select “Set,” “Cal,” and “Zero.” Allow the 2020 to set its zero point.

6. Select “Set,” “Cal,” and “Span.” The 2020 asks for the span gas concentration (usually on bottle). Enter the known span gas concentration, hook up the gas cylinder, open the regulator, and press ENTER.

7. When the display reverts to the default display, the 2020 is calibrated and ready for use.

8. Remove the adapter tubing from the inlet and close the regulator.

Isobutylene is nontoxic and safe to use in confined areas. There are no listed exposure levels at any concentration. The regulator sets and controls the flow rate of gas at a value preset at the factory. Do not use the cylinder below about 30 psi as readings below that level can deviate up to 10% from the rated value.

2.3 ORGANIC VAPOR ANALYZER (OVA)

2.3.1 Startup/Shutdown Procedures

A. Startup procedures for the OVA are as follows:

1. Connect the probe/readout connectors to the side-pack assembly.

2. Check battery condition by moving the pump switch to ON and moving the instrument switch to the battery position. The needle should deflect past the white line in the probe.

3. For measurements taken as methane equivalent, check that the GAS SELECT dial is set at 300.

4. Turn the electronics on by moving the INST switch to the ON position, and allow 5 minutes for warm-up.

5. Set CALIBRATE switch to X10; use CALIBRATE knob to set indicator at zero.

6. Open the H_2 tank valve all the way and the H_2 supply valve all the way. Check that the hydrogen supply gauge reads between 8.0 and 12.0 psi. (About 150 psi of H_2 is required per each hour of survey operation.)

7. Turn the PUMP switch ON, and check the flow system according to the procedures in Subsection 2.3.2.

8. Check that the BACKFLUSH and INJECT valves are in the UP position.

9. To light the flame, depress the igniter switch until a meter deflection is observed. The igniter switch may be depressed for up to 5 seconds. Do not depress for longer than 5 seconds, as it may burn out the igniter coil. If the instrument does not light, allow the instrument to run several minutes and repeat ignition attempt.

10. Confirm OVA operational state by using an organic source, such as a “magic marker.”

11. Establish a background level in a clean area or by using the charcoal scrubber attachment to the probe (depress the sample inject valve) and by recording measurements referenced to background.

12. Set the alarm level, if desired, by turning the calibrate volume knob fully clockwise.

B. Shutdown procedures for the OVA are as follows:

   1. Close H_2 supply valve and H_2 tank valve (do not over tighten valves).

   2. Turn INST switch to OFF.

   3. Wait until H_2 supply gauge indicates system is purged of H_2; then switch off pump (approximately 10 seconds).

   4. Put instrument on electrical charger at completion of day's activities.

2.3.2 Pump System Checkout Procedure

The procedure to ensure that the pump system is in proper working order is as follows:

1. With the pump on, hold unit upright and observe flow gauge.

2. See if ball level is significantly below a reading of 2; if so, flow is inadequate.

3. Check connections at the sample hose.

4. Clean or replace particle filters if flow is impaired or if it is time for scheduled service.

5. Reassemble and retest flow.

6. If flow is still inadequate, replace pump diaphragm and flow valves.

7. If flow is normal, plug air intake. Pump should slow and stop.

8. If there is no noticeable change in pump, tighten fittings and retest.

9. If there is still no change, replace pump diaphragm and valves.

10. Document this function in the field logbook and the maintenance logbook.

2.3.3 Maintenance and Calibration Schedule

The maintenance and calibration schedule listed below should be followed. Instruments should be thoroughly checked before their first use.

Function	Frequency
Check particle filters	Weekly or as needed
Check quad rings	Monthly or as needed
Clean burner chamber	Monthly or as needed
Check secondary calibration	Prior to project startup; daily
Check primary calibration	Monthly or if secondary check is off by more than ±10 percent
Check pumping system	Before project startup
Replace charcoal in scrubber attachment	120 hours of use or when background readings are higher with the inject valve down than with the inject valve up in a clean environment
Factory service	At least annually

2.3.4 Calibration Procedure

A. Primary calibration procedures for operation of the OVA are listed below:

1. Remove instrument components from the instrument shell.
2. Turn on ELECTRONICS and ZERO INSTRUMENT on X10 scale. Turn GAS SELECT dial to 300.
3. Turn on PUMP and HYDROGEN. Ignite flame. Go to SURVEY MODE.
4. Introduce a methane standard near 100 parts per million (ppm).
5. Adjust R-32 Trimpot on circuit board to make meter read to standard.
6. Turn off hydrogen flame and adjust meter needle to read 40 ppm (calibrate @ X10) using the calibration adjust knob.

7. Switch to X100 scale. The meter should indicate 0.4 on the 1-10 meter markings (0.4 x 100 = 40 ppm). If the reading is off, adjust with R33 Trimpot.

8. Return to X10 scale and adjust meter needle to 40 ppm with calibration; adjust knob, if necessary.

9. At the X10 scale, adjust meter to read 0.4 on the 1-10 meter markings using the calibration adjust. Switch to X1 scale. The meter should read 4 ppm. If the reading is off, adjust using R31 Trimpot.

B. Secondary calibration procedures are listed below:

1. Fill an air sampling bag with 100 ppm (certified) methane calibration gas.

2. Connect the outlet of the air-sampling bag to the air-sampling line of the OVA.

3. Record the reading obtained from the meter on the calibration record.

2.4 COMBUSTIBLE GAS INDICATOR (MODEL MSA 361)

2.4.1 Operation/Calibration Procedures

Before calibration of the combustible gas indicator (CGI) Model MSA 361 can be checked, the instrument must be in operating condition.

Operating Instructions

A. Turn the FUNCTION control to the HORN OFF position; the HORN OFF indicator will light, and the descriptor % LEL will show in the readout.

B. Set the readout to zero by adjusting the LEL ZERO control. (NOTE: this must be done within 30 seconds of turning ON to prevent the possibility of activating the off-scale LEL latching alarm).

C. Press the SELECT button firmly to obtain % OXY on the readout; then set the readout to 20.8% by adjusting the OXY CALIBRATION control.

D. Press the SELECT button firmly to obtain PPM TOX on the readout; then set the readout to zero by adjusting the TOX ZERO control.

E. Press the RESET button.

F. Turn the FUNCTION control to MANUAL for continuous readout of any one gas, or to SCAN for automatic scanning of the three gas readings.

G. Momentarily place a finger over the sample inlet fitting or the end of the sample line, if one is used. Observe that the FLOW indicator float drops, indicating no flow. If it does not, check the flow system and sample line for leaks.

H. The instrument is ready for sampling. Move it to the area for sampling, or place the end of the sampling line at the point the sample is to be taken.

Calibration

I. Calibration of the CGI Model MSA 361 will be performed once each working day. If there is a reason to suspect that the instrument is producing incorrect readings, the instrument will be calibrated more frequently during the day. The following calibration procedure should be followed:

   1. Attach the flow control to the 75% pentane/15% oxygen calibration gas tank.
   2. Connect the adapter-hose fitting to the flow control.
   3. Open the flow control valve.
   4. Connect the adapter-hose fitting to the inlet of the instrument; within 30 seconds, the LEL meter should stabilize and indicate between 47 and 55%. If the indication is not in the correct range, remove the right end of the indicator and adjust the LEL SPAN control to obtain 50%.
   5. Verify the oxygen reading; it should be between 13 and 17%.
   6. Disconnect the adapter-hose fitting from the instrument.
   7. Close the flow control valve.
   8. Remove the flow control from the calibration gas tank.

9. Attach the flow control to the 10 ppm hydrogen sulfide calibration gas tank. (40 ppm gas may be used; the choice of H_2S calibration gas will depend upon concentrations anticipated in the work place.)

10. Open the flow control valve.

11. Connect the adapter-hose fitting to the inlet of the instrument; after approximately 1 minute, the TOX readout should stabilize and indicate between 7 to 13 ppm (35 to 45 ppm for 40 ppm H_2S). If the indication is not in the correct range, remove the right end of the indicator and adjust the TOX SPAN control to obtain 10 ppm (40 ppm for 40 ppm H_2S).

12. Disconnect the adapter-hose fitting from the instrument.

13. Close the flow control valve.

14. Remove the adapter-hose fitting from the flow control.

15. Remove the flow control from the calibration gas tank.

J. Calibration gas tank contents are under pressure. Do not use oil, grease, or flammable solvents on the flow control or the calibration gas tank. Do not store calibration gas tank near heat or fire, nor in rooms used for habitation. Do not throw in fire, incinerate, or puncture.

2.4.2 Maintenance Procedures

A. The primary maintenance item of the CGI Model MSA 361 is the rechargeable, 4.0-volt lead-acid battery. Using the appropriate battery charger (240 VAC), insert charger plug into charge jack.

B. Use only the chargers specified above to charge the instrument; otherwise, damage to the battery pack and/or the instrument circuitry may result.

C. The POWER ON lamp indicates that the charger is receiving power from the 240 VAC line. The FAST CHARGE lamp indicates that the battery voltage is low and that the charger has automatically switched to the higher charge rate.

D. The battery pack may not supply full power capacity after repeated partial use between charging; therefore, it is recommended that the battery pack be “exercised” at least once per month by operating the fully charged instrument for 8 hours and then recharging.

E. Recommended charging time is 16 hours.

F. The battery pack should be charged after each day of use (or before use if the instrument has not been operated for 30 days).

G. When the rechargeable 4.0-volt lead-acid battery pack no longer responds to recharging or no longer “holds” a charge, the pack should be replaced according to the following procedure:

    1. Loosen the knurled screws holding the handle and remove handle.

    2. Looking at the front panel of the instrument, remove the right (audible alarm side) panel by unscrewing the four side-panel screws.

    3. Gently pull the side panel loose and tilt the instrument to help slide out the battery case. Disconnect the molded nylon plug from the battery case. (NOTE: Do not disconnect the alarm speaker.)

    4. Install the new battery by reversing the above steps 1 through 3.

2.5 Horiba U-10 Water Quality Meter

2.5.1 Calibration Procedures

The calibration of the meter should be checked at the start of each day, and again during the day if there is a reason to suspect that the meter may be producing incorrect readings. The meter should be calibrated as follows:

1. Rinse the probe in distilled water. Be sure to remove the protective cap from the pH probe.

2. Fill the calibration beaker to about 2/3 with the standard solution. Note the line on the beaker. Fit the probe over the beaker.

3. Turn the unit on, and press the MODE key. The cursor should be on the AUTO sub-mode. If it is not, use the MODE key to move the cursor.

4. Press the ENTER key. The readout will show "*Cal*." The upper cursor will move across the screen as the four auto-calibration parameters are calibrated (pH, Cond, Turb, and DO). Once the cursor has stopped blinking, the auto-calibration is complete.

5. Should an error occur during calibration, the parameter where the error occurred will blink. Check the instruction manual for a list of error codes and redo the calibration.

2.5.2 Routine Preventive Maintenance and Storage

A. Preventive maintenance protocol for the pH/conductivity meter involves replacement of the battery when the low battery is signaled on the LCD display. Replacement batteries will be available.

B. The pH electrode should be covered by the provided protective cap when the meter is not in use. The protective cap should be removed prior to calibration.

2.6 DISSOLVED OXYGEN METER

2.6.1 Procedure for Calibration

A. Place the probe in a water sample of known dissolved oxygen concentration composed of a freshly air-saturated water sample of known temperature.

B. Consult a table, provided by the manufacturer, that lists the solubility of oxygen in water at different temperatures and pressures.

2.6.2 Calibration Schedule

Instrument readings should be checked every hour in sampling areas where the temperature is not constant. Otherwise, the instrument should be calibrated daily.

2.7 OIL/WATER INTERFACE PROBE

The oil/water interface probe will be used to measure groundwater and separate phase product levels in monitoring wells and tanks. The battery for the interface probe should be checked before and after each measurement is taken to ensure proper operation. Daily battery checks should also be performed before conducting any measurement activities. Replace the battery on a regular basis as specified in the operator's manual.

The probe should be thoroughly cleaned before and after each measurement, especially when measuring separate phase product levels. Removal all excess product and any sediment from the probe with a paper towel. Decontaminate the probe and graduated tape in accordance with SOP No. 500. Do not lower the probe all the way to the bottom of the well to avoid contact with bottom sediments and/or damaging the probe.

2.8 ELECTRONIC WATER LEVEL SOUNDER

The electronic water level sounder will be used to measure groundwater levels in monitoring wells. Check the battery for the sounder before and after each measurement to ensure proper operation. Perform daily battery checks before conducting any measurement activities. Replace the battery regularly as specified in the operator's manual. Decontaminate the sounder in accordance with SOP No. 500.

3.0 DOCUMENTATION

A. The following information will be kept on file in the field trailer:

1. Calibration certifications provided by the manufacturer or other outside agency (periodic calibrations only).

2. Date of last calibration and date when next calibration is due.

3. Manufacturer's operating instructions.

4. Manufacturer's calibration and maintenance instructions.

5. Nearby location for purchase of spare and replacement parts (when applicable).

B. General information that must be recorded for each measuring device is listed below:

1. Name of equipment
2. Equipment identification/serial number
3. Manufacturer
4. Calibration frequency (daily, weekly, monthly, etc.)

C. The following calibration information will be recorded in the field logbook:

1. Name of equipment
2. Equipment identification/serial number

3. Date and time of calibration/maintenance check
4. Results of calibration
5. Signature/initials of individual who performed the calibration
6. Description of maintenance performed

TABLES

EXHIBIT A

ACTIVE EQUIPMENT LOG

UNIQUE ITEM NO.	DATE CALIBRATED	DATE DUE FOR RECALIBRATION	DATE CALIBRATED	DATE DUE FOR RECALIBRATION	REMARKS

EXHIBIT B

SPECIALTY EQUIPMENT LOG

ITEM NO.	DATE CALIBRATED	DATE USED	USAGE	REMARKS

Volatile Organic Compounds Analyte List

Petro-Chem Processing Group of Nortru, LLC
Detroit, Michigan

1,2,3-Trimethylbenzene
Cyclohexane
Diisopropyl ether
Ethyl tert-Butyl ether
Hexachloroethane
tert-Amylmethyl ether
tert-Butyl alcohol
Diethyl ether
Iodomethane
trans-1,4-Dichloro-2-butene
Acetone
Acrylonitrile
Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
2-Butanone
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon Disulfide
Carbon tetrachloride
Chlorobenzene
Chloroethane
Chloroform
Chloromethane
1,2-Dibromo-3-chloropropane
Dibromochloromethane
1,2-Dibromoethane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethylbenzene
2-Hexanone

Volatile Organic Compounds Analyte List

Petro-Chem Processing Group of Nortru, LLC
Detroit, Michigan

Isopropylbenzene
4-Isopropyltoluene
2-Methylnapthalene
4-Methyl-2-Pentanone
Methyl tert-butyl ether (MtBE)
Methylene Chloride
Naphthalene
n-Propylbenzene
Styrene
1,1,2,2-Tetrachloroethane
1,1,1,2-Tetrachloroethane
Tetrachloroethene
Tetrahydrofuran
Toluene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
Vinyl Chloride
o-Xylene
m,p-Xylene

Semi-Volatile Organic Compounds Analyte List

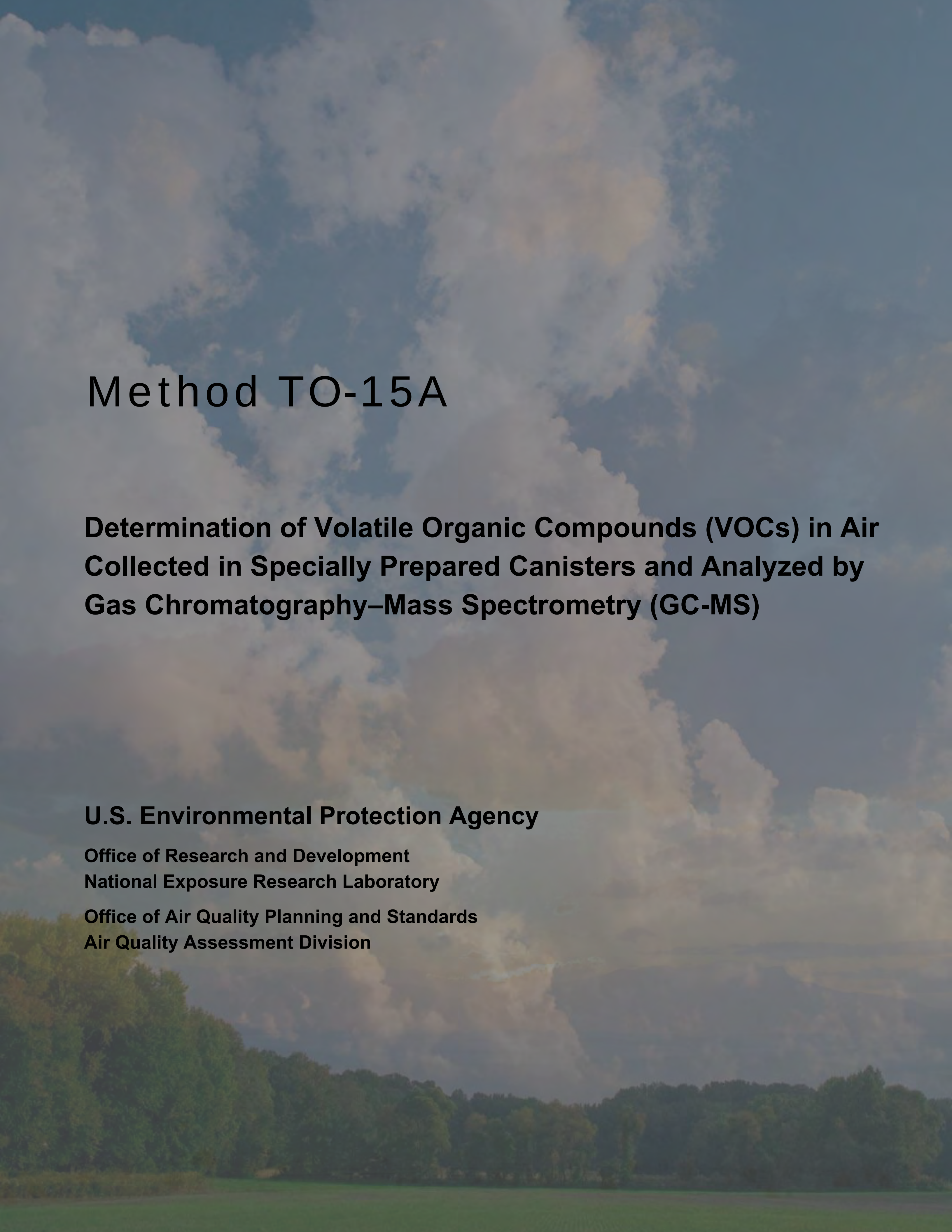
Petro-Chem Processing Group of Nortru, LLC
Detroit, Michigan

2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
2-Chloronaphthalene
2-Chlorophenol
2-Methylnaphthalene
2-Methylphenol
2-Nitroaniline
2-Nitrophenol
3-Nitroaniline
4,6-Dinitro-2-methylphenol
4-Bromophenyl phenyl ether
4-Chloro-3-methylphenol
4-Chlorophenyl phenyl ether
4-Methylphenol & 3-Methylphenol
4-Nitroaniline
4-Nitrophenol
Acenaphthene
Acenaphthylene
Anthracene
Azobenzene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Bis(2-chloroethoxy)methane
Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl)ether
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Carbazole
Chrysene
Dibenzo(a,h)anthracene
Dibenzofuran
Diethyl phthalate
Dimethyl phthalate
Di-n-butyl phthalate
Di-n-octyl phthalate
Fluoranthene
Fluorene
Hexachlorobenzene

Semi-Volatile Organic Compounds Analyte List

Petro-Chem Processing Group of Nortru, LLC
Detroit, Michigan

Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Indeno(1,2,3-cd)pyrene
Isophorone
Naphthalene
Nitrobenzene
N-Nitrosodimethylamine
N-Nitrosodi-n-propylamine
N-Nitrosodiphenylamine
Pentachlorophenol
Phenanthrene
Phenol
Pyrene
1,2-Dichlorobenzene-d4
2,4,6-Tribromophenol
2-Chlorophenol-d4
2-Fluorobiphenyl
2-Fluorophenol
4-Terphenyl-d14
Nitrobenzene-d5
Phenol-d5



Method TO-15A

Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography–Mass Spectrometry (GC-MS)

U.S. Environmental Protection Agency

Office of Research and Development
National Exposure Research Laboratory

Office of Air Quality Planning and Standards
Air Quality Assessment Division

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Disclaimer

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Acronyms and Abbreviations

BFB	bromofluorobenzene
BP	boiling point
CAS	Chemical Abstracts Service
CB	calibration blank
CCV	continuing calibration verification
CDCF	canister dilution correction factor
COC	chain of custody
DB	dilution blank
EI	electron impact
EPA	U.S. Environmental Protection Agency
FEP	fluorinated ethylene propylene
GC	gas chromatography or gas chromatograph
HAP	hazardous air pollutant
HCF	hydrocarbon-free
HPLC	high-performance liquid chromatography
IB	instrument blank
ICAL	initial calibration
I.D.	inner diameter
ID	identification
IDCF	instrument dilution correction factor
IDL	instrument detection limit
IS	internal standard
MB	method blank
MDL	method detection limit
MFC	mass flow controller
MFCD	mechanical flow controlling device
MFM	mass flow meter
MS	mass spectrometry or mass spectrometer
MW	molecular weight
m/z	mass-to-charge ratio
NATTS	National Air Toxics Trends Stations
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
PAMS	Photochemical Assessment Monitoring Stations
PFA	perfluoroalkoxy
PM	particulate matter
PT	proficiency test
PTFE	polytetrafluoroethylene
QA	quality assurance

QC	quality control
RH	relative humidity
RPD	relative percent difference
RRF	relative response factor
RSD	relative standard deviation
RT	retention time
SIM	selected ion monitoring
SIS	selected ion storage
S:N	signal-to-noise ratio
SOP	standard operating procedure
SSCV	secondary source calibration verification
TO	toxic organic
TOF	time-of-flight
UATMP	Urban Air Toxics Monitoring Program
VOC	volatile organic compound

Units of Measure

*Note: A conversion chart for commonly used vacuums and pressures is included as **Appendix A**.*

amu	atomic mass unit(s)
ata	atmosphere(s) absolute (pressure at sea level, 101.3 kPa or 14.7 psia)
atm	atmosphere(s)
°C	degree(s) Celsius
cc	cubic centimeter(s)
cm	centimeter(s)
eV	electronvolt(s)
g	gram(s)
h	hour(s)
Hz	hertz
in.	inch(es)
in. Hg	inch(es) mercury
K	Kelvin
kPa	kilopascal(s)
L	liter(s)
µL	microliter(s)
µm	micrometer(s)
m	meter(s)
MΩ	megaohm(s)
mbar	millibar(s)
mg	milligram(s)
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
mm Hg	millimeter(s) mercury
mol	mole(s)
mTorr	millitorr(s)
ng	nanogram(s)
ppbv	part(s) per billion by volume
ppmv	part(s) per million by volume
pptv	part(s) per trillion by volume
psi	pound(s) per square inch
psia	pound(s) per square inch absolute
psig	pound(s) per square inch gauge
s	second(s)
V	volt(s)

1 Scope

Guidance presented in this 2019 Method TO-15A update of the 1999 Method TO-15 document is intended to provide users with basic canister sampling and analysis information, incorporate current technologies, define performance criteria, and recommend specific procedures associated with collection and analysis of trace levels (approximately 20 to 5,000 parts per trillion by volume [pptv]) of volatile organic compounds (VOCs) in ambient air using specially prepared canisters. However, this method update cannot address all situations analysts might encounter in the present—much less in the future. Therefore, in instances where this guidance is found to be inadequate, development of improved techniques and technologies is encouraged provided that, at a minimum, the performance requirements outlined in this document are met.

This canister air sampling and analysis method provides procedures for measuring a subset of the 97 VOCs included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990 (see **Appendix B** for a list of the 97 compounds). VOCs are defined here as organic compounds with a vapor pressure ≥ 0.1 mm Hg at 25 °C and standard pressure of 760 mm Hg. The subset of toxic organic (TO) VOCs and other environmentally important VOCs that may be measured in ambient air with this method are listed in Table 1-1 in order of highest to lowest vapor pressure. While this list includes compounds usually analyzed in canisters, it does not include many VOCs, notably non-HAP hydrocarbons, such as various ozone precursors including various straight- and branched-chain alkanes, that may be measured with this method. This method's primary application is to measure trace levels of VOCs in ambient air. However, provided the method performance criteria are met, users of TO-15A may, at their discretion, choose to measure other VOCs or implement this method for applications such as vapor intrusion studies, indoor air investigations, and source emissions characterization, among others.

Table 1-1: Volatile Organic Compounds Quantifiable with EPA Method TO-15A

VOC (Alternative Name)[a]	Empirical Formula	CAS[b] Number	Boiling Point (°C)	Vapor Pressure at 20 °C (mm Hg)[c]	Molecular Weight (g/mol)	Typical Ions Monitored
Propene (propylene)	C_3H_6	115-07-1	-48.0	***8686***	42.1	41/39
Dichlorodifluoromethane (Freon 12)	CCl_2F_2	75-71-8	-29.8	4260	120.9	85/87
Chloromethane (methyl chloride)	CH_3Cl	74-87-3	-23.7	3672	50.5	50/52
Chloroethene (vinyl chloride)	C_2H_3Cl	75-01-4	-13.8	2505	62.5	62/64
1,3-Butadiene (butadiene)	C_4H_6	106-99-0	-4.0	1838	54.1	39/54
1,2-Dichlorotetrafluoroethane (Freon 114)	$C_2Cl_2F_4$	76-14-2	4.1	1444	170.9	85/135
Bromomethane (methyl bromide)	CH_3Br	74-83-9	3.5	1420	94.9	94/96
Ethylene oxide	C_2H_4O	75-21-8	10.6	1095	44.1	29/44/15
Chloroethane (ethyl chloride)	C_2H_5Cl	75-00-3	12.5	1000	64.5	64/66
Trichlorofluoromethane (Freon 11)	$CFCl_3$	75-69-4	23.7	690	137.4	101/103
1,1-Dichloroethene (vinylidene chloride)	$C_2H_2Cl_2$	75-35-4	31.7	500	96.9	61/96

VOC (Alternative Name)[a]	**Empirical Formula**	**CAS[b] Number**	**Boiling Point (°C)**	**Vapor Pressure at 20 °C (mm Hg)[c]**	**Molecular Weight (g/mol)**	**Typical Ions Monitored**
Dichloromethane (methylene chloride)	CH_2Cl_2	75-09-2	39.8	350	84.9	49/84
Carbon disulfide (methanedithione)	CS_2	75-15-0	46.0	297	76.1	76/44
1,1,2-Trichlorotrifluoroethane (Freon 113)	$C_2Cl_3F_3$	76-13-1	47.7	285	187.4	101/151
2-Propenal (acrolein)	C_3H_4O	107-02-8	52.3	217	56.1	56/55
2-Methoxy-2-methylpropane (methyl *tert*-butyl ether, MTBE)	$C_5H_{12}O$	1634-04-4	55.2	203	88.2	73/41
2-Chloro-1,3-butadiene (chloroprene)	C_4H_5Cl	126-99-8	59.4	188	88.5	88/53
1,1-Dichloroethane (ethylidene chloride)	$C_2H_4Cl_2$	75-34-3	57.4	182	99.0	63/65
cis-1,2-Dichloroethene (*cis*-1,2-dichloroethylene)	$C_2H_2Cl_2$	156-59-2	55.0	180–265	96.9	61/96
trans-1,2-Dichloroethene (*trans*-1,2-dichloroethylene)	$C_2H_2Cl_2$	156-60-5	48.7	180–265	96.9	61/96
2-Propanone (acetone)	C_3H_6O	67-64-1	56.1	180	58.1	43/58
Trichloromethane (chloroform)	$CHCl_3$	67-66-3	61.2	160	119.4	83/85
Tetrahydrofuran (oxolane)	C_4H_8O	109-99-9	66.0	132	72.1	42/41
Hexane	C_6H_{14}	110-54-3	68.7	120	86.2	57/43
Isopropyl ether (diisopropyl ether)	$C_6H_{14}O$	108-20-3	69.0	119	102.2	45/43
1,1,1-Trichloroethane (methyl chloroform)	$C_2H_3Cl_3$	71-55-6	74.0	100	133.4	97/99
2-Ethoxy-2-methylpropane (ethyl *tert*-butyl ether, ETBE)	$C_6H_{14}O$	637-92-3	72.6	96	102.2	59/87
Methanol (methyl alcohol)	CH_4O	67-56-1	64.7	92	32.0	31/29
Carbon tetrachloride (tetrachloromethane)	CCl_4	56-23-5	76.5	91	153.8	117/119
Ethenyl acetate (vinyl acetate)	$C_4H_6O_2$	108-05-4	72.7	83	86.1	43/86
2-Propenenitrile (acrylonitrile)	C_3H_3N	107-13-1	77.3	83	53.1	53/52
2-Butanone (methyl ethyl ketone, MEK)	C_4H_8O	78-93-3	79.6	78	72.1	43/72
Cyclohexane	C_6H_{12}	110-82-7	80.7	78	84.2	56/84
Benzene	C_6H_6	71-43-2	80.1	76	78.1	78/77
Acetonitrile (cyanomethane)	C_2H_3N	75-05-8	81.6	73	41.1	41/40
Ethyl acetate	$C_4H_8O_2$	141-78-6	77.1	73	88.1	43/61
2-Methoxy-2-methylbutane (*tert*-amyl methyl ether)	$C_6H_{14}O$	994-05-8	86.3	68	102.2	73/43
1,2-Dichloroethane (ethylene dichloride)	$C_2H_4Cl_2$	107-06-2	83.5	64	99.0	62/64
1,1,2-Trichloroethene (trichloroethylene)	C_2HCl_3	79-01-6	87.2	58	131.4	130/132
Bromodichloromethane	$CHBrCl_2$	75-27-4	90.0	50	163.8	83/85
Ethanol (ethyl alcohol)	C_2H_6O	64-17-5	78.3	44	46.1	31/45
1,2-Dichloropropane (propylene dichloride)	$C_3H_6Cl_2$	78-87-5	96.0	42	113.0	63/62
Heptane	C_7H_{16}	142-82-5	98.4	35	100.2	43/41
2-Propanol (isopropanol)	C_3H_8O	67-63-0	82.3	33	60.1	45/43
2-Methyl-2-propanol (*tert*-butyl alcohol, TBA)	$C_4H_{10}O$	75-65-0	82.3	31	74.1	59/31
1,4-Dioxane (*p*-dioxane)	$C_4H_8O_2$	123-91-1	101.2	29	88.1	88/58
Methyl methacrylate (methyl 2-methylprop-2-enoate)	$C_5H_8O_2$	80-62-6	100.5	29	100.1	41/69
trans-1,3-Dichloropropene (*trans*-1,3-dichloropropylene)	$C_3H_4Cl_2$	10061-02-6	108.0	28	111.0	75/39
cis-1,3-Dichloropropene (*cis*-1,3-dichloropropylene)	$C_3H_4Cl_2$	10061-01-5	104.3	26	111.0	75/39
Toluene (methylbenzene)	C_7H_8	108-88-3	110.6	21	92.1	91/92
1,1,2-Trichloroethane	$C_2H_3Cl_3$	79-00-5	114.0	19	133.4	97/83

VOC (Alternative Name)[a]	Empirical Formula	CAS[b] Number	Boiling Point (°C)	Vapor Pressure at 20 °C (mm Hg)[c]	Molecular Weight (g/mol)	Typical Ions Monitored
4-Methyl-2-pentanone (methyl isobutyl ketone, MIBK)	$C_6H_{12}O$	108-10-1	116.5	16	100.2	43/58
1,1,1,2-Tetrachloroethane	$C_2H_2Cl_4$	630-20-6	130.5	***14***	167.8	133/131
Tetrachloroethene (perchloroethylene)	C_2Cl_4	127-18-4	121.3	14	165.8	166/164
1,2-Dibromoethane (ethylene dibromide)	$C_2H_4Br_2$	106-93-4	131.0	11	187.9	107/109
Chlorobenzene	C_6H_5Cl	108-90-7	131.6	9	112.6	112/77
m-Xylene (1,3-xylene)	C_8H_{10}	108-38-3	139.1	9	106.2	91/106
p-Xylene (1,4-xylene)	C_8H_{10}	106-42-3	138.3	9	106.2	91/106
Isopropylbenzene (cumene)	C_9H_{12}	98-82-8	152.4	8	120.2	105/120
Ethylbenzene	C_8H_{10}	100-41-4	136.2	7	106.2	91/106
o-Xylene (1,2-xylene)	C_8H_{10}	95-47-6	144.5	7	106.2	91/106
Dibromochloromethane (chlorodibromomethane)	$CHBr_2Cl$	124-48-1	122.0	***6***	208.3	129/127
Styrene (vinylbenzene)	C_8H_8	100-42-5	145.3	5	104.2	104/103
1,1,2,2-Tetrachloroethane (tetrachloroethane)	$C_2H_2Cl_4$	79-34-5	146.0	5	167.9	83/85
Tribromomethane (bromoform)	$CHBr_3$	75-25-2	149.5	5	252.8	173/171
2-Chlorotoluene (1-chloro-2-methylbenzene)	C_7H_7Cl	95-49-8	159.2	3	126.6	91/126
4-Ethyltoluene (1-ethyl-4-methylbenzene)	C_9H_{12}	622-96-8	162.0	***3***[d]	120.2	105/120
n-Propylbenzene	C_9H_{12}	103-65-1	159.2	***3***	120.2	91/120
sec-Butylbenzene (2-phenylbutane)	$C_{10}H_{14}$	135-98-8	173.5	***2***	134.2	105/134
tert-Butylbenzene	$C_{10}H_{14}$	98-06-6	169.1	***2***	134.2	119/91
m-Dichlorobenzene (1,3-dichlorobenzene)	$C_6H_4Cl_2$	541-73-1	173.0	***2***	147.0	146/148
Hexachlorobutadiene (hexachloro-1,3-butadiene)	C_4Cl_6	87-68-3	215.0	2	260.8	225/227
2-Hexanone (methyl butyl ketone, MBK)	$C_6H_{12}O$	591-78-6	127.2	2	100.2	43/58
2-Isopropyltoluene (*o*-cymene)	$C_{10}H_{14}$	527-84-4	178.0	***2***	134.2	119/134
1,2,4-Trimethylbenzene (pseudocumene)	C_9H_{12}	95-63-6	169.0	***2***	120.2	105/120
1,3,5-Trimethylbenzene (mesitylene)	C_9H_{12}	108-67-8	165.0	2	120.2	105/120
n-Butylbenzene	$C_{10}H_{14}$	104-51-8	183.3	***1***	134.2	91/92
Chloromethylbenzene (benzyl chloride)	C_7H_7Cl	100-44-7	179.0	1	126.6	91/92
o-Dichlorobenzene (1,2-dichlorobenzene)	$C_6H_4Cl_2$	95-50-1	180.1	1	147.0	146/148
p-Dichlorobenzene (1,4-dichlorobenzene)	$C_6H_4Cl_2$	106-46-7	174.0	1	147.0	146/148
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	120-82-1	213.0	1	181.4	180/182
Naphthalene (naphthene)	$C_{10}H_8$	91-20-3	218.0	***0.1***	128.2	128/127

[a] Compound information is derived from PubChem (https://pubchem.ncbi.nlm.nih.gov/), an open chemistry database from the National Institutes of Health, U.S. National Library of Medicine, National Center for Biotechnology Information.

[b] Chemical Abstracts Service.

[c] Vapor pressures shown in bold italics are values at 25 °C.

[d] ThermoFisher Scientific, 4-Ethyltoluene Safety Data Sheet, Revised January 26, 2018.

In this method, ambient air samples are collected using specially prepared and precleaned evacuated stainless-steel canisters. VOCs contained in up to 1 L of air are subsequently preconcentrated and injected into a gas chromatograph–mass spectrometer (GC-MS) for separation, identification, and quantitation. The method performance specifications defined in this document have been demonstrated for many of the compounds listed in Table 1-1 at relevant concentrations (pptv and low parts per billion by volume [ppbv]) in ambient air (**Wang and Austin, 2006**; **Ochiai et al., 2002**; **Ochiai et al., 2003**). However, rigorous studies of the temporal stability in and recovery from canisters at pptv concentrations have not been performed for the entire list of compounds. Some of the compounds with higher molecular weight (MW) and lower volatility may behave poorly in the preconcentrator and GC-MS systems. Therefore, users of this method must determine if the method is suitable for a given purpose. To emphasize this point, fitness for purpose is demonstrated by attainment of the method's performance specifications described in this document.

Method performance for a given VOC or suite of VOCs with similar physicochemical properties is driven by several factors, many of which are related to the collection medium. For example, VOC loss and transformation may be caused by adsorption of VOCs to the interior surfaces of the canister, adsorption of VOCs to particulate matter (PM) entrained in the canister, chemical reactions of VOCs within the canister with co-collected reactive species (such as ozone or nitrogen oxides) or other substances in combination with exposed catalytic surfaces within the canister, dissolution of VOCs in water condensed in the canister, and aqueous hydrolysis and biological degradation (**Ochiai et al., 2002**). As a result of loss of certain compounds, reaction byproduct VOCs may form and increase in concentration within the canister.

This method applies under most conditions encountered when sampling ambient air into rigid, opaque containers, typically a specially treated, surface-deactivated stainless-steel canister. Note that glass bottles or similar inert containers may be employed; however, in such cases users may encounter limitations with respect to container pressurization, safety hazards such as increased potential for rupture of the container, and/or an inability to sufficiently decontaminate the container for reuse. While such alternative containers are addressed briefly, this method revision retains the focus on the use of specially prepared and cleaned stainless-steel canisters for collection of whole air samples.

Method performance may be optimized for a specific set of target analytes selected from Table 1-1, and users are encouraged to do so. However, users must consider that optimization, such as selection of preconcentration and GC-MS separation and analysis conditions, may degrade performance for other compounds. For the analysis of alkanes, for example, co-collected moisture likely need not be of primary concern; however, good water management practices are of critical importance for measuring more polar, water-soluble VOCs.

EPA Method TO-15A should be considered for use when a subset of the 97 Title III VOCs constitutes the target list. Applications of this method for the measurement of VOCs in ambient air include assessment of health impacts due to inhalation exposures to HAP source emissions dispersing into downwind areas and long-term monitoring for HAPs at various urban-scale, neighborhood-scale, and regional background, nonsource-impacted sites. These applications form the basis for operation of the U.S. EPA National Air Toxics Trends Stations (NATTS) ambient air monitoring program.

2 Summary of Method

A whole air sample is collected by passing ambient air through a particulate filter into an evacuated, specially prepared stainless-steel canister. Air may be collected as a "grab" sample or as a time-integrated sample, and the final pressures of the collected samples can be subatmospheric, at atmospheric, or pressurized. A grab sample is taken by simply opening the canister valve and allowing the canister to fill quickly (within seconds to minutes) to atmospheric pressure. A time-integrated sample is collected by filling the canister at a constant rate over a known time period (typically over hours or days). Specific information on the air sampling equipment and its cleaning, handling, and preparation are described in **Sections 7** and **10**, respectively.

Subatmospheric sampling employs the canister vacuum to draw the sample into the canister, with the flow regulated by a critical orifice, a mechanical flow controlling device (MFCD), or an electronic mass flow controller (MFC). Note that an adequate pressure differential is necessary with each type of flow controlling device to provide constant flow, and the flow control will fail when the differential falls below the minimum required for that particular device. The final pressure of the canister should be below ambient pressure at the time of sample retrieval.

Pressurized sampling typically employs a commercially available canister sampling unit that uses a pump and a flow regulation system to pressurize the canister. Pressurized sampling requires electrical power to operate the pump system and the MFC that is used to control the flow and pressurize the canister. Users of the method are cautioned that pressurized sampling methods may result in condensed water within the canister, which can have negative effects on the integrity of the VOCs in the sample (**McClenny et al., 1999**).

Whether grab or time-integrated sampling is performed, programmable timers with solenoid valves are commercially available to permit unattended sample collection. For operation when electrical power is not available, battery-powered models are commercially available.

Canister vacuum should be verified prior to sampling, preferably as close to the time of sampling setup as possible and with a high-quality, calibrated vacuum gauge (±0.25% full-scale accuracy). Ideally, sample setup occurs as close to sample collection as possible to ensure the canister remains at vacuum at the commencement of sampling.

Once the air sample is collected, the canister valve is closed, the canister pressure is measured, and the canister is transported to the laboratory for analysis. Upon receipt at the laboratory, the sample collection information is verified, the canister pressure is measured, and the canister is stored at ambient laboratory temperature until analysis. Suitable compound recovery has been demonstrated for many VOCs for storage times of up to 30 days (**Ochiai et al., 2002**; **Ochiai et al., 2003**; **Kelly and Holdren, 1995**). Users are strongly encouraged to demonstrate acceptable performance over storage times applicable to their needs.

For analysis, a known volume of air is directed from the canister into a preconcentrator. The preconcentrator captures VOCs from the sample aliquot and permits most bulk gases (e.g., nitrogen, oxygen, argon, and carbon dioxide) and water vapor to pass through to vent. Following trapping of the VOCs, the preconcentration path should be dry purged with dry carrier gas to further remove water prior to thermally desorbing the VOCs. The VOCs may be trapped further for focusing (to improve chromatography) or may be introduced to the GC column for separation. Several preconcentrator configurations are described in more detail in Section 14.1.

The analytical strategy for EPA Method TO-15A involves using a high-resolution GC coupled to a low- or high-resolution MS, which may consist of a linear quadrupole, ion trap, or time-of-flight (TOF) system. Target VOCs are identified by a combination of the retention times (RTs) and the associated mass spectra by comparing observed fragmentation patterns to reference spectral patterns and relative ion abundances established during calibration. For any given VOC, the intensity of the observed quantitation ion in the unknown sample is compared with the system response to the same ion for known amounts of the compound. The presence of one or more secondary ions in a known relative abundance to the chosen quantitation ion increases certainty of the identification.

Mass spectrometric detection is considered a more definitive identification technique than nonspecific detectors such as flame ionization detectors, electron capture detectors, photoionization detectors, or a multidetector arrangement of these. The use of both gas chromatographic RTs and the mass fragmentation patterns reduces the likelihood of compound misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

3 Significance

EPA Method TO-15A compiles the best practices and lessons learned by users of the method over the past 20 years since Method TO-15 was published in 1999. It also addresses and incorporates improvements in canister, sampling, preconcentration, and analytical instrumentation technology. Many of the method performance specifications, procedures, and best practices described herein were identified through comments submitted by air toxics stakeholders and the community of analysts currently implementing Method TO-15. With the increased availability and improvements in commercially built equipment, most of the diagrams and descriptions of the “home built” systems that were prevalent in the early years of TO-15 have been removed from this method. This revision incorporates advances in measurement technology and the increased availability of commercial instruments and software systems for the various measurements and data-handling needs to perform the method.

This method focuses on the collection and analysis of VOCs in ambient air. The method is written as a performance-based procedure whereby equipment, instruments, operations, best practices, and acceptance and performance criteria are described. Users may modify portions of the method such as using alternative instrumentation or basing their application on a desired suite of target VOCs or concentration ranges for measurement. However, the modified application must meet the quality control (QC) and performance criteria described in Section 18. These criteria have been developed to ensure high-quality data. Laboratories should develop their own standard operating procedure (SOP) documents describing the equipment, desired target VOCs, procedures, and quality assurance (QA) activities specific to that laboratory and instrumentation. Users should describe any modifications or deviations from this guidance within the SOPs.

EPA Method TO-15A is tailored for analysis of the target VOCs listed in Table 1-1 at concentrations present in ambient air, which typically range from approximately 10 to 10,000 pptv (0.010 to 10 ppbv).

Concentrations of certain target VOCs may be present at higher concentrations in ambient air impacted by sources of VOCs such as refineries or chemical production facilities. Some of the compounds that may be measured with this method are present in ambient air at concentrations to which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be greater.

The minimum concentration for which the method is applicable has been reduced from 500 to 20 pptv (0.5 to 0.020 ppbv), and canister cleanliness requirements have been reduced from 200 to 20 pptv (0.2 to 0.020 ppbv). This is in acknowledgment of general reductions to date and expected continued reductions of ambient air concentrations of VOCs in the United States of America as well as improvements in canister technology, canister hygiene practices, and analytical instrument sensitivity. Moisture management and preconcentration techniques are established and robust, and target analyte behavior is better understood. Bench-top MSs have become more sensitive and offer higher resolution than those available when the method was released in 1999.

The target VOCs may also be measured in soil gas during vapor intrusion investigations and in indoor air, both of which are outside the scope of this method. To be suitable for these other purposes, method modifications may be required; such modifications include, but are not limited to, instrument calibration, reduction of the preconcentrated volume, and less aggressive canister cleaning techniques. Furthermore, different method performance specifications may also be applicable to these other uses. For more information on vapor intrusion application, refer to *OSWER Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air* (**U.S. EPA, 2015**).

4 Applicable Documents

4.1 EPA Documents

- *Quality Assurance Handbook for Air Pollution Measurement Systems*, Volume II, Ambient Air Quality Monitoring Program, U.S. Environmental Protection Agency, EPA-454/B-17-001, January 2017.
- Technical Assistance Document for the National Air Toxics Trends Stations Program, Revision 3, U.S. Environmental Protection Agency, October 2016.
- Clean Air Act Amendments of 1990, U.S. Congress, Washington, D.C., November 1990.

4.2 ASTM Standards

- Method D1356, Standard Terminology Relating to Sampling and Analysis of Atmospheres
- Method E355-96, Standard Practice for Gas Chromatography Terms and Relationships
- Method D5466, Standard Test Method for Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology)

5 Definitions

Absolute pressure: pressure measured with reference to absolute zero pressure, usually expressed in units of kPa absolute or psia.

Accepted reference value: A value that serves as an agreed-upon reference for comparison and which is derived as follows: (1) a theoretical or established value, based on scientific principles; (2) an assigned or certified value, based on experimental work of some national or international organization; or (3) a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or engineering group (**ASTM, 2014**).

Audit accuracy: the difference between the concentration measured by the audited laboratory and the theoretical or target value (or other agreed-to reference value, such as the average of all reported results) as determined by the audit authority for an audit sample (typically contained within a canister or high-pressure cylinder), divided by the assigned theoretical or target value and expressed as a percentage.

Collocated precision: precision determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters and collected through two separate sampling inlets (e.g., two MFCDs that are individually attached to two canisters). This determines the precision of the method including the sampling and analysis processes. Collocated precision is determined by calculating the absolute relative percent difference (RPD) for the collocated measurements (the absolute value of the difference between the two collocated sample results divided by their average value and expressed as a percentage).

Cryogen: a refrigerant used to obtain subambient temperatures in the preconcentrator and/or the GC oven. Typical cryogens are liquid nitrogen (boiling point [BP] -195.8 °C), liquid argon (BP -185.7 °C), and liquid carbon dioxide (BP -79.5 °C).

Diluent gas: gas in which target VOCs are mixed, typically consisting of nominally hydrocarbon-free (HCF) synthetic “zero” air or ultrapure nitrogen. Diluent gases should be evaluated to ensure they are fit for use such that various blanks meet method performance specifications of target VOCs < 20 pptv (refer to **Section 12.2** and **Section 15.3.3**).

Duplicate precision: precision determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters collected through the same sampling inlet (e.g., a rack-mounted system that employs one inlet to fill two canisters at the same time). This determines the precision of the method including the sampling and analysis processes. Duplicate precision is determined by calculating the absolute RPD for the duplicate measurements (the absolute value of the difference between the two duplicate sample results divided by their average value and expressed as a percentage).

Dynamic dilution: means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with a diluent gas (such as humidified HCF zero air) in a mixing chamber or manifold so that a flowing stream of calibration mixture is created.

Gauge pressure: pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psig. Gauge pressure is zero-referenced against ambient air pressure; zero is equal to the local atmospheric (barometric) pressure, which is nominally 101.3 kPa absolute or 14.7 psia (standard pressure at sea-level).

Mass spectrometer: instrument that ionizes molecules and atoms (typically into electrically charged fragments), separates these ions according to their mass-to-charge ratio (*m/z* or *m/e*), and responds to the impact of the ions based on their population. MS systems suitable for this method include quadrupole, ion trap, and TOF detectors. Quadrupole and ion trap MS operating modes can be selected to optimize the ion mass collection range:

> **SCAN mode:** mass spectrometric mode of operation in which the quadrupole or ion trap MS is programmed to scan all ions repeatedly over a specified mass range.
>
> **SIM mode:** mass spectrometric mode of operation in which the quadrupole MS is programmed to scan a selected suite of ions repeatedly.
>
> **SIS mode:** mass spectrometric mode of operation in which the ion trap MS is programmed to store a selected suite of ions.

Nominal concentration: a requested, target, or named concentration that approximates the true, reference, or certified concentration. For example, a nominal 200 pptv standard may have an actual certified concentration of 206 pptv.

Qualitative identification criteria: set of rules or guidelines for establishing the identification or presence of an analyte using a measurement system (U.S. EPA, 2016a).

Quantitative accuracy: the degree of measurement accuracy required to measure the concentration of an identified compound, within a given tolerance of uncertainty, with an analytical system.

Replicate precision: precision determined from repeated analysis of a gas sample from one canister, which may be evaluated by calculating the absolute RPD for pairwise measurements ($N = 2$) or by determining the relative standard deviation (RSD) for replicate measurements where $N \geq 3$. Replicate analyses are used to determine precision of the analysis processes and do not provide information on sampling precision.

Static dilution: means of preparing calibration mixtures in which standard gas(es) and diluent gases are added to a fixed-volume vessel or chamber at a known ratio. Standard and diluent gas amounts may be measured gravimetrically, by volume, and/or by pressure differential from pressurized cylinders or as neat materials and blended with a known amount of diluent gas (such as humidified zero air) in a mixing chamber or manifold.

Target concentration: desired, estimated, or approximate concentration (see “nominal concentration” above).

Theoretical concentration: a reference concentration derived by applying measurements performed with calibrated instruments with known tolerances to a certified reference standard concentration value. Measurements of VOC concentrations are to be determined using a calibration that is developed based on theoretical concentrations.

Time-of-flight mass spectrometry: MS method that determines the ion’s mass-to-charge ratio by measuring the time the ion takes to reach the detector.

Wetted surfaces: surfaces of the flow path, canister, valving, pumps, etc., that contact the gas undergoing collection, mixing, transfer, or analysis.

6 Interferences and Contamination

6.1 Interferences Related to Sample Collection

6.1.1 Leaks in the Sampling Flow Path

Leaks within the sampling flow path will permit air to dilute and likely contaminate field-collected samples. Leaks may also result in unmetered air entering the flow path or canister which may subsequently impact time-integrated sampling. This generally applies to canisters that are placed in an interior location (e.g., sampling shelter) that are drawing outdoor ambient air from a manifold or sampling line.

6.1.2 Contaminants Entering the Flow Path

PM, insect nests, spider webs, and other materials within the sampling flow path may act as sorbents to adsorb VOCs, effectively scrubbing them from the sampled air stream and resulting in a low bias. The VOCs may desorb later from such materials and potentially contaminate subsequent samples. Inlet flow pathways should be inspected for the presence of foreign materials and cleaned regularly. Sintered stainless-steel particulate filters should be installed in the sampling flow path (typically at the canister inlet) to eliminate entrainment of PM into the sampling apparatus. Cleaning of compatible materials is discussed further in Section 10.

6.1.3 Contaminants in Co-collected Samples Employing Sorbent Media–Based Methods

Sampling units are commercially available to facilitate simultaneously collecting canister samples and cartridge samples, such as 2,4-dinitrophenylhydrazine-impregnated cartridges for measuring carbonyls. Such instruments may be configured for the two sampling methods to share a common sample introduction manifold. Residual VOCs from the sampling media may be drawn into the sampling manifold during leak checks and/or sampler purges and contaminate the collected canister sample.

6.1.4 Contaminants in the Sampling Apparatus

Sampling unit flow paths should be constructed of inert materials such as borosilicate glass, quartz glass, or chromatographic-grade stainless steel (minimum type 316 or silicon-ceramic coated). Use of Viton, fluorinated ethylene propylene (FEP) and polytetrafluoroethylene (PTFE) Teflon materials should be minimized, and users are cautioned to demonstrate that sampling devices constructed with these materials (such may be employed in seals or gaskets or pump diaphragms) do not unacceptably bias the collected sample as described in Section 9.5. Absorption/desorption and permeability issues are associated with Viton and Teflon materials. The user is strongly cautioned against the use of any rubber, plastics, and perfluoroalkoxy (PFA) because of contamination and adsorption issues.

Collection of gas samples containing elevated concentrations of VOCs (relative to typical ambient levels) may result in carryover to subsequent samples, particularly if the sampling apparatus is not purged between samples. Each apparatus should be qualified when initially received and periodically thereafter to demonstrate it is not contributing to measurement bias. Conducting sampling apparatus qualification is discussed further in Section 9.5.

6.2 Canister Sampling Media Interferences

Canisters can be the source of interferences resulting from canister manufacturing processes, handling, and/or sampling practices. Such interferences can typically be mitigated by qualifying the canisters when initially purchased and periodically thereafter (as discussed in Section 9.4) and by practicing proper canister hygiene as discussed in Section 10.

Canister interior surfaces are typically passivated by electropolishing or coating with a silicon-ceramic film. Incomplete surface deactivation treatments, such as those that may occur on canister welds, will result in active sites for adsorption or surfaces that facilitate the decomposition of labile VOCs to form other VOCs within the canister. Other potential sources of active sites include canister valves, valve stems, and ferrules. Damage to the canister interior that exposes untreated surfaces may also result in active sites.

Canisters may show increases of concentrations of oxygenated compounds (e.g., ketones, alcohols, aldehydes) and such has been reported by laboratories. Of particular concern in the canister zero checks is acrolein, which evidence suggests may increase in canisters that are stored for extended periods. The mechanism for this increase in acrolein over time is not completely understood; however, this is widely regarded as problematic in performing ambient concentration analysis.

Introduction of PM into canisters may cause interferences with collected samples. As with PM deposits in the sampling pathway, PM within the canister can behave as a sorbent and adsorb VOCs, making them unavailable in the canister gas phase. Such trapped VOCs can potentially desorb at a later time and result in the inability to achieve canister cleanliness performance specifications and/or contaminate subsequent canister sampling events. Additionally, organic PM can react with co-sampled ozone or other oxidative species to form target VOCs. PM entrained in the canister valve can damage the valve seals, threads, and quick-connect mechanisms designed specifically for ambient air sampling, resulting in leaks. PM can also clog tiny openings in critical or restrictive orifices, which impacts collection flow rates.

Under certain conditions, the composition of an air sample may change upon its introduction into the canister and over time such that the air in the canister no longer represents the ambient air from which it was collected. Such changes may be caused by interactions of the VOCs with the interior canister surface or between chemicals in the air matrix. The activity of the interior canister surface is unique to each canister and is based on several factors, including variability in canister manufacturing defects, differences in canister surface deactivation treatments, the presence of PM in the canister, and artifacts from reactions of VOCs on the canister walls. Notably the presence of co-collected moisture has been found to play a key role in canister performance (Coutant, 1992). Under conditions of low humidity, for example, insufficient moisture may be present in the canister to prevent losses of certain VOCs to the interior canister walls, losses that would be less likely and occur to a lesser extent if the relative humidity (RH) of the sample within the canister were higher. However, if the canister is pressurized, condensation of the water present at higher humidities may cause losses of water-soluble compounds.

Condensed water within the canister may result in corrosion of the interior surface of canisters with weak or deficient coatings and may result in the partitioning of hydrophilic polar VOCs to liquid water. Under such circumstances, concentrations of these analytes in the gas phase will be biased low until the condensation is eliminated by reduction of the canister pressure below the vapor saturation pressure of water (McClenny et al., 1999). Therefore, pressurized samples should be collected to a pressure approximately 21 kPa above ambient pressure at the sampling location (approximately 3 psi above ambient pressure at the sampling location) to minimize the likelihood that water will condense within the canister. When this method is used to collect pressurized samples, users should take steps to understand the effect of condensation in the canister on method performance such as VOC recovery (bias), precision, and storage stability over time.

Given that these surface interactions have not been fully characterized on a theoretical basis, an absolute storage stability cannot be assigned to a specific VOC in a specific canister type or specific canister. Rather users of this method must be aware that each canister will have its own specific performance characteristics and be mindful that appropriate cleaning, sampling, and handling procedures are required for attainment of acceptable initial and ongoing method performance. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs covered by this method can be recovered from canisters near their original concentrations after storage times of up to 30 days (**Ochiai et al., 2002**; **Kelly and Holdren, 1995**). Users of this method are encouraged to analyze collected samples as soon as possible after collection to minimize changes that may occur as the canister contents age.

6.3 Analytical Interferences

Interferences in the analytical system can be caused by contamination within the analytical instrument, active sites within the sample introduction or preconcentration flow path, contaminated gases, contaminated water used for humidification, components of the sample matrix such as water or carbon dioxide, or instrument malfunctions:

- Contamination within the analytical system may come from several sources including, but not limited to, offgassing of materials within the sample introduction or preconcentrator flow path, carryover from high-concentration samples or standards, and solvent vapors within the laboratory.
- Active sites within the sample introduction or preconcentration flow path are often caused by use of improper materials or degradation of deactivated surfaces. To minimize the potential for contamination and active sites, analytical system wetted parts should consist of the materials described in **Section 6.1.4**.
- Carrier, diluent, and internal standard (IS) gases may be sources of contaminants. Carrier gases should be dry (dew point < -40 °C) and should be ultrapure (purities > 99.999%). Additional in-line carbon scrubbers and desiccant traps may be necessary to remove residual VOCs and water from the carrier and diluent gases. Impurities in source materials or diluent gases for IS gas mixtures may result in contamination of target VOCs. Qualification of ISs is further discussed in **Section 15.1**.
- Water and the delivery systems used to humidify canisters or diluent gas streams may contaminate the canister contents or humidified gases. Specifications for reagent water are described in **Section 8.7**.
- Moisture in the sample gas may interfere with VOC analysis by GC-MS, whereas a properly configured moisture management system (as discussed in **Section 14.1**) can reduce or eliminate the interference of water. Poor or inconsistent water management during preconcentration can cause peak broadening and RT shifts and result in peak misidentification, particularly for hydrophilic polar compounds. Water management systems

that use semipermeable fluoropolymer membranes are not recommended for use in this method as they remove oxygenated and polar VOCs from the sample matrix and exhibit memory effects for a number of VOCs. VOCs entrained in the fluoropolymer membrane can convert to ketones and alcohols, which are transported across the membrane bidirectionally such that these ketones and alcohols can contaminate the sample stream and VOCs in the sample stream can be adsorbed into the fluoropolymer and removed from the sample stream.

- Carbon dioxide in the collected sample can coelute with more volatile VOCs eluting early in the GC-MS run and interfere with their quantitation.
- Artifacts in chromatograms, such as silanol compounds formed from the breakdown of silicon-ceramic linings of canisters and siloxane compounds from the breakdown of the stationary phase in an analytical column, can interfere with identification and quantitation of less volatile VOCs.

Analysts should be cognizant of compounds that interfere with target analytes when operating in MS modes that do not provide full-scan ion spectra (i.e., selected ion monitoring [SIM] and selected ion storage [SIS]). Such interfering coeluting compounds may share common ions, may have similar mass spectra, and may be difficult or impossible to separate from target VOCs. Examples of such potentially coeluting VOCs that may have identical method-specified quantitation ions include C4 hydrocarbons/1,3-butadiene, propane/propylene, cyclopentane/2,3-dimethylbutane/vinyl acetate, and acetaldehyde/isobutane. When possible, the analyst should add a qualifier ion characteristic to the desired target analyte that is not shared by the interferent. In the case of propane and propylene, however, there is no such ion exclusive to propylene. As propane is ubiquitous in ambient air, propylene concentrations may be overestimated if the two peaks are not sufficiently chromatographically separated. Deconvolution software may assist in distinguishing between minimally resolved peaks; however, users should understand the abilities and limitations of such software, which is generally meant for full-scan spectra. The use of deconvolution software is beyond the scope of this method.

7 Apparatus

7.1 Sample Container

Sample containers should be manufactured expressly for collection and analysis of VOCs in ambient air at trace levels. Before initial use and periodically thereafter, each container and valve combination should be qualified as leak-tight and nonbiasing following the procedure in Section 9.4. This update to TO-15 retains its focus on stainless-steel canisters as the sampling medium of choice, although some information on alternative containers that may meet method performance specifications is also provided.

7.1.1 Stainless-Steel Canisters

Stainless-steel canisters are commercially available with a modest range of options for surface preparation of the canister interior surfaces, valves, and connections. Currently, canister interior surfaces are typically passivated by electropolishing or coating with a silicon-ceramic film. A once common canister surface deactivation process known as SUMMA passivation generated a uniform nickel chromium oxide surface, which increased the inertness of the canister's inner stainless-steel surface. Note that while a number of laboratories may still own and use SUMMA-passivated canisters, they are not currently being manufactured. In general, canisters with silicon-ceramic passivated interior surfaces have been widely adopted. Silicon-ceramic coatings are applied to the interior canister surface to cover active sites to achieve a passivated surface. While electropolished canisters are commercially available at the time this method was approved, they are not as widely used as silicon-ceramic coated canisters.

Stainless-steel canisters are commercially available in a range of sizes (volumes), shapes (e.g., spherical, oblong, oval), valving configurations, and interior surface treatments. Manufacturers typically state whether the canister is suitable for trace gas analysis. Some manufacturers and vendors of canisters at the time of this document's publication are listed in **Appendix C**. Canisters must withstand numerous cycles of evacuation to high vacuum and pressurization to 377 kPa (40 psig). Canisters may experience pressures higher than 377 kPa (40 psig); however, to meet U.S. Department of Transportation regulations (**49 CFR §173.306 (g)**) for shipment, canister pressures should not exceed 377 kPa (40 psig).

Canister size (volume) should be commensurate with the volume of sample to be removed for each analysis, the number of aliquots to be removed from the canister (such as for replicate analysis), and the pressure range for which the preconcentrator can effectively remove gas from the canister. The most common size employed for ambient canister sampling is 6 L; however, other sizes may be advantageous depending on the intended use. Smaller canisters (e.g., 250 cc) may be less expensive, require less purge gas to clean, and be cleaned and evacuated more quickly than larger canisters. Larger canisters (e.g., 32 L) can hold more sample gas and may be useful for longer-term time-integrated sampling as they permit use of higher flow rates that are easier to properly control. However, larger canisters are more expensive to purchase and ship, they require more time to evacuate and clean, and their size may limit the number of canisters that can be cleaned (some canister cleaners may not accommodate larger canisters at all) and/or connected to an autosampler at one time.

Canisters may be purchased with a variety of valves or combinations of valves for connection to the sampling apparatus and preconcentrator. Valves should be designed specifically for ambient air sampling. They should be of packless design and may be bellows, diaphragm, or quick-connect style. Regardless of the configuration or type, the wetted portions of the valve should, at a minimum, be constructed of chromatographic-grade stainless steel (preferably type 316), and the valve seal surfaces should be metal to metal to minimize absorption and offgassing of VOCs and other potential contaminants. Valve designs should have minimal internal volume and surface area to minimize the risk of contamination. Valves and fittings with complex seals and springs may be difficult to clean if they become contaminated. Several manufacturers also offer new-technology valves designed specifically for canisters that are surface deactivated with silicon-ceramic coatings and minimal wetted surfaces. Amorphous silicon-based coatings are also commercially available that are less susceptible to degradation by acidic sulfur compounds such as hydrogen sulfide and other organo-sulfur compounds. Note that valves with threaded connections will typically be compatible with 1/4-in. compression fittings for connections to sampling and analysis instruments. Quick-connect fittings are usually proprietary and require a compatible fitting for gas-tight connections.

7.1.2 Glass Bottles

Glass bottles or jars are commercially available for collecting gas samples. Glass bottles should be amber to protect the sample from photodegradation and should be purposely constructed and intended for gas sampling. Glass bottles that are not intended for this purpose risk implosion upon evacuation and should not be pressurized due to the risk of explosion. Valves should comply with those listed above in Section 7.1.1. Users should closely follow manufacturer recommendations to avoid loss of sample or injury due to container breakage. Glass containers must be carefully packaged for shipping to protect from breakage.

7.1.3 Nonrigid Containers

While nonrigid containers such as Tedlar and Mylar (DuPont, Wilmington, DE) or foil bags may be useful for instrument troubleshooting and other sampling and analytical applications, they cannot be used to collect subatmospheric or pressurized samples. Also, these types of containers cannot be cleaned and reused. As such, nonrigid containers are not included in the scope of this method.

7.2 Canister Cleaning System

Canister cleaning systems are commercially available or may be custom built. Commercially available systems are capable of cleaning multiple canisters. Systems should include the following components:

- Manifold constructed of chromatographic-grade stainless-steel tubing and connections for multiple canisters.
- Rough vacuum pump capable of achieving vacuum of approximately 3.4 kPa absolute (1 in. Hg absolute) (note that oil-free pumps are strongly recommended).
- High-vacuum pump (such as a molecular drag pump) to achieve a final canister vacuum of approximately 0.0067 kPa (0.05 mm Hg or 50 mTorr) or less.
- Heating oven or heating jackets to completely contain canister and allow heating of the valve.
- Humidification system such as an impinger humidifier or bubbler.
- Programmable controller that allows selection of temperature and cycle time and automates switching between evacuation and pressurization. Manually operated systems may also be used.
- A pressure release valve to minimize the likelihood of system overpressurization.
- Trap (cryogenic or molecular sieve) to eliminate backstreaming of contaminants into canisters. This is necessary for systems with a vacuum pump that is not oil-free. Note that the use of oil-free vacuum pumps is strongly recommended.
- Chromatographic-grade stainless-steel tubing and connections to minimize dead volume of the system, which reduces pressurization/evacuation time and provides less surface contact area to reduce potential contamination. Note that butyl rubber and PFA should not be used. Viton, Teflon (e.g., PTFE, FEP), or other materials that may adsorb and/or offgas compounds of interest or introduce other potential interferences are not recommended. If needed for connections or seals, use of Viton and Teflon should be minimized.
- Source of clean purge gas such as HCF zero air or ultrapure nitrogen (such as UHP cylinder nitrogen or liquid nitrogen dewar headspace). Additional scrubbing of purge gas is recommended. Charcoal scrubbing and catalytic oxidation of purge gas will ensure trace contaminants are eliminated from the purge gas and avoid introducing contaminants to the canister during pressurization cycles.

7.3 Sampling Apparatus

7.3.1 Grab Sampling

Canister grab sampling is the simplest whole air sample collection technique, and the sample is generally collected over a few seconds or minutes. Grab sampling is useful for scoping (range finding) prior to conducting actual sampling for studies, determining concentrations at a point in time, or complementing measurements made by other instrumentation. Due to the short time interval intended to be represented by the sample, flow control while filling is not required.

Ambient air grab samples are collected by opening the canister valve and allowing the evacuated canister to fill in a matter of seconds to minutes. During grab sampling, the canister is typically allowed to fill to atmospheric pressure or to slightly below atmospheric pressure. Unattended grab sampling may be performed by employing a solenoid valve and timer to begin and end the sampling cycle. Alternatively, the grab sampler may be configured such that sampling is triggered by a signal from another device based on, for example, wind direction from a meteorological station or measured concentrations from a continuous monitor or sensor. If exposure to rain or heavy dew is possible during unattended sampling, an inverted inlet (e.g., cane) should be installed to prevent entry of water droplets into the canister. Regardless of attended or unattended collection, a particulate filter should always be installed on the canister inlet or in the sampling line to eliminate introduction of PM into the canister and valve. If grab sampling is performed through a sampling line, the internal volume of the line should be < ~1% of the canister's collected volume to ensure that the VOCs in the collected sample are representative of those in the ambient air.

7.3.2 Time-Integrated Sampling

Time-integrated sampling generally requires a more developed sampling apparatus than that for grab sampling. To ensure time-integrated samples are representative of the entire time interval of collection, the collection requires controlled, constant flow of ambient air into the evacuated canister. Several vendors offer purpose-built sampling instruments for this application (see Appendix C). Ambient air monitoring conducted at fixed sites on a routine schedule, such as for state and national monitoring programs, will typically employ a dedicated rack-mounted or bench-top style sampling unit. These units operate on alternating current power and are installed within a climate-controlled shelter. The sampling unit inlet is then attached to an inlet probe to the ambient atmosphere or to a manifold that is continually flushed with ambient outdoor air. Pressurized or subatmospheric samples may be collected depending on the purpose of the monitor and the requirements of the analytical system. Air samples collected at remote or temporary sites for special studies or investigations may employ stand-alone sampling instruments that operate manually or on battery power and do not require fixed shelters.

All time-integrated sampling apparatus should include the following components:

- A flow controller such as a critical orifice, MFCD, or electronic MFC. The flow control device's operational characteristics should be measured and standardized over the intended pressure range of sample collection. Refer to Section 9 for information on characterizing and standardizing flow control.
- A wetted flow path consisting of only chromatographic-grade stainless steel (including silicon-ceramic lined steel), borosilicate glass, quartz glass, or Viton (refer to Section 6.1.4).
- A stainless-steel particulate filter (2- to 7-µm pore size is recommended).

If unattended sampling is desired, several additional components should be included in the sampling apparatus:

- A clock and timer to control start and stop times.
- An electronic solenoid valve to open and close the flow path to the canister. Solenoid valves should be low-temperature rise coils or latching solenoid valves with Viton seals.
- An elapsed-time indicator.
- A computer and software to operate the system (if required).

To ensure method performance specifications are attained and maintained, sampling units should be checked for cleanliness and bias initially upon receipt before field deployment and periodically thereafter, as described in **Section 9.5**.

The sampling apparatus should be protected from weather conditions that may impact sample collection. Some sampling instruments are designed for installation outdoors and operation in inclement weather; however, many sampling instruments require installation within enclosures that provide shelter from the weather and control of environmental conditions (e.g., controlled temperature and RH). Requirements for installation will be stipulated in the instrument manual.

7.3.2.1 Fixed-Site (Installed) Sampling Systems

Sampling instruments intended for installation inside monitoring shelters are commercially available from several manufacturers (see **Appendix C**) and have been in use for canister sampling at EPA Photochemical Assessment Monitoring Stations (PAMS), NATTS, and Urban Air Toxics Monitoring Program (UATMP) sites for over two decades. For collecting samples to subatmospheric pressure, commercially available systems typically employ an MFC to control sample flow into the canister and include a clock and timer to control start and stop of sampling, an elapsed-time indicator, and a vacuum/pressure gauge or pressure transducer to measure the sample pressure. It is recommended that sampling units incorporate a pump (or other suitable vacuum source) to perform leak checks on the sampling pathway as well as a presampling purge of the sampling inlet. For collecting pressurized samples, sampling units should additionally include a sampling pump that draws ambient air into the sampling unit to pressurize the sample gas upstream of the flow controller. Such systems should be designed with a bypass valve that allows a small percentage of sample flow to be directed to the MFC and canister and the remaining supply of fresh ambient air to exit the system. For pressurized sampling, the sampling pump should be a Viton or PTFE diaphragm type pump or a stainless-steel bellows type pump capable of achieving approximately 3 ata pressure at the outlet (at flow rates through the MFC of ~10 mL/min). The pump must be free of leaks, appropriately clean, and uncontaminated by oils or organic compounds.

Automated samplers are available in various configurations that allow unattended sequential sampling and concurrent collection of other media, such as carbonyl cartridges. The units are often self-contained, rack mounted, and programmed for use by computer interfaces.

7.3.2.2 Portable Sampling Systems

Sampling instruments intended for time-integrated sample collection for short-term studies or investigations should be portable and permit operation manually or on battery power. Manual systems require that the canister valve be physically opened and closed by the operator to start and end sample collection. Instruments operating on battery power typically consist of a clock/timer, solenoid valve, and a flow-regulating mechanism such as a restrictive or critical orifice. These units are individually programmed to activate the solenoid valves at the designated times to start and end sample collection.

7.3.3 Flow Control

7.3.3.1 Critical Orifices

The most basic of flow control options consists of a critical orifice whereby air flow is controlled based on the pressure differential across a very small orifice. Volumetric flow through the orifice depends on the orifice size, the upstream and downstream pressures, and the temperature. In order for critical orifices to be useful for collection of time-integrated air samples into evacuated canisters, a critical flow through the orifice must be achieved; otherwise, the flow will be continually decreasing as the canister fills.

Critical flow is achieved when the velocity of air through the orifice reaches sonic conditions (velocity of sound in air). For air at 20 °C, critical flow is achieved when the downstream absolute pressure (P2) is 52.8% of the upstream absolute pressure (P1). Expressed as a simple ratio (P2/P1), 0.528 is the pressure ratio necessary for the air flow to reach maximum velocity. As long as the ratio of the canister absolute pressure (downstream) to the ambient absolute pressure (upstream) is ≤ 0.528, the velocity through the orifice will remain constant. Once the absolute pressure ratio increases above 0.528, the flow no longer meets sonic conditions and the air flow to the canister begins to decrease.

For critical orifices installed on evacuated canisters at high vacuum, the critical pressure ratio condition is initially met, and sample flow remains constant until the absolute pressure ratio exceeds 0.528, at which point the critical flow condition fails and the air flow decreases.

Flow must be constant for time-integrated sampling, otherwise the air sample will be biased toward the period of higher flow. Critical orifices permit collection of approximately half the volume of a canister before the critical pressure ratio is exceeded and constant flow is ceased. Therefore, it is not recommended that critical orifices be used for time-integrated sampling when the vacuum of the canister drives the pressure differential (see Section 9.1 for flow profiles of various types of flow controlling devices, including a critical orifice). In cases where the pressure differential is provided by a pump and the absolute pressure ratio can be maintained below the critical pressure ratio, it may be appropriate to use a critical orifice.

7.3.3.2 Mechanical Flow Controlling Devices

MFCDs designed specifically for use with canisters are available that can maintain constant air flow into an evacuated canister to nearly ambient pressure (17 to 24 kPa below ambient pressure or 5–7 in. Hg vacuum). They are a significant improvement over critical orifices as they are adjustable and extend the range of controlled flow. These devices are effectively used for collecting subatmospheric time-integrated air samples over hours and days, and flow rates are adjustable from < 1 up to several hundred milliliters per minute. MFCDs are designed to maintain a constant pressure drop (and thus a constant flow rate) across a restrictive orifice by allowing a constant leak rate of sample into the canister as the canister vacuum decreases to near ambient pressure. These controllers require no external power to operate as the vacuum of the canister and the resulting pressure differential draws air through the controller into the canister. Battery-powered timers and solenoid valves may be used with these devices to allow remote operation.

MFCDs regulate the air flow with a combination of a restrictive orifice and an adjustable flow mechanism. The flow mechanism consists of a flexible metal diaphragm used in conjunction with an adjustable regulating piston and a precision-bored (typically synthetic sapphire or ruby) flow restrictor. Flow restrictors are available with holes ranging in diameter from 0.0008 to 0.006 in. The flow restrictor determines the approximate flow range, and the piston is adjusted to set the exact flow rate. A diagram of an MFCD is shown in Figure 7-1.

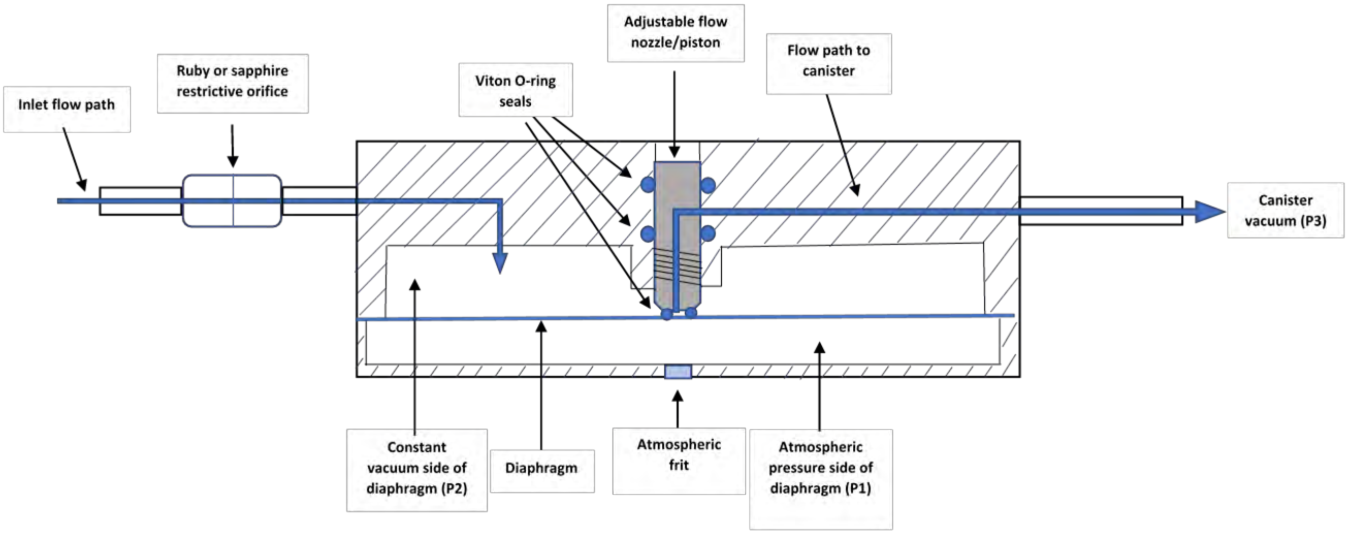


Figure 7-1: Mechanical flow controlling device.

These sampling devices are constructed such that the vacuum of an evacuated canister (P3) draws the air sample in through a stainless-steel particulate filter where it then passes through the restrictive orifice and into the vacuum-regulated chamber (P2). The vacuum in this chamber is balanced by the atmospheric pressure (P1), the vacuum of the canister, and the position of the adjustable piston. The diaphragm is made of thin flexible metal, and one side is open to atmospheric pressure and the other side (sample flow side) is under a slight vacuum as regulated by the piston. The adjustable piston consists of an O-ring that lightly contacts the diaphragm. This piston regulates the vacuum in the chamber, providing the pressure drop that draws the air sample through the restrictor and into the canister. The adjustable piston is moved toward or away from the metal diaphragm by means of screw threads to adjust the vacuum in the chamber. Once set, the pressure drop across the restrictive orifice will be maintained, even with the change in vacuum of the canister, until the vacuum range of the device is exceeded. Figure 7-2 shows the interrelationship of the pressures (P2 and P3) and flow rates of the MFCD/canister system.

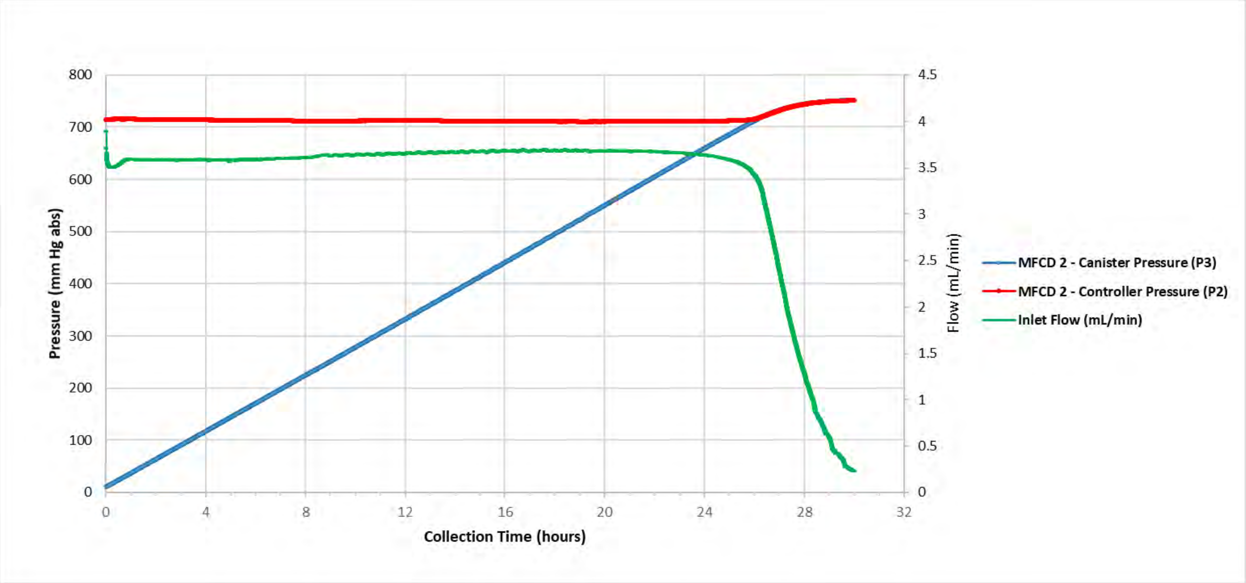


Figure 7-2: MFCD controller chamber pressure, canister pressure, and flow rate during sample collection.

7.3.3.3 Mass Flow Controllers

MFCs regulate flow by sensing the temperature difference across a gas stream and relating this temperature difference to the gas flow according to the density of the gas. MFCs typically perform best when operating at 10% to 90% of the stated flow range. MFCs operate by sensing the change in heat of the metered gas, which is unique to each gas based on the heat capacitance as a function of density, and therefore must be calibrated with the gas for which it will regulate flow. For example, an MFC employed to regulate ambient air flow should not be calibrated with nitrogen as nitrogen is approximately 3% less dense and has a different heat capacitance than air. Such a discrepancy will result in errors in gas flow calibration. MFCs typically require alternating current power, and therefore their use is generally limited to sampling instruments installed for fixed-site or long-term use. MFCs should be able to maintain sample flow to within ±2% of the flow setting over the desired sampling duration. MFC flow characteristics and operation should be precise and predictable such that the selected set point is maintained each time the MFC is employed.

7.4 Vacuum/Pressure Gauges

To verify canister pressure or vacuum, high-quality (accuracy of ±0.25% full scale), calibrated vacuum/pressure gauges or pressure transducers are needed. Gauges may be digital or analog. Commercially available digital gauges that allow programming/selection of units are very useful. Such a gauge or combination of gauges is needed to measure the key pressures, as described in Section 11.3. Gauges for accomplishing these measurements may be incorporated into sampling units, installed on canisters, connected to cleaning manifolds, or be stand-alone and attached at the time of use. For critical processes such as the preparation of standards, the dilution of samples, the determination of acceptable leak rates, and the assessment of minimum canister pressures for analysis, the gauge or combination of gauges should be calibrated over the range of use for the application and have sufficient resolution to permit the user to measure pressure differentials precisely. To verify the accuracy of the laboratory's commonly used gauges, it is recommended that users of the method maintain a National Institute of Standards and Technology (NIST)–certified precision test gauge with accuracy of ±0.1% full scale or better and a range of at least 0 to 207 kPa absolute (0 to 30 psia) or an equivalent electronic digital pressure transducer.

7.5 Gas Regulators, Tubing, and Fittings

Regulators for high-pressure cylinders of dilution gas, stock standard gases, and IS gases should be high-purity stainless steel and may be silicon-ceramic lined (which may be required when analyzing sulfonated VOCs). Regulators should be dedicated to a specific task and labeled for use. For example, a regulator used on a high-concentration stock VOC standard cylinder should not be used on a low-concentration stock VOC cylinder. Teflon products such as PTFE and FEP seals and diaphragms should be avoided where possible to minimize memory effects; PFA should not be used. Regulators for connections to high-pressure cylinders for carrier and make-up gases should be brass or stainless steel and be rated for the pressure and flow used.

Connecting tubing and fittings for dilution gas and standard gases should be of chromatographic-grade stainless steel (preferably 316 type), which includes silicon-ceramic–treated stainless steel. Note that the lining of silicon-ceramic–treated stainless steel tubing can be damaged by bending the tubing too tightly. Follow the manufacturer's recommendations for working with silicon-ceramic–treated tubing. Connections should be metal to metal; PTFE thread sealants and Buna-N rubber components should be avoided.

7.6 Analytical Instrumentation

Analysis by this method may be accomplished with any combination of preconcentrator, GC, and MS provided the performance specifications of the method are met.

7.6.1 Sample Introduction

Commercially available preconcentrator units typically include several ports for the connection of standards, blanks, samples, and ISs. Some users may find the number of ports to be limiting, particularly laboratories with high sample throughput. The connection capacity may be increased by the addition of one or more commercially available multiposition autosamplers.

7.6.2 Sample Preconcentrator

To measure the target VOCs collected within the canister, an aliquot of air is removed and passed through a trap or series of traps where the VOCs are retained (concentrated) while the bulk gases and water are effectively removed. The VOCs are then desorbed from the trap(s) and injected into a GC-MS system.

Several preconcentrator units for this purpose are commercially available. Preconcentrator traps consist of quartz or stainless-steel tubing that may be empty or filled with sorbent material (or combinations of sorbents), such as glass beads, styrene-divinyl copolymers, and graphitized carbon. The traps may also be coated capillary tubing. Parts or all of these traps may be selectively cooled to increase retention of VOCs. Cooling may be accomplished thermoelectrically (for example, with the Peltier effect) or with cryogens such as liquid nitrogen, liquid argon, or liquid carbon dioxide.

Preconcentrators require a vacuum source and a source of clean, dry carrier gas. Vacuum is typically provided by an oil-free pump that meets the manufacturer's specifications for flow and achievable vacuum. Carrier gases may be supplied in high-pressure cylinders or by gas generation systems. Preconcentrators are typically computer controlled to facilitate creating and executing analysis sequences of standards, field-collected canisters, and laboratory QC samples.

7.6.3 Gas Chromatographic–Mass Spectrometric System

7.6.3.1 Gas Chromatograph

The GC must allow temperature programming with quick and accurate temperature ramping. If needed for separation of very light VOCs (such as ethane), the GC should be capable of subambient cooling (e.g., -50 °C). The GC will typically be a stand-alone instrument that is connected to the preconcentrator by a heated chromatographic-grade stainless-steel transfer line or equivalent, such as a length of unlined capillary column, as specified by the preconcentrator or GC manufacturer. Carrier gas connections should be of stainless-steel or copper tubing.

7.6.3.2 Chromatographic Column

A range of suitable capillary chromatographic columns is commercially available for separation of the target analytes. Typical columns are 100% methylpolysiloxane or 5% diphenyl and 95% dimethylpolysiloxane, and the column should have an inner diameter (I.D.) of 0.18 to 0.32 mm for separation of nonpolar compounds. If separation of polar VOCs is desired, the operator may select other stationary phases, as appropriate, such as 6% cyanopropylphenyl–94% dimethylpolysiloxane. The recommended column length is 60 m, but appropriate separation may be achieved by shorter columns (e.g., 30 m), which have the advantage of a shorter GC analysis time. Longer columns (e.g., 100 m) may be employed for better separations, albeit at the cost of longer GC analysis times. However, considering the diversity of the desired target analyte list, the operator should choose a column that is suitable for separating the compounds of interest to meet the performance standards given in **Section 18**.

7.6.3.3 Mass Spectrometer

The MS may consist of a linear quadrupole, ion trap, or TOF unit. The chosen detector should cover the mass range required to evaluate the characteristic ions for each desired target VOC and should have minimum resolution of 1 amu or less. The typical mass range used for monitoring the VOCs in Table 1-1 is 35 to 270 amu; however, depending on the desired suite of target analytes, the range may require adjustment to include lower masses (e.g., down to approximately 20 amu) or higher masses (e.g., up to approximately 300 amu) when characterizing high-MW nontarget VOCs. The upper limit of the range may be preferentially limited to 200 amu, which will increase dwell time and MS sensitivity for quadrupole and ion trap MSs. The MS must be capable of analyzing the desired mass range every 1 s or less and ideally would operate with an acquisition rate such that at least 10 (**Boyd et al., 2008**), and preferably 12 or more, measurements are performed over a typical 6-s-wide (full width at half maximum) chromatographic peak. Quadrupole and ion trap systems employing electron impact (EI) ionization mode should provide 70 V (nominal) electron energy in EI mode to produce a mass spectrum that meets all the instrument performance acceptance criteria as specified by the manufacturer.

Quadrupole MS units may be operated in full-scan (SCAN) mode, which monitors for all ions in the chosen scan range, or SIM mode, which permits the operator to define the ions to be monitored at various time points in the chromatogram. With SIM, the dwell times are increased when compared to SCAN, which consequently increases signal strength of the desired ions and decreases the background noise, leading to lower detection capabilities. SIM historically has had the advantage of providing additional sensitivity for the selected ions; however, it does not provide information on ions that were not purposely selected for monitoring. More sophisticated quadrupole systems are available that allow operation in SCAN and SIM modes simultaneously, which provides the full ion profiles of SCAN and the sensitivity benefits of SIM. If qualitative identification of nontarget VOCs is desired, the MS instrument should be capable of full-scan mode and producing library-searchable mass spectra, which are typically based on a quadrupole MS operated with EI at 70 eV. Note that some instrument systems may also permit the use of “soft” ionization techniques with EI of < 70 eV; however, users of the method should note that ion spectra libraries typically contain spectra generated with EI at 70 eV.

Ion trap MS units similarly may operate in full-scan or SIS mode. As with the quadrupole MS in SIM, SIS provides greater sensitivity than full-scan mode by eliminating unselected ions from the detector and thereby increasing the signal-to-noise ratio (S:N) of the desired ions.

TOF instruments operate on a different measurement principle than the quadrupole and ion trap MS units. TOF instrument operation does not involve filtering the ion fragments as is done with quadrupole and ion trap MSs. All ion fragments impact the detector, and thus TOFs are more sensitive than the quadrupole and ion trap counterparts. The instrument measures the duration from when the ions are electrically pulsed into the analyzer until impact at the detector and correlates the time of impact with the ion *m/z*, providing ion measurement ranges from single-digit *m/z* to approximately 1000 *m/z*, at a resolution that varies according to *m/z* and the analyzer design. The ionization and detection cycles can occur thousands of times per second, resulting in thousands of spectra per analyte peak, which may be co-added to report the spectra at more modest acquisition rates.

7.6.4 Calibration Gas Standard Preparation Equipment

The GC-MS may be calibrated by several conventions, all of which involve varying a known mass of target VOCs introduced to the instrument for analysis. This section discusses the methods of preparing working-level standards for calibrating the GC-MS by dilution of a higher concentration stock standard gas. This dilution can be performed dynamically or statically using commercially available dilution instruments or a custom-built unit constructed of individual components. Refer to Section 13 for calculations for preparing dilutions.

7.6.4.1 Dynamic Dilution Instrumentation

Dynamic dilution preparation methods involve mixing a known standard gas stream or streams with a diluent gas at known flow rates to effectively dilute the standard gas to the desired concentration. The combined gas streams are typically routed through a chamber or area of the flow path with baffles or other turbulence-inducing features to encourage thorough mixing of the resulting gas stream. The diluted gas mixture can be plumbed directly to the preconcentrator inlet or captured in an evacuated canister for later introduction to the preconcentrator. The diluent gas should be humidified to approximately 40% to 50% RH to ensure proper quantitative transfer of target VOCs through the dilution system. The humidity aids in transfer of VOCs with higher BPs from the mixing area to the canister or directly to the preconcentrator. Refer to Section 8.7 for humidification of diluent gases. Deionized water can be added to the canister to adjust the humidity level as needed, as described in Section 13.1.

For dynamic dilution, the system requires, at a minimum, a flow control device for the diluent gas flow and each standard gas to be diluted and a mixing area such as a manifold where the gases and diluent can be sufficiently mixed before introduction to the preconcentrator or canister. Connection tubing should be of chromatographic-grade or silicon-ceramic–coated stainless steel. Mixing chambers or manifolds should be of chromatographic-grade or silicon-ceramic–coated stainless steel, borosilicate, or quartz glass.

Dynamic dilution gas flows are typically controlled by calibrated electronic MFCs with flow ranges appropriate to achieve the desired dilution factor(s). Purpose-built dynamic dilution systems are commercially available with MFCs to meter standard and diluent gases into an included mixing chamber. Such systems should be chosen to provide the desired dilution factor ranges. For example, if a 25 pptv (0.025 ppbv) standard concentration is desired and the stock gas concentration is 100,000 pptv (100 ppbv), the dilution system will need to provide a 1:4000 dilution. Periodic recertification of MFCs is required unless flows are verified with a flow calibration device each time gas standards are prepared.

Alternatively, mechanical flow devices such as needle valves may be used. If these devices are used, flows must be manually adjusted and verified. Use of MFCs is generally preferable as flows are automatically adjusted to maintain a specified rate, whereas mechanical flow devices require an initial manual adjustment and are assumed to maintain the set flow.

7.6.4.2 Static Dilution Instrumentation

Static dilution preparation methods involve the delivery of precise volumes of gas or liquid standards and diluent gas into a container of constant volume. Static dilution of standards is performed in a fixed-volume vessel such as a canister or through a manifold where known amounts of certified standards are transferred. The known amounts may be measured based on partial pressure measurements, volumetric transfers, and/or mass difference. Precise and sensitive pressure transducers or pressure gauges are used to measure the partial pressures of added standard and dilution gases. Volumetrically certified gas-tight syringes may be employed when transferring known volumes of liquids or small gas volumes into vessels for dilution. Sensitive high-capacity analytical balances may be employed to measure masses of added neat materials and diluent gases.

At least four types of static dilution approaches can be used for preparation of standard gas dilutions:

- **Static dilution performed directly into canisters based on partial pressures.** Gas volumes are measured using pressure transducers or pressure gauges to determine the gas volumes added. A pressure transducer or gauge is connected to an evacuated canister, and the canister pressure is monitored and recorded before and after each standard and diluent gas is added. These pressures are input into the calculation of the dilution factor and final concentrations.
- **Static dilution through a manifold based on partial pressures.** A pressure transducer or combination of pressure transducers is employed to monitor the pressures of added standard and diluent gases plumbed through valves into a manifold constructed of chromatographic-grade or silicon-ceramic–coated stainless steel. A canister is attached to the manifold to receive the diluted standard gas. Commercially available static diluters designed for the preparation of calibration gas standards operate on this principle and meter gas standards and dilution gases into canisters based on precise measurements of pressures with pressure transducers.
- **Static dilution into canisters based on known standard volumes.** A known volume of standard gas is added to an evacuated canister with a gas-tight syringe, and the diluent gas is added to a known final pressure. The final pressure of the diluted canister is used to calculate a final volume of the mixture, assuming the volume of the canister is known. Users

are cautioned that this method of dilution preparation is difficult to perform reproducibly and requires practice and excellent technique to perform accurately and consistently. Additionally, due to deviation from the indicated volume of the canister (e.g., 6 L), this method may be subject to errors in the final theoretical concentration as the canister is not volumetrically certified. This is not the preferred method for standards preparation, and it is highly recommended that standards prepared in this manner be verified against standards prepared in a robust manner.

- **Static dilution into canisters based on gravimetric methods.** Gravimetric dilution of standards requires access to a high-sensitivity, high-capacity analytical balance that can resolve and register the addition of small amounts of gas or neat material to a fixed-volume vessel such as a canister or cylinder. Known masses of standard gases or neat materials are added to the vessel. The vessel's mass is measured before and after addition of each material and the added mass is calculated by difference. The vessel mass is then measured prior to and following the addition of diluent gas to determine the final concentration(s). This convention, especially when using neat source material, requires excellent technique and hygiene to prepare an accurate and contaminant-free standard. In general, preparation of standards should be performed by diluting gaseous standards unless exploratory or experimental work is to be conducted for which gaseous standards are not commercially available.

8 Standards, Materials, and Reagents

Standards and reagents should be used within their expiration period. Working-level standards prepared in canisters should be evaluated within 30 days of preparation.

8.1 VOC Standard Stock Gas Mixtures

Standard gaseous mixtures with certified concentrations of desired target VOCs can be sourced from reputable gas vendors (see **Appendix C**). The concentrations of the VOCs in the mixture should be commensurate with the anticipated dilution factor achievable by the laboratory needed to dilute the mixture to the desired working range. Typical concentrations of the stock standard gas mixtures range from approximately 100 ppbv to 1 ppmv, and analytical accuracy is typically cited to be within ±10% tolerance. Note that gas vendors may cite wider allowable deviations for certain labile analytes. When available, standard mixtures of target VOCs in high-pressure cylinders should be traceably certified to a NIST Standard Reference Material or to a NIST/EPA-approved Certified Reference Material. Gas standard certificates of analysis should be retained.

Several gas vendors maintain a readily available stock calibration gas mixture with a predetermined suite of approximately 65 VOCs. The balance of these gas mixtures is ultrapure nitrogen, and the gas mixtures are typically given an expiration of 1 year from certification or production. Note that certain labile analytes may be given shorter or no expiration periods. Gas vendors or third-party certification laboratories may offer recertification services of the target compound concentrations and extend the expiration of the cylinder contents. Recertification is particularly useful and typically costs less than sourcing a new standard if large cylinders of standard gas are purchased. Gas standards that are in use must not have exceeded their current expiration period.

8.2 Neat Materials

Neat VOCs can be procured from reputable chemical providers as gases or neat liquids. The purity for the neat materials should be ≥ 98% and be evidenced by a certificate of analysis or purity. These neat materials are diluted to desired concentrations in evacuated fixed-volume vessels. Masses of these neat materials are added to the canister or cylinder with calibrated glass gas-tight syringes, by pressure differential, or gravimetrically as described in **Section 13.3**. The expiration of a prepared gas mixture is the earliest expiration date of the parent materials.

8.3 Internal Standards

Standard gaseous mixtures with certified concentrations of IS compounds in ultrapure nitrogen are available from reputable gas vendors. IS gases should be sufficiently free of target VOCs. IS compounds chosen should represent the MW range of the desired target VOC suite and may be deuterated isotopes of target analytes or VOCs that are not expected to be found in unknown samples.

8.4 Secondary Source Gas Standard

A secondary source calibration verification (SSCV) is used as a QC measure to verify the accuracy of the primary VOC standard used for quantitation. A best practice is to procure the certified secondary source stock calibration standard from a different supplier than that of the primary calibration standard. A less desirable option is to obtain a second certified standard from the same supplier but from a different lot. The standard must meet the criteria listed in **Section 8.1**. The SSCV should contain all compounds in the calibration mix. As with the calibration stock gases, at time of use the secondary source stock must be within the expiration period of the most recent certification or recertification.

8.5 Gases

Carrier gas: Helium is used as a carrier gas in the GC. Ultrapure (99.999% pure or better) helium is available in high-pressure cylinders. Hydrogen and nitrogen may also be used as carrier gases if all performance criteria are met.

Air: HCF zero air may be purchased in high-pressure cylinders from reputable gas vendors or may be prepared by passing ambient air through molecular sieves, catalytic oxidizers, and subsequent charcoal filters or similar substrate to effectively remove impurities to a concentration of < 20 pptv per compound of interest.

Nitrogen: Ultrapure (99.999% pure or better) nitrogen may be sourced from cylinders procured from commercial gas vendors or from the headspace gas from a liquid nitrogen dewar. (*Note: Dewar headspace is theoretically VOC-free as VOCs in the source nitrogen gas should stay frozen in the liquid phase of the dewar contents. Users are encouraged to analyze headspace gas from each dewar or dewar refill prior to use to ensure the gas is fit for use in this method.*)

8.6 Cryogens

Cryogens such as liquid nitrogen, liquid argon, and liquid carbon dioxide will be specified by the instrument manufacturer, if needed.

8.7 Water for Humidification

Water used to humidify canister contents and diluent gases or to clean canisters should be high-performance liquid chromatography (HPLC) grade or ASTM Type I (resistivity ≥ 18 MΩ·cm), ultrapure, or equivalent. Water should be evaluated for potential VOC contamination by analyzing humidified zero air samples. If VOC contamination is found, removal may be attempted by boiling for approximately 10 min to degas or by sparging for approximately 10 min (or until the VOC background is reduced) with ultrapure helium or nitrogen.

9 Physical and Chemical Characterization and Qualification of Field and Analytical Instruments and Canisters

Prior to field deployment, sampling apparatus flow profiles should be characterized, instrumentation flow rates set or calibrated, and the instrumentation qualified to be nonbiasing. Similarly, analytical instrumentation and canisters should be qualified as nonbiasing prior to use.

9.1 Characterization of Sampling Devices and Systems

The goal for time-integrated sampling is to achieve a constant flow rate during the desired sampling time period. For subatmospheric sampling, when the evacuated canister provides the differential pressure to draw air into the canister, a constant flow rate should be maintained until at least 75% of the canister volume is collected, which is equivalent to approximately 28 kPa (4 psi or 7 in. Hg) below atmospheric pressure. Manufacturers typically provide instructions regarding recommended fill times and flow rates based on designated restrictors and canister sizes. This is addressed in greater detail in Section 11.1.2.

To verify that the flow controlling device is operating properly, the sampling device may be characterized by assembling an evacuated canister, a calibrated vacuum/pressure gauge, the flow controlling device to be tested, a particulate filter, and a certified flow meter, as shown in Figure 9-1. The canister pressure downstream of the flow controlling device and the flow upstream of the flow controlling device are monitored and manually or electronically logged over the desired sample collection period. To verify flow control systems intended for very low flows, such as those required for a two-week sampling period, the flow verification may be performed on an accelerated schedule by employing a smaller-volume canister. The differential pressure is the critical variable for determining flow rate, so a smaller canister will enable the user to verify flow control across the desired pressure differential (vacuum) range in a shorter period due to the more rapid filling of smaller-volume canisters when compared to larger-volume canisters (e.g., 0.4 L vs 6 L).

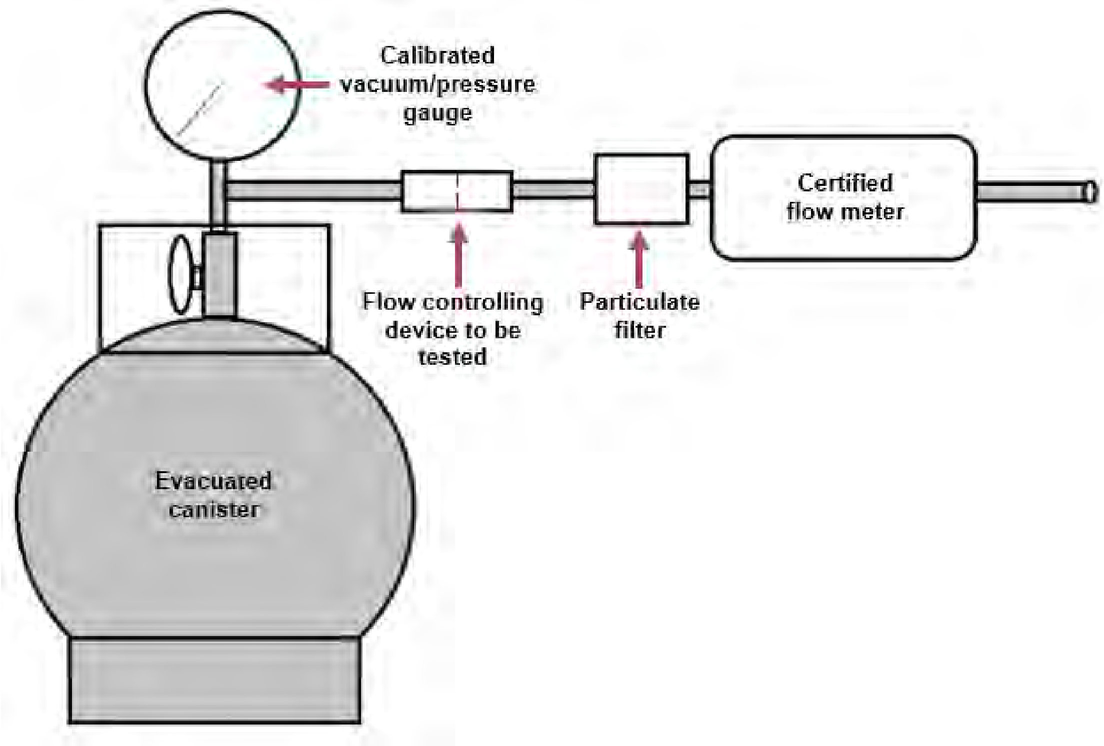


Figure 9-1: Flow controlling device characterization apparatus.

A certified flow meter should be employed, which may consist of a calibrated mass flow meter (MFM), a dry piston meter, or other similar measurement device with the calibrated measurement range appropriate to measure the flow (typically in low single-digit milliliters per minute). For low flow rates (single-digit), the flow measurement device itself must not interfere with the flow measurement—that is, the pressure drop across the measuring device should not be such that it impacts the flow being measured.

An example of a simple test system for characterizing sampling devices can be constructed that continuously logs the output signals from an electronic vacuum/pressure gauge and calibrated MFM using a datalogger to record the pressure (vacuum) of the canister, the flow passing through the controlling device, and the time. Pressure and flow measurement data collection should be of sufficient frequency (e.g., readings every hour or more frequently) to ensure adequate time resolution for determining the critical pressure differential—the pressure ratio above which flow rate is no longer constant. Example plots of flow vs. pressure for various types of flow controlling devices experimentally determined using this test system are shown in Figure 9-2.

Characterization of the flow/pressure profiles for pump-driven canister sampling systems is not necessary as these systems generally maintain a constant flow across the desired flow range. Commercially available rack-mounted canister sampling systems should have been tested and characterized by the manufacturer.

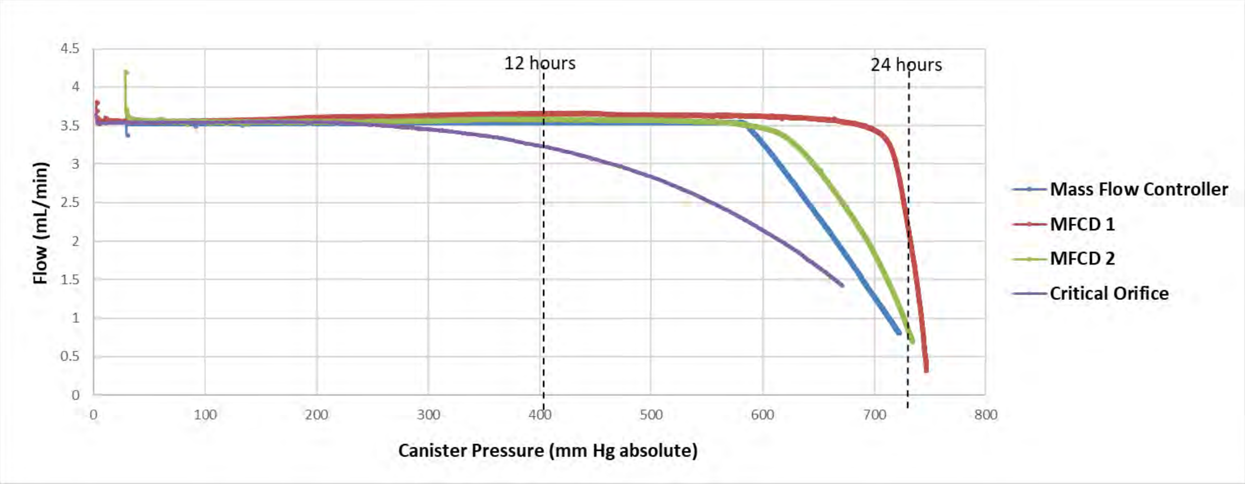


Figure 9-2: Examples of flow vs. pressure plots for various flow controllers.

9.2 Calibration of Flow Controlling Devices and Systems

9.2.1 Calibration and Verification of Mass Flow Controllers

If calibration of an MFC is required, the unit should be sent to the manufacturer or a third-party metrology laboratory. The chosen metrology laboratory should be accredited and have the capability to adjust or repair the MFC in the event it is found to be out of tolerance.

To establish or verify calibration of an MFC, the user should supply air pressure or vacuum to the MFC in the appropriate operating range as stated by the manufacturer and that approximates the pressure during routine use. If the MFC is an integral part of a sampling system, flow verifications should be conducted while it is installed in the system. If the MFC is used as a stand-alone controller attached to an individual canister, it should be verified using the power source and readout that will be used during sampling. The direction of flow indicated on the MFC must be observed and will depend on whether the source of air is pushed or pulled through it. If pressure is applied, the output flow downstream of the MFC is measured with a calibrated flow measurement device. If vacuum is applied, the inlet flow upstream of the MFC is measured with a calibrated flow measurement device.

Preferred flow measurement devices are graphite piston flow calibrators (positive displacement technology such as DryCal technology [Mesa Labs, Butler, NJ]) and calibrated MFMs capable of accurately measuring flow rates under both vacuum and pressure conditions. In either case, a calibrator or MFM of the appropriate calibration range must be used. For very low air flow rates (10 mL/min and below), the pressure drop across the measuring device must be considered as the measurement device may change the performance of the flow control device undergoing verification such that the performance is not representative of the performance under conditions of use.

If verification of flow measurement demonstrates that the MFC readout display is accurate, flows may be set directly using the MFC digital display. However, if the MFC-displayed readings are outside the flow tolerance specified in Section 7.3.3.3 or the manufacturer-defined tolerance from the measured flow, the unit should be returned to the manufacturer or metrology laboratory for recalibration or it may be necessary to measure the flow during each use.

If the MFC-displayed readings are outside of the acceptable tolerance, flows can be measured and set at each use by adjusting the flows according to calibration device measurements. Alternatively, calibration verification can be accomplished by measurement at a minimum of three different flow rates: two flows bracketing the intended flow and one at the intended flow. The MFC display reading is then plotted against the actual measured flow, and the points are modeled by linear regression. The linear regression is then used to provide the corresponding readout display setting for the desired flow rate.

9.2.2 Adjustment and Verification of Mechanical Flow Controlling Devices

Flow rates for MFCDs must be set and/or verified prior to each use. The adjustment process requires that the MFCD be attached to an evacuated canister (or other vacuum source) and a calibration device of the appropriate flow range be attached to the inlet of the MFCD. The canister valve is opened, and as the air is drawn through the flow calibration device, the flow adjustment piston of the MFCD is carefully adjusted until the desired flow is attained. Initial flow adjustment for MFCDs is typically performed prior to sample deployment with the sampling unit attached to an evacuated test canister. This allows adjustments to be made without impacting sample collection. If flows are initially set at an off-site location prior to deployment, it is strongly recommended that flow rates be verified at the sampling location at the time of deployment. If the flow rate has changed and is outside the desired range, the controller will need to be adjusted.

Typical flow measurement devices that meet the necessary criteria for setting and verifying MFCD flow rates are graphite piston flow calibrators (positive displacement technology such as DryCal Technology [Mesa Labs, Butler, NJ]) and calibrated MFMs. Suitable devices for flow measurement must be noncontaminating; therefore, bubble flow devices should not be used. They must also operate based on vacuum and have a sufficiently low pressure drop so as not to impact the flow being measured. Flow measurement devices must be in the appropriate operating range for the target flow range, typically 0–10 mL/min or 0–100 mL/min, depending on the canister volume and sampling duration. Adjustment of MFCDs to flows below 1 mL/min is challenging and requires special measurement devices. MFMs are commercially available that are capable of measuring flows below 1 mL/min.

A simple technique can be used to verify that the MFCD is properly set at time of deployment. This technique requires an evacuated canister, the MFCD with vacuum/pressure gauge, and a timing device. The MFCD is installed on the evacuated canister, and the canister valve is momentarily opened, allowing a vacuum to be established in the controller. The canister valve is then closed, and the time required for the vacuum reading to rise 34 kPa (10 in. Hg) is measured. The time is then referenced to a chart developed by the user specifically for the controller design that relates the leak rate to the flow rate. For this technique to work, the internal volume of the system between the canister valve and the restrictor must always be the same.

9.3 Qualification of Analytical Instrumentation

9.3.1 Zero-Air Challenge of Analytical Instrumentation

To fundamentally demonstrate that the analytical instrumentation (preconcentrator and GC-MS system) is not a source of contamination (positive bias), humidified (40% to 50% RH) HCF zero air from a known clean source (e.g., certified clean canister, clean cylinder gas, zero-air generator) is analyzed to confirm the cleanliness of the system. This procedure should be conducted at installation prior to initial use of the instrument. This basic evaluation does not require establishing calibration or determining quantitative results to assess potential positive bias. This check should be performed by connection of the clean humidified gas sample to the preconcentrator to verify that the analytical instrument and all connections are sufficiently clean. The volume of air analyzed should be consistent with the laboratory's typical canister sample injection volume. Compounds that appear in this zero-air challenge sample indicate contamination attributable to the analytical instrumentation.

Analysis must show that any detected target compounds in the zero-air challenge sample are at response levels that are expected to be < 20 pptv or preferably not detected. Users should examine chromatograms for interferences and other chromatographic artifacts such as nontarget peak responses, large peaks or rises in the chromatogram due to undifferentiated compounds, and baseline anomalies. Where exceedances are noted in the zero-air challenge sample for target compounds, steps should be taken to remove the contamination attributable to the analytical instrumentation by following the manufacturer's instructions. Such steps may include analyzing replicates of humidified clean gas until the contamination is eliminated, which is indicated by measuring decreasing concentrations in subsequent analyses of the target VOCs until a stable concentration (preferably not detected) is reached. The analytical system zero-air challenge is then repeated to ensure that any problems have been mitigated before the analytical instrumentation is suitable for use.

Once the analytical system has been demonstrated to have minimal to no positive bias for target VOCs, the system should be tested with a known standard of target compounds to check for any negative bias.

9.3.2 Known-Standard Challenge of Analytical Instrumentation

To fundamentally demonstrate that the analytical instrumentation (preconcentrator and GC-MS system) is not causing loss of compounds (negative bias), a humidified (40% to 50% RH) reference standard of known integrity containing all target compounds is analyzed to verify that all target compounds are detected by the system, that they respond consistently upon repeated injection, and that they exhibit sufficient response to be quantifiable at low concentrations. This procedure should be conducted at installation prior to initial use of the instrument. This basic evaluation does not require establishing calibration or determining quantitative results to assess potential negative bias. It is recommended that the challenge gas contain all target VOCs at approximately 100 to 500 pptv each, chosen in consideration of the expected concentration in ambient air. The volume of air analyzed should be consistent with the laboratory's typical canister sample injection volume. Compounds demonstrating poor response as indicated by peak absence or minimal peak area may be a result of active sites in the analytical system, cold spots in transfer lines, gas impurities, improper choice of preconcentrator sorbent traps or GC columns, system leaks, and/or poor moisture management. If problems are noted, the instrument manufacturer should be consulted on the necessary steps to eliminate the bias.

9.3.3 Qualification of Autosamplers Associated with Analytical Instrumentation

Once the system has been shown to be fundamentally nonbiasing (positive or negative), the system should be calibrated and evaluated as described in Sections 13 through 16 in order to conduct the canister and sampling device and system qualifications. If an autosampler is used to facilitate analysis of multiple canisters, all ports of the autosampler should be tested once the analytical system has been calibrated and prior to conducting the canister and sampling device and system qualifications.

After establishing the initial calibration (ICAL), each port of the autosampler should be tested to demonstrate cleanliness (positive bias) by analyzing humidified zero air. This is performed by connecting the clean humidified gas sample to the port to verify that transfer lines and all connections are sufficiently clean. Each target VOC's concentration should be < 20 pptv or preferably not detected. This check is performed prior to initial use, upon replacement of transfer lines, or after analysis of potentially contaminating samples.

Next, each port of the autosampler is challenged with a reference standard (approximately 100 to 500 pptv) to demonstrate that the autosampler is not causing bias (typically loss of compounds, or negative bias). Each target VOC's concentration should be within ±15% of theoretical concentration. This is performed prior to initial use and upon replacement of transfer lines.

9.4 Qualification of Canisters

To establish an inventory of canisters suitable for use under Method TO-15A, each canister should be qualified to ensure sample validity. Since canisters may develop problems with use, it is strongly recommended that they be qualified frequently. Canisters that are qualified have been demonstrated to be acceptably leak-tight and nonbiasing. All canisters in use should be qualified at least every 3 years. New canisters should be qualified before initial use and every 3 years thereafter. All canisters in the inventory need not be qualified at the same time but rather a subset of the canister inventory can be qualified on a rolling basis such that all canisters are qualified within a 3-year period. Canisters in an existing inventory that have not been qualified in the past 3 years should be qualified as soon as possible.

9.4.1 Canister Leak Check

Prior to initial use, new canisters should be verified to be leak-free by performing a pressure decay test. This is accomplished by either evacuating or pressurizing the canister. If the evacuation method is used, the canister is evacuated, preferably to high vacuum ≤ 0.0067 kPa absolute (0.05 mm Hg or 50 mTorr), the valve is closed, the vacuum/pressure gauge is attached, the valve is opened, and the initial vacuum is measured and recorded. The valve is then closed, the vacuum/pressure gauge is removed, and the canister valve is left loosely capped until the next pressure reading several days later. In the pressurization method, the procedure is identical except that instead of evacuated, the canister is pressurized to approximately 203 kPa absolute (29.4 psia) with clean fill gas. It is critical that canister valves are loosely capped (brass cap) to ensure that leakage through the valve is accurately assessed while avoiding potential entry of debris into the valve. Vacuum/pressure should be measured with a high-quality, calibrated vacuum/pressure gauge or transducer. Vacuum/pressure should not change by more than 0.69 kPa/day (0.1 psi/day), otherwise the canister leak rate is excessive, and the canister should be removed from service and repaired. As an aid in identifying the location of leaks for possible repair, the canister can be pressurized with helium, which permits quick pinpointing of any leaks with a helium leak detector.

9.4.2 Zero-Air Challenge of Canisters

Canister zero-air challenges are performed by pressurizing clean evacuated canisters with humidified (40% to 50% RH) HCF zero air. Note that performing this qualification with ultrapure nitrogen does not adequately test the canister as the inert nitrogen atmosphere does not permit reactions within the canister that may occur when ambient air is sampled. Each canister should be allowed to equilibrate for a minimum of 24 h prior to an initial analysis. This initial analysis should demonstrate that the target VOCs meet the cleanliness criteria specified in Section 10.2. After the initial analysis, it is recommended that one subsequent analysis be performed for each canister following a holding period equal to or exceeding the typical laboratory holding time, nominally 30 days from the canister fill date. Laboratories may tailor the time of the subsequent analysis to be representative of the maximum holding time experienced by the laboratory (e.g., 21 days if all samples are analyzed within this time frame from sample collection). For this second analysis, the results should continue to meet the cleanliness criteria specified in Section 10.2. Canisters that fail the zero-air challenge should be recleaned and retested. If necessary, more aggressive cleaning techniques such as water rinses or other rinses as specified by manufacturers may be tried. If a canister continues to fail the zero-air challenges for Method TO-15A, it may need to be removed from service or repurposed for other applications. It is recommended that all canisters in the active inventory be retested in this manner at least every 3 years. This can be accomplished by testing a subset of canisters on a periodic basis. This may be coordinated with the cleanliness verification checks that are routinely performed as described in Section 10.2.

9.4.3 Known-Standard Challenge of Canisters

Following the canister zero-air challenge described in Section 9.4.2, it is strongly recommended that canister bias be assessed by filling a clean evacuated canister with a humidified (40% to 50% RH) standard gas in HCF zero air with each target VOC at approximately 100 to 500 pptv. The selected challenge concentration should be chosen to consider the expected measured concentration in ambient air. The canister is filled with the challenge standard and analyzed at least 24 h after preparation. This initial analysis should show that the measured concentrations of the target analytes are within ±30% of the theoretical spiked concentration. After the initial analysis, it is recommended that one subsequent analysis be performed for each canister following a holding period equal to or exceeding the typical laboratory holding time, nominally 30 days from the canister fill date. Laboratories may tailor the time of the subsequent analysis to be representative of the maximum holding time experienced by the laboratory (e.g., 21 days if all samples are analyzed within this time frame from sample collection). For this second analysis, the results should remain within ±30% of the original theoretical value for each target compound. It is recommended that all canisters in the active inventory be retested in this manner at least every 3 years. This can be accomplished by testing a subset of canisters on a periodic basis. Note that the criterion of ±30% is chosen based on the continuing calibration verification (CCV) criterion for acceptable variability in instrument response; however, analysts may choose to set a more stringent criterion for the initial analysis based on the stability of their instrument.

9.5 Qualification of Sampling Devices and Sampling Systems

Prior to use, sampling devices and sampling systems should be determined to be leak-free and nonbiasing. Leak checks should be performed prior to each use. Bias checks should be performed prior to first use and periodically thereafter. Sampling systems that are operated routinely year-round should undergo these checks annually, typically to be conducted after annual calibration and maintenance. Any canisters used during this process should be canisters that have been qualified as described in Section 9.4. Bias checks should be conducted by challenging the systems with humidified zero air and known standards. Ideally the units should not contaminate or adsorb target compounds during sampling.

9.5.1 Leak Checks for Sampling Devices and Sampling Systems

Performance of leak checks on sampling devices and systems during qualification permits users to repair sampling equipment prior to field deployment. Leak checks should also be performed at the time of sample collection, as discussed in Section 11.

A simple technique for leak testing MFCDs with vacuum/pressure gauges is to place the MFCD on an evacuated canister, cap the inlet to the MFCD, open and close the canister valve, and observe the vacuum/pressure gauge for a minimum of 2 min. Ideally there should be no perceivable pressure increase. If a pressure increase is observed, then the device does not qualify, and attempts may be made to determine and eliminate the source of the leak prior to retesting the device.

For qualification of automated rack-mount or bench-top systems, follow the manufacturer's instructions to conduct a leak check to ensure the internal flow path is acceptably leak-free. Ideally, there should be no perceivable leak; however, any leak that is detected should not contribute more than 5% of the total volume collected in the canister. Since manufacturers' leak rates are expressed in psi/min, the user may need to contact the manufacturer to determine the leak rate (psi/min) criteria required to meet the 5% benchmark for a chosen canister volume. Manufacturers' instructions should be followed to correct leaks in the system.

9.5.2 Zero-Air Challenge of Sampling Devices and Sampling Systems

To ensure the sampling device or system is not a source of contamination (positive bias), humidified (40% to 50% RH) HCF zero air collected through the sampling device is analyzed and compared with a reference humidified air sample from the same source. The volume of air analyzed should be consistent with the laboratory's typical canister sample injection volume. Compounds that show increased concentrations in the challenge sample compared to the reference sample indicate contamination attributable to the sampling unit. This challenge should be conducted prior to initial use and on an annual basis thereafter, as well as after cleaning, replacement of components, and collection of potentially contaminating samples.

One technique is to provide humidified zero air flow to a challenge manifold constructed of chromatographic-grade stainless steel or borosilicate or quartz glass. The manifold should include, at a minimum, two ports to be used for connections to the sampling device or system and to a reference canister or analytical system, and a vent to ensure that the manifold remains at ambient pressure. Zero air is to be supplied such that there is excess flow to the manifold at all times as indicated by visible means such as a rotameter, MFM, or piece of tubing inserted in a flask filled with water (bubbling to indicate flow) on the vent. If using a reference canister, its flow should be controlled to approximately the same flow rate as the sampling unit with an MFC or other flow controller. At a minimum, the reference canister should collect a grab sample of the humidified zero-air challenge gas from the manifold. An alternative to using a reference canister is to collect the humidified air directly from the manifold into the VOC preconcentration/analytical system.

Analysis by GC-MS for target compounds must show that the target compounds in the zero-air challenge sample collected through the sampling unit are not > 20 pptv higher than the concentration in the reference sample. Where exceedances are noted in the zero-air challenge sample for target compounds, steps should be taken to remove the contamination attributable to the sampling unit. The sampling unit zero-air challenge is then repeated to ensure the criterion is met before the sampling unit is deployed for sampling. Initial steps to clean the system would involve purging overnight or for longer durations with humidified HCF zero air. If extended purging durations are not adequate to eliminate contaminants, then disassembling and cleaning according to Section 10.6 is recommended. If the unit cannot be cleaned to meet the specifications, then it should be retired from use or repurposed for source sampling.

9.5.3 Known-Standard Challenge of Sampling Devices and Sampling Systems

To ensure the sampling device or system is not causing loss, degradation, or enhancement of compounds, a humidified (40% to 50% RH) standard gas collected through the sampling device is analyzed and compared with a reference sample from the same source. Compounds that show decreased concentrations in the challenge sample as compared to the reference sample indicate that active sites or absorbing materials are present. Increased concentrations as compared to the reference sample indicate contamination or offgassing of target VOCs. This challenge should be conducted prior to initial use, after cleaning or significant maintenance, and after collection of damaging sample matrices that may impact the activity of the flow path surfaces.

The manifold system similar to that described in Section 9.5.2 may be used to accomplish the challenge of the sampling device or system. It is recommended that the challenge gas contain all target VOCs at 100 to 500 pptv each and that the selected challenge concentration be chosen to consider the expected measured concentration in ambient air.

Analysis by GC-MS for target compounds should demonstrate that each VOC in the challenge sample collected through the sampling device or system is within ±15% of the concentration in the reference sample. For compounds exceeding this criterion, steps should be taken to eliminate the bias. This may include cleaning as recommended in Section 10.6 or replacement of compromised parts. Note that this criterion is intentionally tighter than the CCV criterion of ±30%, which characterizes the acceptable drift in instrument calibration response. The reference and challenge canisters are typically analyzed in the same analysis sequence, and therefore calibration drift is expected to not exceed the CCV criterion.

Following completion of the known-standard challenge, the sampling device or system should be flushed with humidified (40% to 50% RH) HCF zero air or ultrapure nitrogen for a minimum of 24 h before field deployment.

10 Cleaning, Handling, and Maintenance of Canisters and Sampling Components

10.1 Canister Cleaning

Canister cleanliness is a critical aspect of Method TO-15A as it directly impacts the quality of VOC measurements. Important cleaning parameters that must be considered are pressure, temperature, humidity, and the number of cleaning cycles. The number of cleaning cycles in particular greatly impacts the final cleanliness of the canisters. Definitive studies have not been published to date recommending specific superior canister cleaning procedures. The canister cleaning recommendations in this section were assembled based on the experience of analysts and procedures generally accepted to be effective. Use of the following procedures should provide canisters of sufficient cleanliness to meet the criteria specified in Section 18. Canister cleaning procedures are discussed below and summarized in Table 10-1.

10.1.1 Gas Source for Canister Cleaning, Pressurization, and Flushing

The purge gas for canister cleaning should be high-purity HCF zero air or nitrogen. Ultrapure nitrogen may be sourced from cylinders, nitrogen generators, or the headspace gas from a liquid nitrogen dewar. Air is generally sourced from cylinders or air generators. Scrubbing of purge gas with additional hydrocarbon traps, moisture traps, and/or catalytic oxidation may be necessary to obtain sufficiently clean purge gas, which should be < 20 pptv for each target analyte. Purge gas cleanliness should be verified upon initial setup by direct analysis if possible or indirectly by filling and analyzing a known clean canister. After initial demonstration of purge gas cleanliness, acceptable canister batch blanks (individual target VOCs ≤ 20 pptv at 101.3 kPa absolute) provide continuing indirect confirmation that the purge gas is suitably clean.

If used, gas scrubbers should be replaced on a regular maintenance schedule. In the event of changes in gas sourcing or after the replacement of scrubbers such as hydrocarbon traps and moisture traps, additional cleanliness verifications may be necessary.

The purge gas should be humidified to approximately 30% to 70% RH; higher humidity levels within this range generally are considered more effective for cleaning canisters. The water assists in removal of polar and high-BP VOCs that may otherwise remain in the canister. Commercial canister cleaning systems usually incorporate a humidifier; however, the supplied humidity may vary considerably based on the type of humidifier that is used. There are generally two types of humidification processes: (1) bubbler humidification systems that incorporate an impinger submerged in water that humidifies by bubbling the purge gas through the water and (2) headspace humidification systems whereby air is simply blown over the surface of the water. Bubbler systems generate higher humidities than headspace systems.

Water for the humidification device should be deionized, distilled, or HPLC grade as specified by the cleaning system manufacturer. If a bubbler-type humidifier is employed, care should be taken to ensure the downstream pressure is lower than the humidifier upstream pressure to avoid backflow of the water. It is recommended that the humidity of the purge gas be measured with a calibrated hygrometer to ensure the desired humidity is attained. Such a measurement can be made by placing a hygrometer probe in the humidified gas stream.

10.1.2 Pre-evacuation of Canisters

Canisters should be pre-evacuated prior to connection to the canister cleaning system to reduce the potential for contamination of the system. Pre-evacuation should be performed on all canisters regardless of whether the contents are ambient air, standards, or samples of high concentrations. Canisters are pre-evacuated by attaching them to an oil-free roughing pump and evacuating to approximately 7 kPa absolute (28 in. Hg vacuum) with the exhaust of the pump directed to a fume hood or passed through a charcoal trap. Canisters are then refilled to ambient pressure with HCF zero air or nitrogen. The pre-evacuation process may need to be repeated for canisters that contain VOCs at higher concentrations. Once the canisters have been pre-evacuated and filled, they are attached to the cleaning system.

10.1.3 Heated Canister Cleaning

Canisters should be heated during cleaning as the heat facilitates removal of compounds. Heating is generally achieved by placing canisters in enclosed ovens. Heating to 80 °C is generally sufficient for cleaning canisters used for ambient air sample collection. Higher temperatures may be used; however, interactions within the canister and the humidified purge gas at temperatures of ≥ 100 °C are not well understood and do not appear to increase cleaning effectiveness. The temperature to which the canister may be subjected during cleaning depends on whether the canister is silicon-ceramic lined, SUMMA, or electropolished; the temperature rating of the valve and vacuum/pressure gauge (if so equipped); and the heating method employed. If using humidified HCF zero air during canister cleaning (specifically in the canister pressurization steps), silicon-ceramic–lined canisters should not be heated above 80 °C as damage to the surface coating due to oxidation may occur, leading to active sites within the canister (**Restek, 2010**).

Canisters used for collection of source-level samples (ppmv concentrations of VOCs) or samples with matrices that include high-MW compounds with high BPs (such as semivolatile organic compounds) may require heating to higher temperatures (100 °C or higher, if permitted by the canister and valve) or specialized cleaning processes. Such canisters typically cannot be sufficiently cleaned with the pressurization and evacuation procedures described in the following sections and should not be used for collecting ambient samples. A best practice is to segregate canister inventories such that canisters used for collection of source-level samples are not used for collection of ambient air samples.

Users are cautioned regarding the following types of heating methods. Heat bands may cause hot spots on the canister where the band contacts the canister, do not evenly heat canister surfaces farther from the bands, and may not adequately heat the valve. Heating jackets and ovens heat the canister evenly but may not be able to isolate the valve from the heat source, which may cause damage to the valve if cleaning is performed at excessive temperatures (> 80 ºC). Some heating jackets or ovens allow the valve to protrude from the heated space and the valve to be exposed only to radiant heat. This may result in cold spots where higher-BP VOCs can accumulate.

10.1.4 Cycles of Evacuation and Pressurization

In general, the greater the number of evacuation and pressurization cycles, the more effective the cleaning. Canisters should be evacuated to minimally 7 kPa absolute (28 in. Hg vacuum) during each evacuation cycle, and higher vacuum is recommended. This vacuum should be maintained for a minimum of 1 min before the pressurization step. Canisters should be pressurized to ≤ 30 psig with humidified purge gas for each pressurization cycle. This pressure should be maintained for a minimum of 1 min before the next evacuation step. At least five cycles of evacuation and pressurization are recommended and 10 or more have been shown to be effective in removing stubborn oxygenated compounds such as ketones, alcohols, and aldehydes (**U.S. EPA, 2016b**). Following the principle of extraction efficiency, in which each cycle recovers a specific percentage of each compound (e.g., 85%), additional evacuation and pressurization cycles (up to 20) may be performed to achieve sufficiently clean canisters. Canisters should undergo final evacuation to ≤ 0.0067 kPa (≤ 50 mTorr). Canisters may be held at this high vacuum for a short period prior to closing the canister valves; however, extended periods (> approximately 5 min) at high vacuum with open connection to the cleaning manifold may result in diffusion of contaminants into the canisters from elsewhere in the manifold. Canisters maintained on the cleaning system at high vacuum for extended periods should be subjected to a subsequent cycle of pressurization prior to final evacuation and closing canister valves. Automated canister cleaning systems are advantageous as they can be programmed to include additional cycles or customize vacuum hold times and thresholds.

For canisters that will be stored for use at a later time, an alternative to storing the canisters under high vacuum is to pressurize the canisters with clean humidified HCF zero air or ultrapure nitrogen purge gas. The stored pressurized canisters are then evacuated to ≤ 0.0067 kPa (≤ 50 mTorr), as stated above, just prior to field deployment.

Table 10-1: Recommended Canister Cleaning Parameters

Canister Type	Pre-evacuate Canister	Temperature[a]		Humidity	Minimum Number of Pressure/Evacuation Cycles	Cycle Time
		Air Purge Gas	Nitrogen Purge Gas			
Silicon-ceramic coated	Yes	≤ 80 °C	≤ 100 °C	50%	5	Varies by system
SUMMA	Yes	≤ 100 °C	≤ 100 °C	50%	5	Varies by system
Electropolished	Yes	≤ 100 °C	≤ 100 °C	50%	5	Varies by system

[a]Do not exceed the manufacturer's recommended maximum temperatures for component parts such as valves and gauges.

10.2 Verification of Canister Cleanliness Prior to Sample Collection

Upon cleaning a batch of canisters, one or more canisters are selected to be pressurized with humidified HCF zero air or nitrogen and analyzed after a minimum of 24 h to verify acceptability of the batch for use. A batch is defined as a set of canisters connected to the same manifold and vacuum source and cleaned simultaneously. At least one canister per batch of up to eight canisters is selected for verification. For batches of 9 to16 canisters, two canisters are selected for verification; for batches of 17 to 24 canisters, three canisters are selected; and so on. This is summarized in Table 10-2.

Table 10-2: Recommended Number of Canisters Verified per Cleaning Batch

Number of Canisters in Batch	Minimum Number Selected for Cleanliness Verification
1 to 8	1
9 to 16	2
17 to 24	3
25 to 36	4

Analysis of more than one canister from each batch is highly recommended. Selection of batch blank canisters for analysis may be random or targeted. Targeted canisters should be those that previously contained high-concentration samples or high-BP VOCs. Targeted canisters may also be those that are to be requalified on a rotating basis as described in **Section 9.4**. Verification of every canister is a best practice and may be necessary for certain studies, depending on the QA requirements.

The canister cleaning criterion is ≤ 20 pptv (0.02 ppbv) per target VOC when a canister is filled to standard ambient pressure (101.3 kPa absolute or 14.7 psia). The criterion is set to meet the challenges of accurately characterizing the ever-lower concentrations of VOCs in ambient air, since the VOC background in canisters should be insignificant in comparison to expected ambient concentrations. Every effort should be made to meet the cleanliness criterion for all compounds of interest. If not achievable, the data must be flagged for those compounds not meeting the criterion.

To maintain more uniform cleaning acceptance criteria across the range of pressures that laboratories may ultimately choose to use for sample collection, the acceptance criterion will vary depending on the final pressure chosen for verifying the canister cleaning batch blanks. This criterion is based on demonstrating that the amount of any given target VOC in a canister is sufficiently low when normalized to the canister volume at ambient pressure at sea level. Filling of canisters to pressures higher than this will dilute the contaminants in the canister, so the acceptance criterion concentration will need to be proportionally reduced. These values (in pptv) are shown in Table 10-3. Canister volumes are included in the table to illustrate the approximate volume of gas in common canister sizes at various absolute pressures.

The acceptable concentration values are based on the fact that increased pressures in a canister correlate with increased volumes of gas that dilute the background contamination. All concentrations stated at the pressures listed in Table 10-3 represent a uniform concentration that is equivalent to 20 pptv at 101.3 kPa absolute (14.7 psia). For example, if a fill pressure of 207 kPa absolute (30 psia) is used for verification of canister cleanliness, then the laboratory would need to meet the cleanliness criterion of ≤ 9.8 pptv for each target compound of interest.

Table 10-3: Canister Blank Acceptance Criteria

Canister Pressure (kPa absolute)	Canister Pressure (psia)	Canister Gauge Pressure (psig)[a]	Final Air/Nitrogen Volume (approx.)				Acceptable Concentration (pptv)
			1-L Canister	2.7-L Canister	6-L Canister	15-L Canister	
310	45.0	30.3	3.1	8.3	18.4	45.9	≤ 6.5
276	40.0	25.3	2.7	7.3	16.3	40.8	≤ 7.4
241	35.0	20.3	2.4	6.4	14.3	35.7	≤ 8.4
207	30.0	15.3	2.0	5.5	12.2	30.6	≤ 9.8
172	25.0	10.3	1.7	4.6	10.2	25.5	≤ 11.8
138	20.0	5.3	1.4	3.7	8.2	20.4	≤ 14.7
101.3	**14.7**	**0**	**1.0**	**2.7**	**6.0**	**15.0**	**≤ 20.0**
89.7	13.0	-1.7	0.9	2.4	5.2	13.3	≤ 23.0

[a] Gauge pressures shown represent those expected at sea level for barometric pressure at standard pressure, 101.3 kPa absolute. Gauge pressure readings under barometric pressure conditions other than sea level will need to be adjusted based on the ambient barometric pressure at a specific location.

The equation used for calculating the canister final air/nitrogen volume (V_{calc}) is given below. It may be used to calculate approximate volumes in the canisters at a given pressure and the acceptance concentration criteria for pressures not shown in Table 10-3:

$$V_{calc} = \left(\left((P_{clean} - P_{std})/P_{std}\right) * V_{can}\right) + V_{can}$$

where:

V_{calc} = approximate calculated volume of gas contained in the canister (L)

P_{clean} = absolute pressure of canister cleaning batch blank, kPa absolute

P_{std} = 101.3 kPa absolute, standard atmospheric pressure

V_{can} = nominal canister volume (L)

The equation used for calculating the acceptable concentration criterion (C_{acc}) is given below. It may be used to calculate acceptance concentration values for pressures not shown in Table 10-3. Calculations are based on the pressure change and specified target concentration of 20 pptv relative to 101.3 kPa absolute (14.7 psia):

$$C_{acc} = C_{atm} * (P_{std}/P_{clean})$$

where:

C_{acc} = acceptance limit concentration at measured canister pressure (pptv)

C_{atm} = 20 pptv, acceptance limit concentration at standard atmospheric pressure

P_{std} = 101.3 kPa absolute, standard atmospheric pressure

P_{clean} = absolute pressure of canister cleaning batch blank, kPa absolute

For example, a laboratory pressurizes cleaned canisters to 178 kPa absolute for batch cleaning analysis. The acceptance criterion for each target VOC is ≤ 11.4 pptv (20 pptv · 101.3 kPa/178 kPa).

The canister cleanliness criterion should be commensurate with the intended measurements to be characterized. Air samples with generally higher concentrations may not require such rigorous canister cleaning. In this case, the laboratory should ensure that canister background levels are kept to ≤ 5% of the concentration measured in the sample.

Canisters that meet the batch blank criterion are ready to be evacuated for use. If one canister representing the batch fails, either the entire batch can be recleaned (recommended) or two additional canisters from the batch can be selected and analyzed to determine whether the batch meets the criterion. If both canisters meet the cleanliness criterion, only the failing canister should be recleaned. If either canister fails, however, the entire batch should be recleaned. If each cleaned canister from the batch is tested, only those canisters that fail the criterion should be subjected to further cleaning. Actions should be taken to investigate an ongoing failure of batch blanks to meet the cleanliness criterion. In a system where batch blanks normally meet the cleanliness verification criterion, continued failure of batch blanks may indicate that the purge gas, cleaning manifold, or other system components have become contaminated. If it is determined that failures are related to specific canisters, more aggressive cleaning techniques such as water rinses or other rinses as specified by manufacturers may be tried.

10.3 Cleaning of Glass Bottles

Prior to cleaning glass bottles, vacuum or pressurization must be released and the vessel must be at atmospheric pressure. Bottles containing standards or unknown contents exceeding ambient pressure should be vented into a fume hood or other exhaust outlet. Once at atmospheric pressure, the cap and valving hardware are removed from the bottle. Bottles are then placed into a heated oven at approximately 75 °C and flushed with humidified purge gas for approximately 12 h. Valving hardware should be connected to a source of humidified purge gas and flushed for several hours. Following cleaning, the bottle and valving should be reassembled, the bottle evacuated to ≤ 0.0067 kPa absolute (≤ 50 mTorr), the bottle filled with a clean diluent gas to the pressure of ambient field samples, and the contents analyzed to ensure all target VOCs are ≤ 20 pptv at standard ambient pressure (101.3 kPa absolute), as discussed in Section 10.2. Once demonstrated to be clean, the bottle assembly is ready for evacuation and field deployment.

10.4 Canister Preventive Maintenance and Best Practices

Maintenance of canisters involves a combination of preventive and routine actions and best practices. The following subsections detail activities and best practices related to canister qualification, sample collection, cleaning, and general handling.

10.4.1 Particulate Filters

Whole air sampling into canisters should be performed using a particulate filter, as discussed in Section 7.3, because particulates are difficult to remove with typical evacuation and pressurization cleaning techniques once they have been drawn into a canister. With use, particulate filters will trap airborne particles and become partially clogged, potentially impacting the concentrations of compounds being drawn into the canister. Particulate filters should be cleaned or replaced frequently to reduce the likelihood of negative impacts on the air sample being collected. Replacement of the filter element is preferred due to the ease of replacement and associated difficulty with cleaning and decontaminating the filter element. If cleaned, sintered metal filters should be removed from the sampling inlet and sonicated in water and/or methanol for 15 min, after which they should be rinsed with fresh methanol, dried in an oven (preferably a vacuum oven) set to approximately 50 °C for a minimum of 12 h, and flushed for several hours with humidified HCF zero air or nitrogen.

Particulate residue inside a canister creates active sites that may have a detrimental effect on target VOC recovery. Particulates may deposit into canister valves, potentially damaging threads and seals, which results in leaks. Furthermore, typical cleaning techniques that employ evacuation and pressurization of canisters do little to remove particulate residue interferences, which may result in canister compound behavior indistinguishable from that caused by degradation of the interior surfaces of the canister. Canisters that cannot be remediated successfully may need to be retired. Alternatively, canister manufacturers offer canister reconditioning and valve replacement parts or services that can restore canisters to new condition.

10.4.2 Canister Valves

Valves currently supplied with new canisters have been specifically designed for canister use to address common issues with early valves that were adapted from other technologies. Early valves were typically of a stainless-steel bellows design, and overtightening the valve damaged valve seats, which caused leaks. Older SUMMA canisters still in service may have valves of the original bellows design, so care must be taken not to overtighten them. Newer valves are generally of a stainless-steel diaphragm design that are often silicon-ceramic coated and have minimal wetted surface area. These valves are less prone to damage from improper tightening; however, the proper torque required to close the valve depends on the specific valve design, and the manufacturer’s recommendation should be followed. Valves should only be hand tightened to close—never tightened with tools (e.g., adjustable or locking pliers).

Faulty or leaking valves generally fall into two categories: (1) those with damaged internal valve seat components or (2) those with damaged external threads. Valves with damaged valve seat components should either be replaced entirely or rebuilt using kits available from the manufacturer. Valves with damaged external threads due to careless handling or deformation from overtightening of sampling inlets require replacement of the entire valve. Using a thread chaser to restore damaged threads is rarely effective in reversing the thread damage and is not recommended.

When not connected for cleaning, sample collection, or analysis, the canister valve opening should always be capped with a brass plug to protect the exposed threads and to ensure particulates do not deposit into the valve opening. Care must be used to properly tighten the brass plugs and to attach the canister to sampling devices and cleaning ovens to minimize chances of distortion of the threads. To avoid galling or cross-threading the threads of the valve connection, caps, plugs, or nuts should be finger tightened and then snugged slightly with a wrench.

10.5 General Canister Handling

Canisters should be handled with care to ensure that the interior canister surface is not compromised, the valve-to-canister connection remains intact, and weld integrity is maintained. Excessive torque on unbraced canister valve stems when making connections to the canister may cause damage and potentially leaks in the valve stem weld or at the ferrule sealing the canister valve and canister stem. Shocks resulting in dents to the surface of the canister may damage welds or create small cracks in the interior canister surface that may expose active sites.

Shipment of canisters in protective hard-shell boxes and/or sturdy cardboard boxes is required to ensure canister longevity. Boxes that have lost integrity or rigidity should be replaced.

10.6 Cleaning of Sampling Components

The manufacturer’s instructions should be followed for cleaning components such as flow controllers and sampling unit parts. Note that disassembly of such instruments may void warranties or calibrations.

Metallic and glass components of sampling units, canister cleaning apparatuses, and wetted pathways such as stainless-steel tubing, sintered particulate filters, critical orifices, and connecting components should be flushed with humidified HCF zero air or ultrapure nitrogen to remove contamination. They may be further cleaned by disassembling and sonicating in water and/or methanol for 15 min, after which they should be rinsed with fresh methanol and dried in an oven (preferably a vacuum oven) set to approximately 50 °C for a minimum of 12 h. Ovens may be set to higher temperatures if the components can withstand the temperatures. To avoid damage to deactivated stainless-steel components due to oxidation in the presence of oxygen-containing atmospheres (e.g., HCF zero air), components treated with silicon-ceramic coatings should not be heated above 80 °C unless evacuated or under an inert atmosphere (e.g., nitrogen).

Nonmetallic components such as Viton seals and O-rings should be disassembled and inspected for cracks, abrasions, and residue (such as from PM) and sonicated in ASTM Type I water for 15 min. After sonication, components should be rinsed with fresh ASTM Type I water and dried in an oven (preferably a vacuum oven) set to approximately 50 °C for a minimum of 12 h.

Following drying, components should be inspected (e.g., to be sure critical orifices are not cracked or compromised), reassembled, and flushed with humidified HCF air or ultrapure nitrogen for at least 12 h.

11 Sample Collection

Before any sample collection is undertaken, decisions need to be made and activities performed to ensure success. Planning and attention to details are important for the generation of high-quality and trusted data. This section addresses the application of the many components and operations previously discussed in Sections 7, 9, and 10. In addition to the actual collection of samples, the associated presampling and postsampling activities are described.

11.1 Presampling Activities

11.1.1 Preparing SOPs and Quality Assurance Project Plan

Prior to collection of samples, SOPs should be prepared for each process (e.g., canister cleaning, standards preparation, operation of canister air sampling device) specific to the project or program. Additionally, a quality assurance project plan should be prepared that establishes the overall project details and the QA and QC aspects of the process.

11.1.2 Determining Sample Collection Specifics

- Determine the type of sampling to be conducted (subatmospheric, grab, or pressurized).
- Determine the type of sample collection apparatus to be used (MFCD, MFC, commercially available rack-mount or bench-top sampling system). Refer to Section 7.3 for discussion.
- Determine the number of canisters and sampling apparatus required.
- Determine the required sampling time and flow rates needed. *Note: Flow controllers should be calibrated against a reference flow standard prior to field deployment. If the flow controllers are calibrated and shipped to a sampling location, flows must be verified at local conditions and adjusted as necessary prior to deployment.*
  - ► For subatmospheric sampling, refer to Table 11-1 for typical sampling flow rates for commercially available MFCDs and common canister sizes and sampling times.

Table 11-1: Typical Sampling Flow Rates (mL/min) for Subatmospheric Sampling Using Common MFCDs

Canister Size (L)	Sampling Time					
	1 h	8 h	12 h	24 h	1 week	2 weeks
1	13.2 to 14.9	1.6 to 1.9	1.1 to 1.2	0.56 to 0.62	—	—
2.7	35.5 to 40.2	4.4 to 5.0	3.0 to 3.4	1.5 to 1.7	0.21 to 0.24	—
3	39.5 to 44.7	4.9 to 5.6	3.3 to 3.7	1.6 to 1.9	0.23 to 0.27	—
3.2	42.1 to 47.2	5.3 to 6.0	3.5 to 4.0	1.8 to 2.0	0.25 to 0.28	—
6	78.9 to 89.5	9.9 to 11.2	6.6 to 7.5	3.3 to 3.7	0.47 to 0.53	0.23 to 0.27
15	197.4 to 223.7	24.7 to 28.0	16.4 to 18.6	8.2 to 9.3	1.8 to 1.3	0.59 to 0.67

Note: Values populating Table 11-1 are calculated based on the actual flow vs. pressure plots of MFCDs 1 and 2 shown in Figure 9-2. Flow adjustments may need to be made for sampling at higher elevations or at low temperatures. These flows should result in time-integrated canister samples at a slight vacuum (10 to 20 kPa below ambient or 3 to 6 in. Hg vacuum). For the MFCDs, the pressure at which the flow controller ceases to maintain constant flow is used as the final canister pressure. It is recommended that laboratories determine the flow vs. pressure characteristics for MFCDs in their inventories and apply the results as appropriate to establish the sampling flow rates for desired sampling volumes and times.

  - ► For samples collected at high elevations, the flow rates may need to be adjusted to account for changes in ambient pressures due to elevation. As a general rule, approximately a 0.2 L decrease in potential collection volume occurs for each 305-m (1000-ft) rise in elevation. For example, at 1524 m (5000 ft), a maximum of approximately 5 L of gas at standard conditions can be collected in a 6-L canister due to the lower ambient pressure and the differential required to drive MFCDs. Larger volumes can be collected if pumps are used.

- ► For pressurized sampling and for canister sizes or times not listed in Table 11-1, the following equation can be used to calculate the required flow rate at local conditions for sample collection. The flow rate is determined so the canister is filled to the desired final pressure over the specified sampling period. Note that this formula does not correct for differences in temperature:

$$F = \frac{P_c \cdot V}{P_a \cdot D}$$

where:

F = flow rate (mL/min) at local conditions

P_c = final absolute canister pressure (kPa absolute)

V = volume of the canister (mL) at standard conditions (101.3 kPa absolute and 25 °C)

P_a = atmospheric pressure (kPa absolute) at time of sampling

D = sampling duration (min)

For example, if a 6-L canister is to be filled to 21 kPa (3 psi) above ambient (122 kPa [17.7 psia] for ambient pressure of 101.3 kPa [14.7 psia]) in 24 h, the flow rate can be calculated as follows:

$$F = \frac{122\ \text{kPa} \cdot 6000\ \text{mL}}{101.3\ \text{kPa} \cdot 1440\ \text{min}} = 5.0\ \text{mL/min}$$

Note: Users are strongly encouraged to limit final pressures of pressurized samples to ≤ 21 kPa above ambient pressure (3 psig) to minimize the likelihood of condensation within the canister as discussed in Section 6.2.

11.1.3 Preparing Field Materials and Supplies for Use

- Clean canisters and verify that cleanliness and vacuum criteria are met (refer to Section 10.2 and Table 10-3).
- If canisters were previously cleaned and stored pressurized while awaiting use, evacuate prior to field deployment. If canisters were stored at vacuum, verify that they still meet vacuum threshold requirements.

Note: It is recommended that at the time of canister cleaning and preparation, an identification (ID) tag such as a 2 3/8-in. x 4 3/4-in. manila or plastic shipping tag with wire (or similar tag) be attached to each canister to provide a convenient place to record the cleaning date, canister pressure, and other information associated with each canister. This also provides a suitable location to attach sample labels without defacing the canister.

- Establish sample codes (unique identifiers) and develop chain of custody (COC)/sample collection data form(s) (hardcopy and/or electronic).
- *(Optional)* Prepare field QC samples (canister field blanks and field spikes) by filling canisters with clean air or standards as described in Section 15.3.5.

- Clean and verify the cleanliness of sample collection devices (MFCD, rack-mount or bench-top system, etc.) that will be used. Ensure a clean particulate filter is in place.
- Preset flow rates and test the operation of sample collection devices.
- If timers and solenoid valves are used, test their operation. Ensure batteries have adequate voltage to operate the timer and solenoid for the duration of sample collection or replace as necessary. Preprogram time/day and sampling times if practical.
- Prepare at least one backup timer and sample collection device for use in the event that problems arise during deployment (e.g., failed solenoid valve) and replacement is required.
- Assemble wrenches and other needed tools, flow calibration devices, and spare components such as batteries, fittings, etc., to accommodate moderate field repairs in the event of problems during deployment.

11.2 Sample Setup Activities

11.2.1 Extra Samples

It may be desirable to collect a few extra samples at the beginning of a study or when sampling in a new area to provide additional analyses that address analytical method development such as unexpected target compounds, tweaks to analysis volumes, or fine-tuning of GC programs for compound separations. Collection of extra samples depends on the specific project and may not be necessary as generally multiple analyses can be made from a single canister, and one of the initial collected canisters may suffice for this purpose.

11.2.2 Sampling Site Requirements

Specific site requirements generally depend on the project goals; regardless of the goals, it is important that sampler placement provides samples that are representative of the air being monitored. Refer to Section 7.3.2 for a general description of time-integrated sampling apparatus and general sampling considerations.

11.2.2.1 Existing Air Monitoring Shelters

Many sites where canister samples are collected are associated with existing air monitoring shelters that have been established using EPA guidelines as outlined in the *Code of Federal Regulations,* Network Design Criteria for Ambient Air Quality Monitoring (**40 CFR Part 58 Appendices D and E**), and Sections 6 and 7 of *EPA's Quality Assurance Handbook for Air Pollution Measurement Systems* (**U.S. EPA, 2017**). The requirements for these sites have generally already been determined, and the primary VOC canister sampling decisions deal with whether the air samples are drawn from a multiuse manifold or a dedicated collection line. The canisters are typically placed inside a climate-controlled shelter. For established shelters, the manifold/collection line intake should be positioned so that it is not impacted by local sources such as roadways; parking lots (vehicle exhaust); shelter roofing materials; heating, ventilation, and air conditioning units/building exhausts; outdoor fuel storage areas; and outdoor smoking areas, to name a few. Also, there should be no nearby obstructions such as buildings or vegetation that block air flow. Manifold or dedicated sampling line intakes must be located to avoid bias to the sample. Intakes must extend beyond building overhangs.

11.2.2.2 Special Studies or Investigations

For air samples collected for special studies or investigations using temporary sampling sites, the following criteria should be considered:

- The canister should be placed in a secure location that protects the canister and sampling inlet from unwanted tampering, damage, or theft.
- Canister and sampling inlets are typically designed to withstand outdoor elements (rain, snow, sun exposure) but should be further protected from the elements by being placed under shelter if possible. Air flow around inlets should not be restricted, and inlets should not be located under building overhangs. The level of protection required will depend on the type of sampling devices used.
- Canister MFCD inlets and manifold intakes should be protected to prevent rain from being drawn directly into the MFCD or manifold. Commercial units are typically designed to address this.
- Consider the use of sturdy speaker tripod stands or metal sign posts modified with hook bolts to hang the canisters. Be aware that any posts that are driven into the ground must be in an area known to be free of underground wiring and/or plumbing.
- There should be no biasing sources in the immediate vicinity, such as outdoor smoking areas; vehicle exhaust; heating, ventilation, and air conditioning units/building exhaust; outdoor fuel storage areas; shelter roofing materials; or exhaust from other sample collection devices. In general, horizontal distances should be > 10 m from biasing sources.
- Placement near vegetation or structures that block or significantly restrict air flow should be avoided.
- Inlet height placement is generally project specific. At temporary locations such as residential indoor or outdoor monitoring sites, inlet heights should be in the breathing zone, approximately 1 to 2 m above ground level. For special studies conducted at established monitoring shelters, inlet heights generally should be between 2 and 6 m. For collection of collocated samples, inlets should be placed as close together as possible, generally within 12 in. (both vertically and horizontally).
- Length and diameter of any tubing used to connect to manifolds or penetrate through shelters should be minimized to maximize linear velocity, thus minimizing residence time of the sampled air in the sampling line. Use inert silicon-ceramic–coated tubing (preferred) or high-grade stainless steel for this purpose. Do not use PTFE, PFA, FEP, or polyethylene tubing. Use of tubing with 1/16- or 1/8-in. outer diameter is recommended.

11.2.3 Sample Setup and Deployment

Whether using manual or automated techniques to collect canister air samples, certain prescribed steps should be followed to ensure successful deployment and sample collection. Deployment of canisters with insufficient starting vacuums, use of improperly functioning sampling apparatus, or improperly labeled samples may result in invalid samples.

Canisters scheduled for deployment can be tracked from cleaning to the point of deployment using the manufacturer-assigned serial number found on each canister, an identifier created by the laboratory's information management system, or some other convention. Regardless of the identifier used, it must be unique. As noted in Section 11.1.3 an ID tag such as a 2 3/8-in. x 4 3/4-in. manila or plastic shipping tag with wire (or similar tag) provides a convenient place to record the canister identifier, cleaning date, canister pressure, and other information associated with each canister until the time of deployment.

At the time of successful deployment, the canister must be assigned a unique sample code that either includes information or links to information providing when and where the sample was collected. This code should also link the sample with any other pertinent collection information and should be affixed to the canister or canister tag as a label that is water resistant or waterproof. A COC form (see Figure 11-1 for an example) should accompany the canisters during shipment and collection to document sample handling and transport. COC forms may be electronic or hard copy.

Canister vacuum should be verified prior to deployment and must be measured at the time of setup to minimize contamination, bias, and/or incomplete sample volumes due to leakage and inadequate starting vacuum. If using a sampling apparatus with an incorporated calibrated vacuum/pressure gauge, the canister vacuum should be read and recorded at the time the canister is connected to the sampling apparatus. Automated computerized sampling units may include routines to facilitate measuring and verifying canister vacuum upon sample setup. If the sampling apparatus does not have an incorporated gauge or if the gauge is not calibrated or functioning properly, the vacuum should be measured and recorded using an auxiliary calibrated digital or analog gauge just prior to connecting the canister to the sampling apparatus. Automated rack-mount and bench-top canister samplers may be programmed to automatically test and record vacuum prior to sample collection.

Starting canister pressure should ideally be high vacuum (≤ 0.0067 kPa absolute or ≤ 50 mTorr) and should not permit more than an overall 5% dilution of the sample collected into the canister. Such a dilution is equivalent to a starting canister pressure of approximately 4 kPa absolute (0.6 psia) for samples collected to a subatmospheric pressure of 81 kPa absolute (11.7 psia) or approximately 7 kPa absolute (1 psia) for samples collected to 122 kPa absolute (17.7 psia). Starting canister pressure should not exceed 7 kPa absolute, which is equivalent to 28 in. Hg vacuum at standard barometric pressure.

The sampling apparatus should be tested for proper connection to the canister and the connection verified to be leak free. If battery-powered timers and solenoids are used, verify that sufficient battery charge is available and that programmed times are correct.

Perform the following steps at the time of sample setup and deployment:

1. Ensure each canister is labeled with unique canister and sample ID codes.
2. Measure and record the canister vacuum to verify that the canister has not leaked and has sufficient vacuum to collect the sample (refer to Table 11-2). Replace the canister if the initial vacuum criterion is not met.
3. Connect the canister to the sampling apparatus (if not already performed as part of the measurement of the canister vacuum).
4. Conduct a leak check.
    - For MFCDs:
        - Tightly cap the inlet.
        - If the gauge is upstream of the solenoid, manually activate the solenoid (if so equipped).
        - Open and close the canister valve to generate a vacuum at the gauge.

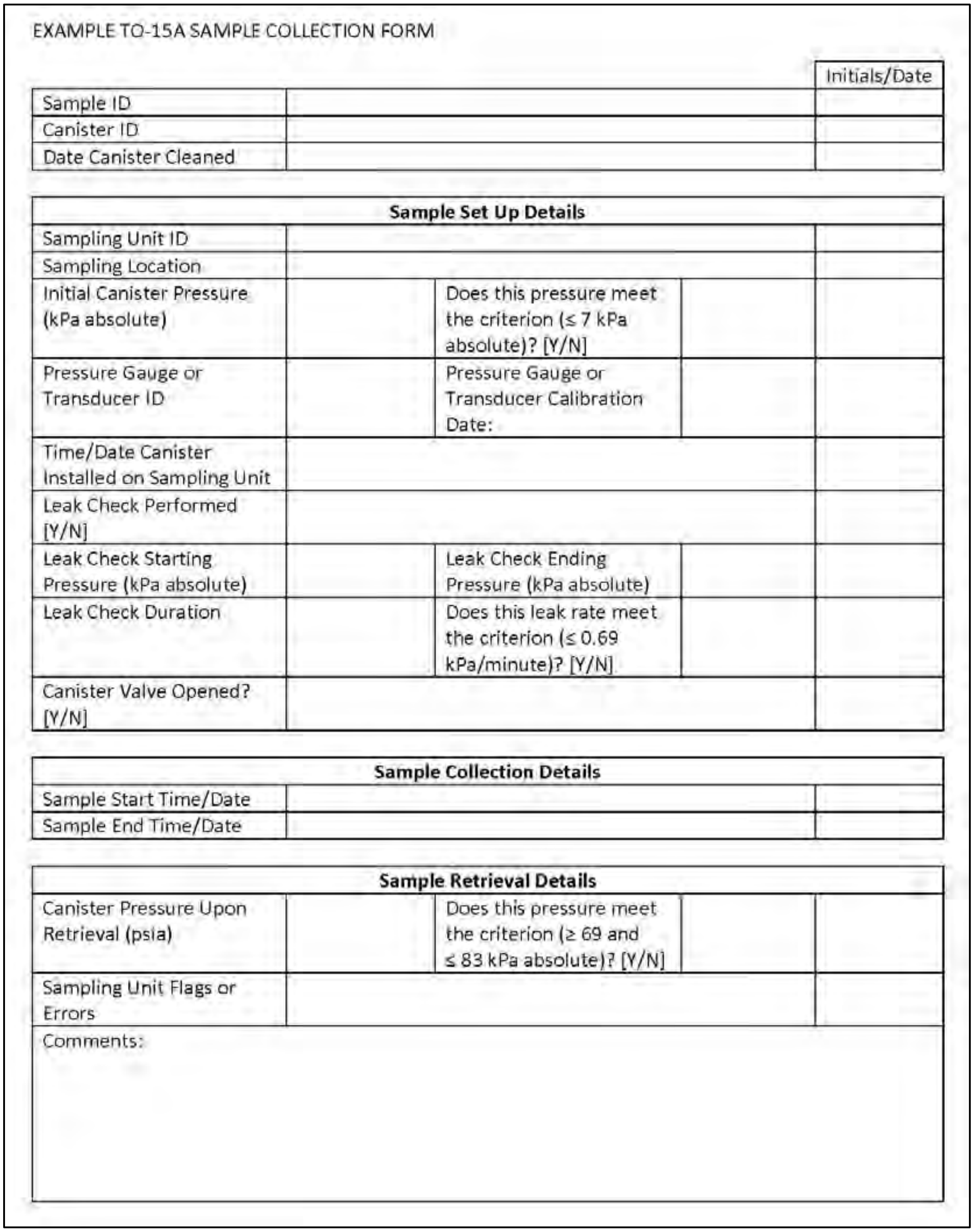
    - Observe the gauge to assess the leak rate. There should be no perceivable pressure increase.
    - If there is a leak, gently snug the fittings and retest. If the leak persists, replace the sampling apparatus and/or canister and test.
    - Following a successful leak check, remove the inlet cap.
  - For rack-mount or bench-top sampling instruments:
    - Follow the manufacturer's instructions for performing onboard automated leak check routines, if so equipped.
    - Open and close the canister valve, or, if so equipped, activate the vacuum pump to generate a vacuum in the system.
    - Observe the gauge to assess the leak rate.

5. Open the canister valve.
6. Record the time that the valve is opened as the start time if the sampling apparatus is manually operated. If the sampling apparatus is controlled by a timer, record the time that the timer is scheduled to turn on as the start time.
7. If the sampling apparatus uses a timer to activate the solenoid, verify the timer program and flow rate (if possible). (Refer to **Section 9.2.2** for a discussion on flow measurements.)
8. Document pertinent information (listed below) on the COC/sample collection data form(s) and canister tag.

Sampling details should be documented on the COC/sample collection data form(s) (refer to the example form shown in Figure 11-1). The following are typical parameters that should be recorded along with the operator's initials and date recorded:

- Unique sample ID
- Unique canister ID
- Date canister cleaned
- Unique sampling unit ID (MFCD, orifice, rack-mount or bench-top unit, and channel)
- Initial canister vacuum measured at time of sample setup
- Gauge/transducer ID used for initial canister vacuum measurement
- Acceptable canister vacuum threshold met/not met (optional)
- Date/time canister was installed on sampling unit
- Performance of a leak check and pass/fail status
- Confirmation of opening canister valve (as applicable)
- Sample collection start time and date
- Sample collection end time and date
- Sample retrieval time and date (may be the same or different from collection end time)
- Canister vacuum/pressure upon retrieval
- Acceptable final canister pressure threshold met/not met *(optional)*
- Sampling flags or error messages provided by the sampling unit
- Comments such as unusual events or conditions that may impact sample results

Sample collection details, or a portion of them, may also be recorded on the tag attached to the canister (see Section 11.1.3). It is recommended that the following information, at a minimum, be recorded on the canister tag: unique sample ID; canister ID; date, time, and vacuum at time of deployment; and date, time and vacuum/pressure at time of retrieval.



EXAMPLE TO-15A SAMPLE COLLECTION FORM

		Initials/Date
Sample ID		
Canister ID		
Date Canister Cleaned		

Sample Set Up Details				
Sampling Unit ID				
Sampling Location				
Initial Canister Pressure (kPa absolute)		Does this pressure meet the criterion (≤ 7 kPa absolute)? [Y/N]		
Pressure Gauge or Transducer ID		Pressure Gauge or Transducer Calibration Date:		
Time/Date Canister Installed on Sampling Unit				
Leak Check Performed [Y/N]				
Leak Check Starting Pressure (kPa absolute)		Leak Check Ending Pressure (kPa absolute)		
Leak Check Duration		Does this leak rate meet the criterion (≤ 0.69 kPa/minute)? [Y/N]		
Canister Valve Opened? [Y/N]				

Sample Collection Details		
Sample Start Time/Date		
Sample End Time/Date		

Sample Retrieval Details				
Canister Pressure Upon Retrieval (psia)		Does this pressure meet the criterion (≥ 69 and ≤ 83 kPa absolute)? [Y/N]		
Sampling Unit Flags or Errors				

Comments:

Figure 11-1: Example TO-15A COC/sample collection data form.

11.3 Sample Retrieval

If canister air samples are collected using a manually operated sampling apparatus, meaning that a valve (e.g., the canister valve) must be manually opened and closed to collect the sample, it is important that the operator be present at the designated time to close the canister valve. If the samples are collected using a flow control device attached to a programmed solenoid valve timer, the solenoid valve will close at the programmed time and the operator does not need to be present at the designated stop time to close the canister valve. However, the operator should return within a reasonable amount of time (within 1 to 2 days) to close the canister valve. Operators should ensure that the solenoid is not programmed to open again prior to retrieval.

If using a manually operated sampling apparatus with a calibrated vacuum/pressure gauge attached, the vacuum/pressure reading should be recorded before closing the canister valve. For sampling apparatus with a programmed solenoid timer, if the gauge is on the upstream side of the solenoid and the solenoid is closed, a temporary override (or manual activation) will be necessary to open the solenoid to measure the vacuum/pressure. For automated sampling devices with vacuum/pressure gauges downstream of the solenoid, the vacuum/pressure can be read directly. For sampling systems without gauges or with improperly functioning gauges, or as an alternative to using an incorporated gauge, the canister vacuum/pressure can be measured using an auxiliary calibrated digital or analog vacuum/pressure gauge.

The following steps should be performed at the time of retrieval for sampling apparatus with properly functioning calibrated incorporated vacuum/pressure gauges:

1. Read and record the final canister vacuum/pressure measurement.
2. Close the canister valve (and record the time if closing the valve concludes the sampling period).
3. Disconnect the sampling apparatus from the canister.
4. Cap the canister valve inlet with a brass plug cap.

The following steps are performed at the time of retrieval when an auxiliary digital or analog vacuum/pressure gauge is used for vacuum/pressure measurements:

1. Close the canister valve.
2. Record the sampling end time (if closing the canister valve stops the sample collection).
3. Disconnect the sampling apparatus from the canister.
4. Attach the calibrated vacuum/pressure gauge.
5. Momentarily open the canister valve.
6. Allow the vacuum/pressure reading to stabilize and record the final measurement.
7. Close the canister valve and remove the gauge.
8. Cap the canister valve inlet with a brass plug cap.

The following steps are performed at the time of retrieval when an automated rack-mount or bench-top system is used for sample collection:

1. Close the canister valve(s).
2. Disconnect the canister(s) from the sampling apparatus.
3. Cap the canister valve inlet with a brass plug cap.

4. Retrieve and record pertinent sampling information stored by the system on the COC/sample collection data form(s).
5. Transfer electronic data collection files from the sampler system to a backup device.

The ending vacuum/pressure reading is compared to the expected ending reading to evaluate whether the sample was collected appropriately. Refer to Table 11-2 for typical pressure ranges for collected samples. An additional conversion chart is provided in Appendix A. Sampling units that log the sampling flow rate and canister pressure should be checked for error messages or alarms (flags) that may be generated due to sampling errors. As a final step, the canister air samples should be prepared and secured for the transport method of choice.

Table 11-2: Key Pressure Measurements and Gauge Ranges Expressed in Commonly Used Units (approximate conversions)

	Typical Pressure Use Ranges							
	kPa		psi		in. Hg		mm Hg (Torr)	
Measurement	**Absolute**	**Gauge**[a]	**Absolute**	**Gauge**[a]	**Absolute**	**Gauge**[a]	**Absolute**	**Gauge**[a]
Cleaning – final evacuation	≤ 0.0067	~ –101	≤ 0.001	~ –14.7	≤ 0.02	~ –29.9	≤ 0.05 (≤ 50 mTorr)	~ –760
Canister vacuum prior to sample collection	≤ 7	≤ ~ –94.1	≤ 1	≤ ~ –13.7	≤ 2	≤ ~ –28	≤ 52	≤ ~ –708
Subatmospheric sampling pressure range at completion	64 to 88	–37 to –13	9 to 13	–5 to –2	19 to 26	–11 to –4	484 to 662	–276 to –98
Pressurized sampling pressure range at completion[b]	110 to 122	9 to 21	16 to 18	1 to 3	32 to 36	2 to 6	827 to 915	67 to 155

[a] Gauge reading = (absolute pressure) – (atmospheric pressure at sea level); conversions obtained from the ENDMEMO website, http://www.endmemo.com/.

[b] Users of the method are cautioned that pressurized sampling methods may result in condensed water within the canister, which may have negative effects on the integrity of the VOCs in the sample.

12 Canister Receipt and Preparation for Analysis

12.1 Measurement of Canister Receipt Pressure

Upon receipt at the laboratory, the sample custodian should review the sample collection information documented on the COC/sample collection data form(s) for completeness and accuracy. The sample custodian should also compare the canister label with the sample collection data sheet and verify that the canister and sample IDs are correct, that the sample collection start and stop times are reasonable, and that the starting and ending sample pressures are as expected.

The canister pressure is then measured with a calibrated vacuum/pressure gauge or transducer and recorded. For samples collected to subatmospheric pressure, the measured canister absolute pressure must be within ±3.5 kPa (0.5 psi) of that measured upon retrieval. This criterion permits a change of pressure (and therefore volume change, or potential dilution) equivalent to approximately 5% of the total pressure of a sample collected to 90 kPa absolute. Pressure differences exceeding this criterion indicate the canister has leaked, permitting contamination of the collected sample. Results from subatmospheric pressure samples exhibiting leaks should be flagged as invalid unless the pressure difference can be confidently attributed to a temperature difference from sample collection to measurement in the laboratory. Note that for samples collected in a temperature-controlled monitoring shelter, a temperature difference is not expected to contribute to a discernible pressure change.

For canisters collected to pressures above atmospheric pressure, the absolute pressure measured upon receipt should ideally also be within ±3.5 kPa (0.5 psi) of that measured at sample retrieval but should minimally exceed ambient pressure at the laboratory. Results from positive pressure samples that have leaked to atmospheric pressure may be suspect and should, at a minimum, be flagged as an “estimated” value for conditional use unless the pressure difference can be confidently attributed to a temperature difference from collection location to laboratory pressure measurement as noted above for subatmospheric pressure sampling.

12.2 Dilution of Canister Samples

Canister samples collected at subatmospheric pressures may require pressurization with HCF zero air or ultrapure nitrogen to provide sufficient pressure for analysis. Minimum sample pressures will depend on the size of the canister and the capability of the preconcentrator to remove the desired aliquot of the sample and will be indicated by the instrument manufacturer. Canisters with target VOC concentrations exceeding the calibration curve range may also require dilution.

When such dilution is performed, the source of diluent gas must be demonstrated to be free of contaminants to ensure that the dilution process does not contaminate the collected samples. This may be done by collecting diluent gas in a separate certified clean canister as a dilution blank (DB) and analyzing. The DB should not be prepared through a dilution system used for preparing standards. The concentrations of the target VOCs in the DB must be < 20 pptv. Ideally a DB is prepared and analyzed with each set of samples that are diluted and at a minimum is prepared and analyzed when the source gas and/or filters are changed.

The canister pressure must be measured with a calibrated vacuum/pressure gauge or pressure transducer just prior to dilution and immediately following dilution. A canister dilution correction factor (CDCF) is calculated from the two absolute pressure readings as follows:

$$\mathrm{CDCF} = \frac{\mathrm{P_d}}{\mathrm{P_i}}$$

where:

P_d = pressure of the canister following dilution (kPa)

P_i = pressure of the canister immediately preceding dilution (kPa)

Diluted canisters should be equilibrated minimally overnight and preferably 24 h before analysis.

13 Preparation of Calibration Standards

Calibration standards will typically be prepared from stock standard gases by dilution using humidified HCF zero air or ultrapure nitrogen. Standards may be prepared by dynamic or static dilution methods employing the equipment described in **Section 7.6.4**. Dynamic dilution techniques involve blending the standard gas mixture with the diluent gas in a manifold prior to transfer to the canister. Static dilution techniques involve dilution of the standard gas mixture with the diluent gas directly in the canister. Standards should be humidified to approximately 40% to 50% RH. Following preparation, it is recommended that each canister be allowed to equilibrate for a minimum of 24 h prior to an initial analysis.

13.1 Humidification of Canisters

The humidity of the gas within a canister is important in the preparation of calibration standards and impacts analysis in several ways. First, water vapor within a canister displaces gases from the interior surfaces of the canister, retaining them in the gas phase. This is especially important for VOCs with higher BPs and for electropolished canisters (**Ochiai et al., 2002**). Insufficient humidification of calibration standards may result in incomplete quantitative transfer of VOCs from the calibration manifold and/or canister(s) containing the calibration mixture to the preconcentrator. Insufficient humidification may also impact transfer to or from subsequent canisters when canister gas standards serve as intermediates for preparing lower level standards. Second, depending on the meteorological conditions at the time of collection, ambient air samples will include some humidity, typically above 10% RH and may be saturated to 100% RH. Since matrix matching between collected samples and the associated standards and blanks is desirable, standard and blank canisters should be humidified to approximately 40% to 50% RH at ambient laboratory temperature. The range of 40% to 50% RH represents a practical compromise to ensure sufficient humidification given the impracticality of matching humidity for the variety of humidity levels possible in collected samples. This helps ensure that hydrophilic and high-BP VOCs meet relevant method performance specifications.

Humidification can be accomplished in several ways: employing a bubbler or impinger within the dilution gas stream, addition of deionized water to the canister, or a combination of these two methods. Adding water to canisters with a syringe via rubber septum is not recommended as the syringe needle can core the septum and result in deposits of rubber into the canister and valve. This may lead to potentially irreproducible and biased VOC recoveries from the canister. For direct injection of water into a canister with a syringe, a high-pressure PTFE-sealed septum (such as a Merlin Microseal [Merlin Instrument Company, Newark, DE]) should be installed on the canister. For canisters to be connected to a gas source for pressurization via a dynamic or static dilution system, the water can be added to the valve opening of the evacuated canister prior to connecting to the dilution system. Once connected, the valve is opened, and the water is pulled into the canister along with the diluted standard gas.

The following formula is used to determine the volume of water to add to a canister to achieve the desired % RH (**Herrington, 2013**):

$$\mathrm{V_w = D_{sat} \cdot RH_d \cdot V_c \cdot \frac{P_c}{P_s} \cdot \frac{1}{D_w}}$$

where:

V_w = water volume to add to canister (µL)
D_{sat} = saturation vapor density of water (mg/µL) at ambient laboratory temperature (refer to Table 13-1)
RH_d = desired RH level expressed as a decimal
V_c = nominal internal volume of canister (L)
P_c = final pressure of canister (kPa absolute)
P_s = standard ambient pressure (101.3 kPa absolute)
D_w = density of water (1 mg/µL)

*Notes: The formula above does not correct the density of water for the ambient temperature and assumes the density of water to be 1 g/mL. It also assumes that 100% of the added water is in the gas phase. Water may condense inside the canister if the temperature is reduced to the point at which the amount of water in the canister exceeds the saturation density. For more information regarding canister humidity, refer to "Variation of the Relative Humidity of Air Released from Canisters after Ambient Sampling" (**McClenny et al., 1999**).*

Table 13-1: Water Saturation Vapor Density at Various Temperatures

Temperature (°C)	Water Saturation Vapor Density (mg/L)[a]
15	12.8
16	13.6
17	14.4
18	15.3
19	16.3
20	17.3
21	18.3
22	19.4
23	20.6
24	21.8
25	23.1
26	24.4
27	25.9
28	27.3
29	28.9
30	30.5
31	32.2
32	34.0
33	35.8

[a] Values are generated according to the following formula (**Nave, 2017**):

$$vapor\ density\ (mg/L) = 5.018 + 0.32321 \cdot T + 8.1847 \times 10^{-3} T^2 + 3.1243 \times 10^{-4} T^3$$

where: T = temperature in °C

Example:

An analyst prepares a VOC standard in a 6-L canister, diluting to a final pressure of 202.6 kPa (2 ata) with dry HCF zero air. The laboratory temperature is 25 °C and the analyst wants the standard to be 50% RH. The volume of water needed is calculated as follows:

$$\mathrm{V_W} = 23.1\ \mathrm{mg/L} \cdot 0.50 \cdot 6\ \mathrm{L} \cdot 1\ \mathrm{\mu L/mg} = 139\ \mathrm{\mu L}$$

13.2 Dynamic Dilution

13.2.1 Calibration of Dynamic Dilution Systems

For dynamic dilution, the system requires a separate flow control device for the diluent gas and each gas standard to be diluted as well as a mixing area such as a manifold where the gases can be sufficiently mixed before introduction to the preconcentrator or canister. Dynamic dilution gas flows are typically controlled by employing calibrated electronic MFCs with flow ranges appropriate to achieve the desired dilution factor(s).

MFCs in dynamic dilution systems should be calibrated, with the calibration verified at least annually by comparison to a certified or primary reference flow standard. MFCs that fail a calibration check criterion of ±2% should be recalibrated. For commercially available dilution instruments, the manufacturer’s instructions should be followed for recalibration. For laboratory-built systems that employ MFCs, the controllers may either be removed and shipped to a manufacturer or third party for recertification. Alternatively, a regression calibration curve can be generated by challenging the MFC with the appropriate gas, recording the MFC setting, and measuring the flow with a flow calibrator for a minimum of five points covering the 10% to 100% portion of the flow range of the MFC. The resulting regression slope and intercept is then used to provide the MFC setting for a given desired flow. As a best practice, flows should be measured at each use with a primary reference flow standard if possible, depending on the system configuration and accessibility to the MFCs.

13.2.2 Standards Preparation by Dynamic Dilution

Dynamic dilution systems should be powered on and the diluent and stock gases allowed to flow through the respective MFCs for a minimum of 1 h prior to use. A best practice is to experimentally determine the actual equilibration times necessary for each concentration level and document this in the SOP as appropriate. This equilibration period allows passivation and equilibration of the system to ensure the concentrations of the VOCs in the blended gas are stable prior to transferring to the canister (or directly to the preconcentrator).

Before proceeding with the preparation of canister standards by dynamic dilution, determine the method of humidification to be used as discussed in Section 13.1. Standards should be prepared from low concentration to high concentration. When changing stock gas flow rate(s) to prepare a different concentration, calibration gas should flow through the system for a minimum of 30 min prior to preparation of the working calibration canister (or delivering the working standard directly to the preconcentrator). These equilibration times are particularly important for laboratories analyzing compounds with higher BPs such as hexachlorobutadiene and 1,2,4-trichlorobenzene. Extended equilibration times may be necessary to fully passivate the flow path and mixing chamber of the dynamic dilution system when higher BP compounds are included in the standard.

Note: Final pressures of calibration standard canisters must not exceed the maximum pressure permitted by the preconcentrator unit. Closely matching the pressure of the calibration standard canisters to the expected pressure of the collected field samples is recommended when analysis is performed with preconcentrators that measure volumes with MFCs. Consult the preconcentrator instrument manual for further guidance on matching canister pressures.

The final concentration of the diluted standard is calculated as follows:

$$C_f = \frac{C_s \cdot F_s}{F_s + F_d}$$

where:

C_f = final diluted standard concentration (pptv)
C_s = certified concentration of stock standard (pptv)
F_s = flow of stock standard (mL/min)
F_d = flow of diluent gas (mL/min)

Note: If multiple gas standards are combined for dilution, the denominator is the sum of all gas flows combined for preparing the dilution.

13.3 Static Dilution

Static dilution methods involve the precise measurement of the pressure changes in, or delivery of known volumes of gas into, a container of known constant volume. Static dilution is performed into a fixed-volume vessel such as a canister or into a manifold where the known volumes or partial pressures of each gas are measured. Before proceeding with the preparation of canister standards by static dilution, determine the method of humidification to be used as discussed in Section 13.1.

13.3.1 Static Dilution by Addition of Partial Pressures into Canisters

Starting with an evacuated canister, a pressure transducer or gauge is connected to the canister to monitor the canister pressure as gases are added. Stock and diluent gases are added separately by direct connection of the gas to the canister. The canister pressure is measured before and after standard and diluent gases are bled into the canister, and these pressures are input into the calculation of the dilution factor and final concentrations.

The final concentration of each VOC in the diluted standard is calculated as follows:

$$C_f = \frac{C_s \cdot (P_{sa} - P_{sb})}{P_f}$$

where:

C_f = final diluted standard concentration (pptv)
C_s = certified concentration of stock standard (pptv)
P_{sa} = absolute pressure of canister after adding standard gas (kPa)
P_{sb} = absolute pressure of canister before adding standard gas (kPa)
P_f = final absolute pressure of canister after adding standard and diluent gases (kPa)

13.3.2 Static Dilution by Addition of Partial Pressures into Manifolds

Diluent gas and standard gas(es) are introduced stepwise into a manifold constructed of chromatographic-grade stainless steel or silicon-ceramic–coated stainless steel to which a canister is connected. The pressure of the manifold and canister is measured with a pressure transducer or combination of pressure transducers prior to and after the addition of each gas to the manifold.

The final concentration of the diluted standard is calculated as follows:

$$C_f = \frac{C_s \cdot (P_{sa} - P_{sb})}{(P_{sa} - P_{sb}) + (P_{da} - P_{db})}$$

where:

C_f = final diluted standard concentration (pptv)

C_s = certified concentration of stock standard (pptv)

P_{sa} = absolute pressure of manifold and canister after adding standard gas (kPa)

P_{sb} = absolute pressure of manifold and canister before adding standard gas (kPa)

P_{da} = final absolute pressure of manifold and canister after adding diluent (kPa)

P_{db} = absolute pressure of manifold and canister before adding diluent (kPa)

13.3.3 Static Dilution by Addition of Known Volumes into Canisters

Note: This method of dilution preparation is difficult to perform reproducibly and requires practice and excellent technique to perform consistently. Additionally, due to deviation from the vendor-stated volume of the canister (e.g., 6 L), this method may be subject to errors in the final theoretical concentration as the canister is not volumetrically certified.

A known volume of standard gas is added to an evacuated canister with a gas-tight syringe through a septum, and the diluent gas is added to a known final pressure. The canister contents should be humidified as described in Section 13.1. The final concentration of the diluted standard is calculated as follows:

$$C_f = \frac{C_s \cdot V_s}{V_c(\frac{P_f}{P_a})}$$

where:

C_f = final diluted standard concentration (pptv)

C_s = certified concentration of stock standard (pptv)

V_s = volume of stock standard added to canister (mL)

V_c = nominal volume of canister (mL)

P_f = absolute pressure of final dilution (kPa)

P_a = ambient absolute pressure (kPa)

13.3.4 Static Dilution into Canisters by Gravimetric Methods

Gravimetric dilution of standards requires access to a high-sensitivity, high-capacity analytical balance that can resolve and register the addition of small amounts of gas or neat material to a fixed-volume vessel such as a canister or cylinder. Known masses of standard gases or neat materials are added to the canister. The canister mass is measured before and after addition of each material, and the added mass is calculated by difference. The canister mass or pressure is measured before and after the addition of diluent gas to determine the final concentration in the canister. This convention, especially when using neat source material, requires excellent technique and hygiene to prepare an accurate and contaminant-free standard. In general, this technique is employed for experimental or exploratory work for which diluted standard gases are not available from commercial sources.

The masses of the added standard and diluent materials are measured directly with the analytical balance, if all materials are gases. Liquid standard material masses may be measured directly with the analytical balance when added to the canister or may be measured volumetrically and the mass determined according to the density of the liquid material at the temperature when weighed according to the following equation:

$$\mathrm{m_{std}} = \mathrm{V_{ls}} \cdot \mathrm{d_{ls}}$$

where:

m_{std} = mass of standard material (g)
V_{ls} = liquid volume of neat standard material at temperature of preparation (mL)
d_{ls} = density of the neat standard (g/mL) at temperature of preparation

For example, 0.0100 mL of 1,2,4-trichlorobenzene at 25 °C (density of 1.46 g/mL at 25 °C) is added to a canister.

0.00100 mL · 1.46 g/mL = 0.0146 g 1,2,4-trichlorobenzene

The gaseous volumes of the standards and diluent are determined from the mass of each gas added to the fixed-volume vessel according to the following equation. Gaseous volumes of standards are corrected according to their purity listed on the certificate of analysis. Diluent gases are assumed to have 100% purity:

$$\mathrm{V} = \frac{\mathrm{m} \cdot \mathrm{R} \cdot \mathrm{T} \cdot p}{\mathrm{MW} \cdot \mathrm{P_s}}$$

where:

V = gaseous volume of added gas at 25 °C and 101.3 kPa absolute (L)
m = mass of the gas added (g)
R = gas constant, 8.314 L-kPa/mol·K
T = standard temperature, 298 K
P_s = standard pressure, 101.3 kPa absolute (1 atm)
MW = molecular weight of the gas (g/mol)
p = purity of neat material as listed on the certificate of analysis (as a decimal)

For example, 0.0114 grams of 99.2% pure benzene (MW 78.11 g/mol), 0.0146 grams of 99.7% pure 1,2,4-trichlorobenzene (MW 181.45 g/mol), and 4585.12 grams of high-purity nitrogen (MW 28.013 g/mol) are added to a cylinder:

(0.0146 g · 8.314 L-kPa/mol·K ·298 K · 0.997)/(181.45 g/mol · 101.3 kPa) = 0.00196 L 1,2,4-trichlorobenzene

(0.0114 g · 8.314 L-kPa/mol·K ·298 K · 0.992)/(78.11 g/mol · 101.3 kPa) = 0.00354 L benzene

(4585.12 g · 8.314 L-kPa/mol·K ·298 K · 1.00)/(28.013 g/mol · 101.3 kPa) = 3999.25 L nitrogen

The final concentration (in pptv) is then calculated using the following equation:

$$C_f = \frac{V_s}{V_t} \cdot 10^{12}$$

where:

C_f = final diluted standard concentration (pptv)

V_s = volume of stock standard gas added to vessel at 25 °C and 101.3 kPa absolute (L)

V_t = total volume of standard and diluent gases at 25 °C and 101.3 kPa absolute (L)

For the example above, the concentrations of 1,2,4-trichlorobenzene and benzene are 490,000 pptv (0.00196 L/3999.26 L · 10^{12}) and 885,000 pptv (0.00354 L/3999.26 L · 10^{12}), respectively.

13.4 Storage of Standards

Standards prepared in canisters should be stored at ambient laboratory conditions for up to 30 days. Users should note that many target VOCs may not be stable over this time frame, so it is strongly recommended that users demonstrate storage stability in the canisters to be employed by following the canister bias checks described in **Section 9.4**. Storage locations should be free of potential contaminants.

14 Sample Preconcentration and Analytical System Operation

The introduction of standards and samples to the analytical system is handled by a preconcentrator unit configured as a multitrap system whose function is to quantitatively trap the target VOCs while allowing bulk gases and water to pass through the system. Elimination of bulk gases and water improves the GC separation of the target VOCs. Target VOCs with high temporal resolution are separated with fused-silica capillary columns and detected by a linear quadrupole, ion trap, or TOF MS.

14.1 Sample Preconcentration

A measured aliquot of the whole air sample (typically 100 to 1000 mL) is drawn from the sample canister by vacuum through a preconcentrator. Moisture and bulk atmospheric gases such as oxygen, nitrogen, argon, and carbon dioxide must be largely removed from the sample aliquot prior to introduction of the target VOCs to the GC. Instrument manufacturers have developed different methods for removal of moisture and bulk gases, most of which typically involve freezing water from the sample aliquot by cryogenic or electronic cooling.

One general convention passes the sample aliquot through an empty metal or quartz trap cooled to approximately -30 to -50 °C to freeze the water but permit the target VOCs and bulk gases to pass through to a sorbent bed trap. The empty trap containing the ice is then isolated from the sorbent bed trap, warmed to melt the ice, swept with a dry purge gas to vent, and readied for the next sample (**Entech Instruments, 2015**).

In another convention, the sample aliquot is routed through an empty trap or a trap packed with glass beads that is cooled to approximately -110 to -160 °C to retain all of the target VOCs and water while permitting the bulk gases to pass through. The trap is then warmed slightly above the freezing point of water and flushed with dry carrier gas to sweep the target VOCs onto a subsequent sorbent bed trap and retain most of the water on the first trap (**Agilent Technologies, 2017**).

In either convention described above, the second trap may contain sorbent beds with one or more sorbents arranged to selectively trap the target VOCs and permit water and the bulk gases to pass through. Following trapping of the target VOCs on this second trap, it is isolated, heated quickly to desorb the target VOCs, and backflushed to the GC column or to a subsequent focusing trap (typically a cooled empty trap). The focusing step delivers the VOCs to the GC column in a small volume of carrier gas, which facilitates sharp chromatographic peaks and improved baseline separation of peaks. If multiple sorbents are employed in the trap, the sorbents are arranged such that the sample aliquot first enters the weakest sorbent and then successively stronger sorbents. This configuration permits trapping of the higher-BP VOCs in the weaker sorbent. Lower-BP VOCs are not retained as completely on the weaker sorbents and partially pass through to the stronger sorbents where they are retained. Once trapping is complete, the trap may be purged with dry carrier gas to remove excess moisture, or the preconcentration may progress directly to heated desorption. During heated desorption, the trap is rapidly heated and backflushed to release the target VOCs from the sorbents. Such multisorbent bed arrangements allow efficient trapping and desorption of target VOCs. Sorbent configurations, trap cooling temperatures, flush volumes, and desorption temperatures are recommended by the preconcentrator instrument manufacturers and are tailored to the suite of target VOCs desired for quantification.

A third type of preconcentration uses a series of capillary columns to trap and maintain target VOCs while allowing water and bulk gases to pass through. Upon backflushing, the target VOCs are trapped onto a second series of capillary columns for focusing and then backflushed for injection onto the GC column.

Preconcentrator instrument manufacturers will typically indicate the optimum factory default settings for the sample aliquot volume, trapping time, trapping temperature, gas flows, and additional preconcentration parameters. Each of these variables may be adjusted based on the needs of the individual user and the suite of desired VOCs for measurement.

14.2 Preconcentration System Operation

Preconcentrator traps should be conditioned when first installed to eliminate contaminants that act as interferences or chromatographic artifacts. Conditioning may be performed with prolonged baking of the trap at an elevated temperature (e.g., 200 to 300 °C) while flowing dry, inert carrier gas (hydrogen or helium as recommended by the manufacturer) through the trap. The conditioning temperature depends on the sorbents in the trap and is typically recommended by the sorbent or trap manufacturer. Note that preconcentrator traps with multiple sorbent beds should be conditioned at the lowest temperature of the sorbents contained in the trap (**Brown, 2013**). For example, if a sorbent trap contains both Tenax-TA (MilliporeSigma, St. Louis, MO, recommended conditioning temperature 320 °C) and Carbopack (available from MilliporeSigma, St. Louis, MO, recommended conditioning temperature 350 °C), the trap conditioning temperature should not exceed 320 °C. The temperature during conditioning should be raised slowly in a stepwise manner (e.g., 20 °C/h) until the conditioning temperature is achieved. Bakeout periods of approximately 48 h at the conditioning temperature have shown to be effective; however, manufacturer recommendations should be followed. After this 48-h period, most of the trap contamination will have been removed. Lower concentration (sub-ppbv) levels of target compounds may still evolve from the trap for an extended period following conditioning. Analysis of instrument blanks (IBs) and method blanks (MBs) will demonstrate sufficient trap conditioning when criteria in Table 18-1 are met.

Differing configurations of preconcentrator systems and the associated sorbent traps and conventions for moisture management require the operating conditions and settings of the preconcentrator to be optimized based on the desired suite of target VOCs. The manufacturer's guidelines should be used as a starting point.

14.3 GC-MS System

The instrument operator should optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methylpolysiloxane stationary phase is an indication of acceptable chromatographic performance. GC carrier gas flows, oven temperature program, and instrument run time should be based on the manufacturer's recommendations and customized for separating the list of desired target VOCs. In general, heated transfer lines from the preconcentrator to the GC should be set to manufacturer recommendations, typically approximately 80 to 100 °C.

14.3.1 Example GC Conditions

Example GC analytical conditions are given in Table 14-1 for carrier gas, carrier gas flow rate, and oven program. These conditions assume the use of a 60-m length fused-silica column with an I.D. of 0.25 or 0.32 mm and a polydimethylsiloxane film thickness of 1 μm.

Table 14-1: Example GC Analytical Conditions

Parameter	Specification	
Carrier gas:	Helium	
Carrier gas flow rate:	1–3 mL/min as recommended by manufacturer	
Oven temperature program:	Initial temperature[a]:	35 °C
	Initial hold time:	2 min
	Ramp rate:	8 °C/min
	Final temperature:	220 °C
	Final hold time:	Until all target compounds elute

[a] This is a default initial temperature, and users may need to employ a subambient initial oven temperature to effectively separate VOCs and interferences eluting in the early portion of the chromatogram.

14.3.2 Example MS Conditions

The MS instrument manufacturer's recommendations should be followed for detection of the desired suite of target VOCs. The following are examples of MS settings for linear quadrupole, ion trap, and TOF MS detectors:

- Linear quadrupole MS instruments should be operated in EI mode at nominal ionization energy of 70 eV. The scan range should be commensurate with the target analytes; the recommended range is 35 to 270 amu unless the desired target VOCs require a different scan range. Scan ranges that include *m/z* 28 and 32 may experience interference problems with nitrogen and oxygen, respectively. Creation of custom scan ranges that are tailored to specific analyte RTs may be appropriate and may avoid these interferences when an expanded scan range is needed. The MS should be configured to perform at least one scan per second. Ideally, the scan rate should be fast enough that at least 10 (**Boyd et al., 2008**), and preferably 12 or more, scans are available for each peak.
- Ion trap MS instruments should be operated in EI mode at nominal ionization energy of 70 eV. As with linear quadrupole instruments, the scan range should cover the desired target VOC suite, and the recommended range is 35 to 270 amu unless an expanded range is needed. The same interferences with nitrogen and oxygen apply when including lower masses in the scan range. The scan time should be set to approximately 0.4 to 1 s/scan; faster scan rates will provide improved resolution. Axial modulation, manifold temperature, and emission current should be adjusted to the manufacturer's recommendations.
- TOF MS instruments should be configured to the manufacturer's recommendations. The following are typical settings: EI setting of 70 eV, ion source temperature of 260 °C, and transfer line temperature of 260 °C. Spectral acquisition rates of approximately 2 to 4 Hz (2 to 4 scansets/s) or higher will provide appropriate resolution for eluting peaks.

14.3.3 Data Acquisition Method

Based on the type of MS that is in use, the analyst must decide on a specific data acquisition method (SIM, full scan, SIM/SCAN, SIS) as discussed in **Section 7.6.3.3**. The data acquisition parameters are set up based on the manufacturer's specific software package. Typically monitored ions are listed in **Table 1-1**.

14.4 Tuning/Optimizing the Mass Spectrometer and Verifying the Tune

14.4.1 General Mass Spectrometer Tuning/Optimizing Considerations

The MS (quadrupole, ion trap, or TOF MS) is tuned/optimized according to the manufacturer's specifications upon initial installation of the instrument and following significant preventive maintenance or repair activities that impact the performance of the GC-MS system. This includes, but is not limited to, cleaning the ion source or analyzer, trimming or replacing the capillary column, and adjusting MS tune or optimization parameters. Once optimized, the MS tune should be verified according to the manufacturer's specifications each day of use. The purpose of MS tuning is to demonstrate acceptable performance across the selected ion mass range, where acceptable performance demonstrates sufficient responses of desired masses, correct mass ratios, and adequately low vacuum leak rates.

Note: The analytical instrument (quadrupole, ion trap, or TOF MS) should be tuned/optimized according to the manufacturer's specifications. Method TO-15 previously required a bromofluorobenzene (BFB) tune verification. This BFB tune verification is no longer required in Method TO-15A, although analysts may choose to continue using this protocol as outlined below.

14.4.2 Optional Tune Verification Using BFB

To confirm that the MS meets tuning and standard mass spectral abundance criteria prior to initiating data collection, the GC-MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the system are then verified by analysis of the tuning check compound, BFB. Most modern MS systems include an automatic tuning optimization routine that is operated through the instrument software. The use of BFB as the tuning compound is specific to ensure acceptable MS response ratios up to approximately 200 amu.

14.4.2.1 Introducing the BFB

If the BFB is included in the IS stock gas mixture, it is introduced to the preconcentrator with the IS mixture through the dedicated port. If not a component of the IS mixture, BFB can be purchased as a stand-alone compound in a high-pressure cylinder and introduced to the preconcentrator through a step-down regulator or diluted appropriately into a canister. The tuning check is performed by introducing 1 to 2 ng into the preconcentrator and analyzing the standard using the preconcentrator, GC, and MS parameters established and used for the analysis of calibration standards, QC samples, and field samples. The method integration and analysis parameters employed should also be those for routine analysis of standards, QC samples, and field samples.

14.4.2.2 BFB Tuning Verification Frequency

Before analyzing samples, blanks, or calibration standards on each day of analysis, the analyst should confirm that the GC-MS system meets the mass spectral ion abundance criteria, as listed in Table 14-2, for the BFB tuning check for linear quadrupole or ion trap MS instruments. The tuning check should be analyzed and pass criteria before the ICAL and every 24 h of analysis thereafter. The 24-h time period for the tuning check begins at the injection (acquisition time) of the BFB.

Table 14-2: BFB Tuning Check Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria[a]
50	8.0% to 40.0% of *m/z* 95
75	30.0% to 66.0% of *m/z* 95
95	Base peak, 100% relative abundance
96	5.0% to 9.0% percent of *m/z* 95
173	< 2.0% of *m/z* 174
174	50.0% to 120.0% of *m/z* 95
175	4.0% to 9.0% of *m/z* 174
176	93.0% to 101.0% of *m/z* 174
177	5.0% to 9.0% of *m/z* 176

[a] All ion abundances must be normalized to *m/z* 95, the nominal base peak, even though the ion abundance of *m/z* 174 may be up to 120% that of *m/z* 95.

14.4.2.3 BFB Tuning Corrective Action

If the BFB tuning criteria in Table 14-2 are not met, the analyst should adjust the tune of the MS, which may require adjusting the ion focus or lens settings, for example. Repeated failure to meet tuning abundance acceptance criteria requires corrective action, which may include cleaning the ion source, checking for leaks, and/or servicing the MS vacuum pump. If the analyst cannot attain an acceptable MS tune after performing instrument maintenance, a service technician visit may be required. The manufacturer's manual should be consulted for assistance with instrument troubleshooting. Automated tuning routines may be helpful in adjusting MS tuning parameters to achieve an acceptable tune.

15 Internal Standards, Calibration, and Quality Control

Method users should strive to meet acceptance criteria for the calibration and QC listed in the following section for the suite of target VOCs; however, method users may identify target VOCs of importance that they require to meet calibration and QC criteria to continue analysis and may identify other target VOCs that are still of interest but need not meet the most stringent calibration and QC criteria to continue analysis. In all cases, sample measurements for target VOCs associated with nonconformance of calibration and/or QC criteria should be flagged to indicate the criteria failure(s).

15.1 Selection and Use of Internal Standards

ISs are added to the air matrix during preconcentration to permit tracking of and correction for variability in instrument performance and detector response over time. IS compounds should be selected to include a minimum of three VOCs covering the approximate early, middle, and late elution range of the target VOC elution order. At a minimum, a single IS compound should be used. ISs should be VOCs that are not expected to be present in collected field samples and should either be deuterated VOCs or VOCs that are chromatographically similar to, but are not, target VOCs. Three typical VOC ISs are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other suitable IS compounds include 1,2-dichloroethane-d_4, hexane-d_{14}, toluene-d_8, and 1,2-dichlorobenzene-d_4.

IS stock gases are commercially available at 100 ppbv in ultrapure nitrogen or can be purchased with a custom suite of compounds at desired concentrations from reputable gas providers. IS stock gases should be evaluated upon receipt for the presence of contaminants that may interfere with the quantitation of target VOCs. This evaluation can be performed by analyzing increasing volumes of the IS (e.g., 25, 50, 100, 250 mL) and examining the results for VOC contaminants whose responses increase proportionally with the increasing volume of IS analyzed. IS gas standards that contribute unacceptable levels of target VOCs, such that, for instance, MBs fail acceptance criteria, should not be employed for analysis and should be replaced. Typical contaminants in IS mixtures include methylene chloride and carbon disulfide.

The IS is added at the same concentration to each injection (standard, sample, blank, etc.) to monitor instrument sensitivity and assess potential matrix effects. Significant changes in the IS RT and response may be warning signs of chromatographic issues such as leaks, column degradation, or insufficient water management techniques. ISs are not added directly to the sample canister but instead are introduced through a different dedicated nonsample port in the preconcentrator and trapped along with the sample aliquot on the trapping module in the preconcentrator. The concentration of IS added to each injection should be chosen such that the IS compound peak area response approximates target compound area responses in the lower half of the calibration curve range, but that minimally provides a peak that is on scale and does not exceed the area response of the highest calibration standard.

15.1.1 Internal Standard Retention Time

Each IS compound in each injection should be within ±2 seconds of the average RT for each IS compound in the ICAL. An occasional outlier may not be problematic but may indicate a poor injection, in which case the analysis should be repeated. If RTs are consistently outside of this window of the average RT, then the operator should further investigate possible reasons for the shift.

The average RT for each IS in the ICAL is calculated using the following equation:

$$\overline{\mathrm{RT}}=\sum_{i=1}^{n}\frac{\mathrm{RT}_i}{n}$$

where:

$\overline{\mathrm{RT}}$ = average RT for the IS compound (min)

RT_i = RT for the IS compound for each calibration level (min)

n = number of concentration values used to generate the calibration (minimum of 5)

15.1.2 Internal Standard Response

The area response for each IS compound in each injection (calibration standard, field sample, blank, CCV, etc.) must be within ±40% of the mean area response of the IS compound determined from the ICAL per the following equation:

$$\overline{Y}=\sum_{i=1}^{n}\frac{Y_i}{n}$$

where:

$\overline{Y}$ = average area response for the given IS compound

Y_i = area response for the IS for each calibration level

n = number of concentration values used to generate the calibration (minimum of 5)

The quantitation ion for each IS compound is chosen as the most abundant ion (base peak) unless there is a spectral interference from a coeluting or nearby compound or interference that impacts the quantitation of the base peak. In such cases, another abundant ion that is distinguishable from the other compounds may be selected for quantitation.

Changes in the IS response may be due to leaks in the system, issues associated with the IS delivery, matrix effects, or a decline in detector sensitivity. It is advised that a control chart of all IS area responses (temporal plot of IS response vs. chronological sample analyses), such as that shown in Figure 15-1, be maintained and monitored on a daily basis to aid in the detection and diagnosis of problems. Erratic increases and decreases of approximately 15% in IS response can indicate system leaks, issues with delivery of the IS, and/or other problems with the analytical system. A trending decline of IS responses typically indicates a decline in detector sensitivity. If there is a trending decline, sequences involving multiple samples should not be started if there is a likelihood that the IS responses (based on the indicated trend) will fall outside the ±40% range. Otherwise samples falling outside this range will need to be reanalyzed once the instrument sensitivity is restored. In any event, IS responses should be evaluated and appropriate action taken to resolve issues before analysis is resumed. Any samples for which the IS area response differs by more than 40% from the mean IS area response as determined from the ICAL should be reanalyzed or flagged.

Note that while changes in the instrument sensitivity are quantitatively adjusted using the IS response through the use of relative response factors (RRFs) (see Section 15.2.3), loss of sensitivity due to detector issues can cause some low-concentration compounds to produce reduced signals that fall below detection levels. Maintaining a tight IS response range minimizes the impact of this effect and improves the comparability of data. In light of this, laboratories may choose to implement a ±30% acceptance criterion for IS response tracking.

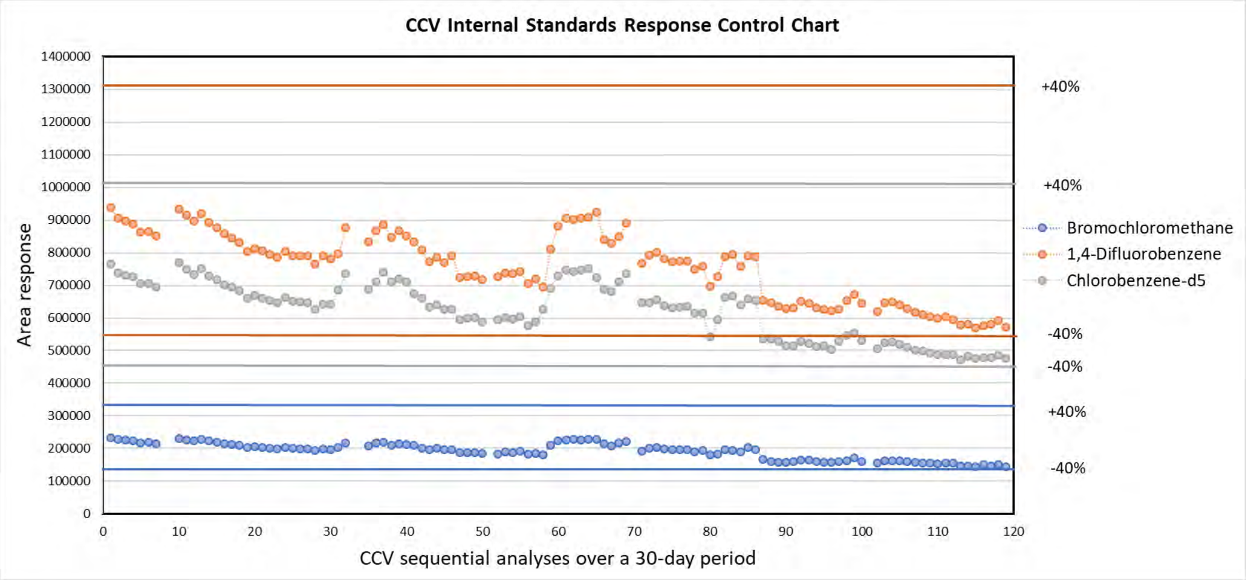


Figure 15-1: Example control chart for internal standards response.

15.2 Establishing Calibration

The GC-MS is calibrated initially and when the system is out of control as indicated by IS responses or CCV standards failing acceptance criteria. Once the decision has been made to calibrate or after the instrument has been tuned/optimized, it is recommended that a sufficient number of humidified HCF zero air blanks or humidified check standards be analyzed to verify that instrument sensitivity is stable, as indicated by IS response. This will minimize potential instrument drift during the ICAL. When this has been completed, the ICAL can proceed as discussed below.

15.2.1 Preparation for Calibration

The calibration curve is prepared by analysis of different concentration levels covering the concentration range desired by the laboratory as determined by the expected concentration of the samples, the sensitivity of the instrumentation, and the mass of analytes delivered to the column. A typical calibration range for ambient air analysis is approximately 20 to not more than 5000 pptv (ranging from tens of picograms to tens of nanograms on column). A best practice is to include a calibration point to approximate concentrations of target VOCs typically measured in ambient air, approximately 20 pptv. Five levels must be included in the ICAL at a minimum, and more levels are recommended, especially at the lower end of the calibration curve if the lowest standard concentration is in the tens of pptv. If a quadratic regression is used to model the curve, a minimum of eight levels is recommended. While not required, analysis of up to three replicates at each calibration level should be considered to verify injection precision and provide a more robust calibration curve.

The inclusion of a true zero calibration point (a calibration blank [CB], which is a humidified matrix blank with no standards added, as discussed in Section 15.3.3.3) should be considered for calibration models that permit inclusion of a zero concentration point (note that calibrations employing the average RRF cannot accommodate a zero concentration point). However, even if the calibration model does not allow a zero point to be used as a data point, a zero point may still be analyzed and used for assessment purposes since the zero-concentration point should ideally demonstrate no target VOC detections.

Calibration curves may be established on the instrument by two conventions:

- **Individual standards method.** Prepare a separate canister for each level of the calibration curve and analyze the same volume from each canister. This method is straightforward. For example, to establish an eight-level calibration curve, the analyst prepares canisters at concentrations of 20, 50, 100, 250, 1000, 2000, and 5000 pptv and analyzes the same volume (e.g., 250 mL) of each standard as is performed for field samples.
- **Effective dilution method.** Prepare canisters at different concentrations from which proportional volumes are analyzed to establish the calibration curve. For example, the analyst prepares two standard canisters: 250 and 5000 pptv. The typical injection volume for samples is 250 mL; therefore, to establish a calibration curve of 20, 50, 100, 250, 1000, 2000, and 5000 pptv, the analyst injects 20, 50, 100, and 250 mL from the 250 pptv canister and 50, 100, and 250 mL from the 5000 pptv canister. Users should employ a minimum of two different canisters for generating calibration curves. When using a single canister for introducing standards, an error in preparation of the canister will not be apparent as the calibration will meet the technical linearity and accuracy criteria. When employing a single standard canister to generate the calibration curve, it is necessary to verify the calibration with a canister prepared independently from the primary calibration canister. The SSCV described in Section 15.3.1 can serve this purpose.

Note that when the individual standards method is employed to establish calibration, the same gas volume from each canister is delivered to the preconcentrator resulting in the same amount of moisture and the same degree of penetration of compounds onto the preconcentrator sorbent trap. When the effective dilution standards method is employed to establish calibration, various gas volumes are delivered to the preconcentrator resulting in differing amounts of moisture and degrees of penetration of the compounds on the preconcentrator sorbent trap. As a result, it is important to demonstrate that the sample introduction volume measurements are reproducible, linear, and proportional and that the moisture and penetration do not impact the analysis. To accomplish this, analysts should follow any manufacturer procedures for demonstrating linear and proportional volume metering of gases for preconcentration. Acceptance should also be demonstrated by establishing a calibration based on the individual standards method followed by establishing a second calibration based on the effective dilution method by injecting various volumes of the individual standard method's high calibration standard. A comparison of the two calibration curves should demonstrate linearity of compounds covering the volatility range of the target analyte suite. This demonstration then validates the effective dilution is appropriate.

For measuring low (tens of pptv) levels of VOCs as is needed for ambient air analysis, it is important to properly characterize instrument response at these lower concentrations by including a greater number of calibration points toward the bottom of the calibration curve (as shown in the examples above). Including more lower concentration points better defines the calibration curve at the low end and minimizes calibration bias due to the influence of the higher concentration standards.

Note: To establish the calibration curve, the theoretical concentrations of the working calibration standards should be calculated using the certified concentration from the gas vendor or neat standard provider. Certificates of analysis for stock standard gas mixtures typically include both a nominal (or "requested") concentration (e.g., 100 ppbv) for each analyte and a certified concentration (e.g., 108 ppbv), which should be within a specified tolerance (e.g., ±10%). These tolerances may permit the certified concentration to differ from the nominal concentration by 10% to 20%, resulting in final theoretical concentration errors for the working-level standards when the nominal concentration is input into standard concentration calculations instead of the certified concentration. Calibration standards prepared with neat materials must account for the standard purity when calculating the working standard concentrations.

15.2.2 Analysis of Calibration Standards

Once the calibration convention has been decided and standards have been prepared, the calibration standards are analyzed to establish the ICAL.

An air/water check of the MS also should be performed prior to any analyses to ensure that the system is leak-free. Prior to starting the ICAL analytical sequence, the operator should conduct a thorough system bakeout per the manufacturer's instructions for the preconcentrator and also ramp the GC column temperature. This readies the system by effectively removing any accumulated impurities in the analytical system. Analysis of an IB (**Section 15.3.3.1**) or performing a BFB tune check (**Section 14.4.2**) accomplishes this as well. An MB (**Section 15.3.3.2**) should be analyzed before beginning the analysis of the calibration standards. Analysis of the MB should demonstrate that the system is acceptably clean and meets the canister blank acceptance criteria in **Table 10-3** (i.e., ≤ 20 pptv at 101.3 kPa absolute). Once the criteria have been met, analysis of the calibration standards from lowest to highest concentration can be performed. It is recommended that an additional MB be analyzed following the highest calibration standard in preparation for analysis of the SSCV, as discussed in **Section 15.3.1** (strongly recommended after ICAL). If calibration standards and samples are to be analyzed sequentially, analyze field samples and additional CCV standards and MBs to complete the sequence, ending with a CCV, as discussed in **Section 15.3.2**.

The recommended steps for readying the system and performing the GC-MS analytical sequence are as follows:

1. Perform an air/water check.
2. Bake out the system.
3. Analyze a preliminary IB or perform the BFB instrument tuning check.
4. Analyze a laboratory MB.
5. Analyze the calibration standards to establish the ICAL (includes CB).
6. Analyze a laboratory MB.
7. Analyze a SSCV.
8. Analyze field samples, CCV standards (every 10 samples), and MBs, ending with a CCV. (*Note: This step is applicable for laboratories that run samples immediately following an ICAL.*)

15.2.3 Calibration Curve Models

Following analysis of all calibration standards, a calibration curve is prepared for each target analyte by determining the RRF of each concentration level. Following data acquisition for the calibration standards, the RRF of each target compound in each calibration level is determined as follows:

$$\mathrm{RRF} = \frac{\mathrm{A_s} \cdot \mathrm{C_{IS}}}{\mathrm{A_{IS}} \cdot \mathrm{C_s}}$$

where:

A_s = peak area for quantitation ion of the target compound

C_{IS} = concentration of the assigned IS compound (pptv)

A_{IS} = peak area for quantitation ion of the assigned IS compound

C_s = concentration of the target compound (pptv)

The quantitation ion for each target VOC is chosen as the most abundant ion (base peak) unless there is a spectral interference from a coeluting or nearby compound or interference that impacts the quantitation of the base peak. In such cases, another abundant ion that is distinguishable from the other compounds may be selected for quantitation.

Method TO-15 previously required the use of an average RRF calibration model. This calibration model is no longer required in Method TO-15A. Analysts should use their professional judgment to select an appropriate calibration model, which may include using average RRFs or linear or quadratic regressions.

If using an average RRF calibration model, the RSD of the RRF for each target VOC should be ≤ 30%. Chromatographic software programs typically include these calculations and can be configured to generate the RRF at each level, the average RRF for all calibration standards, and the RSD of the RRF for each target compound and to flag calibrations that exceed the RSD criterion.

Note that the calibration model using average RRF assumes the curve intercept goes through the origin. For analytes with calibration behavior known to demonstrate background or other behavior where the curve is not expected to pass through the origin, the analyst should carefully consider an alternative calibration model. For example, a calibration curve may be prepared by linear or quadratic regression of the ratios A_S/A_{IS} as the dependent variables and the ratios C_S/C_{IS} as the independent variables. The user should be aware that use of quadratic regression may mask nonlinear behavior that is due to errors in standards preparation or introduction and is not a function of the compound behavior or instrument limitations. The coefficient of determination (R^2) for linear or quadratic curves should be ≥ 0.995 for each target VOC. Such linear or quadratic curves may be weighted (e.g., 1/concentration or 1/concentration^2) to provide better representation at the low end of the curve. However, better representation at the low end of the curve may be achieved without employing weighted regression models by including more calibration levels at the low end, as described in **Section 15.2.1**, where half the calibration levels are less than or equal to 100 pptv.

Linear or quadratic curves should pass through the origin unless the system exhibits consistent elevated background levels of target VOCs. Consistent low-concentration background levels in the calibration may be introduced from contamination in canisters, diluent gas, humidification processes, or the analytical system. Presence of background may be confirmed by analysis of a CB (see **Section 15.3.3.3**) canister prepared identically to calibration standards without introduction of standard gas (i.e., only containing standard diluent gas), which is the zero-calibration point (see **Section 15.2.1**) when employed in the calibration curve. In such cases, the calibration behavior may be better characterized with a calibration regression curve fit using a calculated y-intercept, which will typically be positive in magnitude. However, analysts should use caution when employing calculated intercepts and calibration models including a zero point, especially in situations where the compound background is an artifact of the calibration process (such as in dilution gases, canisters selected for preparing calibration standards, or the gas dilution system) and not a consistent behavior of the measurement system that affects all measurements (such as low-level contamination in the preconcentrator, ISs, or transfer line). In instances where the positive calibration y-intercept is due to the calibration process (including any contribution from a zero-calibration point), negative concentration measurements may result when measuring individual samples that do not exhibit the same level of background contamination.

Irrespective of the curve-fit method selected, the calculated concentration for each VOC at each calibration level should be within ±30% of the theoretical concentration when quantitated against the resulting calibration curve. Exclusion of calibration standard levels is not permitted unless justifiable (for example, a known error in standard preparation or a known poor injection of the standard). This evaluation of each concentration level is important to properly demonstrate calibration curve accuracy across the chosen concentration levels as both the coefficient of determination and RSD assessment of linear regression are poor overall estimation of the goodness of fit of the curve. Corrective action should be taken for target compounds that fail this criterion.

Note: Since this method may be employed to analyze numerous target VOCs with a wide range of chemical properties (volatility, polarity, etc.), some target VOCs may not meet the calibration criteria. Target VOCs of high importance to the laboratory should meet the calibration criteria; however, compounds of lesser importance may fail the criteria. In such instances of failed calibration criteria, the concentrations measured in samples should be labeled (flagged) accordingly based on the laboratory policy.

15.3 Quality Control

15.3.1 Second Source Calibration Verification Standard

Following each successful calibration, it is strongly recommended that an SSCV standard be analyzed to verify the ICAL for each target VOC. The SSCV standard should be prepared independently from the calibration standards using a certified secondary source calibration standard. A humidified SSCV standard is prepared in a canister at a concentration in the lower third of the calibration curve. The SSCV standard should contain all compounds in the calibration mixture. Each target VOC in the SSCV standard should be recovered within ±30% of the theoretical concentration.

15.3.2 Continuing Calibration Verification Standard

On a daily basis, the operator should verify that the system continues to meet sensitivity and quantitation criteria for each target VOC prior to analyzing samples. This is accomplished through analysis of a CCV standard. Sensitivity is based on monitoring the IS responses, and quantitation is based on comparing the measured amount of target compounds to the theoretical amount. A humidified CCV standard is prepared as a dilution of a certified standard in a canister at a concentration in the lower third of the calibration curve. This certified standard is preferably the cylinder that was used for the ICAL standards but may be another certified cylinder standard containing the target VOCs.

At a minimum, a CCV standard is analyzed at the beginning and end of the analytical sequence unless the sequence begins with an ICAL. Additionally, and as a best practice, it is recommended that a CCV standard be analyzed after every 10 sample injections. The IS area responses for each CCV standard should meet the criteria outlined in Section 15.1.2, and the quantitated concentrations of the target compounds for each CCV standard should be within ±30% of the theoretical concentrations. CCV failures indicate a drift in calibration response or degradation of the gas within the CCV standard canister. Therefore, corrective action should be taken to investigate and address CCV failures, including, for example, reanalyzing the CCV, preparing and analyzing a new CCV or standard canister, and preparing a new ICAL. Additional steps may require system maintenance including, for example, trimming or replacing the column, cleaning MS components followed by retuning the MS, or replacing preconcentrator traps, all of which require establishing a new ICAL.

The following equation is used to calculate the percent difference of the measured concentration of each target VOC in the CCV standard ($\%D_{CCV}$) from the theoretical concentration:

$$\%D_{CCV} = \frac{C_{CCV} - C_{theoretical}}{C_{theoretical}} \times 100$$

where:

C_{CCV} = measured concentration of the CCV for each target VOC (pptv)

$C_{theoretical}$ = theoretical concentration of the CCV for each target VOC (pptv)

Alternatively, percent recoveries may be calculated as follows and should fall between 70% and 130%:

$$\%Recovery_{CCV} = \frac{C_{CCV}}{C_{theoretical}} \times 100$$

where:

C_{CCV} = measured concentration of the CCV for each target VOC (pptv)

$C_{theoretical}$ = theoretical concentration of the CCV for each target VOC (pptv)

15.3.3 Blank Analyses

Blank analyses confirm for the analyst that the analytical system and reagent gases are suitably clean and free of interferences. Analysis of all blanks should demonstrate each target compound is < 20 pptv.

15.3.3.1 Instrument Blank

An IB should be analyzed at the beginning of the sequence and prior to analysis of the ICAL and daily CCV standard as a preliminary demonstration that the carrier gas and analytical system show acceptably low levels of target VOCs and potential interferences. The IB is a preconcentration analysis cycle performed where all preconcentration steps are taken without introduction of diluent (e.g., HCF zero air or ultrapure nitrogen) or sample gas into the preconcentrator. Preconcentration traps are desorbed and swept with carrier gas to the GC to evaluate contaminants within the preconcentrator sample introduction and concentration pathways. ISs should be included in this injection to ensure proper quantitation of contaminants and to aid in conditioning the IS lines and loop.

15.3.3.2 Method Blank

A laboratory MB is analyzed at least once in each analytical sequence. The MB not only indicates possible laboratory contamination but also fully verifies that target VOCs and potential interferences are acceptably low in the system as a whole. The MB consists of a canister filled with humidified (40% to 50% RH) clean diluent gas and is analyzed via the same instrument method as the standards and field samples in the analytical sequence (i.e., if 250 mL of field sample are typically analyzed, the MB analysis volume will also be 250 mL). The humidified air of the MB more fully characterizes and purges the system of contaminants than analysis of the dry carrier gas in the IB.

The MB is analyzed prior to and following the ICAL in an ICAL sequence or prior to the initial daily CCV standard. This should demonstrate acceptably low carryover in the analytical system prior to analysis of samples (ICAL standards, CCVs/SSCVs, and field samples). Samples with expected high concentrations of target VOCs may be followed by one or more MB injections to flush the analytical system. In such instances where a blank is used to clean the instrument, additional MB aliquots should be run until the instrument is demonstrated to be acceptably clean. This will ensure the analyst's confidence in the subsequent data.

15.3.3.3 Calibration Blank

A CB is prepared with each set of standard canisters to be used for an ICAL. The CB used for this purpose is a canister filled with the humidified (40% to 50% RH) clean diluent gas sourced through the dilution system employed to prepare standards. For laboratories that do not employ a dynamic or automated static dilution system, the CB consists of a humidified canister of the gas used to dilute the calibration standard. The purpose of the CB is to demonstrate that the diluent gas and dilution apparatus (if employed) is sufficiently clean such that little or no positive bias is imparted to the calibration. The CB is analyzed via the same instrument method as standards and field samples when the ICAL is established and may be included in the calibration curve as a zero-concentration level (this is optional). The typical analysis volume is to be analyzed (i.e., if 250 mL of field sample are typically analyzed, the CB analysis volume will also be 250 mL).

15.3.4 Precision Measurements

Precision of the method may be assessed by analysis of collocated or duplicate samples as well as replicate sample analyses, as defined in Section 5. Precision is evaluated by calculating the absolute RPD of the measurement pair using the following formula:

$$\mathrm{RPD} = \left| \frac{\mathrm{X}_1 - \mathrm{X}_2}{\left(\frac{\mathrm{X}_1 + \mathrm{X}_2}{2}\right)} \right| \times 100$$

where:

X_1 = target VOC concentration measured in first measurement of the precision pair (pptv)

X_2 = target VOC concentration measured in second measurement of the precision pair (pptv)

Acceptable precision analyses will demonstrate RPD ≤ 25% for each target analyte when both measurements are ≥ fivefold the method detection limit (MDL). Failure to meet this criterion should prompt the analyst to investigate the reason for the discrepancy. Associated results should be flagged to indicate poor precision was observed.

15.3.4.1 Field Sample Precision

Precision of the method inclusive of the field collection activities is evaluated through measurements of collocated or duplicate samples. When collecting samples for a study, a number of samples equal to approximately 5% of the total samples (at minimum three) are collected as duplicate or collocated samples.

15.3.4.2 Laboratory Analysis Precision

Replicate analyses are used to demonstrate precision of the instrumental analysis and do not provide information on field-sampling precision. Each analysis sequence should include a replicate analysis of a field-collected sample. Each analytical sequence should include analysis of either one replicate or replicates of 5% of the field samples, whichever is greater.

15.3.5 Field Quality Control Samples

Note: Field QC samples are optional but may be required by QA/QC staff for particular projects or as outlined in a quality assurance project plan.

Field QC samples provide additional verification that the data which are being collected are reliable. The canister valve is not opened in the field; therefore, field QC samples should not become contaminated or otherwise compromised. Field QC samples that do not meet acceptance criteria should prompt users to examine the preparation and sample handling procedures and to qualify the concentration data reported for associated field collected samples (those samples accompanying the field QC samples through handling and transport).

- **Canister field blank.** Blank field QC sample prepared by filling a canister with humidified clean diluent gas (prepared in the same manner as an MB as described in Section 15.3.3.2). The canister is transported to the field site(s) to accompany field-collected canisters and treated identically to field-collected samples in the field and laboratory. The field blank canister valve is not opened in the field (users may remove and reinstall the brass plug, if so equipped). The field blanks are analyzed by interspersing them among the field samples. Field blank acceptance criteria should be approximately 20 pptv or less.
- **Field spike.** Positive field QC sample prepared by filling a canister with humidified standard gas at a concentration in the lower third of the calibration curve. The field spike canister is transported to the field site(s) to accompany field-collected canisters and treated identically to field-collected samples in the field and laboratory. The field spike canister is not opened in the field (users may remove and reinstall the brass plug, if so equipped). The field spikes are analyzed by interspersing them among the field samples. Field spike acceptance criteria should be within ±30% of the theoretical spiked concentrations.

15.3.6 Audit Accuracy

A measure of analytical accuracy is the degree of agreement with an independently prepared audit standard. An audit standard is prepared by an individual or entity other than the analyst, and the concentrations can be known or blind to the analyst. These samples are also known as performance evaluation or proficiency test (PT) samples. The results measured by the analyst are compared to an accepted reference value to evaluate the analytical method bias, which is defined as the difference between the target compound’s accepted reference value and the measured value divided by the accepted reference value and expressed as a percentage as follows:

$$\text{Audit Accuracy (\%)} = \frac{\text{Measured Value} - \text{Accepted Reference Value}}{\text{Accepted Reference Value}} \text{ x } 100$$

The recommended audit accuracy criterion for this method is that the analyzed result be within ±30% of the accepted reference value, which is in agreement with the bias specification for the calibration standard levels, SSCV, and CCV.

Aggregated audit accuracy data from the NATTS PT Program from 2016 and 2017 are shown in Table 15-1. The NATTS PT Program requires the measurement of 15 target VOCs and requires that measurements provided by participating laboratories be within ±25% of the accepted reference value for an acceptable evaluation. *N* is the is the number of participating laboratories measuring and reporting a concentration value for the analyte.

Table 15-1: Example Proficiency Test/Audit Accuracy Results for Trace-Level VOC Analysis

National Air Toxics Trends Stations (NATTS) Proficiency Test (PT)
Mean Percent Difference of Participating Laboratories' Reported Values from Accepted Reference Values
Calendar Year (CY) 2016 and 2017, Calendar Quarters (QTR) 1 and 3

Target VOC	**CY2016 QTR1**			**CY2016 QTR3**			**CY2017 QTR1**			**CY2017 QTR3**		
	RV[a] (pptv)	**Bias %**	***N***	**RV[a] (pptv)**	**Bias %**	***N***	**RV[a] (pptv)**	**Bias %**	***N***	**RV[a] (pptv)**	**Bias %**	***N***
2-Propenal	261	44.4	20	313	16.1	18	NS[b]	N/A	N/A	NS[b]	N/A	N/A
Benzene	228	–1.6	26	507	0.4	22	256	–7.4	21	438	0.4	22
1,3-Butadiene	366	3.1	25	572	–5.5	21	460	–12.3	21	539	–8.9	22
Carbon tetrachloride	NS[b]	N/A	N/A	86	32.2	22	59.7	16.5	21	219	7.0	23
Trichloromethane	667	–1.9	26	409	0.1	23	192	2.4	22	590	2.8	23
1,2-Dibromoethane	906	–0.8	25	344	–3.1	22	345	–6.1	21	567	–5.2	22
1,2-Dichloroethane	524	–3.8	25	351	1.7	22	286	–3.7	22	346	0.3	23
Dichloromethane	363	–5.2	25	117	13.9	21	186	67.4	22	NS[b]	N/A	N/A
1,2-Dichloropropane	421	2.2	22	434	1.2	21	547	–10.4	20	473	–0.3	20
***cis*-1,3-Dichloropropene**	735	–12.4	25	541	–12.7	21	430	–17.2	20	380	–1.9	20
***trans*-1,3-Dichloropropene**	426	–4.2	25	399	–8.2	21	243	–5.6	19	597	–12.5	20
1,1,2,2-Tetrachloroethane	291	–1.0	24	124	14.0	21	37.2	43.4	16	89.3	–4.8	20
Tetrachloroethene	211	0.3	26	460	–1.8	22	268	–7.6	21	379	1.3	22
1,1,2-Trichloroethene	264	–6.2	26	442	–8.5	23	246	–8.2	22	447	–7.3	23
Chloroethene	366	1.6	26	344	2.5	22	425	–6.0	21	270	–3.9	22

[a] RV = reference value.

[b] NS = not spiked. VOC not included in PT to evaluate laboratories incorrectly reporting false-positive detections.

15.3.7 Ambient Air Check

Several of the chlorofluorocarbon VOCs are ubiquitous in ambient air due to their long half-life in the atmosphere. These compounds include trichlorofluoromethane (Freon 11), dichlorodifluoromethane (Freon 12), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), carbon tetrachloride, and 1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon 114). The National Oceanic and Atmospheric Administration (NOAA) periodically updates the global background concentrations of these compounds, which can be queried at the NOAA halocarbon website, https://www.esrl.noaa.gov/gmd/hats/. Analysts can compare their measured concentrations of these analytes to the values reported by NOAA to increase confidence in the representativeness of the field-collected sample and in the precision, accuracy, and sensitivity of the collection and analysis methods. However, this comparison should not serve as the basis for invalidation of sample data.

16 Sample Analysis and Compound Identification and Quantitation

16.1 Sample Analysis

This section addresses the analysis of samples after an ICAL has been established. See Section 15.2.2 for discussion of sample analysis when an ICAL is performed at the beginning of each sequence.

Samples are analyzed using the same acquisition methods as were used for establishing calibration. This includes the preconcentrator operation parameters, GC oven program, MS parameters, and integration methods. Field-collected samples and QC samples should be at ambient laboratory temperature for analysis. A typical sample aliquot volume is used for all samples. Adjustment of this sample aliquot volume requires adjustment of a dilution factor to account for the difference in relative analyzed volume, as discussed in Section 16.1.4.

16.1.1 Sample Introduction

Sample canisters are connected to the preconcentration unit through a port. Instrument manufacturers offer configurations that consist of a single port or a series of ports on a manifold, with each port connected through a rotary valve, solenoid valve, or other means that permits connection of sample canisters. Regardless of the sample introduction configuration, each canister should be isolated and verified to have a leak-free connection prior to beginning the analysis sequence.

The sample aliquot volume should be accurately measured for analysis. This can be accomplished by metering the sample with an MFC or with the combination of a fixed-volume vessel and a pressure transducer. Sample introduction volume measurements must be reproducible to ensure that analyzed volumes of samples and standards are consistent. It is critical that the metering system operates reproducibly, linearly, and proportionally. This is particularly important if the effective dilution method is employed for samples that fall outside the calibration range.

16.1.2 Leak Check of Preconcentrator Connections

Prior to beginning an analytical sequence, including an ICAL sequence, each canister connection must be verified as leak-free through the preconcentrator. Manufacturers generally incorporate a leak test routine in their software. During the leak check, canisters are connected to the autosampler or sample introduction lines and the canister valves are kept closed. Each port of the autosampler or sample introduction line is evacuated, and the pressure is monitored over 30 s to 1 min for a change in pressure. Pressure changes of < 3.4 kPa/min (0.5 psi/min) are generally acceptable although no change in pressure is preferable. Should a canister fail the leak check, a typical corrective action includes rechecking the tightness of all fittings and then retesting. If leaks persist, then other troubleshooting measures should be undertaken as per the manufacturer’s recommendations. Analysis must not be performed using any canister connection that does not pass the leak check. Canisters that do not pass the leak check may leak to atmospheric pressure, allowing laboratory air into the analyzed sample stream. Many preconcentration control software systems include a leak check function that provides standard QC reports. Following the leak check, all autosampler ports or sample introduction lines are evacuated and the canister valves are opened. Leak check results should be documented in the analysis records.

16.1.3 Analysis of Field Samples

An air/water check of the MS should be performed prior to any analyses to ensure that the system is acceptably leak-free. Prior to starting an analytical sequence, the operator should conduct a thorough system bakeout per the manufacturer's instructions for the preconcentrator and also ramp the GC column temperature. This readies the system by effectively removing any accumulated impurities in the analytical system. Analysis of an IB (**Section 15.3.3.1**) or performing a BFB tune check (**Section 14.4.2**) accomplishes this as well. An MB (**Section 15.3.3.2**) should be analyzed before beginning the analysis of the samples. Analysis of the MB should demonstrate that the system is acceptably clean and that each target compound is < 20 pptv. Once these checks meet criteria (summarized in **Table 18-1**), the instrument calibration is verified by analysis of a CCV and sample analysis can begin.

The recommended steps for readying the system and performing the GC-MS analytical sequence are as follows:

1. Perform an air/water check.
2. Bake out the system.
3. Analyze a preliminary IB or perform the BFB instrument tuning check.
4. Analyze a laboratory MB.
5. Analyze a CCV to verify the calibration.
6. Analyze field samples and additional CCV standards (every 10 samples) and MBs to complete the sequence, ending with a CCV, as discussed in **Section 15.3.2**.

16.1.4 Sample Dilution

If the on-column concentration of any compound in any sample exceeds the calibration range, the sample should be diluted for reanalysis. A dilution can be performed either by reducing the sample aliquot volume for an effective dilution or adding diluent gas to the sample canister to physically dilute the sample. To select an appropriate dilution factor, the analyst should estimate the concentration of the sample requiring dilution and aim to have diluted concentrations fall into the upper third of the calibration range (e.g., 3500 pptv for a calibration with a 5000 pptv high standard). The dilution factor is then equal to the estimated concentration divided by this desired diluted concentration.

It is recommended that an effective dilution be used first, if an appropriate dilution factor can be achieved. This eliminates the need to add diluent gas to the canister. Note that this dilution method is limited by the ability of the preconcentrator to accurately extract smaller volumes from the canister. For some preconcentrators this lower limit is approximately 20 mL. For example, if an analyst needs to perform a 10-fold dilution on a sample and the typical injection volume is 250 mL, the analyst would inject 25 mL. If a larger dilution is necessary, physical dilution of the canister sample with diluent gas may be necessary in combination with effective dilution, as described in **Section 12.2**. If a 30-fold dilution is needed, for example, a twofold physical dilution (doubling the sample pressure) is suggested, followed by a 15-fold effective dilution. These dilution factors are multiplied to calculate the total dilution factor. Refer to **Section 16.3** for resulting sample concentration calculations.

16.2 Compound Identification

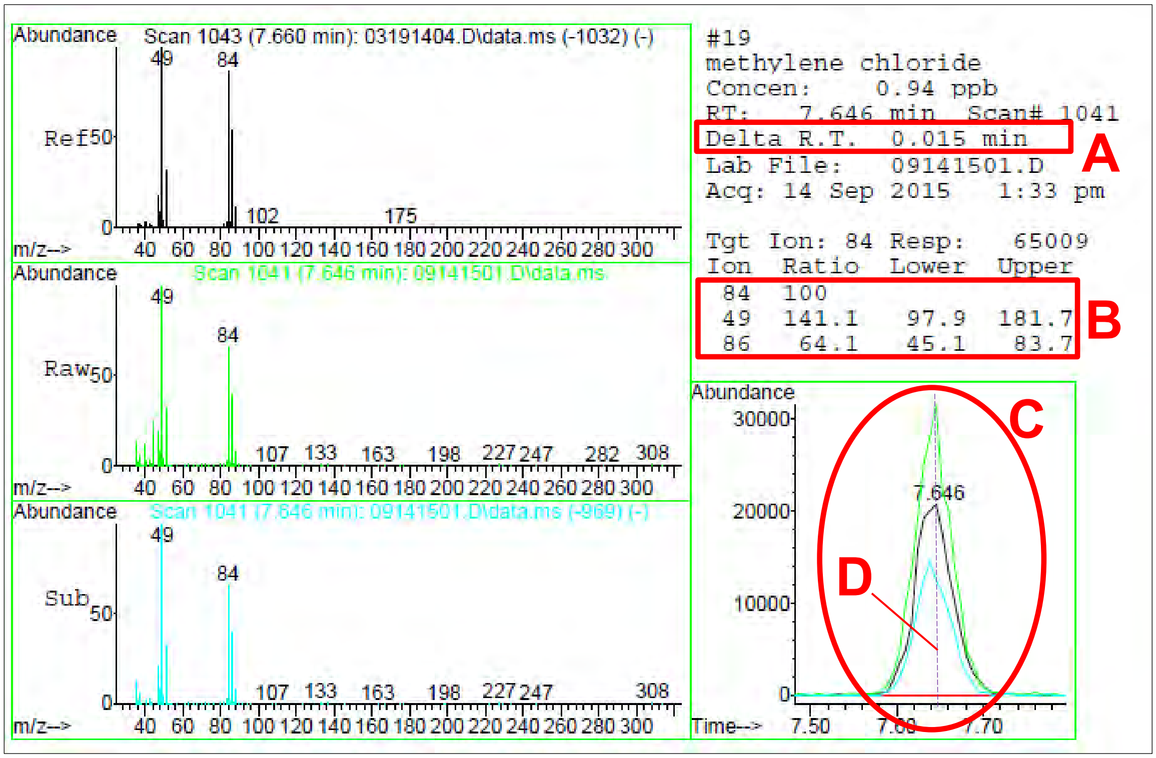
Once data acquisition is complete, each chromatogram should be examined. Chromatographic peaks should be appropriately resolved, and integration should not include peak shoulders or inflections indicative of a coelution. Subject to the judgment of an experienced operator, any peaks that have not been integrated properly may need to be manually integrated. Deconvolution techniques may be available to the operator to help resolve compound coelutions, depending on the particular instrument and chromatography software package that is in use.

Target VOCs are identified based on their RT and the relative abundance of their characteristic ions from the MS. Four criteria must be met to positively identify a target compound qualitatively:

1. The RT of the compound must be within the RT window of ±2 s as determined from the ICAL average.
2. The relative abundance ratio of qualifier ion response to target ion response for at least one qualifier ion must be within ±30% of the average relative abundance ratio from the ICAL.
3. The S:N of the target and qualifier ions must be > 3:1, preferably > 5:1.
4. The target and qualifier ion peaks must be co-maximized (peak apexes within one scan of each other) (**Axys Analytical Services, 1992**).

Figure 16-1 shows an example of the qualitative identification criteria listed above. The RT is within the RT window defined by the method (red box A), and the relative abundance ratios of the qualifier ions are within ±30% of the ICAL average relative abundance ratio (red box B). The S:N of the peak is shown to be > 5:1 (red oval C), and the target and qualifier ion peaks are co-maximized (dotted purple line D). Note that it is critical that ion abundance ratios are relative to the average relative abundances established with the ICAL. Incorrectly assigning abundance ratios as absolute abundance percentages will lead to improperly wide or narrow acceptance ranges. Improperly wide acceptance ranges may include an abundance ratio of 0%, which the chromatography data systems/software may show as an acceptable identification even though the qualifier ion may not in fact be present. For the example in Figure 16-1, the average relative abundance of *m/z* 49 and 86 are 141.1% and 64.1%, respectively. Calculating lower and upper relative abundance ranges based on these averages results in acceptance ranges of 97.9% to 181.7% and 45.1% to 83.7%, respectively.

Refer to Figure 16-2 for the following example for determining the S:N. To determine the S:N, the characteristic height of the noise of the baseline (A) just before the peak and the height of the analyte peak (B) are measured. The ratio of the analyte peak height (B) is divided by the noise height (A) to calculate the S:N. In the example, the peak at 17 min is discernible from the noise but is not well resolved and is very close to an S:N of 3. In the example, the peak heights of the noise and the analyte peaks (at approximately 17 min) are approximately 700 units and 1700 units, respectively, for an S:N of 2.4. Analysts may choose instead to determine the S:N by determining the average area of a selected portion of the chromatogram characteristic of the noise (e.g., 0.2 minutes before the target peak) and the area of the target peak.



```
#19
methylene chloride
Concen:     0.94 ppb
RT:      7.646 min   Scan# 1041
Delta R.T.   0.015 min
Lab File:    09141501.D
Acq: 14 Sep 2015    1:33 pm

Tgt Ion: 84 Resp:   65009
Ion  Ratio  Lower  Upper
 84  100
 49  141.1   97.9  181.7
 86   64.1   45.1   83.7
```

Figure 16-1: Qualitative identification of GC-MS target analytes.

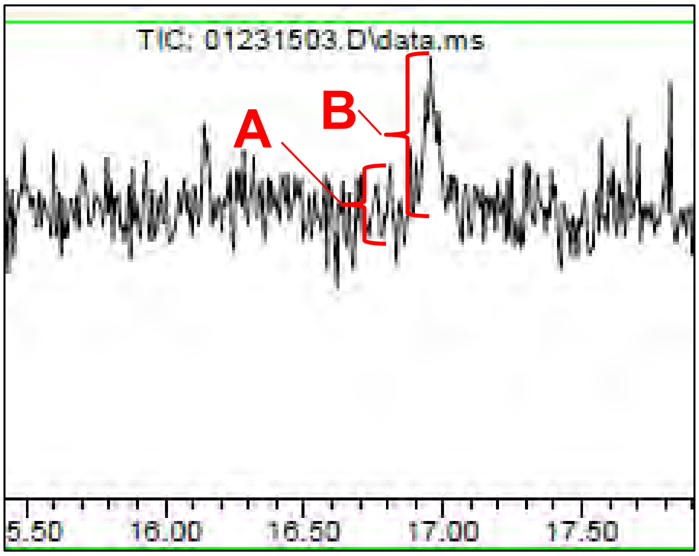


Figure 16-2: Determination of chromatographic peak signal-to-noise ratio.

Determining the S:N is somewhat subjective based on an individual analyst's characterization of the noise and analyte peak. Some chromatography data systems/software programs include S:N functions that require the analyst to assign the noise range in the chromatogram and target peak. For well-resolved peaks, the S:N will greatly exceed 5:1 and does not need to be measured. For peaks with low S:N that are questionable as to whether they meet criterion 3 above, the 3:1 S:N is only a guideline; it is unnecessary to measure each peak, and the experienced analyst's opinion should weigh heavily on whether the peak meets the S:N criterion.

As with the S:N determination, evaluation of whether target and qualifier ion peaks are co-maximized does not need to be rigorously evaluated with each peak. Rather interpretation by an experienced analyst is sufficient for deciding whether the qualifier ion peaks are co-maximized with the target ion.

Evaluation of criteria 1 (RT) and 2 (relative ion abundances) may be automated by the analytical data system such that they are automatically flagged when exceeded. Such automation reduces the time required for analyst data review; however, it is important that the RT windows and ion abundances be updated with each new ICAL.

If any of the four criteria are not met, the compound cannot be positively identified. The only exception to this is when the compound is positively identified in the opinion of an experienced analyst. The rationale for such an exception should be documented and the associated reported data flagged to indicate that identification criteria were not met. Note that in some instances of large peaks where the detector response is saturated or close to saturation, the relative ion abundances may not fall within the ±30% range. Such peaks typically require dilution of the sample and reanalysis. If the abundance criterion is not met and the sample cannot be reanalyzed, the experienced analyst's opinion should be considered for compound identification.

16.3 Compound Quantitation

16.3.1 Quantitation Using Relative Response Factors

Once the peak areas are determined, the quantitation process is initiated using the software package of choice to provide quantitative results based on the selected calibration model (see Section 15.2.3). Quantitation of the target VOC concentration is performed by relating the area response ratio of each target ion (typically the base peak, or most abundant, ion) and assigned IS in the unknown sample to the RRF of the ICAL curve as follows:

$$C_D = \frac{A_t \cdot C_{IS}}{A_{IS} \cdot RRF}$$

where:

C_D = instrument-detected analyte concentration (pptv)

A_t = area response of target compound quantitation ion

C_{IS} = concentration of assigned IS (pptv)

A_{IS} = area response of assigned IS quantitation ion

RRF = RRF from the ICAL curve

16.3.2 Dilution Correction Factors

If an aliquot is analyzed from the sample canister that is different from the typical analysis volume (as described in Section 16.1.4 for performing effective dilution), an instrument dilution correction factor (IDCF) is calculated:

$$\mathrm{IDCF} = \frac{\mathrm{V_{nom}}}{\mathrm{V_{inj}}}$$

where:

V_{nom} = nominal volume of sample injected (typical volume analyzed)

V_{inj} = volume of sample injected

The final concentration of each target compound in air is determined by multiplying the instrument-detected concentration by the CDCF (see Section 12.2) and the IDCF:

$$\mathrm{C_F} = \mathrm{C_D} \cdot \mathrm{CDCF} \cdot \mathrm{IDCF}$$

where:

C_F = concentration of the target compound in air (pptv)

C_D = concentration measured at the instrument (pptv)

CDCF = canister dilution correction factor

IDCF = instrument dilution correction factor

Note: The MDL reported with the final concentration data will be corrected by multiplying the MDL by the CDCF and IDCF applied to the sample concentrations. For example, if the benzene MDL is 9.1 pptv for an undiluted sample and the sample was diluted by 2.5, the MDL becomes 23 pptv.

17 Method Detection Limits

17.1 Overview

MDLs for VOCs are determined as part of the initial validation of the method and annually thereafter by following the guidance from EPA's Office of Water listed in the *Code of Federal Regulations* (U.S. EPA, 2016a; 40 CFR Part 136 Appendix B). The MDL procedure described was updated in August 2017 to address shortcomings of the original MDL process first promulgated in 1984. The purpose of the MDL is to capture the routine variability in the method and is defined as the minimum measured amount of a target analyte that is distinguishable above background (MB) levels with 99% confidence. The MDL process involves estimating the MDL concentration, preparing and analyzing a series of blanks and known-standard "spike" samples prepared in matrix (e.g., humidified HCF zero air), calculating the MDL for each target VOC, and confirming the representativeness of the MDL.

The MDL process is designed to account for background contaminants present in the canisters themselves as well as the contaminants that may be introduced during canister handling, preparation, and analysis. Statistical confidence is estimated from the observed method variability across instruments, operators, and time and requires that canisters be selected randomly from among a laboratory's inventory of canisters in routine use. Separate spiked canisters and MBs must be prepared using the same procedures as those with which field-collected canisters are prepared and analyzed. It is not acceptable to analyze replicate samples from a single canister, to intentionally choose the best-performing canisters, or to select only a specific vendor's canisters for determining MDLs.

To initially determine the MDL, laboratories must prepare a minimum of seven MB canisters and seven spiked canisters in at least three batches on three separate calendar dates. These canisters are analyzed on at least three separate calendar dates. Separate MDLs are calculated for each target VOC based on the results from the spiked canisters and the MBs (MDL_{sp} [Section 17.6] and MDL_b [Section 17.7], respectively), and the higher of the two concentrations is chosen as the laboratory MDL.

All steps performed in the preparation and analysis of field sample canisters (such as dilution) must be included in the MDL procedure. Canisters are prepared at the selected spiking concentration with humidified (40% to 50% RH) HCF zero air. While the MDL capabilities of each laboratory may vary due to a number of factors (canister hygiene, condition of equipment, cleanliness of diluent gases, etc.), spiking concentrations for VOC MDLs of approximately 10 to 100 pptv are typical to achieve realistic MDLs. It is not appropriate to prepare a higher concentration spike and analyze a smaller aliquot than analyzed for field-collected samples (e.g., perform an effective dilution). For example, laboratories that analyze 250 mL of field-collected sample should choose a spike concentration of 60 pptv. The spiked canisters should be prepared at 60 pptv with humidified HCF zero air, and 250 mL should be analyzed. It would not be acceptable for the laboratory to prepare spikes at 300 pptv and analyze only 50 mL of the sample as this would not be representative of the procedure for field-collected samples. This would underrepresent any potential contamination that may remain in the canisters from inadequate canister cleaning. Moreover, potentially anomalous canister behavior will be more evident at lower concentrations, thereby better representing the expected behavior of VOCs in ambient air at concentrations near MDLs.

17.2 Frequency of Method Detection Limit Determination

MDLs are determined initially and, at a minimum, annually thereafter or when changes to the instrument or preparation procedure result in significant changes to the sensitivity of the instrument and/or procedure. Situations that require redetermination of the MDL include, but are not limited to, the following:

- Detector replacement or major preventive maintenance activities
- Replacement of the entire analytical instrument
- Replacement of a large (e.g., > 50%) portion of a laboratory's canister inventory
- A change to the cleaning procedure for sample collection media or labware that results in a marked reduction in contamination levels

After the initial MDL determination, laboratories may choose to perform and update MDLs on an ongoing basis. This may be beneficial for laboratories that run samples routinely. In this scenario MDL spiked canister samples are prepared and analyzed along with scheduled MBs that are interspersed with samples. The MDL samples are analyzed over the course of days or weeks. After a minimum of seven data points have been collected for the MDL spikes and for seven associated MBs, the MDLs for each can be calculated. This eliminates the need to dedicate a significant continuous block of time to preparing and analyzing MDL samples and MBs. All criteria outlined in Section 17.1 must be met.

For laboratories that do not run samples continuously but rather are more research focused, determining MDLs for each new calibration or project may be more appropriate. In this situation, the laboratory should repeat the process for determining the initial MDL.

17.3 Selecting a Spiking Level

An estimated spiking level for the replicate canister samples must be determined before preparing the spiked MDL canisters for analysis. If the analyst chooses a spiking level that is too low, the analyte may not be reliably detected. If a spiking level is chosen that is too high, the variability of the method near the actual limits of detection may not be properly characterized. An appropriate spiking level may be selected by considering the following (in order of importance):

1. Concentration at which the instrument S:N is threefold to fivefold for the analyte.
2. Concentration at which qualitative identification criteria for the analyte are lost. (Note that this will be approximately the concentration determined from the MDL process absent of blank contamination.)
3. The concentration estimated as the equivalent of three times the standard deviation of the area response from the analysis of at least three MBs.
4. Concentrations from previously acceptable MDL studies and related experience.

Note that the MDL spiking level should not be within the calibration curve; rather the MDL spiking level should be less than the lowest calibration standard (excluding a potential zero calibration point) to best approximate the MDL. Concentrations within the calibration curve will meet precision and bias acceptance criteria and are of a high enough concentration that qualitative identification is certain. Note that it is expected and acceptable that the relative abundance and S:N for qualifier ions may not meet the identification criteria listed in **Section 16.2**; however, the RT and qualifier ion (when of sufficient S:N) must be met.

At least once per year the spiking level should be reevaluated by analyzing samples at the MDL spike level. If more than 5% of the spiked samples do not provide positive numerical results that meet all the method qualification criteria (see **Section 16.2**), then the spiking level must be increased and the initial MDL redetermined.

17.4 Preparing the Spiked and Method Blank Samples

A minimum of seven separate spiked samples (at the level determined in **Section 17.3**) and a minimum of seven separate MB samples are prepared for analysis to determine the MDL. To best mimic field-collected samples, each spiked and blank sample must include, to the extent feasible, all portions of the sample matrix and be subjected to the same procedures performed to process field samples in preparation for analysis. MBs and spiked samples should be prepared over the course of three different preparation batches, preferably on nonconsecutive days.

The following should be considered when preparing MDL samples:

- Spiked samples must be prepared in matrix (humidified HCF zero air in a canister). Following preparation, it is recommended that each canister be allowed to equilibrate for a minimum of 24 h prior to initial analysis.

- Selection of canisters should include as much variety as possible (e.g., different canister manufacturers or types of canisters such as electropolished and silicon-ceramic lined) to best characterize the variability of the method attributable to the use of field-collection sample media.
- MBs that do not meet cleanliness criteria for a given target VOC should trigger root-cause analysis to determine the source of the contamination and should not be used to determine the MB portion of the MDL.

17.5 Analyzing MDL Samples

The MDL samples (blanks and spikes) are analyzed against a valid calibration curve on three separate calendar dates. QC criteria for the analytical sequences should be met. All MDL calculations should be performed in the final units (e.g., pptv).

*Note: The MDL Method Update (**U.S. EPA, 2016a**; **40 CFR Part 136 Appendix B**) allows multiple instruments in the same laboratory to be assigned the same MDL values if the results of the required seven MDL spike and seven MB analyses are distributed across the instruments (minimum two spikes and two blanks per instrument) and the resulting standard deviation from the combined instrument data is used to calculate the MDLs. This is not a recommended practice for Method TO-15A.*

17.6 Calculating MDLs from Spiked Samples (MDL_{sp})

After acquisition of the concentration data for each of the seven or more spiked canisters, the standard deviation of the concentrations for the spiked samples (S_{sp}) is calculated. All replicates are included unless a technically justified reason can be cited (faulty injection, unacceptably low IS response, etc.) or if a result can be statistically excluded as an outlier.

The MDL for the spiked samples (MDL_{sp}) is calculated by multiplying S_{sp} by the Student's *t*-value appropriate for the single-tailed 99th percentile *t*-statistic and a standard deviation estimate with $n - 1$ degrees of freedom corresponding to the number of spiked samples analyzed according to Table 17-1. Other values of *t* for additional samples ($n > 13$) may be found in standard statistical tables.

$$\mathrm{MDL_{sp}} = \mathrm{t}_{(n-1,1-\alpha=0.99)} \mathrm{S_{sp}}$$

where:

$\mathrm{t}_{(n-1,1-\alpha=0.99)}$ = the Student's' *t*-value appropriate for the single-tailed 99th percentile *t*-statistic and a standard deviation estimate with $n - 1$ degrees of freedom

S_{sp} = sample standard deviation of the replicate spiked sample measured concentrations

The analyst compares the resulting calculated MDL_{sp} value to the theoretical spiked amount. The theoretical spiked level must be greater than MDL_{sp} and less than 10-fold MDL_{sp}, otherwise the determination of MDL_{sp} must be repeated with an adjusted spiking concentration. For MDL_{sp} values greater than the theoretical spike level, the MDL spiking level should be adjusted higher by approximately twofold or threefold. For theoretical spike levels that are greater than 10-fold the MDL_{sp}, the MDL spiking level should be adjusted lower by approximately twofold or threefold. The goal is to spike at a concentration within approximately three times the MDL_{sp} to best estimate the method variability at concentrations near the MDL.

Table 17-1: Single-Tailed 99th Percentile **Student's** *t*-Statistics

Number of MDL Samples (*n*)	**Degrees of Freedom (*n* – 1)**	$t_{(n-1,1-\alpha=0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
12	11	2.718
13	12	2.681

17.7 Calculating MDLs from Method Blanks (MDL_b)

There are three scenarios for determining MDL values for the MBs: (1) if none of the MBs provides numerical results, (2) if some (but not all) of the MBs provide numerical results, and (3) if all the MBs provide numerical results.

Non-numerical values such as "ND" (not detected) are reported when the analyte is not positively identified and only those target VOCs having peaks in the MB that meet the specified qualitative criteria for identification listed in Section 16.2 are given a numerical result. A numerical result includes both positive and negative values for analytes that are positively identified.

The procedure to calculate MDL_b for each of the three scenarios is as follows:

1. If none of the MBs provides a numerical result for the individual analyte, the MDL_b does not apply.
2. If some, but not all, of the MBs provide numerical results for an individual analyte, the MDL_b is set to the highest of the MB concentration results. If 100 or more MB results are available for the analyte, the MDL_b is set to the level that is no less than the 99th percentile concentration of the MBs. In other words, for n MBs where $n \geq 100$, the concentrations should be rank ordered with all non-numerical and zero results placed before the lowest numerical result. The value of the 99th percentile concentration ($n \cdot 0.99$) is the MDL_b. For example, to determine MDL_b from a set of 129 MBs where the highest ranked MB concentrations are … 1.10, 1.15, 1.62, 1.63, and 2.16, the 99th percentile concentration is the 128th value ($129 \cdot 0.99 = 127.7$, which rounds to 128), or 1.63. Alternatively, spreadsheet programs may be employed to interpolate the MDL_b more precisely.
3. If all concentration values for the MBs are numeric values, the MDL_b is calculated as follows:
   - Calculate the average concentration of the MBs ($\bar{x}_b$). If $\bar{x}_b < 0$, let $\bar{x}_b = 0$.
   - Calculate the standard deviation of the MB concentrations, S_b.
   - Multiply S_b by the Student's *t*-value appropriate for the single-tailed 99th percentile *t*-statistic and a standard deviation estimate with $n - 1$ degrees of freedom corresponding to the

number of blanks analyzed according to **Table 17-1**. Other values of *t* for additional samples ($n > 13$) may be found in standard statistical tables.

- Calculate MDL_b as follows:

  $$\mathrm{MDL_b} = \bar{\mathrm{x}}_\mathrm{b} + \mathrm{t}_{(\mathrm{n}-1,1-\alpha=0.99)}\mathrm{S_b}$$

  where:

  $\bar{x}_b$ = average concentration of the MBs

  $\mathrm{t}_{(\mathrm{n}-1,1-\alpha=0.99)}$ = the Student's *t*-value appropriate for the single-tailed 99th percentile *t*-statistic and a standard deviation estimate with $n-1$ degrees of freedom

  S_b = sample standard deviation of the replicate MB concentrations

- As an option, if $n \geq 100$, MDL_b may be determined as in procedure 2 above.

17.8 Selecting and Confirming the MDL

MDL_{sp} and MDL_b are compared and the higher of the two values is selected as the MDL for a given analyte. If MDL_{sp} is determined to be the MDL, laboratories may choose to perform a confirmation of the determined MDL as follows:

1. Prepare one or more spiked samples at onefold to fivefold the determined MDL and analyze the sample per the method to ensure the determined MDL is reasonable. At the MDL_{sp} concentration, there is a 50% chance that the analyte will not be detected (i.e., meet the qualitative identification criteria listed in **Section 16.2**) (**Keith, 1991**); however, the analyte should be reliably detected at twofold to fivefold the determined MDL_{sp}.
2. Develop a reasonable acceptance criterion for the measured concentrations in the MDL_{sp} verification. An appropriate starting point for acceptance limits is to double or triple the acceptance window prescribed by the method for the given analyte. For example, 40% to 160% recovery doubles the method bias criteria of ±30% (see **Section 15.3.6**).
3. Examine the MDL_{sp} procedure for reasonableness if the verification sample is outside the laboratory-defined acceptance criteria. Such an examination might include investigating the S:N of the analyte response in the spiked samples, comparing the MDL_{sp} to the existing instrument detection limit (IDL) (if known, as discussed in #4 below), and relying on the analyst's experience and expertise to evaluate the MDL_{sp} procedure and select a different spiking level. The MDL_{sp} portion of the study should then be repeated with a different spiking level. A very low S:N for the spiked samples may indicate the MDL_{sp} is not representative of the estimated MDL and that the chosen spiking concentration was too low and should be increased several-fold. If the MDL_{sp} is several-fold higher than the IDL, canister hygiene or the standards preparation process should be investigated. If the canister and standards preparation issues cannot be resolved, the spiking concentration may need to be increased several-fold.
4. Troubleshooting may include determination of the IDL to evaluate whether the poor or elevated recovery is due to the instrument. The IDL is determined by analyzing seven or more aliquots of a standard from the same canister, calculating the standard deviation of the measurements, and multiplying the standard deviation by the appropriate Student's *t*-value. The IDL is an estimate of the concentration that can be detected above instrument background and is typically much lower than the MDL_{sp} since it does not involve the variability of multiple canisters and preparation steps.

The MDL_{sp} should not theoretically be less than the IDL, and if such is the case, it indicates the MDL_{sp} measurements are overly precise and the spiking level should be decreased several-fold.

MDLs determined by a NATTS laboratory employing a quadrupole MS in SIM mode are shown in Table 17-2. Analytes were spiked in seven separate canisters at a target concentration of 10 pptv except *m,p*-xylenes, which were spiked at 20 pptv.

Table 17-2: Example MDLs for EPA Method TO-15A

Compound	MDL (pptv)
Dichlorodifluoromethane	2
Chloromethane	4
1,2-Dichlorotetrafluoroethane	2
Chloroethene	3
1,3-Butadiene	7
Bromomethane	2
Chloroethane	1
2-Propenal	7
Trichlorofluoromethane	2
2-Propenenitrile	2
1,1-Dichloroethene	1
Dichloromethane	3
1,1,2-Trichlorotrifluoroethane	2
1,1-Dichloroethane	2
cis-1,2-Dichloroethene	1
Trichloromethane	2
1,2-Dichloroethane	2
1,1,1-Trichloroethane	1
Benzene	2
Carbon tetrachloride	1
1,2-Dichloropropane	1
1,1,2-Trichloroethene	2
cis-1,3-Dichloropropene	2
trans-1,3-Dichloropropene	2
1,1,2-Trichloroethane	2
Toluene	3
1,2-Dibromoethane	2
Tetrachloroethene	2
Chlorobenzene	2
Ethyl benzene	1
m,p-Xylenes	4
Styrene	2
o-Xylene	2
1,1,2,2-Tetrachloroethane	2
1,3,5-Trimethylbenzene	2
1,2,4-Trimethylbenzene	6
m-Dichlorobenzene	2
p-Dichlorobenzene	2
o-Dichlorobenzene	2
1,2,4-Trichlorobenzene	4
Hexachlorobutadiene	2

17.9 Reporting Concentrations Outside the Calibration Range

Measured concentrations between the determined MDL and the lowest calibration standard and measurements exceeding the calibration range are not expected to meet method specifications for bias and precision. Depending on the reporting requirements, laboratories may opt to report a non-numeric value for concentrations below the lowest calibration standard, also referred to as the lower limit of quantitation. Laboratories reporting concentrations measured below the lowest calibration level should identify such measurements and should also identify reported concentrations measured below the MDL. Additionally, concentrations exceeding the calibration range that were not diluted into the calibration range for measurement should be identified when reported.

18 Method Quality Control Parameters and Performance Specifications

Method QC parameters and performance specifications for TO-15A are listed in Table 18-1.

Table 18-1: Quality Control Parameters and Performance Specifications for EPA Method TO-15A

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Zero-air challenge of analytical instrument systems	Test of instrumentation to demonstrate cleanliness (positive bias) by analyzing humidified zero air; performed by connecting the clean humidified gas sample to the preconcentrator to verify that the analytical instrument and all connections are sufficiently clean	At installation prior to initial use of the instrument	Analysis must show that any detected target compounds in the zero-air challenge sample are at response levels that are expected to be < 20 pptv or preferably not detected (see Section 9.3.1)
Known-standard challenge of analytical instrument systems	Test to demonstrate that the analytical instrumentation (preconcentrator and GC-MS system) is not causing loss of compounds (negative bias)	At installation prior to initial use of the instrument	Verifies that all target compounds are detected by the system, that they respond consistently upon repeated injection, and that they exhibit sufficient response to be quantifiable at low concentrations (see Section 9.3.2)
Zero-air challenge of autosamplers associated with analytical instrument systems	After establishing the ICAL, each port of the autosampler is tested to demonstrate cleanliness (positive bias) by analyzing humidified zero air; performed by connecting the clean humidified gas sample to the port to verify that transfer lines and all connections are sufficiently clean	Prior to initial use, upon replacement of transfer lines, or after analysis of potentially contaminating samples	Each target VOC's concentration should be < 20 pptv or preferably not detected (see Section 9.3.3)
Known-standard challenge of autosamplers associated with analytical instrument systems	After establishing the ICAL, each port of the autosampler is tested with a reference standard (approximately 100 to 500 pptv) to demonstrate that the autosampler is not causing bias (typically loss of compounds or negative bias)	Prior to initial use and upon replacement of transfer lines	Each target VOC's concentration within ±15% of theoretical concentration (see Section 9.3.3)

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Canister leak check	Verification that canisters are leak-free by performing a pressure decay test of a canister pressurized to approximately 203 kPa absolute (29.4 psia) over the course of several days	Prior to initial use and recommended periodically thereafter (e.g., every 3 years)	Remove from service and repair any canister that exhibits a pressure change ≥ 0.69 kPa/day (see Section 9.4.1)
Zero-air challenge of canisters for qualification	Test of canisters to determine that they remain acceptably clean (show acceptably low positive bias) over the course of a known time period, typically 30 days or the laboratory holding time, by filling with humidified zero air (not nitrogen)	Initially upon receipt in the laboratory and every 3 years thereafter	Upon initial analysis after a minimum of 24 h and a subsequent time period (e.g., 30 days), each target VOC's concentration ≤ 20 pptv at 101.3 kPa absolute (14.7 psia) (refer to Table 10-3 and Section 9.4.2)
Known-standard challenge of canisters for qualification	Test of canisters to determine bias by filling with a known reference standard (approximately 100 to 500 pptv) prepared in humidified zero air (not nitrogen) and analyzing	Initially upon receipt in the laboratory and every 3 years thereafter	Upon initial analysis after a minimum of 24 h and subsequent analysis at 30 days or typical laboratory holding time, each target VOC's concentration must remain within ±30% of theoretical concentration (see Section 9.4.3)
Zero-air challenge of sampling devices/systems	Assessment of positive bias of sampling system by collecting humidified zero air through the sampling device/system and comparing it to the reference sample collected upstream of the sampling device/system	Prior to initial field deployment and periodically thereafter (e.g., annually), following maintenance (component replacement), or after collection of potentially contaminating samples	Analysis must show that the target compounds in the zero-air challenge sample collected through the sampling unit are not > 20 pptv higher than the concentration in the reference sample (see Section 9.5.2)
Known-standard challenge of sampling devices/systems	Assessment of bias of sampling system by collecting a known reference standard (approximately 100 to 500 pptv) through the sampling device/system and comparing it to the reference standard collected upstream of the sampling device/system	Prior to initial field deployment and periodically thereafter (e.g., annually), following maintenance (component replacement), or after collection of potentially contaminating samples or damaging sample matrices that may impact the activity of the flow path surfaces	Each target VOC's concentration within ±15% of concentrations in the reference sample (see Section 9.5.3)
Purge gas check	Analysis of canister cleaning purge gas to ensure contaminants are acceptably low	Verified upon initial setup and in the event of changes in gas sourcing or after the replacement of scrubbers such as hydrocarbon traps and moisture traps, or following maintenance of zero-air generator	Each target VOC's concentration < 20 pptv (see Section 10.1.1)
Canister cleaning batch blank	Analysis of a sample of humidified diluent gas in a canister from a given batch of clean canisters to ensure acceptably low levels of VOCs in the batch of cleaned canisters	One or more canisters from each batch of cleaned canisters (chosen canister should represent no more than eight total canisters) Alternatively, each canister checked for cleanliness	Upon analysis 24 h after filling, each target VOC's concentration should meet the canister blank acceptance criterion in Table 10-3 (i.e., ≤ 20 pptv at 101.3 kPa absolute, 14.7 psia) (see Section 10.2)
Dilution blank (DB)	Canister filled with clean, humidified diluent gas that is used to dilute samples; indicates that diluent gas and dilution apparatus do not contribute target VOCs to the samples; the DB should not be prepared through a dilution system used for preparing standards	Ideally one DB is prepared and analyzed with each set of samples that are diluted, and at minimum one DB is prepared and analyzed when source and/or filters are changed	DB should be sufficiently clean such that no positive bias is imparted to the samples; each target VOC's concentration should be < 20 pptv (see Section 12.2).

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Holding time	Duration from end of sample collection or canister preparation to analysis	Each field-collected or laboratory QC (standard or blank) canister	≤ 30 days unless longer stability can be demonstrated (see Section 13.4)
MS tune check, as applicable	May be accomplished by injection of 1 to 2 ng BFB for tune verification of quadrupole or ion trap MS detector	Prior to ICAL and prior to each day's analysis	Abundance criteria for BFB listed in Table 14-2 (see Section 14.4.2)
Retention time (RT)	RT of each IS and target compound	All qualitatively identified compounds and internal standards	IS compounds within ±2 s of their mean ICAL RTs (see Section 15.1.1) Target VOCs within ±2 s of their mean ICAL RTs (see Section 16.2)
Internal standards (IS)	Deuterated or other compounds not typically found in ambient air co-analyzed with samples to monitor instrument response and assess matrix effects	Co-analyzed along with all calibration standards, laboratory QC samples, and field-collected samples	Area response for each IS compound preferably within ±30% of the average response as determined from the ICAL and may not exceed ±40% (see Section 15.1.2)
Initial calibration (ICAL)	Analysis of a minimum of five calibration levels (minimum eight levels if using quadratic regression) covering approximately 20 to 5000 pptv	Before sample analysis; following failed BFB tune check (as applicable), failed IS criteria, or failed CCV criteria; or when changes/maintenance to the instrument affect calibration response	Average RRF ≤ 30% RSD and each calibration level within ±30% of theoretical concentration; for quadratic or linear curves, coefficient of determination ≥ 0.995, and each calibration level within ±30% of theoretical concentration (see Section 15.2.3)
Second source calibration verification (SSCV)	Analysis of a secondary source standard in the lower third of the calibration curve to verify ICAL accuracy for each target analyte	Immediately after each ICAL	Measured concentrations of VOCs should be within ±30% of theoretical concentration (see Section 15.3.1)
Continuing calibration verification (CCV)	Analysis of a known standard in the lower third of the calibration curve to verify ongoing instrument calibration for each target analyte	Prior to analyzing samples in an analytical sequence and at the end of a sequence; recommended after every 10 sample injections	Measured concentrations of VOCs within ±30% of theoretical concentration (see Section 15.3.2)
Instrument blank (IB)	Analysis of an injection where no sample or standard is introduced to the preconcentrator to preliminarily demonstrate the carrier gas and instrument are sufficiently clean to begin analysis	Prior to ICAL and at the beginning of an analytical sequence	Each target VOC's concentration should be < 20 pptv (see Section 15.3.3.1)
Method blank (MB)	Canister filled with clean, humidified gas; indicates that target VOCs and potential interferences are at acceptably low levels in the system as a whole; the MB is to help assess overall quality of the data	Prior to and following the ICAL and prior to the initial daily CCV/SSCV	This should demonstrate acceptably low carryover in the analytical system prior to analysis of samples; each target VOC's concentration should generally be < 20 pptv (see Section 15.3.3.2)
Calibration blank (CB)	Canister filled with clean, humidified diluent gas; indicates that diluent gas and dilution apparatus do not contribute target VOCs, imparting a positive bias to the ICAL; may also serve as zero point in the ICAL	Prepare one CB with each set of calibration standard canisters and analyze with each ICAL	CB should be sufficiently clean such that little or no positive bias is imparted to the calibration (see Section 15.3.3.3)

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Method precision	Duplicate samples: precision is determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters collected through the same sampling inlet (e.g., a rack-mounted system that employs one inlet to fill two canisters at the same time; this determines the precision of the sampling and analysis processes OR Collocated samples: precision is determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters collected through two separate sampling inlets (e.g., two MFCDs that are individually attached to two canisters); this determines the precision of the sampling and analysis processes	Applicable to the collection of samples: collect approximately 5% of total samples or minimum of three samples	Precision ≤ 25% RPD of target VOCs in the compared samples when both measurements are ≥ fivefold MDL (see Section 15.3.4)
Instrument precision	Precision is determined from repeated analyses of a gas sample from one canister; replicate analyses are used to determine precision of the analysis processes and do not provide information on sampling precision	One replicate analysis with each analytical sequence or 5% of field samples in each analytical sequence, whichever is greater	Precision ≤ 25% RPD for target VOCs when both measurements are ≥ fivefold MDL (see Section 15.3.4)
Field blank	Canister filled with clean, humidified diluent gas transported to the field site(s) with field collected samples; indicates that sample handling practices do not contaminate samples	*Optional:* prepared for transport with field-collected samples; frequency determined by method user	Each target VOC's concentration should be approximately 20 pptv or less (see Section 15.3.5)
Field spike	Canister filled with humidified standard gas at a concentration in the lower third of the calibration curve and transported to the field site(s) with field collected samples; indicates that sample handling practices do not deteriorate sample integrity	*Optional:* prepared for transport with field-collected samples; frequency determined by method user	Measured concentrations of VOCs within ±30% of theoretical spiked concentrations (see Section 15.3.5)
Audit accuracy	Analysis of an independently prepared audit standard to determine analytical accuracy	Annually at a minimum	Within ±30% of accepted reference value (see Section 15.3.6)
Preconcentrator leak check	Pressurize or evacuate the canister connection to verify as leak-free	Each canister connected to the instrument prior to analysis	< 3.4 kPa (0.5 psi) change per minute or as recommended by the manufacturer (see Section 16.1.2)
Method detection limit (MDL)	Establishes the minimum amount of a target analyte distinguishable above background with 99% confidence; determined from spiked canisters and MB canisters	Annually at a minimum	MDLs are recommended to be < 20 pptv or should meet program goals (see Table 17-2 for example MDLs)
MDL confirmation sample	Known standard prepared at approximately onefold to fivefold the determined MDL_{sp} to confirm the determined MDL is reasonable	*Not required* but recommended for MDLs determined as the MDL_{sp} (and not for those determined as the MDL_b)	Recommended recovery within 40% to 160% or other in-house defined limits (see Section 17.8)

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Appendix A: Vacuum and Pressure Units Conversion Chart

% Vacuum[a]	in. Hg Vacuum[a]	in. Hg (absolute)	mm Hg and Torr (absolute)	mbar (absolute)	psia (absolute)	kPa (absolute)
0%	0	29.92	760	1013.3	14.7	101.325
10%	2.99	26.93	684	912.2	13.23	91.217
20%	5.98	23.94	608	810.8	11.76	81.082
30%	8.98	20.94	532	709.5	10.29	70.947
40%	11.97	17.95	456	608.1	8.82	60.812
50%	14.96	14.96	380	506.8	7.35	50.676
60%	17.95	11.97	304	405.4	5.88	40.541
70%	20.94	8.98	228	304.1	4.41	30.406
80%	23.94	5.98	152	202.7	2.94	20.271
90%	26.93	2.99	76.0	101.4	1.47	10.135
91%	27.23	2.69	68.4	91.0	1.32	9.101
92%	27.53	2.39	60.8	81.4	1.18	8.136
93%	27.83	2.09	53.2	71.0	1.03	7.102
94%	28.13	1.79	45.6	60.7	0.88	6.067
95%	28.42	1.50	38.0	50.3	0.73	5.033
96%	28.72	1.20	30.4	40.7	0.59	4.068
97%	29.02	0.90	22.8	30.3	0.44	3.034
98%	29.32	0.60	15.2	20.0	0.29	1.999
99%	29.62	0.30	7.6	10.3	0.15	1.034
99.10%	29.65	0.27	6.8	8.96	0.13	0.896
99.20%	29.68	0.24	6.1	8.27	0.12	0.827
99.30%	29.71	0.21	5.3	6.89	0.10	0.689
99.40%	29.74	0.18	4.6	6.21	0.09	0.621
99.50%	29.77	0.15	3.8	4.83	0.07	0.483
99.60%	29.80	0.12	3.0	4.14	0.06	0.414
99.70%	29.83	0.09	2.3	2.76	0.04	0.276
99.80%	29.86	0.06	1.5	2.07	0.03	0.207
99.90%	29.89	0.03	0.8	0.69	0.01	0.069
100%	29.92	0	0	0	0	0

[a] The % vacuum and in. Hg vacuum assume that the reference barometric pressure is at standard conditions of 101.325 kPa.

Appendix B: The 97 VOCs Included in the 189 Hazardous Air Pollutants Listed in the Clean Air Act Amendments

Compound (Alternative Name)[a]	Empirical Formula	CAS Number
Chloromethane (methyl chloride)	CH_3Cl	74-87-3
Carbonyl sulfide	COS	463-58-1
Chloroethene (vinyl chloride)	C_2H_3Cl	75-01-4
Diazomethane	CH_2N_2	334-88-3
Formaldehyde	CH_2O	50-00-0
1,3-Butadiene (butadiene)	C_4H_6	106-99-0
Bromomethane (methyl bromide)	CH_3Br	74-83-9
Phosgene (carbonyl dichloride)	CCl_2O	75-44-5
Vinyl bromide (bromoethene)	C_2H_3Br	593-60-2
Ethylene oxide	C_2H_4O	75-21-8
Chloroethane (ethyl chloride)	C_2H_5Cl	75-00-3
Acetaldehyde (ethanal)	C_2H_4O	75-07-0
1,1-Dichloroethene (vinylidene chloride)	$C_2H_2Cl_2$	75-35-4
Propylene oxide	C_3H_6O	75-56-9
Methyl iodide (iodomethane)	CH_3I	74-88-4
Dichloromethane (methylene chloride)	CH_2Cl_2	75-09-2
Methyl isocyanate	C_2H_3NO	624-83-9
Allyl chloride (3-chloropropene)	C_3H_5Cl	107-05-1
Carbon disulfide (methanedithione)	CS_2	75-15-0
2-Methoxy-2-methylpropane (methyl *tert*-butyl ether, MTBE)	$C_5H_{12}O$	1634-04-4
Propionaldehyde (propanal)	C_3H_6O	123-38-6
1,1-Dichloroethane (ethylidene chloride)	$C_2H_4Cl_2$	75-34-3
2-Chloro-1,3-butadiene (chloroprene)	C_4H_5Cl	126-99-8
Chloromethyl methyl ether (chloro(methoxy)methane)	C_2H_5ClO	107-30-2
2-Propenal (acrolein)	C_3H_4O	107-02-8
1,2-Epoxybutane (1,2-butylene oxide)	C_4H_8O	106-88-7
Trichloromethane (chloroform)	$CHCl_3$	67-66-3
Ethyleneimine (aziridine)	C_2H_5N	151-56-4
1,1-Dimethylhydrazine	$C_2H_8N_2$	57-14-7
Hexane	C_6H_{14}	110-54-3
Propyleneimine (2-methylaziridine)	C_3H_7N	75-55-8
2-Propenenitrile (acrylonitrile)	C_3H_3N	107-13-1
1,1,1-Trichloroethane (methyl chloroform)	$C_2H_3Cl_3$	71-55-6
Methanol (methyl alcohol)	CH_4O	67-56-1
Carbon tetrachloride (tetrachloromethane)	CCl_4	56-23-5
Ethenyl acetate (vinyl acetate)	$C_4H_6O_2$	108-05-4
2-Butanone (methyl ethyl ketone, MEK)	C_4H_8O	78-93-3

Compound (Alternative Name)[a]	**Empirical Formula**	**CAS Number**
Benzene	C_6H_6	71-43-2
Acetonitrile (cyanomethane)	C_2H_3N	75-05-8
1,2-Dichloroethane (ethylene dichloride)	$C_2H_4Cl_2$	107-06-2
Triethylamine (N,N-diethylethanamine)	$C_6H_{15}N$	121-44-8
Methylhydrazine	CH_6N_2	60-34-4
1,2-Dichloropropane (propylene dichloride)	$C_3H_6Cl_2$	78-87-5
2,2,4-Trimethylpentane (isooctane)	C_8H_{18}	540-84-1
1,4-Dioxane (*p*-dioxane)	$C_4H_8O_2$	123-91-1
bis(Chloromethyl) ether (chloro(chloromethoxy)methane)	$C_2H_4Cl_2O$	542-88-1
Ethyl acrylate (ethyl prop-2-enoate)	$C_5H_8O_2$	140-88-5
Methyl methacrylate (methyl 2-methylprop-2-enoate)	$C_5H_8O_2$	80-62-6
cis-1,3-Dichloropropene (*cis*-1,3-dichloropropylene)	$C_3H_4Cl_2$	10061-01-5
Toluene (methylbenzene)	C_7H_8	108-88-3
1,1,2-Trichloroethene (trichloroethene)	C_2HCl_3	79-01-6
1,1,2-Trichloroethane	$C_2H_3Cl_3$	79-00-5
Tetrachloroethene (perchloroethylene)	C_2Cl_4	127-18-4
Epichlorohydrin (2-(chloromethyl)oxirane)	C_3H_5ClO	106-89-8
1,2-Dibromoethane (ethylene dibromide)	$C_2H_4Br_2$	106-93-4
N-Nitroso-N-methylurea (1-methyl-1-nitrosourea)	$C_2H_5N_3O_2$	684-93-5
2-Nitropropane	$C_3H_7NO_2$	79-46-9
Chlorobenzene	C_6H_5Cl	108-90-7
Ethylbenzene	C_8H_{10}	100-41-4
Xylenes (isomer and mixtures)	C_8H_{10}	1330-20-7
Styrene (vinylbenzene)	C_8H_8	100-42-5
p-Xylene (1,4-xylene)	C_8H_{10}	106-42-3
m-Xylene (1,3-xylene)	C_8H_{10}	108-38-3
4-Methyl-2-pentanone (methyl isobutyl ketone, MBK)	$C_6H_{12}O$	108-10-1
Tribromomethane (bromoform)	$CHBr_3$	75-25-2
1,1,2,2-Tetrachloroethane (tetrachloroethane)	$C_2H_2Cl_4$	79-34-5
o-Xylene (1,2-xylene)	C_8H_{10}	95-47-6
Dimethylcarbamoyl chloride (dimethylcarbamyl chloride)	C_3H_6ClNO	79-44-7
N-Nitrosodimethylamine (N,N-dimethylnitrous amide)	$C_2H_6N_2O$	62-75-9
beta-Propiolactone	$C_3H_4O_2$	57-57-8
Isopropylbenzene (cumene)	C_9H_{12}	98-82-8
Acrylic acid (2-propenoic acid)	$C_3H_4O_2$	79-10-7
N,N-Dimethylformamide	C_3H_7NO	68-12-2
1,3-Propane sultone	$C_3H_6O_3S$	1120-71-4
Acetophenone	C_8H_8O	98-86-2
Dimethyl sulfate	$C_2H_6O_4S$	77-78-1
Chloromethylbenzene (benzyl chloride)	C_7H_7Cl	100-44-7
1,2-Dibromo-3-chloropropane	$C_3H_5Br_2Cl$	96-12-8
bis(2-Chloroethyl)ether	$C_4H_8Cl_2O$	111-44-4

Compound (Alternative Name)[a]	**Empirical Formula**	**CAS Number**
2-Chloroacetic acid	$C_2H_3ClO_2$	79-11-8
Aniline (aminobenzene)	C_6H_7N	62-53-3
p-Dichlorobenzene (1,4-dichlorobenzene)	$C_6H_4Cl_2$	106-46-7
Ethyl carbamate (urethane)	$C_3H_7NO_2$	51-79-6
Acrylamide (2-propenamide)	C_3H_5NO	79-06-1
N,N-Dimethylaniline	$C_8H_{11}N$	121-69-7
Hexachloroethane (1,1,1,2,2,2-hexachloroethane)	C_2Cl_6	67-72-1
Hexachlorobutadiene (hexachloro-1,3-butadiene)	C_4Cl_6	87-68-3
Isophorone	$C_9H_{14}O$	78-59-1
N-Nitrosomorpholine (4-nitrosomorpholine)	$C_4H_8N_2O_2$	59-89-2
Styrene oxide (2-phenyloxirane)	C_8H_8O	96-09-3
Diethyl sulfate	$C_4H_{10}O_4S$	64-67-5
Cresylic acid (cresol isomer mixture)	C_7H_8O	1319-77-3
o-Cresol (2-methylphenol)	C_7H_8O	95-48-7
Catechol (1,2-dihydroxybenzene)	$C_6H_6O_2$	120-80-9
Phenol	C_6H_6O	108-95-2
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	120-82-1
Nitrobenzene	$C_6H_5NO_2$	98-95-3

[a] Compound information is derived from PubChem (https://pubchem.ncbi.nlm.nih.gov/), an open chemistry database from the National Institutes of Health, U.S. National Library of Medicine, National Center for Biotechnology Information.

Appendix C: Some Commercial Vendors of Analytical and Sample Collection Instruments and Supplies

Agilent
5301 Stevens Creek Blvd
Santa Clara, CA 95051
(877) 424-4536
www.agilent.com
[GC, MS]

Airgas USA, LLC
(formerly Air Liquide America, LLC)
259 N. Radnor-Chester Road, Suite 100
Radnor, PA 19087
800 255-2165
www.airgas.com
[Scott calibration standards]

Apel Riemer Environmental, Inc.
1295 NW 163rd Street
Miami, FL 33169
(786) 925-6201
Email: **riemer@apelriemerenvironmental.com**
[VOC standards]

ATEC
9727 Cotharin Road
Malibu, CA 90265
(310) 457-2671
www.atec-online.com
[sampling instruments]

Bruker BioSpin Corporation
15 Fortune Drive
Billerica, MA 01821
(978) 667-9580
www.bruker.com
[preconcentration, GC, MS]

Entech Instruments, Inc
2207 Agate Court
Simi Valley, CA 93065
(805) 527-5939
www.entechinst.com
[sampling hardware, preconcentration,
canister cleaner]

Essex Industries
7700 Gravois Road
St. Louis, MO 63123
(314) 832-4500
www.essexindustries.com
[sampling media]

Lab Commerce, Inc.
681 E. Brokaw Road
San Jose, CA 95112
(408) 265-6482
www.labcommerce.com
[sampling media, sampling instruments]

LECO Corporation
3000 Lakeview Avenue
Saint Joseph, MI 49085
(269) 985-5496
www.leco.com
[MS]

Markes International, Inc.
2355 Gold Meadow Way
Gold River, Sacramento, CA 95670
(866) 483-5684
www.markes.com
[preconcentration, GC, MS]

Messer North America, Inc.
(formerly Linde North America, Inc.)
200 Somerset Boulevard, Suite 7000
Bridgewater, NJ 08807
(800) 755-9277
www.messer-us.com
[environmental/VOC standards]

NuTech
651 N. Plano Road #429
Richardson, TX 75081
(972) 480-8908
http://www.nutechins.com
[sampling instruments, preconcentration]

PerkinElmer
710 Bridgeport Avenue
Shelton, CT 06484-4794
(203) 925-4600
www.perkinelmer.com
[GC, MS]

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823
(800) 356-1688
www.restek.com
[sampling hardware, GC, canister cleaner]

Shimadzu Scientific Instruments, Inc.
7102 Riverwood Drive
Columbia, MD 21046
(800) 477-1227
www.ssi.shimadzu.com
[GC, MS]

ThermoFisher Scientific
(formerly Finnigan/ThermoQuest)
168 Third Avenue
Waltham, MA 02451
https://www.thermofisher.com
(800) 678-5599
[GC, MS]

Tisch Environmental
145 South Miami Avenue
Cleves, OH 45002
(877) 263-7610
tisch-env.com
[sampling instruments]

Wasson-ECE Instrumentation
101 Rome Court
Fort Collins, CO 80524
(970) 221-9179
wasson-ece.com
[canister cleaner]

Xonteck, Inc.
4009 Clipper Court
Fremont, CA 94538
(805) 547-2022
www.xonteck.com
[sampling instruments, canister cleaner]

Stericycle®
Environmental Solutions

May 17, 2016

Mr. Daniel Dailey, P.E.
Michigan Department of Environmental Quality
525 West Allegan Street
Lansing, Michigan 48933

RE: Petro-Chem Processing Group of Nortru, LLC Inc.
Ambient Air Monitoring Program Update
Minor License Modification Request

Dear Mr. Dailey:

This letter is in response to your June 1, 2016 communication which specifically discusses the Petro-Chem Processing Group of Nortru, LLC Inc. (PCPG), located in Detroit, Michigan and the current Environmental Monitoring Program. The Michigan Department of Environmental Quality (MDEQ) provided comments to assist in updating and/or changing the current ambient air monitoring program and completing a minor modification of the operating license from using the TO-17 (tubes) method to the TO-15 (canisters) method.

To provide a greater consistency in collection methodology and to achieve requested method detection limits PCPG is proposing the described minor modification. The revised Ambient Monitoring Network Plan and Form EQP 5111 Attachment B5 (appropriate sections) are attached for your review and approval. Your comments provided have been incorporated.

We would like to initiate the change to the TO-15 Method as soon as possible following your direction. If there are any questions or comments, please contact me at either (313) 824-5840, Ext. 155, or ed.burk@stericycle.com. We look forward to your response.

Sincerely,

STERICYCLE ENVIRONMENTAL SOLUTIONS

Edward C. Burk, Jr.
Compliance Manager

enclosures

c: S. Kilmer, MDEQ
J. Day, MDEQ
A. Jones, Stericycle
M. Frohriep, Stericycle

resourceful. naturally.
engineering and environmental consultants
BARR

Memorandum

To: Dan Dailey, EGLE MMD
From: Barr Engineering Co.
Subject: Petro-Chem Processing Group of Nortru (PCPG) Air Monitoring Network
Date: May 19, 2022
Project: 22821113.05
c: Ed Burk, Jr., Clean Earth, Greg Patten and Teresa Kinder, Barr Engineering Co.

Petro-Chem Processing Group of Nortru, LLC (PCPG) is requesting approval of a waiver of the monitoring program pursuant to Rule 611(4) following a three-month testing period once the new container management building commences operation. Rule 611(4) allows the director to grant the waiver if the owner or operator demonstrates that monitoring is not required or that a lesser degree of monitoring can be utilized to demonstrate compliance with the provisions of Part 111.

The data presented in this memorandum supports the reduction of the monitoring locations to only MS-2, analyzing for only TCE monthly. In addition, after three months of operations occurring in the new container management building (CMB-2) that will capture and control the loading/unloading commingling emissions with an activated carbon system and if TCE is below the AQD ITSL, all air monitoring requirements should be waived.

Executive Summary

Currently PCPG is required to operate an air monitoring network pursuant to Michigan Environment, Great Lakes, and Energy (EGLE) Materials Management Division (MMD) Rule R 299.9611(2)(a). The air monitoring network consists of four (4) monitoring stations that collects eight hours of samples over a 24-hour period for analysis of Benzene, Carbon Tetrachloride, Chloroform, Methylene Chloride, Tetrachlorethene (PCE), Trichloroethene (TCE), Vinyl Chloride, 1,1,1-Trichloroethane, Toluene and Xylene. Of these analytes, Benzene, PCE, Toluene and TCE have EGLE Air Quality Division (AQD)-established 24-hour average initial threshold screening levels (ITSL), which would align with the appropriate sampling averaging period. Of these compounds, TCE is the only compound that has resulted in samples above the AQD 24-hour average ITSL of 2 ug/M^3, with the sampling predominantly at one of the monitoring stations, MS-2. The other three monitoring stations had a few observations above the TCE ITSL of 2 ug/M^3, described as follows. Monitoring station MS-1 only experienced four (4) observations above the TCE AQD 24-hour average ITSL, with just two of the samples potentially traceable to PCPG due to the wind direction coming from offsite for the other two sampling events. MS-3 did not experience any samples above the ITSL, and MS-4 only one observation above the ITSL for the previous 2-year time period. The single observation at MS-4 had winds predominately out of the south and east, which indicates the source of the TCE is not PCPG. Therefore, the single reading would not be attributable to PCPG. Accordingly, this leaves only monitoring station MS-2 with readings that could reliably be attributed to PCPG operations. The air monitoring network data presented in this memorandum has already been provided to MMD in the monthly report submittals. See attached figure for the locations of the monitoring stations.

PCPG is proposing to relocate the existing container loading/unloading (commingling) operations into a new enclosed container management building (CMB-2). It is proposed that the new CMB-2 building will be designed to control emissions from the container loading/unloading operation by capturing the air in the building and controlling it through an activated carbon system. The enclosure of the loading/unloading operations as well as the addition of the activated carbon system will result in a reduction of volatile organic compounds (VOCs), which is potentially a source of monitoring station MS-2 TCE readings.

Based on this information presented in this memorandum, PCPG is requesting to maintain only MS-2 air monitoring station and sampling for only TCE on a monthly schedule until the proposed CMB-2 is in operation. After the new container management operations has commenced, PCPG proposes to continue monitoring MS-2 for three months and will assess if any samples are above the AQD 24-hour average ITSL. If no observations above the AQD 24-hour average ITSL for TCE of 2 mg/M^3 occur during the three-month period, the air monitoring network will no longer be needed and PCPG will cease operation of the air monitoring network.

Monitoring Sampling Results Summary

Currently, the PCPG Detroit facility hazardous waste operating license pursuant to Part 111 requires an air monitoring network. The air monitoring network updated plan (Plan) was submitted to EGLE and approved in 2011. The Plan consists of four monitoring locations that collect an 8-hour composite sample over a 24-hour period (1 minute on, two minutes off) every six days. See the attached figure for the four monitoring station locations. The samples are then sent to a laboratory for analysis in accordance with USEPA Method TO-15. The following lists the analytes reported monthly.

- Benzene
- Carbon Tetrachloride
- Chloroform
- Methylene Chloride
- Tetrachlorethene
- Trichloroethene
- Vinyl Chloride
- 1,1,1-Trichloroethane
- Toluene
- Xylene

Of these compounds, Benzene, Tetrachloroethene (PCE), Toluene and Trichloroethene (TCE) have AQD-established 24-hour average initial threshold screening levels (ITSL). Of these compounds, TCE is the only compound that has observed results above the AQD 24-hour average ITSL of 2 ug/M^3. These TCE analytical results for the most recent two-year time period (2020/2021) for each monitoring station (MS-1, MS-2, MS-3 and MS-4) are presented in the tables attached to this memorandum. Of note, MS-3 did not experience any results above the TCE ITSL for the two-year time period and MS-4 only experienced one sample above the ITSL. The remaining four analyte results for 2016 through 2021 are presented in the attached tables. The air monitoring network data presented in this memorandum has already been provided to MMD in the monthly report submittals.

For each day that any of the monitors with the TCE result above the 24-hour average ITSL, the wind speed and direction were captured to evaluate the potential source of the TCE. As noted, and what would be expected, the winds shift throughout the 24-hour sample collection period, resulting with uncertainty of the source of the TCE. Monitoring station MS-3 did not experience any readings above the ITSL for all samples collected in 2020 and 2021. For MS-4 located on the southern property line, the single reading above the AQD ITSL threshold most likely would be coming from offsite with the winds mainly coming from the south and southeast for that day. For MS-1, only four readings out of the 121 sampling days in 2020/2021 were measured above the AQD ITSL. Of the four days, only two days had wind directions that could potentially attribute the TCE to PCPG. Whereas MS-2 appears to have readings that could potentially be attributed to PCPG. With that, PCPG proposes to continue collecting samples and analysis on a monthly basis from only the MS-2 location. In addition, because none of the other compounds experienced readings above the associate AQD screening threshold, the need for analysis of those analytes is not warranted and PCPG proposes limiting the analyte sampling/monitoring at MS-2 to only TCE.

PCPG is requesting the installation and operation of a new CMB2 to enclose the current loading/unloading operations. PCPG is proposing to capture and control the emissions from the loading/unloading waste commingling operations with an activated carbon control system. After the operation of the proposed container management building with activated carbon control commences, PCPG recommends continuing the operations of MS-2 for three months and sampling on a monthly basis. The continued operation of MS-2 for the first three months after operation of the new container management along with maintaining the leak detection and repair (LDAR) program according to the AQD approved LDAR plan as noted in the Regulatory Background section below is sufficient to demonstrate compliance with the applicable requirements, specifically the AQD TCE air quality screening threshold and Part 111 Rule 611.

Regulatory Background

The MMD and AQD have federally approved programs for Resource Conservation Recovery Act (RCRA) and delegation for applicable Clean Air Act (CAA) federal programs such as New Source Performance Standards (NSPS) and National Emission Standards for Hazardous Air Pollutants (NESHAP) programs.

Michigan RCRA regulations are contained in Part 111, which includes Rule 611 (R 299.9611). The specific ambient air monitoring requirement is as follows:

(2) An owner or operator shall do all of the following as part of the environmental monitoring program:

> *(c) Conduct an ambient air monitoring program approved by the director or his or her designee to detect violations of the provisions of part 55 of the act.*

As noted, the air monitoring program is to detect violations of the provisions of part 55 of the act. Because part 55 is the driver for the air network, it is important to understand the applicable part 55 requirements. Part 55 grants AQD the powers to promulgate rules to establish standards for ambient air quality and for emissions. Rules 336.1224 through 336.1228 and 336.1901 are the applicable regulations to Rule 611 ambient air monitoring program for PCPG. These rules apply to a facility subject to the requirements of Rule 201 Permit to Install (PTI) review. Because PCPG is not undergoing activities that would trigger air permitting pursuant to Rule 201, Rules 336.1224 through 336.1228 would not apply. PCPG did apply for and receive an air PTI for their existing operations. The facility has been subjected to several Rule 201 PTI reviews with the issuance of PTI Nos. 84-04B, 84-04C, and 184-13, which were voided upon issuance of PTI No. 6-19 on June 18, 2019. AQD had several opportunities to evaluate PTI No. 6-19 with Rules 336.1224 through 336.1228 requirements and resulted in an emission limit of 6.9 VOC tons per year (tpy) for FG-2019 and 8.9/22.5 tpy hazardous air pollutants, which keeps the facility as an area source of the CAA and is not established as a result of Rules 336.1224 through 336.1228. The existing air permits do not contain emission limits of the specific analyte as listed in the air monitoring network plan. The existing air permit does require the implementation of the LDAR plan, a malfunction abatement plan and several other monitoring, recordkeeping requirements, design parameters, and material limits with underlying applicable requirements of R 336.1224 through 336.1228. However, the existing air permit does not limit the specific analytes or require the air monitoring network. In fact, the latest AQD inspection report specifically states that the air monitoring network is regulated by MMD pursuant to Part 111 Hazardous Waste Management operating license.[1] That leaves Rule 901. Rule 901 states:

Rule 901. Notwithstanding the provisions of any other rule, a person shall not cause or permit the emission of an air contaminant or water vapor in quantities that cause, alone or in reaction with other air contaminants, either of the following:

> *(a) Injurious effects to human health or safety, animal life, plant life of significant economic value, or property.*
>
> *(b) Unreasonable interference with the comfortable enjoyment of life and property.*

---

[1] AQD compliance inspection staff activity report dated September 24, 2020. https://www.egle.state.mi.us/aps/downloads/SRN/N0731/N0731_SAR_20200924.pdf

Both Rule 901(a) and (b) would not apply to the PCPG because neither injurious effects or unreasonable interference with the comfortable enjoyment of life and property; also known as nuisance odors, has occurred. As noted in the most recent air compliance inspection staff report dated September 24, 2020, AQD determined the facility to be in compliance with all air requirements.

Part 111, including Rule 611(1)-(3) was part of the original hazardous waste regulations, which was approved by USEPA October 30, 1986. After the original rules package, Rule 611(4) became effective October 15, 1996, which is after the implementation of the CAA regulating hazardous air pollutants and Michigan toxic air contaminant Rules R 336.1224 through R 336.1228. Rule 611(4) allows the director to waive all or portions of the environmental monitoring.

> *(4) The director shall waive the requirements of subrule (2)(c) and (d) of this rule if the owner or operator demonstrates that monitoring is not required or that a lesser degree of monitoring can be utilized to demonstrate compliance with the provisions of part 111 of the act and these rules.*

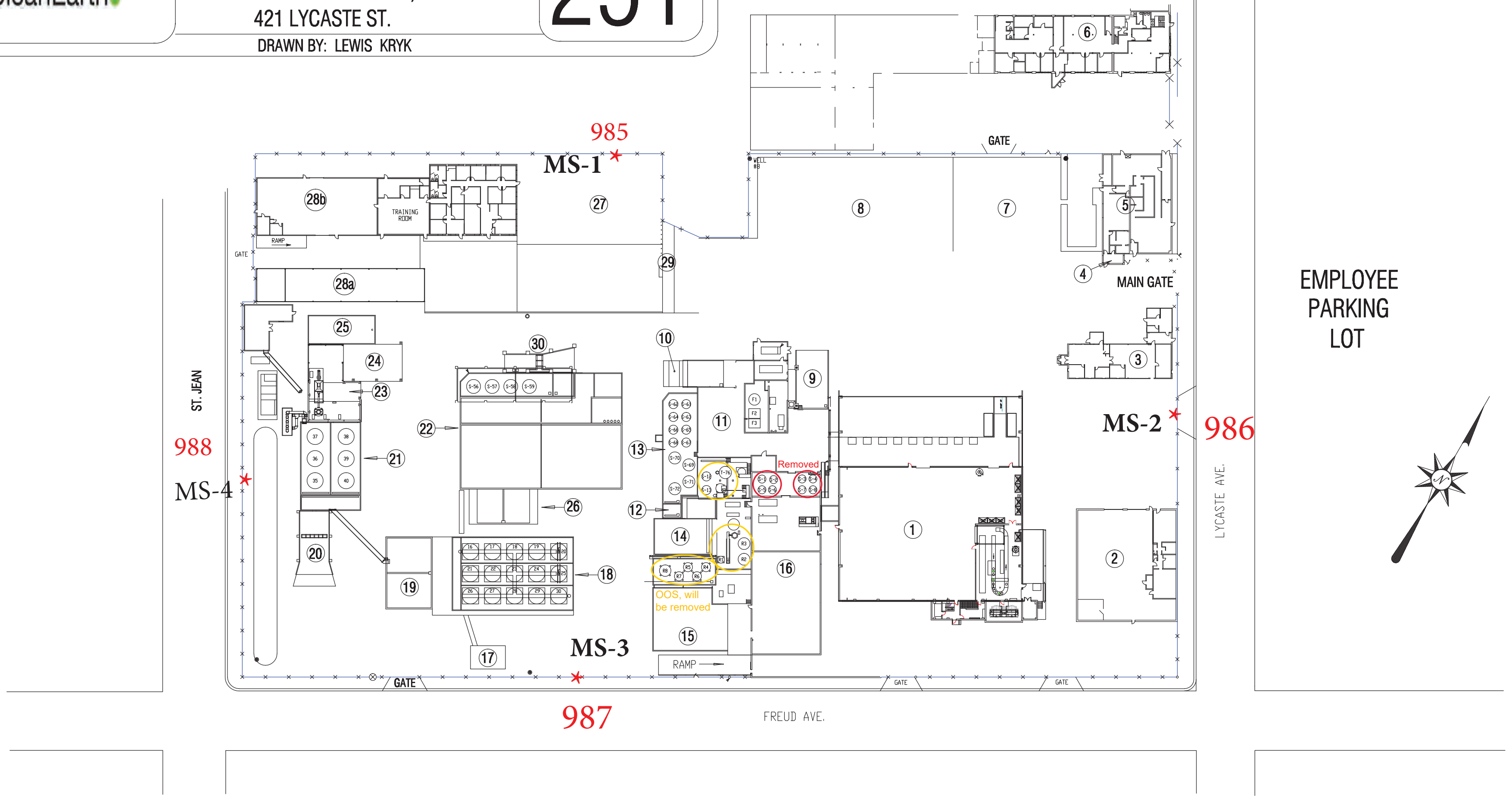
With the implementation of the CAA programs regulating hazardous air pollutants, USEPA understood that TSDF regulated facilities would be subject to overlapping monitoring programs of RCRA AA, BB, and CC air monitoring requirements and the CAA leak detection and repair (LDAR) program.

Specific to the ambient air requirements, state-only toxic regulations for all organic air emission units would subsume the federal CAA provisions. Because the air permit for the facility has been reviewed and determined to be in compliance with the air permit (see Sept 24, 2020 inspection report), PCPG has demonstrated compliance with all of its applicable regulatory air requirements. The USEPA recognized TSDF regulated facilities subject to CAA programs such as LDAR was sufficient with demonstrating compliance with RCRA programs. The analytical results of the existing air monitoring network show only TCE is above the state-only screening threshold periodically at one of the monitoring stations MS-2. As noted above in the monitoring sampling results summary section above and the attached tables, the results support maintaining MS-2 for three months after the operations of the container management building with activated carbon along with implementation of the approved LDAR program. PCPG is requesting approval of a waiver of the monitoring program pursuant to Rule 611(4) following the three-month testing period after the new container management building commences operation. Rule 611(4) allows the director to grant the waiver if the owner or operator demonstrates that monitoring is not required or that a lesser degree of monitoring can be utilized to demonstrate compliance with the provisions of Part 111. The data presented in this memorandum supports the reduction of the monitoring locations to only MS-2, analyzing for only TCE on a monthly basis. In addition, after three months of operations occurring in the new CMB-2 that is proposed to be designed so as to capture and control the loading/unloading emissions with an activated carbon system, and if TCE is below the AQD ITSL, all air monitoring requirements should be waived.

CleanEarth

DATE 07/18/18
PETROCHEM PROCESSING
GROUP OF NORTRU, LLL
421 LYCASTE ST.
DRAWN BY: LEWIS KRYK

251



① — CMB - CONTAINER MANAGEMENT BLDG.
② — MAINTENANCE BLDG.
③ — LABORATORY
④ — SECURITY
⑤ — LOCKER ROOM / BREAK ROOM
⑥ — ADMINISTRATION OFFICE
⑦ — TRUCK STAGING AREA
⑧ — 72 HR. TRUCK STAGING AREA
⑨ — DOCK 4
⑩ — DOCK 3
⑪ — 1ST. FLOOR OPERATIONS
⑫ — CONTAINER STAGING AREA
⑬ — TS3-TANK SYSTEM 3
⑭ — TS3-TRANSFER PAD
⑮ — DOCK 2
⑯ — QA / QC AREA
⑰ — MCC - MOTOR CONTROL CENTER
⑱ — TSI - TANK SYSTEM 1
⑲ — TS1 - TRANSFER PAD
⑳ — TS2 - TRANSFER PAD
㉑ — TS2 - TANK SYSTEM 2
㉒ — TANK SYSTEM 4
㉓ — SBS - SOLIDS AREA
㉔ — SBS - DOCK STORAGE AREA
㉕ — SBS - CONTANER STORAGE
㉖ — TS4 - TRANSFER PAD
㉗ — SOLID WASTE NON HAZARDOUS AREA
(28a) — SUPPLY STORAGE
(28b) — SUPPLY STORAGE
㉙ — PROPANE STORAGE
㉚ — NON HAZ

* MS-1 thru MS-7 = Ambient Air Monitoring Locations

Petro-Chem Processing Group - Air Monitoring
Air Monitoring Networks Results - TCE 2020-2021

TCE	**ITSL 24-hr**	**2 ug/m3**	**DL**	**0.02 ug/m3**
Monitoring Station	**MS-1**	**MS-2**	**MS-3**	**MS-4**
2020-21 No. Sample	121	121	121	121
2020-21 %ND	43.0	37.2	44.6	62.8
2020-21 >2ug/M3	**4**	**16**	**0**	**1**
3/4/2020	ND	4	0	0
7/14/2020	1	23	ND	0
8/19/2020	0	33	0	ND
9/30/2020	ND	8	1	ND
10/12/2020	ND	0	0	3
11/5/2020	0	9	ND	0
2/22/2021	ND	3	0	ND
2/28/2021	ND	3	ND	ND
3/24/2021	ND	9	ND	ND
3/30/2021	ND	3	ND	ND
4/11/2021	1	3	0	0
4/23/2021	2	21	ND	ND
5/5/2021	ND	7	1	0
5/17/2021	7	0	ND	0
5/23/2021	4	1	0	ND
7/22/2021	10	13	ND	0
9/20/2021	24	15	ND	ND
9/26/2021	1	3	ND	ND
10/2/2021	ND	7	ND	ND

Petro-Chem Processing Group - Air Monitoring
Air Monitoring Networks Results 2016-2021

BENZENE	ITSL 24-hr	30 ug/m3	DL	0.05 ug/m3
Monitoring Station	**MS-1**	**MS-2**	**MS-3**	**MS-4**
2016-21 No. Sample	373	373	373	373
2016-21 %ND	94.9	93.0	91.4	95.7
2016-21 >30ug/M3	**0**	**0**	**0**	**0**
2020-21 No. Sample	121	121	121	121
2020-21 %ND	100.0	91.7	100.0	100.0
2020-21 >30ug/M3	**0**	**0**	**0**	**0**

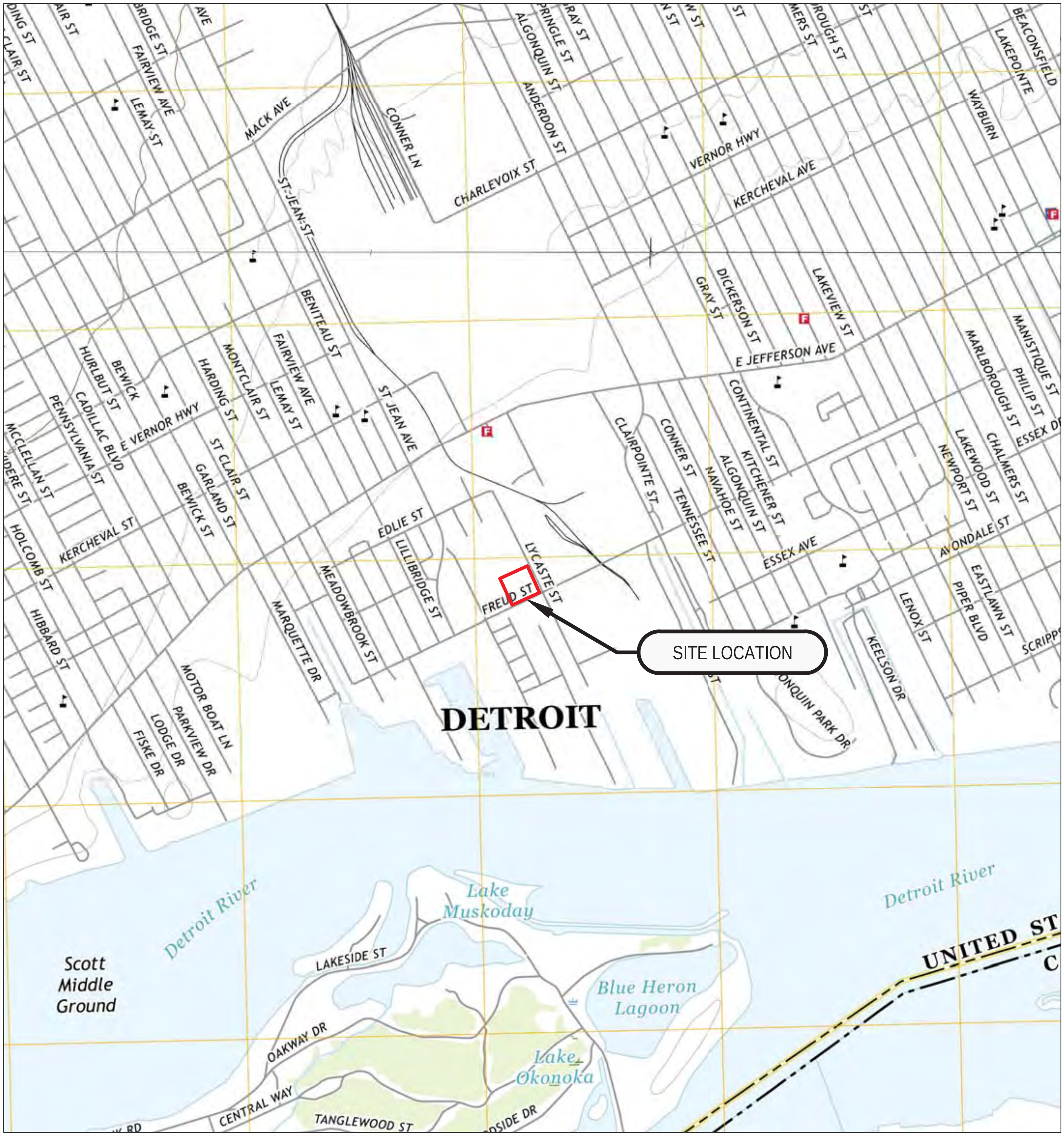
PCE	ITSL 24-hr	1400 ug/m3	DL	0.05 ug/m3
Monitoring Station	**MS-1**	**MS-2**	**MS-3**	**MS-4**
2016-21 No. Sample	312	312	312	312
2016-21 %ND	86.9	91.0	86.2	93.3
2016-21 >1400ug/M3	**0**	**0**	**0**	**0**
2020-21 No. Sample	121	121	121	121
2020-21 %ND	93.4	88.4	96.7	99.2
2020-21 >1400ug/M3	**0**	**0**	**0**	**0**

TOLUENE	ITSL 24-hr	5000 ug/m3	DL	1.00 ug/m3
Monitoring Station	**MS-1**	**MS-2**	**MS-3**	**MS-4**
2016-21 No. Sample	312	312	312	312
2016-21 %ND	39.1	46.8	30.4	59.0
2016-21 >5000ug/M3	**0.0**	**0.0**	**0.0**	**0.0**
2020-21 No. Sample	121	121	121	121
2020-21 %ND	34.7	37.2	38.0	69.4
2020-21 >5000ug/M3	**0.0**	**0.0**	**0.0**	**0.0**

111 TCA	ITSL 24-hr	6000 ug/m3	DL	1.5 ug/m3
Monitoring Station	**MS-1**	**MS-2**	**MS-3**	**MS-4**
2016-21 No. Sample	373	373	373	373
2016-21 %ND	96.8	94.9	95.2	96.8
2016-21 >5000ug/M3	**0.0**	**0.0**	**0.0**	**0.0**
2020-21 No. Sample	121	121	121	121
2020-21 %ND	100.0	96.7	100.0	100.0
2020-21 >5000ug/M3	**0.0**	**0.0**	**0.0**	**0.0**

Appendix B5.1

Ground Water (GW) Contour Diagram



QUADRANGLE LOCATION

Scale 1:24000

0 1/2 1 MILE

1000 0 1000 2000 3000 FEET

SOURCE OF MAP IS US TOPO 7.5 MINUTE QUADRANGLE MAP, BELLE ISLE (2017), MICHIGAN: U.S. GEOLOGICAL SURVEY

SITE LOCATION/BOUNDARIES APPROXIMATED

N

CHECK BY	KW
DRAWN BY	JL
DATE	7/25/2019
SCALE	AS SHOWN
CAD NO.	11.19.076.00A
PRJ NO.	11019-000076.00

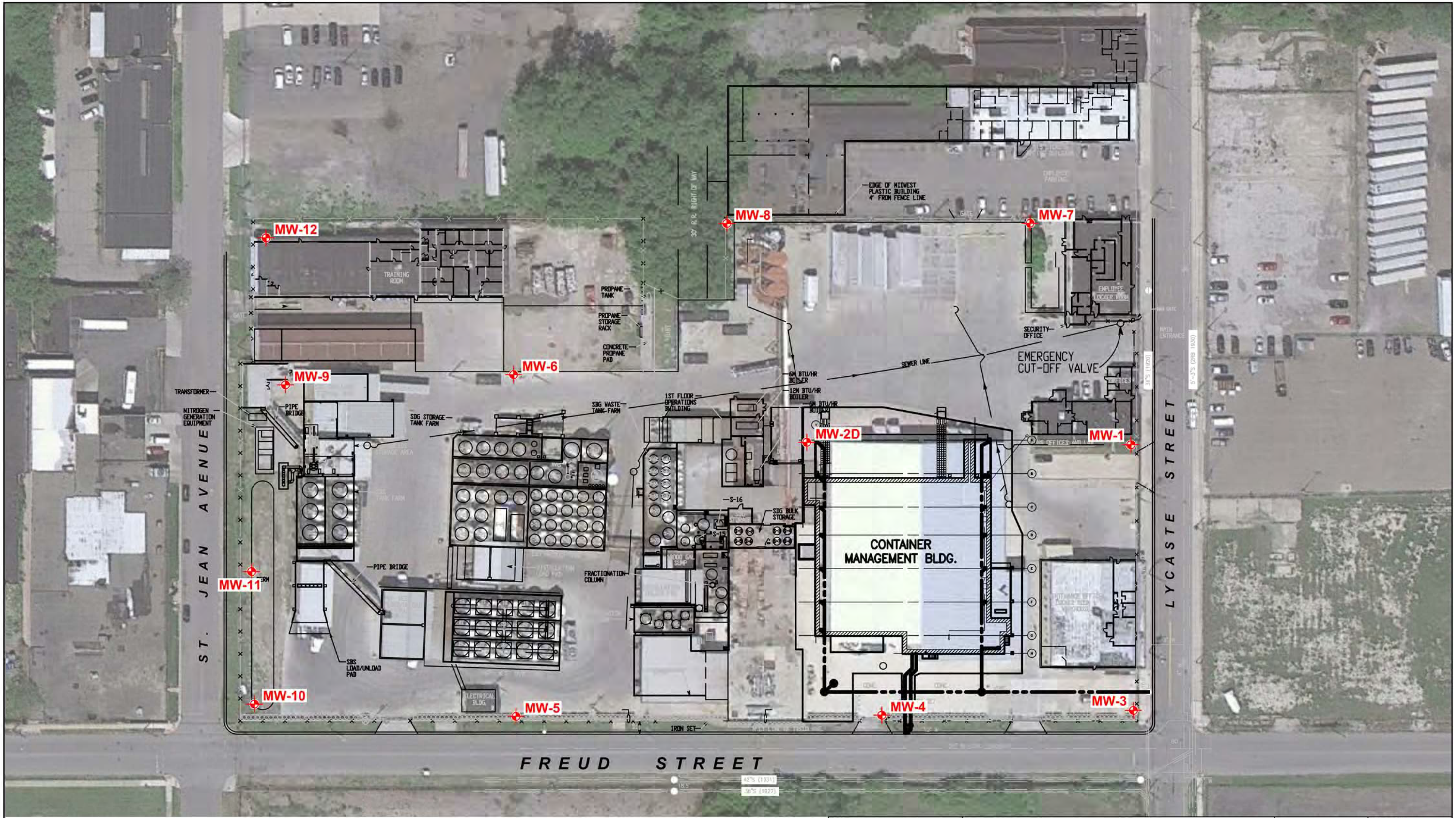
SITE LOCATION MAP

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE

1



LEGEND

MW-# MONITORING WELL LOCATION

SCALE IN FEET

0 40 80 160

CHECK BY KW
DRAWN BY JL
DATE 7/25/2019
SCALE AS SHOWN
CAD NO. 11.16.143.00b
PRJ NO. 11016-000143.00

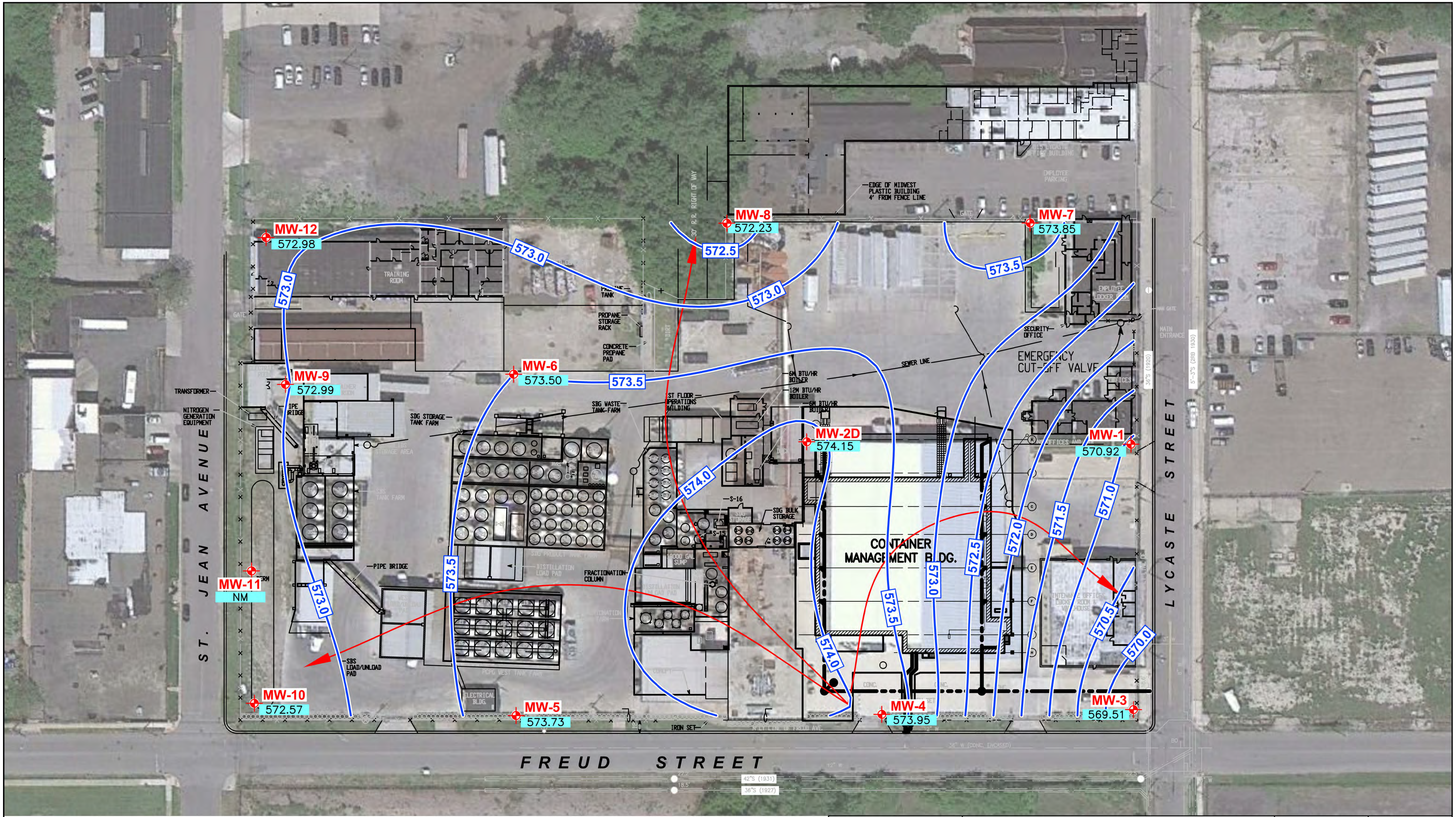
SAMPLING LOCATIONS

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE

2



LEGEND

571.0	GROUNDWATER CONTOUR
569.51	GROUNDWATER ELEVATION (FT.)
←	GROUNDWATER FLOW

SCALE IN FEET
0 40 80 160

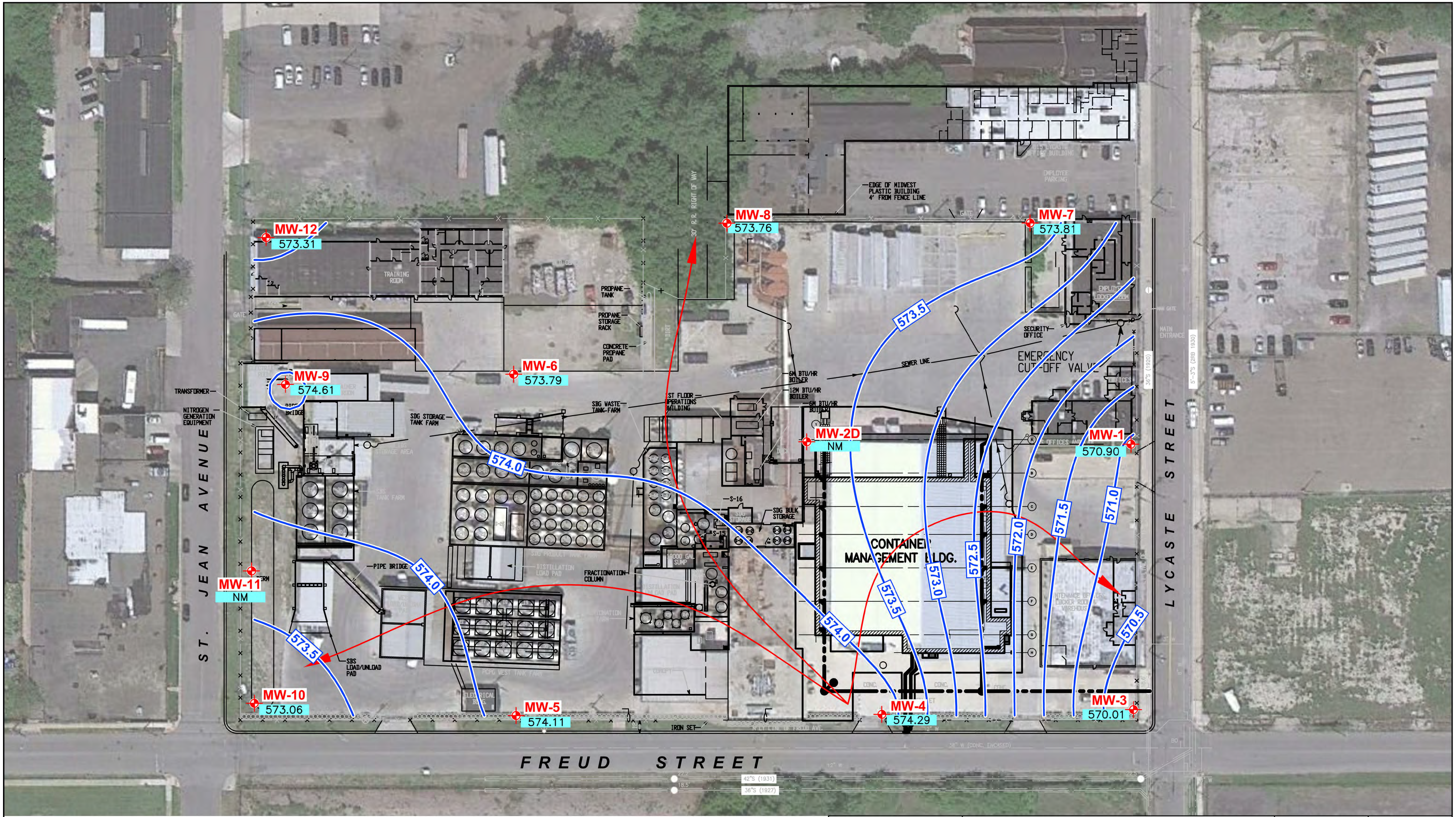
CHECK BY	KW
DRAWN BY	JL
DATE	8/2/2021
SCALE	AS SHOWN
CAD NO.	044.00_gw6-21
PRJ NO.	11021-000044.00

GROUNDWATER ELEVATION CONTOURS
JUNE 24, 2021

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE
3



LEGEND

571.0	GROUNDWATER CONTOUR
570.01	GROUNDWATER ELEVATION (FT.)
←	GROUNDWATER FLOW

SCALE IN FEET

0 40 80 160

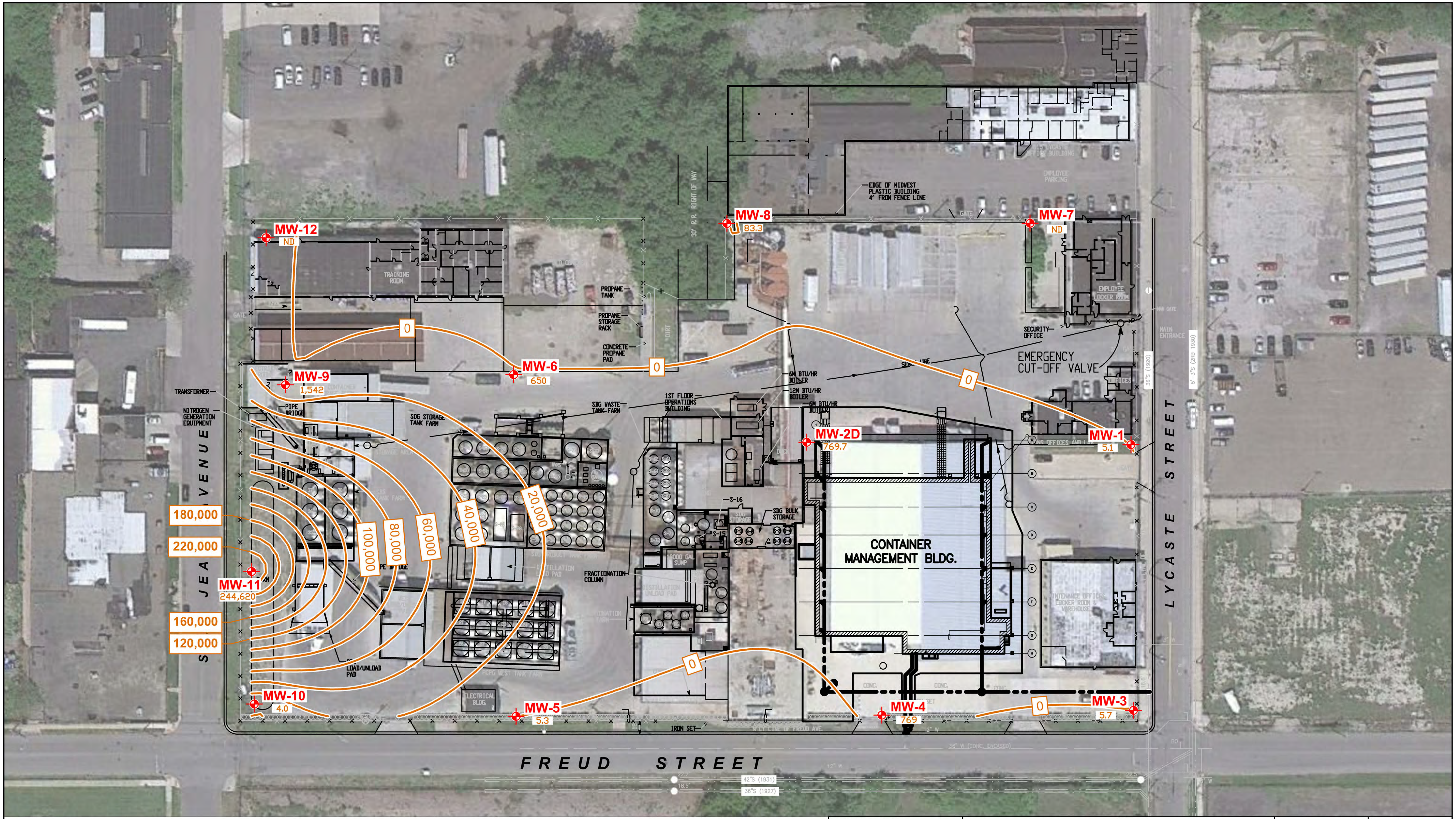
CHECK BY	KW
DRAWN BY	JL
DATE	2/25/2022
SCALE	AS SHOWN
CAD NO.	044.00_gw12-21
PRJ NO.	11021-000044.00

GROUNDWATER ELEVATION CONTOURS
DECEMBER 20, 2021

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE
4



LEGEND

CONTOUR LINE (INTERVAL 20,000)

50 CONCENTRATION LEVEL

MW-# MONITORING WELL LOCATION

NOTES: ND=NOT DETECTED; NS=NOT SAMPLED

SCALE IN FEET

0 40 80 160

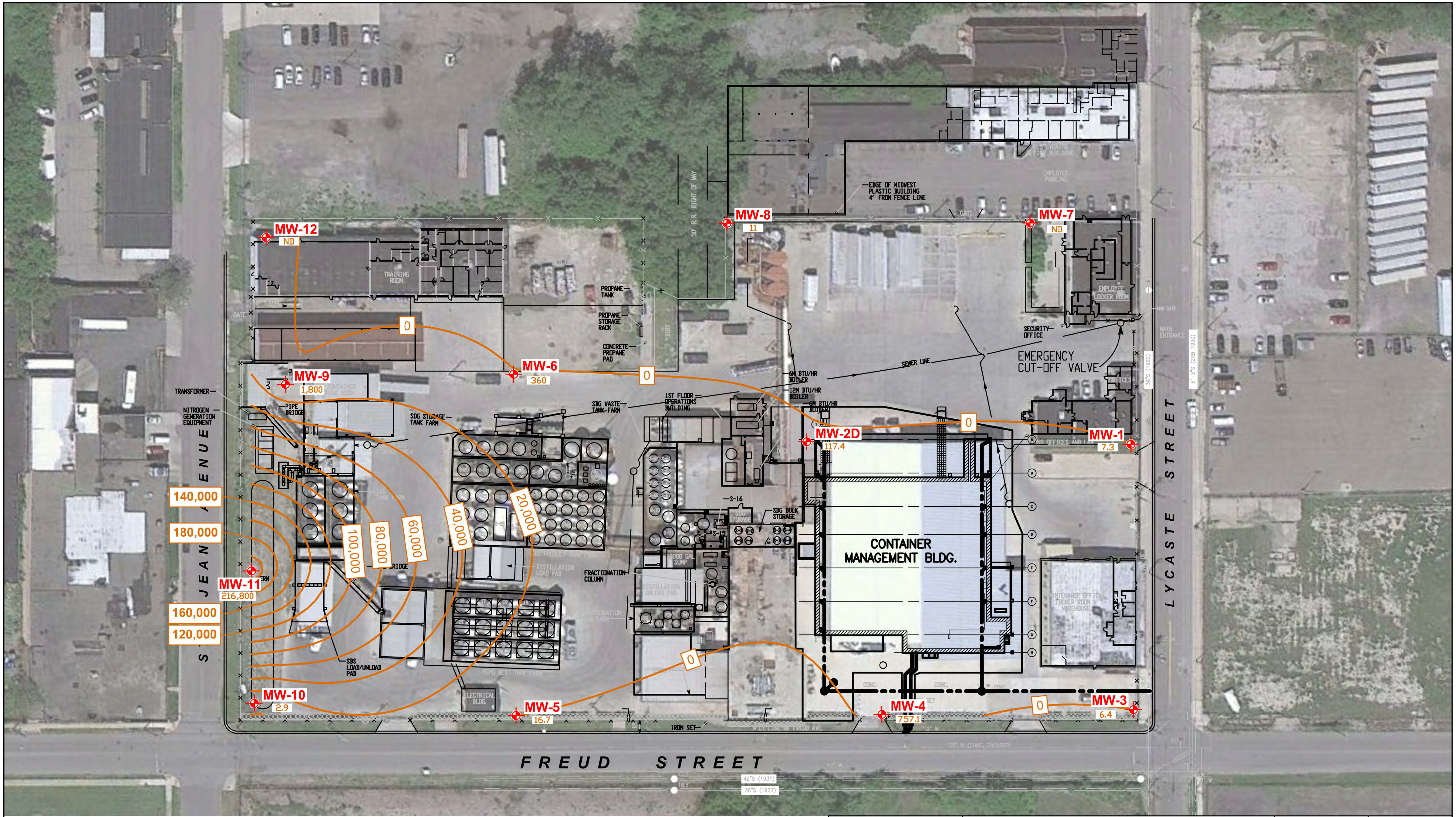
CHECK BY	KW
DRAWN BY	JL
DATE	2/25/2022
SCALE	AS SHOWN
CAD NO.	6-21_044.03v
PRJ NO.	11021-000044.00

TOTAL VOCs
JUNE 2021

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE
5a



LEGEND

	CONTOUR LINE (INTERVAL 20,000)
50	CONCENTRATION LEVEL
MW-#	MONITORING WELL LOCATION

NOTES: ND=NOT DETECTED; NS=NOT SAMPLED

SCALE IN FEET

0 40 80 160

CHECK BY	KW
DRAWN BY	JL
DATE	2/25/2022
SCALE	AS SHOWN
CAD NO.	12-21_044.03v
PRJ NO.	11021-000044.00

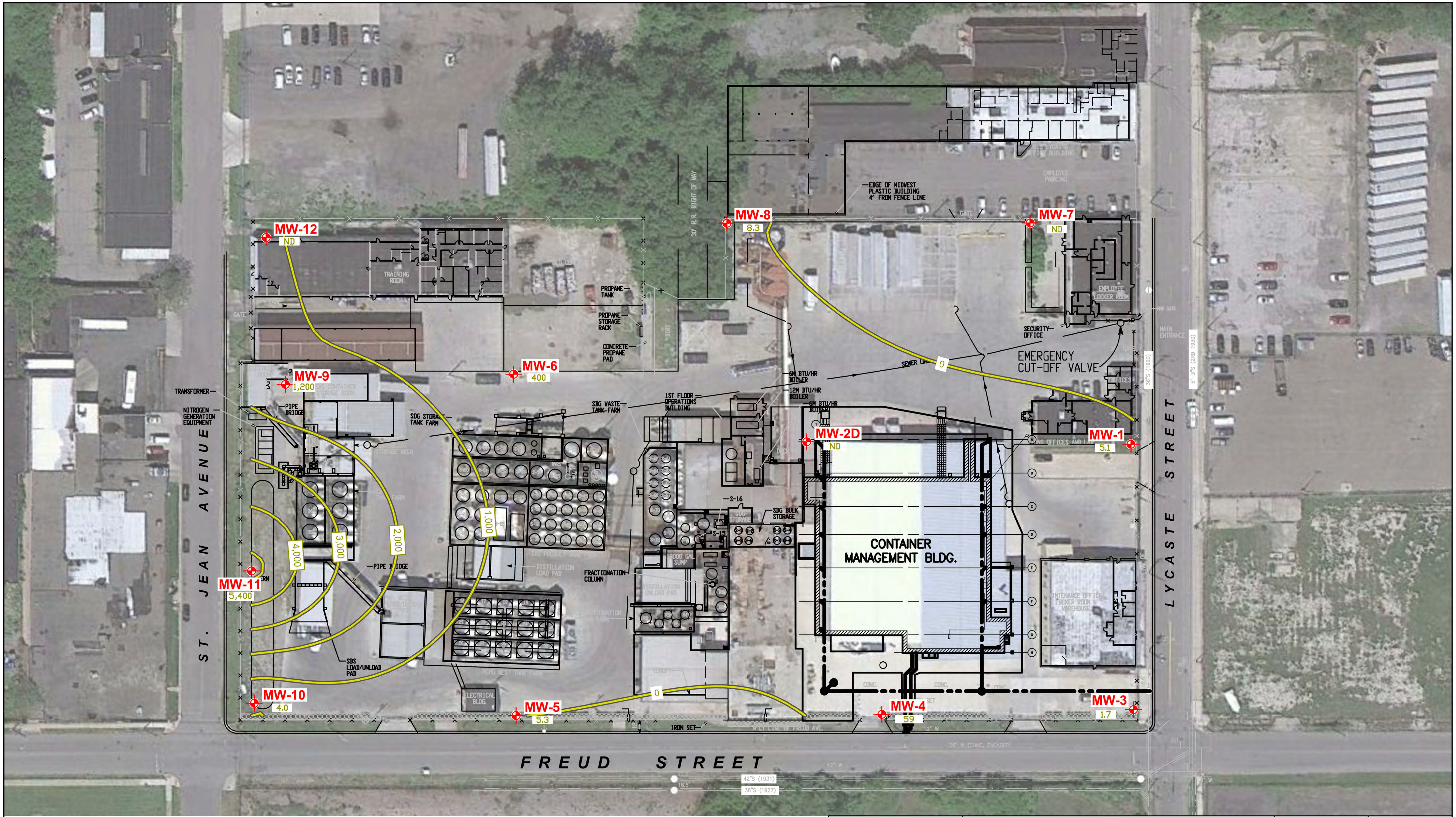
TOTAL VOCs
DECEMBER 2021

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE

5b



LEGEND

CONTOUR LINE (INTERVAL 1,000)

50 CONCENTRATION LEVEL

MW-# MONITORING WELL LOCATION

NOTES: ND=NOT DETECTED; NS=NOT SAMPLED

SCALE IN FEET

0 40 80 160

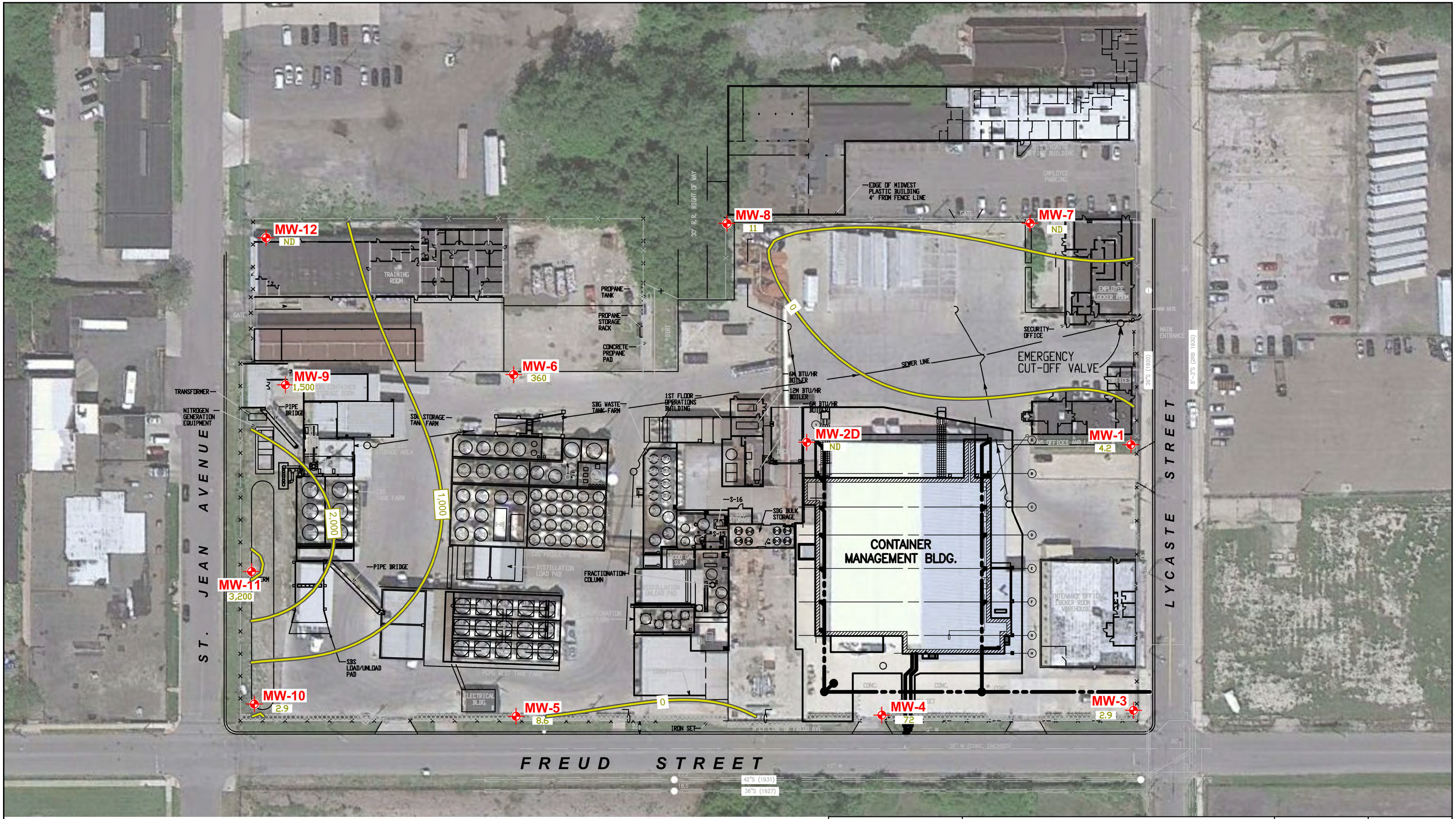
CHECK BY	KW
DRAWN BY	JL
DATE	2/25/2022
SCALE	AS SHOWN
CAD NO.	6-21_044.03m
PRJ NO.	11021-000044.00

MtBE
JUNE 2021

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE
5c



LEGEND

CONTOUR LINE (INTERVAL 1,000)

50 CONCENTRATION LEVEL

MW-# MONITORING WELL LOCATION

NOTES: ND=NOT DETECTED; NS=NOT SAMPLED

SCALE IN FEET

0 40 80 160

CHECK BY	KW
DRAWN BY	JL
DATE	2/25/2022
SCALE	AS SHOWN
CAD NO.	12-21_044.03m
PRJ NO.	11021-000044.00

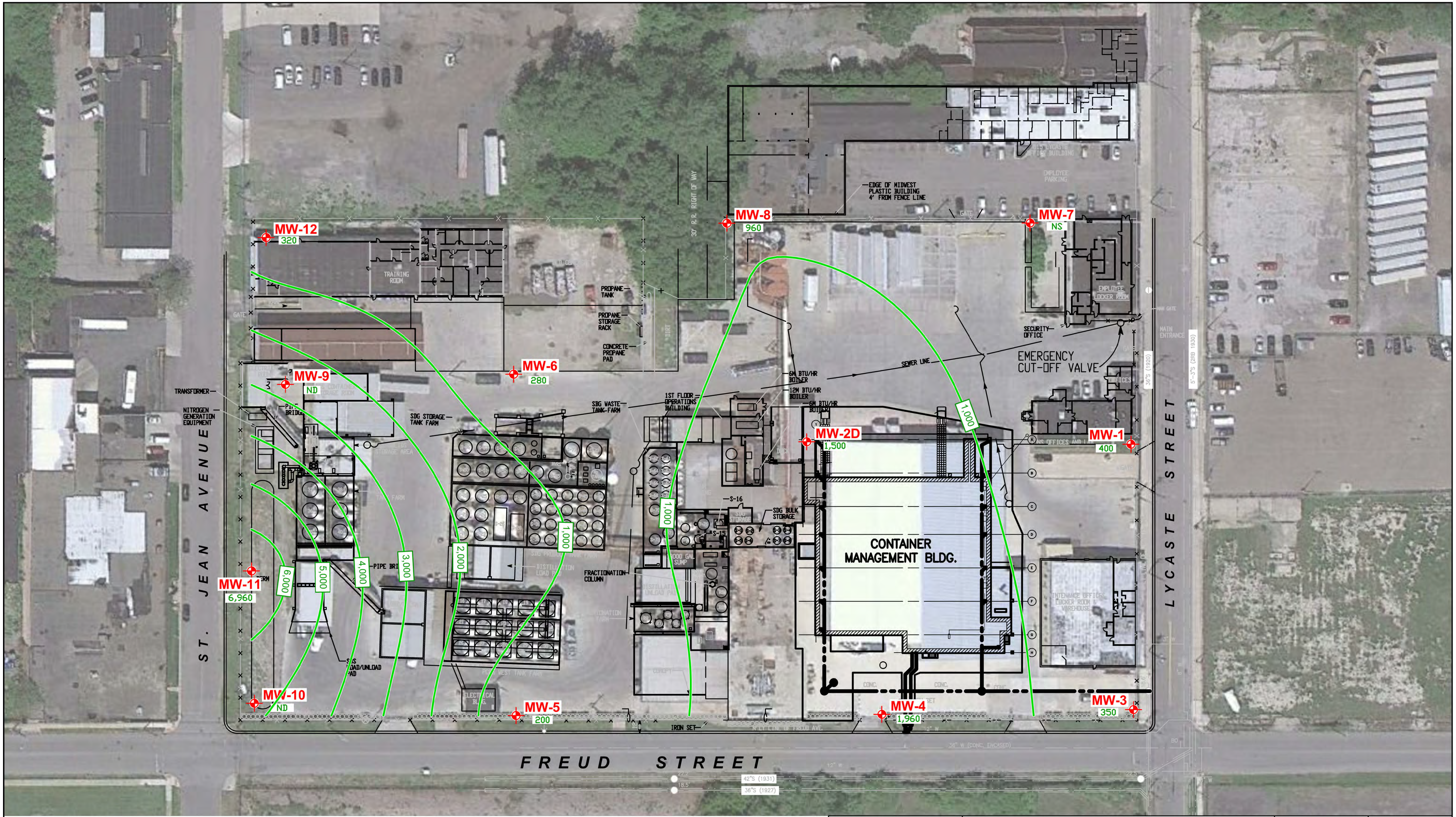
MtBE
DECEMBER 2021

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE

5d



LEGEND

🟩	CONTOUR LINE (INTERVAL 1,000)
50	CONCENTRATION LEVEL
MW-#	MONITORING WELL LOCATION

NOTES: ND=NOT DETECTED; NS=NOT SAMPLED

SCALE IN FEET
0 40 80 160

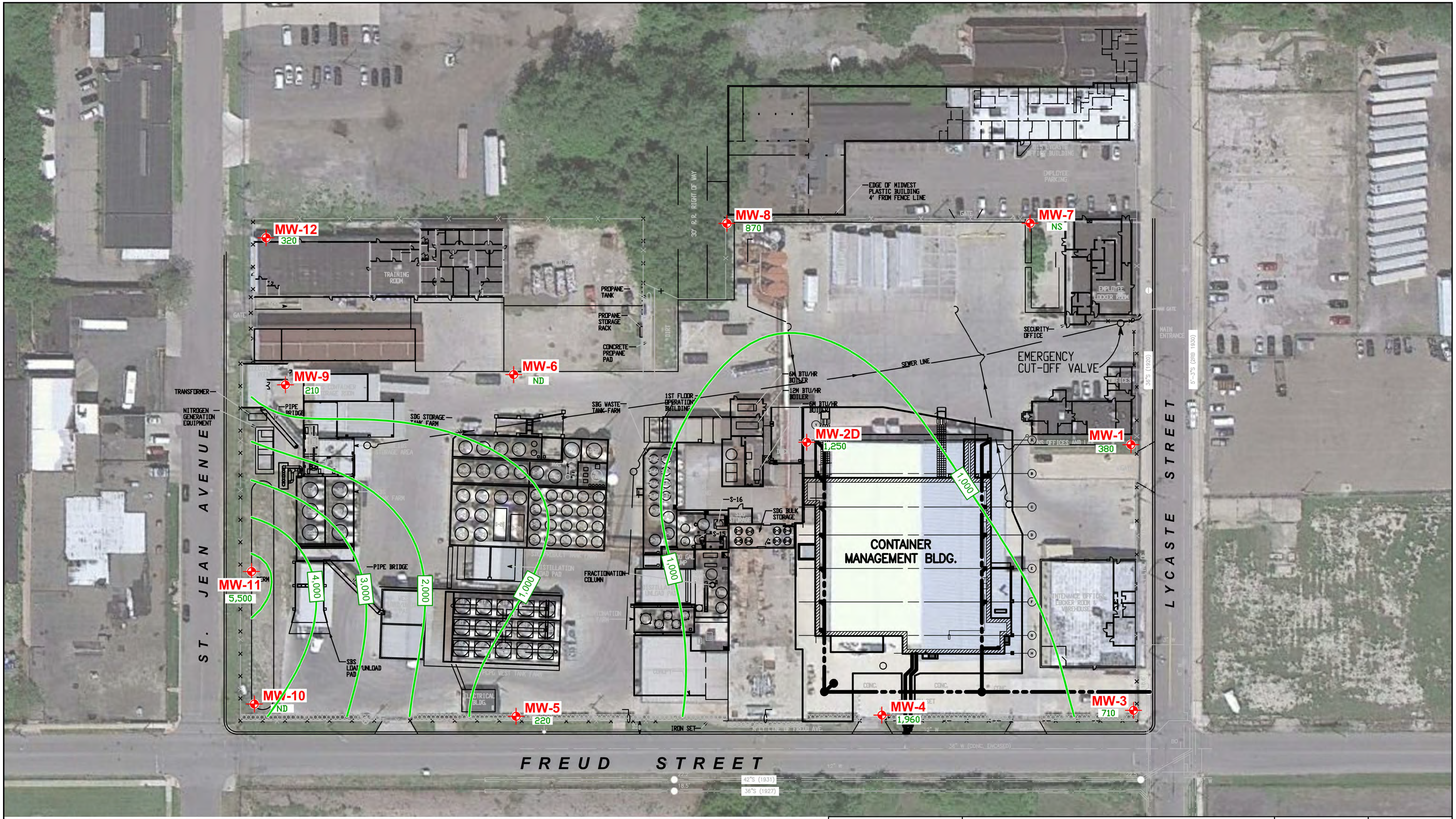
CHECK BY	KW
DRAWN BY	JL
DATE	2/25/2022
SCALE	AS SHOWN
CAD NO.	6-21_035.03d
PRJ NO.	11021-000044.00

DRO/ORO
JUNE 2021

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE
5e



LEGEND

CONTOUR LINE (INTERVAL 1,000)

50 CONCENTRATION LEVEL

MW-# MONITORING WELL LOCATION

NOTES: ND=NOT DETECTED; NS=NOT SAMPLED

SCALE IN FEET

0 40 80 160

CHECK BY	KW
DRAWN BY	JL
DATE	2/25/2022
SCALE	AS SHOWN
CAD NO.	12-21_035.03d
PRJ NO.	11021-000044.00

DRO/ORO
DECEMBER 2021

PETRO-CHEM PROCESSING GROUP
421 LYCASTE STREET
DETROIT, MICHIGAN

APEX

FIGURE

5f

Appendix B5.2

University Labs QA Manual

The objective of University Laboratories QA/QC program is to produce results that are reproducible, representative, comparable, accurate, precise, and as free from bias as possible.

Results are made reproducible by providing ample documentation. University Laboratories Standard Operating Procedures (SOP) provide documentation of the procedure followed, the analytical data sheets provide documentation on the data generated, along with a large array of support documentation throughout the laboratory.

Calibrations are run frequently along with calibration checks to insure that the data generated from the instrumentation is reproducible, and representative.

Surrogates and standards are used to insure that the data generated is comparable to data generated elsewhere. Surrogates are compounds that do not interfere with the target analyte that can be monitored by the instrumentation, and that are added to the sample in a known quantity. The percent of surrogate recovered is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits.

Accuracy is the closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component. Accuracy is monitored by calculating the percent recovery for internal standards, spiked compounds, and surrogates.

Precision is the agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the relative standard deviation (RSD), or the relative percent difference (RPD) when only two samples are available.

The uses of QC samples are the means for which the accuracy and precision is checked. When mentioning QC samples the following terms should be considered; method blank, matrix spike (MS), matrix spike duplicate (MSD)/ sample duplicate, and laboratory control sample (LCS).

Method blank is an aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The method blank is used to determine if method analytes or other interference's are present in the laboratory environment, reagents, or apparatus.

Matrix Spike (MS) is an aliquot of sample spiked with a known concentration of target analytes. The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD) is an intralaboratory split sample spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix by calculating the relative standard deviation (RSD), or the relative percent difference (RPD) of the duplicate samples.

Laboratory Control Sample (LCS) consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

The type and frequency of QC samples employed depends on the analyses being performed.

Heather Schmidt; BS
Quality Control Officer

University Laboratories

Quality Control Manual

September, 2010
Version 5.0

Prepared By: Heather K. Schmidt, B.S.
Quality Assurance Officer

QUALITY MANUAL
FOR
University Laboratories
REVISION 5.0

EFFECTIVE DATE
03-17-2010

Prepared by: Heather Schmidt
39830 Grand River Ave.
Suite B1
Novi, MI 48375
(248) 615-8000

7-8-2008

___________________________________ __________
Bijan Sedghi (Director of Laboratories) Date

___________________________________ __________
Heather K. Schmidt (Quality Assurance Officer) Date

TABLE OF CONTENTS

APPENDICES

TABLES AND FIGURES

1. POLICY STATEMENT

1.1. This Quality Manual summarizes the policies and operational procedures associated with the Quality Department at University Laboratories at 39830 Grand River Ave. Novi, MI 48375. All policies and procedures have been structured in accordance with ISO/IEC 17025: 2005 standards and applicable EPA requirements, regulations, guidance, and technical standards. Further details on these policies and procedures are contained in SOPs and related documents. This Quality Manual, SOPs, and related documentation describe the quality system for University Laboratories.

1.2. University Laboratories performs chemical analyses for inorganic and organic constituents in aqueous, non-aqueous, air, solid, sludge, oil, and soil matrices. University Laboratories' goal is to produce data that is reproducible, representative, comparable, accurate, precise, and as free form bias as possible. The data is to be of known and documented quality in accordance with any applicable state or EPA regulations or requirements.

1.3. University Laboratories analyzes Proficiency Test (PT) samples annually from a National Institute of Standards and Technology (NIST) approved PT provider. All analytes are tested that are within the scope of the laboratory's services and available from a PT provider. The specific analytes and matrices analyzed are based on the current scope of the laboratory services and are documented in an internal audit report for PT sample analyses.

1.4. University Laboratories has developed a proactive program for prevention and detection of improper, unethical or illegal actions. Components of this program include: internal proficiency testing (single and double blind); peer review of data by analysts; post-analysis data review by the QA Officer; and SOPs identifying appropriate and inappropriate laboratory and instrument manipulation practices.

1.5. University Laboratories has made a commitment to its management system and will continually work to improve its efficiency by communication processes that are established within the laboratory regarding the management system. The management system is dedicated to working with quality to ensure the goals and objectives of the QA/QC program are obtained.

2. ORGANIZATION AND RESPONSIBILITIES

2.1. Organization Chart

2.1.1. An organization chart for University Laboratories is shown in Figure 2-1. This chart includes all individuals discussed below.

Figure 2-1: ORGANIZATIONAL CHART

University Laboratories

Director of Laboratories
Bijan Sedghi

Project Coordinator
Megan Sedghi

Technical Team Leader
Mohamed Sayed

Quality Assurance Officer
Heather Schmidt

Senior Chemist
Erica Kotajarvi
Supreet Singh

Technical Staff
Meda Vartanian

2.2. **Director of Laboratories**

2.2.1. The Director of Laboratories is responsible for:

2.2.1.1. Defining the minimal level of experience and skills necessary for all positions in the laboratory. In addition to education and/or experience, basic laboratory skills are considered;
2.2.1.2. Ensuring that all technical laboratory staff have demonstrated proficiency in the activities for which they are responsible;
2.2.1.3. Ensuring that the training of its personnel is kept up-to-date;
2.2.1.4. Ensuring the documentation of all analytical and operational activities;
2.2.1.5. Supervising all personnel;
2.2.1.6. Ensuring that all sample acceptance criteria are verified and that samples are logged into the sample tracking system and properly labeled and stored;
2.2.1.7. Performing an annual Management System Review;
2.2.1.8. Ensuring the documentation of the quality of all data reported by the laboratory;
2.2.1.9. Ensuring that the laboratory has the appropriate resources and facilities to perform requested work;
2.2.1.10. Ensuring that corrective actions relating to findings from the internal audit are completed;
2.2.1.11. Nominating deputies when the Technical Team Leader or QA Officer is absent;
2.2.1.12. Developing a proactive program for prevention and detection of improper, unethical or illegal actions;

2.2.1.13. Ensuring that only those outside support services and supplies that are of adequate quality to sustain confidence in the laboratory's tests are used;

2.3. **Quality Assurance (QA) Officer**

2.3.1. As shown in Figure 2-1, the QA Officer is independent of direct job involvement and day-to-day operations, and has direct access to the Laboratory Director, to resolve any dispute involving data quality. The QA Officer serves as the focal point for QA/QC and is responsible for the oversight and/or review of quality control data. He/she is responsible for auditing the implementation of the Quality System. The QA Officer has sufficient authority to stop work as deemed necessary in the event of serious QA/QC issues. Specific functions and duties include:

2.3.1.1. Annually conducting internal audits on the entire technical operation;
2.3.1.2. Notifying laboratory management of deficiencies in the quality system and monitoring corrective action;
2.3.1.3. Monitoring standards of performance in quality control and quality assurance;
2.3.1.4. Monitoring the validity of the analyses performed and data generated in the laboratory to assure reliable data;
2.3.1.5. Monitoring documentation so that the data is of known quality;
2.3.1.6. Maintaining that the technical laboratory staff has a documented demonstration of proficiency in their required field of analyses; and
2.3.1.7. Approving the data for distribution to its respective clientele;

2.4. **Technical Team Leader**

2.4.1. As shown in Figure 2-1, the Technical Team Leader for Chemical Analyses reports to the Laboratory Director and is responsible for:

2.4.1.1. Responsible for the technical operations and the distribution of those resources needed to ensure the required quality of laboratory operations on a daily basis.
2.4.1.2. Providing educational direction to laboratory staff;
2.4.1.3. The address any complaints, issues, or concerns in a timely manner; and
2.4.1.4. Allocate daily responsibilities to technical staff at daily morning meetings.

2.5. **Project Coordinator**

2.5.1. As shown in Figure 2-1, the Project Coordinator reports directly to the Director of Laboratories. The Project Coordinator is responsible for;

2.5.1.1. Organization and documentation of projects;
2.5.1.2. Sample custodian;
2.5.1.3. Customer service;
2.5.1.4. Preparation of sampling supplies provided to clients;
2.5.1.5. Schedule in-coming or returned samples;
2.5.1.6. The scheduling of the field sampler;

2.5.1.7. Maintenance, preparation, and scheduling the use of the automatic composite water sampler;

2.5.1.8. Confirm invoices for payment; and

2.5.1.9. Ensuring that only those outside support services and supplies that are of adequate quality to sustain confidence in the laboratory's tests are used

2.6. **Senior Chemist**

2.6.1.As shown in Figure 2-1, the Senior Chemist reports directly to the Director of Laboratories. The Senior Chemist is responsible for analysis of chromatograms and identifying and directing corrective action. All personnel is responsible for complying with all quality assurance/ quality control (QA/QC) requirements that pertain to their organization/technical function. As documented in the employee records each Senior Chemist has the experience and education to adequately demonstrated knowledge of chromatography and a general knowledge of laboratory operations, analytical test methods, QA/QC procedures and record management.

2.7. **Technical Staff**

2.7.1.Technical staff is responsible for sample analysis, identification of corrective actions, and instrument maintenance. The staff reports directly to the Technical Team Leader. All personnel are responsible for complying with all QA/QC requirements that pertain to their organizational/technical function. As documented in the employee records, each technical staff member has the experience and education to adequately demonstrate knowledge of their particular function and a general knowledge of laboratory operations, analytical test methods, quality assurance/quality control procedures and records management.

2.8. **Training**

2.8.1.Training records containing documentation of the following six steps are kept with each employee’s personnel files.

2.8.2.Each employee has read, understands, and agreed to the Safety Agreement.

2.8.3.Each employee has read and understands the Material Data Safety Sheets (MSDS).

2.8.4.Each employee has an acceptable knowledge of the Safety issues related to his/her job responsibilities and increased said knowledge by attending safety meetings.

2.8.5.Each employee has knowledge of the basic techniques involved with their respective job responsibilities.

2.8.6.Each employee has read, understood, and is using the latest version of the laboratory's Standard Operating Procedures (SOP), which relates to his/her job responsibilities.

2.8.7. Each employee demonstrates continued proficiency by the acceptable performance of Laboratory Control Sample (LCS) and Initial Demonstrations of Proficiency (IDP).

2.9. **Laboratory Capabilities**

2.9.1. University Laboratories analyzes aqueous, non-aqueous, air, solid, sludge, oil, and soil samples. The table below lists the parameters/analytes measured and references the laboratory Controlled Document Number (CD#).

2.9.2. University Laboratories uses a Laboratory Information Management System (LIMS).

Table 2-1 **University Laboratories Capabilities**

Parameter/Analyte	**Methodology**	**(CD) #**
Asbestos	Out Sourced	none
Bacteria Count	Out Sourced	none
BOD	Dissolved Oxygen	040
BTU	Out Sourced	none
Chloride	Spectrophotometer	037
Chlorinated Herbicides	GC/ECD	029
COD	Spectrophotometer	010
Cyanide	Spectrophotometer	035
Cyanide, Amenable	Spectrophotometer	035
Fluoride	Spectrophotometer	032
FOG	Gravimetric	020
Hexavalent Chromium	Spectrophotometer	054
Low Level Mercury	CVAA	006/007
Metals	ICP-AES	079
Metals	ICP-MS	None
Mercury	CVAA	006/007
Nitrogen	Spectrophotometer	
Organochlorine Pesticides	GC/ECD	066
Phosphorus	Spectrophotometer	081
Phenolic Compounds	Spectrophotometer	021
PCB	GC/ECD	127/136
PH	pH Meter	
Reactive Cyanide	Spectrophotometer	036
Reactive Sulfide	Spectrophotometer	036
Semi-Volatile Organic	GC/MS	065
Sulfate	Spectrophotometer	022
Sulfite	Spectrophotometer	046
TDS	Gravimetric	083
TOC	Out Sourced	none
TSS	Gravimetric	025
Volatile Organic	GC/MS	055

3. QUALITY ASSURANCE OBJECTIVES

3.1. The objective of University Laboratories QA/QC program is to develop and implement procedures for laboratory analysis, chain-of-custody, and reporting that will provide results which are of known and documented quality. The QA/QC program uses the following objectives to monitor and document the quality of results: reproducibility, representativeness, comparability, precision, accuracy (bias), and detection limits. This following section summarizes how these specific QA objectives are achieved. The specific application of these various objectives are outlined in the respective technical SOPs.

3.2. **Reproducibility**

3.2.1.To reproduce something, is to produce it again or anew. So for a laboratory's use, reproducibility would be the ability to produce results again.

3.2.2.Results are made reproducible by providing ample documentation. University Laboratories Standard Operating Procedures (SOP) provide documentation of the procedure followed, the analytical data sheets provide documentation on the data generated, and a large array of support documentation (training records, maintenance logs, Standard/Solution prep logs, etc.) provide documentation on who/what was used to produce the results.

3.2.3.Calibrations are run frequently, along with calibration checks, to ensure that the data generated from the instrumentation is reproducible and representative.

3.3. **Representativeness**

3.3.1.Representativeness expresses the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition within a defined spatial and/or temporal boundary. One that serves as an example or type for others of the same classification.

3.3.2.Representativeness is ensured by using the proper analytical procedures, using certified standards, using appropriate methods, meeting sample holding times, and analyzing field duplicate samples.

3.4. **Comparability**

3.4.1.Comparability is an expression of the confidence with which one data set can be compared to another.

3.4.2.Comparability is achieved by the use of routine analytical methods, analyzing within holding times, reporting results in common units, use of consistent detection levels, and consistent rules for reporting data.

3.4.3.Standards are used to ensure that the data generated is comparable to data generated at other laboratories. Standards are purchased from NIST accredited suppliers at known concentrations and are certified.

3.4.3.1. Surrogates are an example of a type of standard used. Surrogates are compounds that do not interfere with the target analyte, can be monitored by the instrumentation, and that are added to the sample in a known quantity. The percent recovered of this surrogate is used to monitor for unusual matrix effects, gross sample processing errors, etc. By monitoring the surrogate recovery University Laboratories ensures that the data generated is comparable to another laboratory.

3.5. **Precision**

3.5.1. Precision is a measure of the degree to which two or more measurements are in agreement.

3.5.2. Precision is assessed through the calculation of relative percent difference (RPD) and/or relative standard deviation (RSD) for replicate samples. Laboratory precision is usually assessed through the analysis of a matrix spike/ matrix spike duplicate (MS/MSD) or sample/sample duplicate pair. When there is insufficient sample to perform a MS/MSD or sample/sample duplicate pair, two LCS samples are prepared. These LCS pairs are then used to calculate precision.

3.6. **Accuracy**

3.6.1. Accuracy is the degree of agreement between an observed value and an accepted reference or true value.

3.6.2. Accuracy is assessed by the analysis of blanks and through the adherence to all sample handling, preservation, and holding times requirements. Laboratory accuracy is further assessed through the analysis of MS/MSD, reference samples, laboratory control samples (LCS), and surrogate compound spikes.

3.6.3. Accuracy is monitored by calculating the percent recovery for internal standards, spiked compounds, and surrogates.

3.7. **Detection Limits**

3.7.1. Method Detection Limits (MDLs) are determined for all analytes. The MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.7.2. The MDL study should be performed annually for each analyte in each matrix unless other wise stated in the respective SOP or the process or the analytical system has undergone significant changes.

4. SAMPLING PROCEDURES

4.1. University Laboratories performs both grab and composite sampling, along with pH readings. Information about the specific requirement related to sampling can be found in the respective SOP.

5. SAMPLE HANDLING

5.1. This section summarizes policies and practices for sample handling. Further details are contained in the SOP (CD # 135).

5.2. Sample Tracking

5.2.1. University Laboratories uniquely identifies each sample to be tested, to ensure that there can be no confusion regarding identity. A unique identification (ID) number is placed on each sample container. The sample ID number is then used to identification all samples, sub-samples and subsequent extracts and/or digestions.

5.3. Sample Acceptance Policy

5.3.1. University Laboratories has a written sample acceptance policy that outlines the circumstances under which samples will be accepted (CD# 135). Data from any sample, which do not meet the policy, is noted in the laboratory chain of custody (COC) defining the nature and substance of the variation. The COC is then sent to the client and it is their judgment if analyses is performed.

5.4. Sample Receipt Protocols

5.4.1. Proper, full, and complete documentation is required. This includes the sample identification, the location, date and time of collection, collector's name, preservation type, sample type, and any special remarks concerning the sample;

5.4.2. Upon receipt, the condition of the sample, including any abnormalities or departures from standard condition, are recorded on the COC. Some circumstances that would be defined as abnormal include, but are not limited to, the following;

5.4.2.1. The use of inappropriate sample containers.
5.4.2.2. Not receiving the samples within the respective holding time.
5.4.2.3. Inadequate sample volume.
5.4.2.4. If the sample is Radio Active or known to be Hazardous, it must be labeled on the sample as well as on the COC. If there is a MSDS it should be attached to the COC.

5.4.3. All samples that require thermal preservation are considered acceptable if the arrival temperature is either within +/-2°C of the required temperature or the method specified range.

5.4.4. Samples that are hand delivered to the laboratory immediately after collection may not be held to this criteria (sec 5.4.3). In these cases, the samples will be considered acceptable if there is evidence that the chilling process has begun, such as arrival on ice.

5.4.5. Unique identification numbers are assigned to each sample using durable labels completed in indelible ink.

5.4.6. Where applicable, University Laboratories verifies chemical preservation using readily available techniques, such as pH, free chlorine, or temperature, prior to or during sample preparation or analysis. The results of all checks are recorded.

5.4.7. Where there is any doubt as to the sample's suitability for testing, University Laboratories consults its clients for further instruction before proceeding. If the sample does not meet the sample receipt acceptance criteria, University Laboratories notes the condition of the samples on the COC.

5.5. **Storage Conditions**

5.5.1. Samples that require thermal preservation are stored under refrigeration which is +/- 2 degrees from the specified preservation temperature. For samples with a specified temperature of 4°C, samples with a temperature ranging from just above the freezing temperature of water to 6°C are considered acceptable.

5.5.2. Samples are stored in a manner that prevents cross contamination.

5.6. **Chain of Custody**

5.6.1. Chain of custody records are used to establish an intact, continuous record of reception, storage, and disposal of sample containers. The COC forms remain with the samples during transport or shipment. University Laboratories keeps records of all COC received.

5.6.2. If shipping containers and/or individual sample containers are submitted with sample custody seals, and any seals are not intact, the lab shall note this on the COC.

5.6.3. The COC records all changes in custody. For example if the sample is returned to a client it is recorded on the COC.

5.6.4. Access to all samples and sub-samples are controlled. The laboratory area is maintained securely and is restricted to authorized personnel only.

5.7. **Sample Disposal**

5.7.1. All samples, digestates, leachates, and extracts or other sample preparation products are disposed of in accordance with Federal and State laws and regulations, after storage for 45 days, or returned to the client.

5.7.2. If the sample is determined to contain cyanide, mercury, or PCBs, upon analysis, it is marked and returned to the client. If the sample is part of litigation, disposal of the physical sample occurs only with the concurrence of the affected legal authority, sample data user, and/or submitter of the sample.

6. CALIBRATION PROCEDURES AND FREQUENCY

6.1. **Traceability of Calibration**

6.1.1. Wherever applicable, calibration of analytical support equipment and instruments is traceable to national standards of measurement.

6.2. Reference Standards

6.2.1. Reference standards of measurement (such as NIST traceable weights or traceable thermometers) are used for calibration only. Reference standards are subjected to in-service checks between calibrations and verifications.

6.3. General Requirements

6.3.1. Each calibration is dated and labeled so that it is traceable to the method, instrument, analysis date, analytes of interest, concentration, and response (or response factor). Sufficient information is recorded to permit reconstruction of the calibration. Acceptance criteria for calibrations comply with method requirements or are established and documented.

6.4. Analytical Support Equipment

6.4.1. If quantitative results are dependent on their accuracy, as in standard preparation, dispensing, or dilution into a specified volume is considered Analytical Support Equipment. Analytical support equipment includes: balances, ovens, refrigerators, freezers, incubators, water baths, temperature measuring devices, and volumetric dispensing devices. All such support equipment is:

6.4.1.1. Maintained in proper working order. The records of all maintenance activities, including service calls are kept.

6.4.1.2. Calibrated or verified at least annually, using NIST traceable references when available, over the entire range of use. The results of such calibration must be within the specifications required of the application for which the equipment is used or the equipment is removed from service until repaired.

6.4.2. Every other week, ovens, refrigerators, freezers, incubators, and water baths are checked with NIST traceable references (where possible) in the expected use range. The acceptability for use or continued use is according to the needs of the analysis or application for which the equipment is being used. Mechanical volumetric dispensing devices (except Class A glassware) are checked for accuracy annually.

6.5. Instrument Calibration

6.5.1. The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria, and the conditions that will require re-calibration. In all cases, the initial calibration is verified using an independently prepared calibration verification solution.

6.5.2. All results are calculated based on the response curve from the initial calibration.

6.5.3. If the initial calibration fails, the analysis procedure is stopped and evaluated. For example, a second standard may be analyzed and evaluated or a new initial calibration curve may be established and verified. In all cases, the initial calibration must be acceptable before analyzing any samples.

6.5.4. When an initial instrument calibration is not performed on the day of analysis, a calibration verification check standard is analyzed.

6.5.5. For external standard methods (e.g. PCB methods) a calibration verification check standard is analyzed at the beginning and end of each batch.

6.5.6. For internal standard methods (e.g. most organic methods). For these analyses, the calibration check is only analyzed at the beginning of the analytical sequence.

7. TEST METHODS AND STANDARD OPERATING PROCEDURES

7.1. University Laboratories maintains Standard Operating Procedures (SOPs) that accurately reflect all laboratory activities such as corrective actions, non-technical activities, and all test methods. Copies of all SOPs are accessible to all personnel. Each SOP indicates the effective date, the revision number, and the signature(s) of the QA Officer, Director of Laboratories, Technical Team Leader, and the Primary chemist conducting the analysis.

7.1.1. SOPs contain sufficient information to enable reproducibility and to ensure consistency. Any deviation from an established procedure during an analysis is documented on the analytical data sheet at the time of the observation or collection of data.

7.2. SOPs for Sample Management

7.2.1. These SOPs describe the receipt, handling, scheduling, and storage of samples.

7.2.2. Life Cycle of a Sample (CD# 135) -- This procedure describes the precautions to be used in opening sample shipment containers and how to verify that a chain-of-custody has been maintained, examine samples so that they meet the sample acceptance policy, and log samples into the laboratory sample streams.

7.2.2.1. Sample Scheduling -This procedure describes the sample scheduling in the laboratory and includes procedures used to ensure that holding time requirements are met.

7.2.3. Sample Preservation and Holding Time SOP_66 (CD# 80) -This procedure describes the storage conditions for all samples, verification, and documentation of storage conditions, and how to ensure that custody of the samples is maintained.

7.3. SOPs for Reagent/Standard Preparation

7.3.1. The respective SOPs describe how to prepare standards and reagents for each analysis. They also include information concerning specific grades of materials used in reagent and standard preparation and the appropriate glassware or containers for preparation and storage. There is a Labeling SOP for information on the appropriate way to label reagents and standards. There is also a SOP for the appropriate way to record the preparation of reagents, standards, from stock standards, neat compounds, etc.

7.4. SOPs for General Laboratory Techniques

7.4.1. The SOP describes all the essentials of laboratory operations that are not addressed elsewhere. These techniques should include, but are not limited to, glassware cleaning procedures, operation of analytical balances, pipetting techniques, and use of volumetric glassware.

7.5. SOPs for Test Methods

7.5.1. Procedures for test methods describing how the analyses are actually performed in the laboratory are specified in method SOPs. These SOPs for sample preparation, cleanup, and analysis are based on reference methods published by EPA, ASTM, AWWA, and other organizations and on internally developed methods. Each method SOP includes:

1) Applicable Analytical Method;
2) Applicable matrix or matrices;
3) Method Detection Limit;
4) Scope and Application;
5) Method Summary;
6) Definitions;
7) Interference;
8) Safety;
9) Equipment and Supplies;
10) Reagents and Standards;
11) Sample Collection, Preservation, and Handling;
12) Quality Control;
13) Calibration and Standardization;
14) Procedure;
15) Preventative Maintenance;
16) Calculations;
17) Method Performance;
18) Pollution Prevention;
19) Data Assessment;
20) Corrective Action;
21) Waste Management;
22) References; and
23) Any Tables, Diagrams, Flowcharts and Validation Data

7.6. SOPs for Equipment Calibration and Maintenance

7.6.1. Calibration and maintenance of laboratory equipment and instrumentation are in accordance with manufacturers 'specifications or applicable test specifications. Specific maintenance procedures and schedules can be found in the respective SOP. The course of action SOP may also contain calibration or maintenance recommendations.

8. INTERNAL QUALITY CONTROL CHECKS

8.1. Quality Control Samples

8.1.1.The data acquired from QC procedures are used to estimate the quality of analytical data, to determine the need for corrective action in response to identified deficiencies, and to interpret results after corrective action procedures are implemented. Each method SOP includes a QC section, which addresses the QC requirements for the procedure. The QC checks may differ slightly for each individual procedure but in general are described below. The acceptance limits and corrective actions for these QC checks are described in Section 12 and 13 of this Manual.

8.1.2.Method Blanks are performed at a frequency of one per batch of samples per matrix type per sample extraction or preparation test method. The results of these samples are used to determine contamination.

8.1.3.Laboratory Control Sample (LCS) are analyzed at a minimum of one per batch of twenty or fewer samples per matrix type per sample extraction or preparation method. Except for analytes for which spiking solutions are not available. The results of these samples are used to determine batch acceptance.

8.1.4.Surrogates - Surrogate compounds are added to all samples, standards, and blanks for all organic chromatography test methods except when a surrogate is not available. Poor surrogate recovery generally indicates a problem with the sample composition or gross sample processing errors, and is re-analyzed or reported with the appropriate qualifiers.

8.1.5.Matrix Spikes (MS) are performed at a frequency of one in twenty samples per matrix type per sample extraction or preparation method. Except for analytes for which spiking solutions are not available. A representative sample(s) is selected from the extraction/digestion/analytical batch so that various matrix problems may be noted and/or addressed. Poor performance in a matrix spike generally indicates a problem with the sample composition, not the laboratory analysis, and is reported with the appropriate qualifiers.

8.1.6.Matrix Spike Duplicates (MSDs) or Laboratory Duplicates are analyzed at a minimum of one in twenty samples per matrix type per sample extraction or preparation test method. A representative sample(s) is selected from the extraction/digestion/analytical batch so that various matrix problems may be noted and/or addressed. Poor performance in the duplicates generally indicates gross sample processing errors, and is re-analyzed or reported with the appropriate qualifiers.

8.2. Detection Limits

8.2.1.For analytes for which spiking is a viable option, detection limits are determined by a Method Detection Limit (MDL) study as described in Appendix G. The method detection limit is initially determined for the compounds of interest in each method in laboratory pure reagent water or Diatomaceous Earth.

8.2.2. An MDL study is not performed for any component for which spiking solutions are not available. For these types of analytes, the detection limit is based on the restrictions of the respective instrument.

8.3. Selectivity

8.3.1. Absolute and relative retention times aid in the identification of components in chromatographic analyses and help evaluate the effectiveness of a column to separate constituents. Acceptance criteria for retention time windows are documented the respective SOP.

8.3.2. Acceptance criteria for mass spectra are contained in the respective SOPs.

8.4. Demonstration of Method Capability

8.4.1. Prior to acceptance and use of any method, satisfactory initial demonstrations of proficiency (IDP) are required. This IDP is performed each time there is a significant change in instrument type, personnel, or test method. The process is described in Appendix B and in the respective SOPs. A Certification Statement is completed for each analyst documenting that this activity has been acceptably performed. A copy of this statement is found in Appendix C and will be kept in the employee's folder.

9. DATA REDUCTION, REVIEW, REPORTING AND RECORDS

9.1. Data Reduction and Review

9.1.1. Data resulting from the analysis of samples is reduced according to protocols described in the laboratory SOPs. Computer programs used for data reduction are verified regularly by manual calculations. All information used in the calculations (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, sample response, and blank or background-correction protocols) are recorded in order to enable reconstruction of the final result at a later date. Information on the preparation of the sample (e.g., weight or volume of sample used, percent dry weight for solids, extract volume, dilution factor used) is maintained in order to enable reconstruction of the final result at a later date.

9.1.2. All data is reviewed by a second analyst (peer review) and a supervisor, according to laboratory procedures, to ensure that calculations are correct and to detect transcription errors. Spot checks are performed on computer calculations to verify program validity. Errors detected in the review process are referred to the analyst(s) for corrective action.

9.1.3. As described in Section 12.0, the results of all quality control sample analyses are reviewed, and evaluated before data is reported to the client.

9.2. Project Report Format and Contents

9.2.1.The results of each analysis or series of analysis are normally reported in a project report and include all the information necessary for the interpretation of the results.

9.2.2.Each project report typically includes:

1) The title "Report of Analysis";
2) Name and address of laboratory, and phone number with name of contact person;
3) A unique identification number and the total number of pages, with all pages sequentially numbered;
4) Name and address of client;
5) Description and unambiguous identification of the sample(s) including the client identification code;
6) Identification of results for any sample that did not meet sample acceptance requirements;
7) Date and time of receipt of sample, date and time that the project report was printed, date analyzed, and analysis that reported the data;
8) Identification of the test method used;
9) Data qualifiers;
10) Identification of the reporting units such as µg/L or mg/Kg;
12) Clear identification of all test data provided by outside sources; and
13) Clear identification of numerical results with values below the Reporting Limit reported as less the reporting limit.

9.2.3.Exceptions to this standard approach for reporting are allowed with approval of the Director of laboratories and are documented.

9.3.**Records**

9.3.1.Records provide the direct evidence and support for the necessary technical interpretations, judgments, and discussions concerning laboratory results. These records, particularly those that are anticipated to be used as evidentiary data, provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, retrievable, and protected against damage, deterioration, or loss. All records referenced in this section are retained for a minimum of five years.

9.3.2.Laboratory records generally consist of bound notebooks with pre-numbered pages, personnel qualification and training forms, equipment maintenance and calibration forms, analytical data forms, and chain-of-custody forms. All records are recorded in indelible ink and retained for five years. Records that are stored or generated by computers or personal computers (PCs) have hard copy or write-protected backup copies.

9.3.3.Any documentation errors are corrected by drawing a single line through the error so that it remains legible and is initialed by the responsible individual, along with the date of change. The correction is written adjacent to the error. If corrections need to be made in computerized data, a system parallel to the corrections for handwritten data is used. The person who performed the instrumental analysis signs recorder printouts and sequence tables.

9.3.4. Laboratory records include the following:

9.3.4.1. Standard Operating Procedures -- Any revisions to laboratory procedures are written, dated, and distributed to all affected individuals to ensure implementation of changes.

9.3.4.2. Equipment Maintenance Documentation -- Documents detailing the receipt and specification of analytical equipment are retained. A history of the maintenance record of each system serves as an indication of the adequacy of maintenance schedules and parts inventory. As appropriate, the maintenance guidelines of the equipment manufacturer are followed. When maintenance is necessary, it is documented in the respective logbook. Required information documentation within the logbook includes why the maintenance was performed, what was done, when it was done, who performed the corrective action, and the effect the corrective action had, along with any serial numbers, suppliers names, etc. of added parts.

9.3.4.3. Calibration Records & Traceability of Standards/Reagents -- The frequency, conditions, standards, and records reflecting the calibration history of a measurement system are recorded. The preparation of Standards and Reagents is documented. Standards and reagents are labeled with sufficient information to refer to the preparation documentation.

9.3.4.4. Sample Management -- These include records pertaining to:

9.3.4.4.1. Sample preservation including appropriateness of sample container and compliance with holding time requirement;
9.3.4.4.2. Sample identification, receipt, acceptance or rejection and log-in;
9.3.4.4.3. Sample storage and tracking including shipping receipts, transmittal forms;
9.3.4.4.4. Disposal of hazardous samples including the date of sample or sub-sample disposal and name of the responsible person;

9.3.4.5. Original Data -- The raw data and calculated results for all samples are maintained on analytical data sheets, logbooks, workbooks, excel files or other sample tracking or data entry forms. Instrumental output data is stored in a computer file or a hard copy report. These records include:

9.3.4.5.1. Laboratory sample ID number;
9.3.4.5.2. Date of analysis;
9.3.4.5.3. Analysis type and sample preparation information, including sample aliquots processed, cleanup, and separation protocols.;
9.3.4.5.4. All manual, automated, or statistical calculations; and
9.3.4.5.5. Analyst's or operator's initials/signature.

9.3.4.6. QC Data -- The raw data and calculated results for all QC samples and standards are maintained in the manner described in the preceding paragraph. Documentation allows correlation of sample results with associated QC data. Documentation also includes the source and lot numbers of standards for traceability.

QC samples include, but are not limited to, laboratory control samples, method blanks, matrix spikes, and matrix spike duplicates.

9.3.4.7. Correspondence -- Correspondence pertinent to a project is recorded on the COC or paper clipped to the COC and kept in the project files. Correspondence with clients is kept in the closest phone log book.

9.3.4.8. Deviations -- All deviations from SOPs. Deviations are recorded on the analytical data sheet and reviewed / approved by the QA Officer or Technical Team Leader.

9.3.4.9. Final Report – The final report is mailed to the client. An electronic copy of the report is stored in the LIMS system and any supporting documentation is filed with the COC.

9.3.4.10. Administrative Records -- The following are maintained:

9.3.4.10.1. Personnel qualifications, experience and training records.

9.3.4.10.2. Safety records.

9.3.4.10.3. Initial and continuing demonstration of proficiency for each analyst.

9.4. **Document Control System**

9.4.1. The document control system is used to ensure that all staff has access to current policies and procedures at all times, it is also used as a tool to record significant changes made to a controlled document. Documents which are managed by this system are refried to as Controlled Documents (CD) which includes this Quality Manual, analytical data sheets, and all SOPs. The system consists of document review, revision, and approval and a revision recording system within the LIMS system.

9.4.2. All quality documents (this Manual, SOPs, policies, etc.) are reviewed and approved by the QA Officer, the Technical Team Leader, and the Director of Laboratories. Such documents are revised whenever significant changes are made. All documents are reviewed at least every 5 years.

9.4.3. All quality documents are controlled by the QA Officer. Controlled copies are provided to individuals in the laboratory who need copies. Entries into the CD system within the LIMS system are always dated and initialed; nothing is deleted. See the Controlled Document SOP (CD#186) for more information.

9.5. **Confidentiality**

9.5.1. All laboratory results and associated raw data are kept in confidence. Access to laboratory records and LIMS data is limited to laboratory personnel.

9.5.2.Where clients require transmission of test results by telephone, telex, facsimile or other electronic or electromagnetic means, staff will ensure confidentiality is preserved.

9.5.3.There must be written consent from the sample submitter in order for documents to be supplied to a party other then the party that submitted the sample.

10. PERFORMANCE AND SYSTEM AUDITS AND FREQUENCY

10.1. Internal Laboratory Audits

10.1.1. Annual internal audits are performed to verify that laboratory operations continue to comply with the requirements of the quality system. Such audits are done by the quality assurance officer. Where the audit findings cast doubt on the correctness or validity of the laboratory's results, an immediate corrective action is initiated and the Director of the Laboratories is notified.

10.1.2. The internal system audits include an examination of laboratory documentation on sample receiving, sample log-in, sample storage, chain-of-custody procedures, sample preparation and analysis, instrument operating records, etc.

10.2. Managerial Review

10.2.1. At least once per year, laboratory management conducts a review of the quality system to ensure its continuing suitability and effectiveness and to introduce any necessary changes or improvements in the quality system and laboratory operations. The review takes into account reports from managerial and supervisory personnel, the outcome of recent internal audits, assessments by external bodies, the results of proficiency tests, any changes in the volume and type of work undertaken, feedback from clients, corrective actions, and other relevant factors.

10.3. External Audits

10.3.1. Records of external audits are kept for five years.

11. FACILIES, EQUIPMENT, REAGENTS, AND PREVENTATIVE MAINTENANCE

11.1. Equipment and Reference

11.1.1 Records are maintained for all major equipment and all reference materials significant to the tests performed. These records include documentation on all routine and non-routine maintenance activities and reference material verifications.
The records include:

1) The name of the equipment;
2) The manufacturer's name, type identification, and serial number or other unique identification;
3) Date received and date placed in service (if available);

4) Current location, where appropriate;
5) If available, condition when received (e.g. new, used, reconditioned);
6) Copy of the manufacturer’s instructions, where available;
7) Details of maintenance carried out to date and planned for the future; and
9) Record of damage, malfunction, modification or repair.
10) Corrective Action and Results

11.1.1. Glassware Cleaning - Glassware is cleaned to meet the sensitivity of the method. Any cleaning and storage procedures that are not specified by the method are documented in a Glassware Preparation SOP_57 (CD#73).

11.2. **Documentation and Labeling of Standards and Reagents**

11.2.1. Records are kept for all standards, including the manufacturer/vendor, the manufacturer’s Certificate of Analysis or purity (if supplied), the date of receipt, recommended storage conditions, and an expiration date after which the material is not used unless it is verified.

11.2.2. Original containers provided by the vendor are labeled with an opened date.

11.2.3. Detailed records are maintained on reagent and standard preparation. These records indicate traceability to purchased stocks or neat compounds (lot #), reference to the method of preparation, date of preparation, expiration date, and preparer’s initials.

11.2.4. All containers of prepared reagents and standards bear a unique identifier and expiration date and are linked to the documentation requirements above.

11.2.5. Reagents - In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the method are not be used. The labels on the container are checked to verify that the purity of the reagents meets the requirements of the particular method. Such information is documented with the Certificate of Analysis.

11.2.6. Water - The quality of reagent water sources is monitored and documented to meet method specified requirements. For the nanopure system the Ω is recorded in a logbook each day it is used.

11.3. **Computers and Electronic Data Related Requirements**

11.3.1. Where computers or automated equipment are used for the capture, processing, manipulation, recording, reporting, storage or retrieval of test data.

11.3.2. Section 8.1 through 8.11 of the EPA Document “2185 - Good Automated Laboratory Practices” (1995), is used as the standard.

11.3.3. Computer software is documented to be adequate for use;

11.3.4. Procedures are established and implemented for protecting the integrity of data; and

11.3.5. Computer and automated equipment are maintained to ensure proper functioning;

11.4. Preventative Maintenance

11.4.1. A routine preventative maintenance program is used to minimize the occurrence of instrument failure and other system malfunctions. Laboratory employees regularly perform routine scheduled maintenance and repair of all instruments. All maintenance that is performed is documented in the appropriate maintenance logbook. All laboratory instruments are maintained in accordance with manufacturer's specifications.

11.5. Inspection/Acceptance Requirements for Supplies and Consumables

11.5.1. Labels indicating the following information on receipt and testing are to be used for critical supplies and consumables.

11.5.1.1. Unique identification number (if not clearly shown).
11.5.1.2. Date received.
11.5.1.3. Date opened.
11.5.1.4. Date tested (if performed).
11.5.1.5. Date to be re-tested (if applicable).
11.5.1.6. Expiration date.

12. SPECIFIC ROUTINE PROCEDURES USED TO EVALUATE DATA QUALITY

12.1. Quality control acceptance criteria are used to determine the validity of the data based on the analysis of internal quality control check (QC) samples (see Section 8.0). The specific QC samples and acceptance criteria are found in the laboratory technical SOPs. Typically, acceptance criteria are taken from published EPA methods. Where no EPA criteria exist, laboratory generated acceptance criteria are established. In-house proficiency data is generated as acceptance criteria for lab bias. In-house proficiency data is based on the historical mean recovery plus or minus three standard deviation units, and acceptance criteria for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference (RPD) plus three standard deviation units. When in-house proficiency data is available it is used, when its limits are within the limits mentioned by the EPA method.

12.1.1. Analytical data generated with QC samples that fall within prescribed acceptance criteria indicate the laboratory was in control. Data generated with QC samples that fall outside the established acceptance criteria indicate the laboratory was "out-of-control" for the failing tests. This data is considered suspect and the corresponding samples are reanalyzed or reported with qualifiers.

12.1.2. Many published EPA methods do not contain recommended acceptance criteria for QC sample results. In these situations, University Laboratories uses 70 - 130% as an interim acceptance criteria for recoveries of spiked analytes, until in-house limits are developed. In-house limits are based on a 95% confidence interval and must include a minimum of 20 data points, with a maximum of 30 data points.

12.2. **Laboratory Control Samples**

12.2.1. A laboratory control sample (LCS) is analyzed with each extraction, digestion, or analytical batch of samples to verify that the accuracy of the analytical process is within the expected performance of the method. The results of LCS are compared to acceptance criteria to determine usability of the data. Data generated with LCS samples that fall outside the established acceptance criteria are judged to be "out-of-control". These data points are considered suspect and the corresponding samples are re-prepared, reanalyzed, and or reported with appropriate qualifiers.

12.3. **Matrix Spikes/Matrix Spike Duplicates (MS/MSD)**

12.3.1. Results from MS/MSD analyses are primarily designed to assess data quality in a given matrix, and not laboratory performance. In general, if the LCS results are within acceptance criteria, performance problems with MS/MSD results may either be related to the specific sample matrix or to an inappropriate choice of extraction, cleanup, or determinative methods. If any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated acceptance criteria, University Laboratories will determine if the poor recovery is related to a matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data is within acceptance criteria but the matrix spike data exceeds the acceptance criteria. When matrix effect is indicated the corresponding data points are reported with the appropriate qualifiers.

12.3.2. If the samples within an analytical batch, with a failing MS/MSD, have a concentration below the lowest standard the sample can be reported without estimation. This is done because if the concentration detected in the sample were corrected for the lower bias, due to the matrix, the results would still be below the PQL.

12.3.3. If the samples within an analytical batch, with a failing MS/MSD, have a concentration above the lowest standard the sample is reported with the appropriate qualifiers.

12.4. **Surrogate Recoveries**

12.4.1. Surrogates are exclusively used in organic analyses. Surrogate recovery data from individual samples are compared to surrogate recovery acceptance criteria in the methods. As for MS/MSD results, surrogate recoveries are used primarily to evaluate data quality and not laboratory performance.

12.4.2. If surrogate recovery is not within the acceptance criteria the samples are re-prepared, reanalyzed, and or reported with the appropriate qualifiers.

12.5. **Internal Standards**

12.5.1. Internal standard is used primarily in the analysis of organic compounds, ICP-MS, and ICP-AES. If the value of the internal standard is not within the acceptance criteria the samples are re-prepared, reanalyzed, and or reported with the appropriate qualifiers.

12.6. **Method Blanks**

12.6.1. Method blank results indicate contamination. The source of contamination is investigated and measures taken to correct, minimize, or eliminate the problem. The method blank is considered contaminated if:

12.6.1.1. The blank contamination exceeds a concentration or the method detection limit, 5% of the regulatory limit for that analyte, or 5% of the measured concentration in the sample.

12.6.2. Each sample in the affected batch is assessed against the above criteria to determine if the sample results are acceptable. Any sample associated with the contaminated blank is reprocessed for analysis or the results reported with appropriate data qualifiers.

13. CORRECTIVE ACTION

13.1. Corrective action is the process of identifying, troubleshooting, and implementing measures to counter unacceptable procedures or out of control QC performance that can affect data quality. To the extent possible, samples are reported only if all quality control measures are acceptable. If a quality control measure is found to be out of control, and the data is to be reported, all samples associated with the failed quality control measure are reported with the appropriate data qualifier(s). Sample results may also be qualified when there are deviations from the laboratory Standard Operating Procedure for which the sample is reported.

13.2. Corrective action in the laboratory may occur prior to, during, or after initial analyses. A number of conditions such as heterogeneous samples, low/high pH readings, and potentially high concentration samples, may be identified during sample log-in, or just prior to analysis. These conditions would warrant corrective action, such as, taking an appropriate sub-sample, adjusting the pH, or taking a smaller initial volume. These corrective actions should be recorded on the appropriate Analytical Data Sheet.

13.3. The SOPs state specific conditions during or after analysis that may automatically trigger corrective action, such as, dilution of samples, additional sample extract cleanup, and automatic re-injection/re-analysis when certain QC criteria are not met. Corrective action that occurs after analysis should prevents the recurrence of the original problem. These actions can range from correcting equations within an excel worksheet or altering controlled documents that may have been negligible. Specific corrective action procedures are also located in Appendix D and Appendix E, and the corresponding EPA methods.

13.4. Any QC sample result outside of acceptance limits requires corrective action. Once the problem has been identified and addressed, corrective action may include the reanalysis of samples, or reporting the appropriate qualifier with the results.

13.5. When nonconforming work occurs analyst will identify the need for corrective action. The Technical Team Leader will approve the required corrective action to be implemented by the laboratory staff. The QA Officer will ensure implementation and documentation of the corrective action.

13.6. Corrective actions are performed prior to release of data from the laboratory. The corrective action is documented in a narrative on the analytical data sheets or in a notepad file with the data, in the Quality Control section of the database for the project, and when applicable in the maintenance log. The effectiveness of the corrective action is monitored, and the corrective action that is most likely to eliminate and prevent the problem, is chosen and executed.

13.7. Where a complaint, or any other circumstance, raises doubt concerning the laboratory’s compliance with the laboratory’s policies or procedures, or with the quality of the laboratory’s tests, the laboratory shall ensure that those areas of activity and/or responsibility involved are promptly audited. Records of the complaint and subsequent actions are maintained. Such complaints are directed through the Director of Laboratories. If results are determined to be erroneous the customer or customers respectfully are notified and University Laboratories works diligently to rectify the error.

14. SUBCONTRACTING AND SUPPORT SERVICES AND SUPPLIES

14.1. Subcontracting Laboratory Services

14.1.1. The following records of all subcontracted analyses are maintained:

14.1.1.1. a copy of the report from the subcontracted laboratory

14.2. Outside Support Services and Supplies

14.2.1. University Laboratories only uses those outside support services and supplies that are of adequate quality to sustain confidence in the laboratory’s tests. Records of all suppliers for support services or supplies required for tests are maintained. Analyses that are most commonly sent to an outside support service include TOC, Asbestos, BTU, and Bacteria.

15. REFERENCES

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15.2. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMS-005/80, December 29, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, Washington, DC 20460.

15.3. RCRA QAPP Instructions, U. S. EPA Region 5, Revision: April 1998*

15.4. ASTM D-5283-92.Generation of Environmental Data Related to Waste Management Activities: Quality assurance and Quality Control Planning and Implementation

15.5. "American National Standards Specification and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs (ANSI/ASQC E-4)", 1994

15.6. EPA 2185 - Good Automated Laboratory Practices, 1995*

15.7. ISO/IEC Guide 25: 1990. General requirements for the competence of calibration and testing laboratories.

15.8. ISO/IEC 17025, International Standard, General requirements for the competence of testing and calibration laboratories, Reference Number ISO/IEC 17025:2005(E) Second Edition 2005-02-15.

15.9. QA/R-2: EPA Requirements for Quality Management Plans, August, 1994*

15.10. QA/G-4: Guidance for the Data Quality Objectives Process EPA/600/R-96/055, September, 1994*

15.11. QA/R-5: EPA Requirements for Quality Assurance Project Plans Draft - November 1997*

15.12. QA/G-5: Guidance on Quality Assurance Project Plans EPA/600/R-98/018, February, 1998*

15.13. QA/G-6: Guidance for the Preparation of Standard Operating Procedures for Quality-Related Operations EPA/600/R-96/027, November, 1995*

15.14. QA/G-9: Guidance for the Data Quality Assessment: Practical Methods for Data Analysis EPA/600/R-96/084 , January, 1998*

15.15. Manual for the Certification of Laboratories Analyzing Drinking Water EPA/570/9-90/008*