STATE OF MICHIGAN

IN THE CIRCUIT COURT FOR THE COUNTY OF WASHTENAW

ATTORNEY GENERAL FOR THE STATE OF MICHIGAN *ex rel.* MICHIGAN DEPARTMENT OF ENVIRONMENT, GREAT LAKES, AND ENERGY,

Plaintiffs,

-v-

GELMAN SCIENCES INC., a Michigan Corporation,

Defendant.

File No. 88-34734-CE
Honorable Timothy P. Connors

Brian J. Negele (P41846)
Michigan Department of Attorney General
525 W. Ottawa St.
PO Box 30212
Lansing, MI 48909-7712
Telephone: (517) 335-7664
Attorney for the State of Michigan

Michael L. Caldwell (P40554)
Zausmer, P.C.
32255 Northwestern Hwy.
Suite 225
Farmington Hills, MI 48334
Telephone: (248) 851-4111
Attorney for Defendant

FILED IN Washtenaw County Trial Court; 6/1/2021 1:12 PM

# FOURTH AMENDED AND RESTATED CONSENT JUDGMENT

The Parties enter this Fourth Amended and Restated Consent Judgment ("Consent Judgment" or "Fourth Amended Consent Judgment") in recognition of, and with the intention of, furtherance of the public interest by (1) addressing environmental concerns raised in Plaintiffs' Complaint; (2) expediting Remedial Action at the Site; and (3) avoiding further litigation concerning matters covered by this Consent Judgment. Among other things, the Parties enter this Consent Judgment to reflect EGLE's revision of the generic state-wide residential and non-residential generic drinking water cleanup criteria for 1,4-dioxane in groundwater to 7.2 micrograms per liter ("ug/L") and 350 ug/L, respectively, and of the generic groundwater-surface

water interface cleanup criterion for 1,4-dioxane in groundwater to 280 ug/L. The Parties agree to be bound by the terms of this Consent Judgment and stipulate to its entry by the Court.

The Parties recognize that this Consent Judgment is a compromise of disputed claims. By entering into this Consent Judgment, Defendant does not admit any of the allegations of the Complaint, does not admit any fault or liability under any statutory or common law, and does not waive any rights, claims, or defenses with respect to any person, including the State of Michigan, its agencies, and employees, except as otherwise provided herein. By entering into this Consent Judgment, Plaintiffs do not admit the validity or factual basis of any of the defenses asserted by Defendant, do not admit the validity of any factual or legal determinations previously made by the Court in this matter, and do not waive any rights with respect to any person, including Defendant, except as otherwise provided herein. The Parties agree, and the Court by entering this Consent Judgment finds, that the terms and conditions of the Consent Judgment are reasonable, adequately resolve the environmental issues covered by the Consent Judgment, and properly protect the public interest.

NOW, THEREFORE, upon the consent of the Parties, by their attorneys, it is hereby ORDERED and ADJUDGED:

## I. JURISDICTION

A. This Court has jurisdiction over the subject matter of this action. This Court also has personal jurisdiction over the Defendant.

B. This Court shall retain jurisdiction over the Parties and the subject matter of this action to enforce this Consent Judgment and to resolve disputes arising under the Consent Judgment.

## II. PARTIES BOUND

This Consent Judgment applies to, is binding upon, and inures to the benefit of Plaintiffs, Defendant, and their successors and assigns.

## III. DEFINITIONS

Whenever the terms listed below are used in this Consent Judgment or the Attachments that are appended hereto, the following definitions shall apply:

A. "Consent Judgment" or ""Fourth Amended Consent Judgment" shall mean this Fourth Amended and Restated Consent Judgment and all Attachments appended hereto. All Attachments to this Consent Judgment are incorporated herein and made enforceable parts of this Consent Judgment.

B. "Day" shall mean a calendar day unless expressly stated to be a working day. "Working Day" shall mean a day other than a Saturday, Sunday, or a State legal holiday. In computing any period of time under this Consent Judgment, where the last day would fall on a Saturday, Sunday, or State legal holiday, the period shall run until the end of the next working day.

C. "Defendant" shall mean Gelman Sciences Inc.

D. "1,4-dioxane" shall mean 1,4-dioxane released to or migrating from the Gelman Property. This term as it is used in this Consent Judgment shall not include any 1,4-dioxane that Defendant establishes by a preponderance of the evidence to have originated from a release for which Defendant is not legally responsible, except to the extent that such 1,4-dioxane is commingled with 1,4-dioxane released to or migrating from the Gelman Property. Nothing in this Consent Judgment shall preclude Defendant's right to seek contribution or cost recovery from other parties responsible for such commingled 1,4-dioxane.

E. "Eastern Area" shall mean the part of the Site that is located east of Wagner Road, including the areas encompassed by the Prohibition Zone.

F. "EGLE" shall mean the Michigan Department of Environment, Great Lakes, and Energy, the successor to the Michigan Department of Environmental Quality, the Michigan Department of Natural Resources and Environment, the Michigan Department of Natural Resources, and the Water Resources Commission. Pursuant to Executive Order 2019-06, effective April 22, 2019, the Michigan Department of Environmental Quality was renamed the Michigan Department of Environment, Great Lakes, and Energy.

G. "Evergreen Subdivision Area" shall mean the residential subdivision generally located north of I-94 and between Wagner and Maple Roads, bounded on the west by Rose Street, on the north by Dexter Road, and on the south and east by Valley Drive.

H. "Gelman" shall mean Gelman Sciences Inc.

I. "Gelman Property" shall mean the real property described in Attachment A, where Defendant formerly operated a manufacturing facility in Scio Township, Michigan. The Defendant sold portions of the property and retains one parcel only for purposes of operating a water treatment system (the "Wagner Road Treatment Facility").

J. "Generic GSI Criterion" shall mean the generic groundwater-surface water interface ("GSI") cleanup criterion for 1,4-dioxane of 280 ug/L established pursuant to MCL 324.20120e(1)(a).

K. "Groundwater Contamination" shall mean the 1,4-dioxane in the groundwater at a concentration in excess of 7.2 ug/L, as determined by the analytical method(s) described in Attachment B to this Consent Judgment, subject to review and approval by EGLE.

L. "Municipal Water Connection Contingency Plan" or "MWCCP" shall mean a

contingency plan developed to identify the steps necessary to connect properties that rely on a private drinking water well to municipal water in the event those wells are threatened by 1,4-dioxane concentrations in excess of the applicable drinking water cleanup criterion and the estimated time necessary to implement each step of the water connection process.

M. "Part 201" shall mean Part 201 of the Natural Resources and Environmental Protection Act, MCL 324.20101, *et seq.*

N. "Parties" shall mean Plaintiffs and Defendant.

O. "Plaintiffs" shall mean the Attorney General of the State of Michigan *ex rel.* EGLE.

P. "Prohibition Zone" or "PZ" shall mean the area that is subject to the institutional control established by the Prohibition Zone Order and this Consent Judgment. A map depicting the Prohibition Zone established by this Fourth Amended Consent Judgment is attached as Attachment C.

Q. "Prohibition Zone Order" shall collectively mean the Court's Order Prohibiting Groundwater Use, dated May 17, 2005, which established a judicial institutional control, and the March 8, 2011 Stipulated Order Amending Previous Remediation Orders, which incorporated the Prohibition Zone Order into this Consent Judgment and applied the institutional control to the Expanded Prohibition Zone, as defined in the Third Amendment to Consent Judgment.

R. "PZ Boundary Wells" shall mean those wells on or near the boundary of the Prohibition Zone and designated in Section V.A.3.b herein, whose purpose is to detect movement of 1,4-dioxane near the Prohibition Zone boundary.

S. "Remedial Action" or "Remediation" shall mean removal, treatment, and proper disposal of Groundwater and Soil Contamination, land use or resource restrictions, and

institutional controls, pursuant to the terms and conditions of this Consent Judgment and work plans approved by EGLE under this Consent Judgment.

T. "Response Activity" or "Response Activities" shall have the same meaning as that term is defined in Part 201, MCL 324.20101(vv).

U. "Sentinel Wells" shall mean those wells designated in Section V.A.3.a herein, whose purpose is to detect movement of 1,4-dioxane toward the Prohibition Zone boundary.

V. "Site" shall mean the Gelman Property and other areas affected by the migration of 1,4-dioxane emanating from the Gelman Property.

W. "Soil Contamination" or "Soil Contaminant" shall mean 1,4-dioxane in soil at a concentration in excess of 500 micrograms per kilogram ("ug/kg"), as determined by the analytical method(s) described in Attachment D or another higher concentration limit derived by means consistent with Mich Admin Code R 299.18 or MCL 324.20120a.

X. "Verification Process" shall mean the process through which Defendant shall test for and verify concentrations of 1,4-dioxane in excess of the applicable threshold at the relevant monitoring and drinking water wells, using the sampling and analytical method(s) described in Attachment B to this Consent Judgment. Specifically, Defendant shall sample the wells on a quarterly basis unless an alternative schedule is agreed upon with EGLE. Groundwater samples will be analyzed for 1,4-dioxane, either by Defendant's laboratory or a third-party laboratory retained by Defendant. In the event that 1,4-dioxane concentrations in groundwater sampled from any well exceed the applicable threshold, Defendant shall notify EGLE by phone or electronic mail within 48 hours of completion of the data verification and validation specified in the Quality Assurance Project Plan ("QAPP") described in Section V.E. Defendant will resample the same well within five days after the data verification and validation of the original

result or at a time agreed upon with EGLE, if EGLE opts to take split samples. If a second sample analyzed by Defendant's laboratory or a third-party laboratory retained by Defendant has contaminant concentrations exceeding the applicable threshold, the exceedance will be considered verified and Defendant shall undertake the required Response Activities.

In the event that EGLE opts to take split samples, Defendant shall also collect an additional split sample for potential analysis within the applicable holding time by a mutually agreed-upon third-party laboratory at Defendant's expense. If the results from one sample, but not both, confirm a verified exceedance, the third sample analyzed by the mutually agreed-upon third-party laboratory, using the sampling and analytical method(s) described in Attachment B to this Consent Judgment, shall serve as the relevant result for verification purposes.

Y. "Western Area" shall mean that part of the Site located west of Wagner Road.

## IV. IMPLEMENTATION OF REMEDIAL ACTION BY DEFENDANT

Defendant shall implement the Remedial Action to address Groundwater and Soil Contamination at, and emanating from, the Gelman Property in accordance with (1) the terms and conditions of this Consent Judgment; and (2) work plans approved by EGLE pursuant to this Consent Judgment. Notwithstanding any requirements set forth in this Consent Judgment obligating Defendant to operate remedial systems on a continuous basis, at a minimum rate, or until certain circumstances occur, Defendant may temporarily reduce or shut-down such remedial systems for reasonably necessary maintenance according to EGLE-approved operation and maintenance plans.

## V. GROUNDWATER REMEDIATION

Defendant shall design, install, operate, and maintain the systems described below to satisfy the objectives described below. Defendant also shall implement a monitoring program to

verify the effectiveness of these systems.

A. Eastern Area

1. Objectives. The remedial objectives of the Eastern Area ("Eastern Area Objectives") shall be the following:

a. Prohibition Zone Containment Objective. Defendant shall prevent Groundwater Contamination, regardless of the aquifer designation or the depth of the groundwater or Groundwater Contamination, from migrating beyond the boundaries of the Prohibition Zone as may be amended pursuant to Section V.A.2.f. Compliance with the Prohibition Zone Containment Objective shall be determined as provided in Section V.A.4.b, below.

b. Groundwater-Surface Water Interface Objective. Defendant shall prevent 1,4-dioxane from venting into surface waters in the Eastern Area at concentrations above the Generic GSI Cleanup Criterion, except in compliance with Part 201, including MCL 324.20120e ("Groundwater-Surface Water Interface Objective" for the Eastern Area).

2. Prohibition Zone Institutional Control. Pursuant to MCL 324.20121(8) and the Prohibition Zone Order, the following land and resource use restrictions shall apply to the Prohibition Zone depicted on the map attached hereto as Attachment C:

a. The installation by any person of a new water supply well in the Prohibition Zone for drinking, irrigation, commercial, or industrial use is prohibited.

b. The Washtenaw County Health Officer or any other entity authorized to issue well construction permits shall not issue a well construction permit for any well in the Prohibition Zone.

c. The consumption or use by any person of groundwater from the

Prohibition Zone is prohibited.

d. The prohibitions listed in Subsections V.A.2.a–c do not apply to the installation and use of:

i. Groundwater extraction and monitoring wells as part of Response Activities approved by EGLE or otherwise authorized under Parts 201 or 213 of the Natural Resources and Environmental Protection Act ("NREPA"), or other legal authority;

ii. Dewatering wells for lawful construction or maintenance activities, provided that appropriate measures are taken to prevent unacceptable human or environmental exposures to hazardous substances and comply with MCL 324.20107a;

iii. Wells supplying heat pump systems that either operate in a closed loop system or if not, are demonstrated to operate in a manner sufficient to prevent unacceptable human or environmental exposures to hazardous substances and comply with MCL 324.20107a;

iv. Emergency measures necessary to protect public health, safety, welfare or the environment;

v. Any existing water supply well that has been demonstrated, on a case-by-case basis and with the written approval of EGLE, to draw water from a formation that is not likely to become contaminated with 1,4-dioxane emanating from the Gelman Property. Such wells shall be monitored for 1,4-dioxane by Defendant at a frequency determined by EGLE; and

vi. The City of Ann Arbor's Northwest Supply Well, provided that the City of Ann Arbor operates the Northwest Supply Well in a manner that does not prevent

its municipal water supply system from complying with all applicable state and federal laws and regulations.

e. Attachment E (consisting of the map depicting the Prohibition Zone and the above list of prohibitions/exceptions) shall be published and maintained in the same manner as a zoning ordinance at Defendant's sole expense, which may be accomplished by the City of Ann Arbor maintaining a hyperlink on its public webpage that includes the City of Ann Arbor zoning maps, or another appropriate webpage, that directs the visitor to the portion of EGLE's Gelman Sciences website that identifies the extent of the Prohibition Zone and the Summary of Restrictions. EGLE-approved legal notice of the Prohibition Zone expansion reflected in Attachment F shall be provided at Defendant's sole expense.

f. The Prohibition Zone Institutional Control shall remain in effect in this form until such time as it is modified through amendment of this Consent Judgment, with a minimum of 30 days' prior notice to all Parties. The Defendant or EGLE may move to amend this Consent Judgment to modify the boundaries of the Prohibition Zone to reflect material changes in the boundaries or fate and transport of the Groundwater Contamination as determined by future hydrogeological investigations or EGLE-approved monitoring of the fate and transport of the Groundwater Contamination. The dispute resolution procedures of Section XVI shall not apply to such motion. Rather, the Prohibition Zone boundary may not be expanded unless the moving Party demonstrates by clear and convincing evidence that there are compelling reasons that the proposed expansion is needed to prevent an unacceptable risk to human health. The above-described showing shall not apply to a motion if the Prohibition Zone expansion being sought arises from or is related to: (1) inclusion of the Triangle Property under the following subsection; (2) the incorporation of a more restrictive definition of Groundwater Contamination

(i.e., a criterion less than 7.2 ug/L) into this Consent Judgment; or (3) expansion under V.A.6.c up to and including back to the boundary established by this Fourth Amended Consent Judgment.

g. Future Inclusion of Triangle Property in the Prohibition Zone. The triangular piece of property located along Dexter Road/M-14 ("Triangle Property"), depicted in Attachment C, will be included in the Prohibition Zone if the data obtained from monitoring wells MW-121s and MW-121d and other nearby wells, including any water supply well installed on the property, as validated by the Verification Process, indicate that the Groundwater Contamination has migrated to the Triangle Property.

h. Well Identification. To identify any wells newly included in the Prohibition Zone as a result of this modification or any future modification to the Prohibition Zone, pursuant to an EGLE-approved schedule, Defendant shall implement a well identification plan for the affected area that is consistent with the Expanded Prohibition Zone Well Identification Work Plan approved by EGLE on February 4, 2011.

i. Plugging of Private Water Wells. Defendant shall plug and replace any private drinking water wells identified in any areas newly included in the Prohibition Zone by connecting those properties to the municipal water supply. Unless otherwise approved by EGLE, Defendant shall also properly plug non-drinking water wells in any areas newly included in the Prohibition Zone.

j. Municipal Water Connection Contingency Plan ("MWCCP"). Defendant shall develop a MWCCP addressing the potential provision of municipal water to properties using private drinking water wells in the Calvin Street, Wagner Road, and Lakeview Avenue areas. The MWCCP will be developed according to a schedule to be approved by

EGLE.

3. Monitoring and Extraction Well Installation and Operation. Defendant shall install the following additional wells in the Eastern Area according to a schedule approved by EGLE and subject to access and receipt of any required approvals pursuant to Section VII.D:

a. Sentinel Well Installation. Defendant shall install the following three monitoring well clusters to monitor movement of 1,4-dioxane south of the northern Prohibition Zone boundary, in addition to MW-120, MW-123, and MW-129 that are already in place (collectively referred to herein as "Sentinel Wells"):

i. Residential area in the general vicinity of Ravenwood and Barber Avenues (Location "A" on map attached as Attachment G);
ii. Residential area in the general vicinity of Sequoia Parkway and Archwood Avenues between Delwood and Center (Location "B" on map attached as Attachment G); and
iii. Residential area in the general vicinity of Maple Road and North Circle Drive (Location "C" on the map attached as Attachment G).

b. PZ Boundary Well Installation. Defendant shall install the following two monitoring well clusters to monitor the movement of 1,4-dioxane near the PZ Boundary (collectively referred to herein as "PZ Boundary Wells"):

i. Residential, commercial, and vacant area east of South Wagner Road, north of West Liberty Road, west of Lakeview Avenue, and south of Second Sister Lake (Location "D" on map attached as Attachment G); and
ii. Residential area south/southeast of the MW-112 cluster (Location "E" on map attached as Attachment G).

c. Sentinel and PZ Boundary Well Installation and Sampling. Defendant shall install the new well clusters according to a schedule to be approved by EGLE. Each new Sentinel or PZ Boundary Well cluster will include two to three monitoring wells, and

the determination of the number of wells shall be based on EGLE's and the Defendant's evaluation of the geologic conditions present at each location, consistent with past practice. The frequency of sampling these monitoring wells and the analytical methodology for sample analysis will be included in the Eastern Area System Monitoring Plan, as amended.

d. Drilling Techniques. Borings for new wells installed pursuant to Section V.A.3 shall be drilled to bedrock unless a different depth is approved by EGLE or if conditions make such installation impracticable. EGLE reserves the right to require alternate drilling techniques to reach bedrock if standard methods are not able to do so. If the Defendant believes that drilling one or more of these wells to bedrock is not practical due to the geologic conditions encountered and/or that such conditions do not warrant the alternative drilling technique required by EGLE, Defendant may initiate dispute resolution under Section XVI of this Consent Judgment. The wells shall be installed using Defendant's current vertical profiling techniques, which are designed to minimize the amount of water introduced during drilling, unless EGLE agrees to alternate techniques. Any material excavated as the result of well installation shall be properly characterized and disposed of or transferred to an appropriate facility for preservation and future scientific investigation, at Defendant's discretion.

e. Installation of Additional Groundwater Extraction Wells.

i. Defendant shall install an additional groundwater extraction well (the "Rose Well") and associated infrastructure in the general area bounded by Rose Street and Pinewood Street as designated on Attachment G or convert former injection well IW-2 to a groundwater extraction well, or both. The decision to install the Rose Well or to convert IW-2 to an extraction well (or to do both) and exact location of the Rose Well if installed will be based on an evaluation of relevant geologic conditions, water quality, and other relevant factors,

including access.

ii. Subject to V.A.3.g., below, Defendant shall install an additional groundwater extraction well (the "Parklake Well") and associated infrastructure in the parcel owned by the City of Ann Arbor bounded by Parklake Avenue and Jackson Road as designated on Attachment G (the "City of Ann Arbor-owned parcel"). The exact location of the Parklake Well within the City of Ann Arbor-owned parcel will be based on an evaluation of relevant geologic conditions, water quality, and other relevant factors, including access. Terms of access to the City of Ann Arbor-owned parcel shall be governed by an access or license agreement between Defendant and the City of Ann Arbor and Defendant's obligation to install and operate the Parklake Well shall be conditioned on negotiation of a mutually acceptable agreement with the City of Ann Arbor.

f. Eastern Area Groundwater Extraction.

i. The Defendant shall operate the Evergreen Subdivision Area extraction wells, LB-4 and either the Rose Well or IW-2, or both (including EGLE-approved replacement well(s)) (collectively, the "Evergreen Wells"), and TW-19 and TW-23 (or EGLE-approved replacement well(s)) (the "Maple Road Wells"), at a combined minimum purge rate of approximately 200 gallons per minute ("gpm") or the maximum capacity of the existing deep transmission pipeline, whichever is less provided Defendant properly maintains the pipeline, in order to reduce the mass of 1,4-dioxane migrating through the Evergreen Subdivision Area and the mass of 1,4-dioxane migrating east of Maple Road, until such time as the Eastern Area Objectives will be met at a reduced extraction rate or without the need to operate these extraction wells. In the event the maximum capacity of the existing deep transmission pipeline is ever reduced to below 180 gpm, Defendant shall repair and/or reconfigure the pipeline and

related infrastructure, or take other action, including potentially replacing the pipeline or treating and disposing of some portion of the extracted groundwater at a different location, as needed to once again achieve a capacity of 190 – 200 gpm. Defendant shall have the discretion to adjust the individual well purge rates in order to optimize mass removal and compliance with the Eastern Area Objectives, provided that it shall operate the Evergreen Wells at a combined minimum purge rate of approximately 100 gpm, until such time as the Eastern Area Objectives will be met at a reduced extraction rate without the need to operate these wells. Before significantly reducing extraction below the minimum purge rates described above or permanently terminating extraction from either the Evergreen Wells or the Maple Road Wells, Defendant shall consult with EGLE and provide a written analysis, together with the data that supports its conclusion that the Eastern Area Objectives can be met at a reduced extraction rate or without the need to operate these extraction wells. EGLE will review the analysis and data and provide a written response to Defendant within 56 days after receiving Defendant's written analysis and data. If Defendant disagrees with the EGLE's conclusion, Defendant may initiate dispute resolution under Section XVI of this Consent Judgment. The Defendant shall not significantly reduce or terminate extraction from the Evergreen Wells or the Maple Road Wells during the 56-day review period or while Defendant is disputing EGLE's conclusion.

ii. Defendant shall operate the Parklake Well, at a purge rate of approximately 200 gpm, subject to the yield of the aquifer in that area and discharge volume restrictions imposed in connection with the method of water disposal including discharge restrictions during wet weather events, in order to reduce the mass of 1,4-dioxane migrating from that area. Purged groundwater from the Parklake Well shall be treated with ozone/hydrogen peroxide or ultraviolet light and oxidizing agents at the City of Ann Arbor-owned parcel.

Defendant shall operate this extraction and treatment system until the 1,4-dioxane concentration in the groundwater extracted from the Parklake Well has been reduced below 500 ug/L. Once concentrations have been reduced below 500 ug/L, Defendant shall cycle the Parklake Well off and on for several periods of time approved by EGLE to demonstrate that significant concentration rebound is not occurring. Defendant shall not permanently terminate extraction and treatment of water from the Parklake Well before the second anniversary of the date extraction was commenced. Before significantly reducing or terminating extraction from the Parklake Well (beyond the discharge volume restrictions/variations arising from the approved discharge option/above-described cycling), Defendant shall consult with EGLE and provide a written analysis, together with the data that supports its conclusion that the foregoing conditions have been satisfied. EGLE will review the analysis and data and provide a written response to Defendant within 56 days after receiving Defendant's written analysis and data. If Defendant disagrees with EGLE's conclusion, Defendant may initiate dispute resolution under Section XVI of this Consent Judgment. The Defendant shall not significantly reduce or terminate extraction from the Parklake Well during the 56-day review period or while Defendant is disputing EGLE's conclusion.

g. Prerequisites for Parklake Well. Notwithstanding anything else in this Consent Judgment, Defendant shall not be obligated to install and operate the Parklake Well unless and until EGLE issues Defendant an NPDES permit with effluent limitations, discharge limits (other than volume) and other conditions no more restrictive than those included in Defendant's NPDES Permit No. MI-0048453 dated October 1, 2014 ("2014 NPDES Permit") that authorizes discharge of groundwater extracted by the Parklake Well to First Sister Lake following treatment with ozone/hydrogen peroxide technology .

4. Verification Monitoring. Defendant shall amend its Eastern Area System Monitoring Plan dated December 22, 2011 to include the monitoring wells installed under Section V.A.3 within 60 days of their installation. The Eastern Area System Monitoring Plan, as amended (hereinafter the "Verification Plan"), shall be sufficient to meet the objectives of this Section.

a. Objectives of Verification Plan. The Verification Plan shall include the collection of data sufficient to measure the effectiveness of the Remediation and to: (i) ensure that any potential migration of Groundwater Contamination outside of the Prohibition Zone is detected before such migration occurs and with sufficient time to allow Defendant to maintain compliance with the Prohibition Zone Containment Objective; (ii) verify that the Groundwater-Surface Water Interface Objective is satisfied; (iii) track the migration of the Groundwater Contamination to determine the need for additional investigation and monitoring points to meet the objectives in Section V.A.1, including the determination of the fate and transport of Groundwater Contamination when and if it reaches the Allen Creek Drain (including its branches) and the portion of the Huron River that is the easternmost extent of the Prohibition Zone; and (iv) evaluate potential changes in groundwater flow resulting from adjustments in extraction rates at different extraction well locations. The Verification Plan shall be continued until terminated pursuant to Section V.D.

b. Compliance Determination. The Verification Plan shall include the following steps for verifying sampling results and confirming compliance or noncompliance with the Eastern Area Objectives.

i. Verification Process for Sentinel Wells. Defendant shall conduct the Verification Process as defined in Section III.X for each Sentinel Well to verify any

exceedance of 7.2 ug/L. A verified detection above 7.2 ug/L will be considered a "Verified Sentinel Well Exceedance" and Defendant shall take the Response Activities set forth in Section V.A.5.a.

ii. Verification Process for PZ Boundary Wells. Defendant shall conduct the Verification Process as defined in Section III.X for each PZ Boundary Well to verify any exceedance of 4.6 ug/L and/or 7.2 ug/L. A verified detection above 4.6 ug/L will be considered a "Verified PZ Boundary Well Exceedance" and Defendant shall take the Response Activities set forth in Section V.5.b. A verified detection above 7.2 ug/L will be considered a "Confirmed PZ Boundary Well Noncompliance" and Defendant shall take the Response Activities set forth in Section V.5.c.

5. Eastern Area Response Activities. Defendant shall take the following Response Activities:

a. Verified Sentinel Well Exceedance. In the event of a Verified Sentinel Well Exceedance, Defendant shall sample that Sentinel Well monthly. If the concentrations of 1,4-dioxane are less than 7.2 ug/L in samples from any two successive monthly sampling events, Defendant shall return to sampling that Sentinel Well quarterly. If, however, the concentrations of 1,4-dioxane exceed 7.2 ug/L in samples collected from the same Sentinel Well in any three successive monthly sampling events, Defendant shall take the following actions:

i. If involving a Sentinel Well in the north, installation of up to two additional well clusters near the Prohibition Zone boundary (the location of which shall be determined based on the location of the initial exceedance). If more than one Sentinel Well in the north exceeds the trigger level, Defendant and EGLE will mutually agree on the number of

PZ Boundary Wells to be installed. Defendant shall sample the new PZ Boundary Wells monthly until Defendant completes the hydrogeological assessment described in Section V.A.5.a.ii below.

ii. Completion of a focused hydrogeological assessment of the applicable area that analyzes the likelihood that 1,4-dioxane at levels above 7.2 ug/L will migrate outside the Prohibition Zone. The assessment shall also opine on the mechanism causing the exceedances and the potential risk of impact to private drinking water wells. Defendant shall provide this assessment to EGLE within 60 days after installation of the new PZ Boundary Well(s). If the focused hydrogeological assessment determines that there is a low potential for the Groundwater Contamination to migrate beyond the Prohibition Zone boundary, normal quarterly monitoring of the Sentinel Well and applicable PZ Boundary Wells will resume. If the focused hydrogeological assessment determines that there is a reasonable likelihood for 1,4-dioxane greater than 7.2 ug/L to migrate beyond the Prohibition Zone boundary, the Defendant shall initiate the following Response Activities:

(A) Defendant shall continue to monitor the affected Sentinel Well(s) and the Prohibition Zone Boundary Wells on a monthly basis.

(B) If the Verified Sentinel Well Exceedance occurs in a Sentinel Well to be installed near the northern boundary of the Prohibition Zone, Defendant shall develop a "Remedial Contingency Plan" that identifies the Response Activities that could be implemented to prevent Groundwater Contamination from migrating beyond the Prohibition Zone Boundary. The Remedial Contingency Plan may identify expansion of the Prohibition Zone as an option, subject to Section V.A.2.f. Defendant shall submit the Remedial Contingency Plan to EGLE within 45 days after the focused hydrogeological assessment is completed.

(C) Defendant will review the Municipal Water Connection Contingency Plan, if applicable, and initiate preliminary activities related to provision of municipal water to potentially impacted private drinking water wells. The amount of work to be completed will be based on the anticipated time frame for water extension and the projected time of migration to potential receptors.

b. Verified PZ Boundary Well Exceedance. In the event of a Verified PZ Boundary Well Exceedance, Defendant shall sample that PZ Boundary Well monthly. If the concentrations of 1,4-dioxane are less than 4.6 ug/L in samples from any two successive monthly sampling events, Defendant shall return to sampling that PZ Boundary Well quarterly. If, however, the concentrations of 1,4-dioxane exceed 4.6 ug/L in samples collected from the same PZ Boundary Well in any three successive monthly sampling events, Defendant shall take the following actions:

i. Defendant, in consultation with EGLE, shall sample select private drinking water wells in the immediate vicinity of the impacted PZ Boundary Well.

ii. Defendant will review the Municipal Water Connection Contingency Plan, and initiate further activities related to potential provision of municipal water to potentially impacted private drinking water wells as appropriate. The amount of work to be completed will be based on the anticipated time frames for water extension and the projected time of migration to potential receptors.

iii. Subject to Section V.A.2.f, Defendant shall implement the Remedial Contingency Plan as necessary to prevent contaminant levels above 7.2 ug/L from migrating beyond the Prohibition Zone Boundary.

c. Confirmed PZ Boundary Well Noncompliance. In the event of a

Confirmed PZ Boundary Well Noncompliance, Defendant shall sample that PZ Boundary Well monthly. If the concentrations of 1,4-dioxane are less than 7.2 ug/L in samples from any two successive monthly sampling events, Defendant shall return to sampling that PZ Boundary Well quarterly. If, however, the concentrations of 1,4-dioxane exceed 7.2 ug/L in samples collected from the same PZ Boundary Well in any four successive monthly sampling events, Defendant shall take the following actions:

i. Defendant shall sample any active drinking water wells in the immediate vicinity of the impacted PZ Boundary Well on a monthly basis.

ii. Defendant will review the Municipal Water Connection Contingency Plan and implement the remaining activities necessary to provide municipal water to properties serviced by private drinking water wells potentially impacted by 1,4-dioxane concentrations above the applicable drinking water cleanup criterion.

iii. Defendant shall connect any such properties to municipal water on a case-by-case basis as determined by EGLE or if requested by the property owner.

iv. Subject to Section V.A.2.f, Defendant shall undertake Response Actions as necessary to reduce concentrations in the affected PZ Boundary Well(s) to less than 7.2 ug/L.

d. Bottled Water. At any time, Defendant shall supply the occupants of any property with a threatened drinking water well with bottled water if, prior to connection to municipal water, 1,4-dioxane concentrations in the drinking water well servicing the property exceed 3.0 ug/L. This obligation shall terminate if either (i) the 1,4-dioxane concentration in the well drops below 3.0 ug/L during two consecutive sampling events or (ii) the property is connected to an alternative water supply.

e. Triangle Property. If a drinking water well is installed on the Triangle Property in the future, Defendant shall take the necessary steps to obtain permission to sample the well on a schedule approved by EGLE. Defendant shall monitor such well(s) on EGLE-approved schedule unless or until that property is included in the Prohibition Zone, at which time, any water well(s) shall be addressed as part of the well identification process described in Section V.A.2.h.

f. Downgradient Investigation. The Defendant shall continue to implement its Downgradient Investigation Work Plan as approved by EGLE on February 4, 2005, as may be amended, to track the Groundwater Contamination as it migrates to ensure any potential migration of Groundwater Contamination outside of the Prohibition Zone is detected before such migration occurs with sufficient time to allow Defendant to maintain compliance with the Prohibition Zone Containment Objective and to ensure compliance with the Groundwater-Surface Water Interface Objective. Defendant shall, as the next phase of this iterative investigation process investigate the area depicted on the map attached as Attachment G, including the installation of monitoring wells at the following locations subject to access and receipt of any required approvals pursuant to Section VII.D:

i. A monitoring well nest in the residential area in the general vicinity of intersection of Washington and 7th Streets (Location "F" on Attachment G);
iii. A shallow well in the residential area in the general vicinity of current monitoring well nest MW-98 (Location "G" on Attachment G); and
iv. A monitoring well nest in the residential area in the general vicinity of Brierwood and Linwood Streets (Location "H" on Attachment G).

The data from these wells will be used to guide additional downgradient investigations as necessary to ensure compliance with the Eastern Area Objectives.

6. Prohibition Zone Boundary Review.

a. Five years after entry of this Fourth Amended Consent Judgment and then every five years thereafter, Defendant and EGLE shall confer and determine whether the boundary of the Prohibition Zone can be contracted without either: (i) posing a current or future risk to the public health and welfare, including maintaining an adequate distance between the Groundwater Contamination and the Prohibition Zone boundary; or (ii) requiring Defendant to undertake additional Response Activities to contain the Groundwater Contamination within the contracted Prohibition Zone boundary beyond those Response Activities otherwise required immediately before the proposed contraction. This determination will be based on consideration of the totality of all data from existing Eastern Area monitoring wells.

b. If EGLE and Defendant jointly agree that the Prohibition Zone boundary may be contracted under these conditions, the Parties shall move to amend Attachments C and E of this Consent Judgment for the sole purpose of establishing a revised boundary for the Prohibition Zone. If only one Party concludes that the Prohibition Zone boundary may be contracted under these conditions, that Party may move to amend Attachments C and E of this Consent Judgment for the sole purpose of establishing a revised boundary for the Prohibition Zone, but must demonstrate by clear and convincing evidence that the above conditions are satisfied. The non-moving Party may oppose or otherwise respond to such motion and the showing required under Section XVI shall not apply to the Court's resolution of the motion.

c. If the Prohibition Zone boundary is contracted under Section V.A.6 and the Parties, either jointly or independently, subsequently determine that based on the totality of the data, the Prohibition Zone boundary should be expanded up to and including back

to the boundary established by this Fourth Amended Consent Judgment in order to protect the public health and welfare, the Party(ies) may move to amend Attachments C and E of this Consent Judgment for the sole purpose of establishing a revised boundary for the Prohibition Zone. Neither Section XVI nor the showing required under SectionV.A.2.f shall apply to the Court's resolution of the motion, provided that the expansion sought does not extend beyond the boundary established by this Fourth Amended Consent Judgment.

d. To the extent the Prohibition Zone boundary is contracted under Section V.A.6.a, Defendant shall not be required to undertake Response Activities to contain the Groundwater Contamination within the contracted boundary beyond those Response Activities required immediately before the Prohibition Zone was contracted.

7. Operation and Maintenance. Subject to Sections V.A.3.f, V.A.9, and reasonably necessary maintenance according to EGLE-approved operation and maintenance plans, Defendant shall operate and maintain the Eastern Area System as necessary to meet the Prohibition Zone Containment Objective until Defendant is authorized to terminate extraction well operations pursuant to Section V.C.1.

8. Treatment and Disposal. Groundwater extracted by the extraction well(s) in the Eastern Area System shall be treated (as necessary depending on the disposal method(s) utilized) with ozone/hydrogen peroxide or ultraviolet light and oxidizing agent(s), or such other method approved by EGLE to reduce 1,4-dioxane concentrations to the required level and disposed of using methods approved by EGLE, including, but not limited to, the following options:

a. Groundwater Discharge. The purged groundwater shall be treated to reduce 1,4-dioxane concentrations to the level required by EGLE, and discharged to

groundwater at locations approved by EGLE in compliance with a permit or exemption authorizing such discharge.

b. Sanitary Sewer Discharge. Use of the sanitary sewer leading to the Ann Arbor Wastewater Treatment Plant is conditioned upon approval of the City of Ann Arbor. If discharge is made to the sanitary sewer, the Evergreen and Maple Road Wells shall be operated and monitored in compliance with the terms and conditions of an Industrial User's Permit from the City of Ann Arbor, and any subsequent written amendment of that permit made by the City of Ann Arbor. The terms and conditions of any such permit and any subsequent amendment shall be directly enforceable by EGLE against Defendant as requirements of this Consent Judgment.

c. Storm Sewer Discharge. Use of the storm drain or sewer is conditioned upon issuance of an NPDES permit and approval of the appropriate regulatory authority(ies). Discharge to the Huron River via a storm water system shall be in accordance with the relevant NPDES permit and conditions required by the relevant regulatory authority(ies). If a storm drain or sewer is to be used for disposal of purged groundwater, Defendant shall submit to EGLE and the appropriate local regulatory authority(ies) for their review and approval, a protocol under which the purge system shall be temporarily shut down: (i) for maintenance of the storm drain or sewer and (ii) during storm events to assure that the storm water system retains adequate capacity to handle run-off created during such events. Defendant shall not be permitted or be under any obligation under this subsection to discharge purged groundwater to the storm drain or sewer unless the protocol for temporary shutdown is approved by all necessary authorities. Following approval of the protocol, the purge system shall be operated in accordance with the approved protocol.

d. Existing or Additional/Replacement Pipeline to Wagner Road Treatment Facility.

i. The existing deep transmission pipeline, an additional pipeline, or a pipeline replacing the existing deep transmission pipeline may be used to convey purged groundwater from the existing Evergreen Area infrastructure to the Wagner Road Treatment Facility where the purged groundwater shall be treated to reduce 1,4-dioxane concentrations to the level required by NPDES Permit No. MI-0048453, as amended or reissued.

ii. Installation of an additional pipeline or a replacement pipeline from the existing Evergreen Area to the Wagner Road Treatment Facility is conditioned upon approval of such installation by EGLE. If the pipeline is proposed to be installed on public property, the pipeline installation is conditioned upon approval of such installation by the appropriate local authority(ies), if required by statute or ordinance, or by Order of the Court pursuant to the authority under MCL 324.20135a. Defendant shall design and install the pipeline in compliance with all state requirements and install the pipeline with monitoring devices to detect any leaks. If leaks are detected, the system will automatically shut down and notify an operator of the condition. In the event that any leakage is detected, Defendant shall take any measures necessary to repair any leaks and perform any remediation that may be necessary. To reduce the possibility of accidental damage to the pipeline during any future construction, Defendant shall participate in the notification system provided by MISS DIG Systems, Inc., or its successor ("MISS DIG"), and shall comply with the provisions of MCL 460.721, *et seq.,* as may be amended and with the regulations promulgated thereunder. Defendant shall properly mark its facilities upon notice from MISS DIG.

e. Existing, Replacement, or Additional Pipeline from Maple Road

Extraction Well(s). Defendant may operate the existing pipeline or install and operate a replacement pipeline or an additional pipeline from the Maple Road Extraction Well(s) to the existing Evergreen area infrastructure to convey groundwater extracted from the Maple Road Extraction Wells to the Wagner Road Treatment Facility, where the purged groundwater shall be treated to reduce 1,4-dioxane concentrations to the level required by NPDES Permit No. MI-0048453, as amended or reissued. Installation and operation of an additional or replacement pipeline from the Maple Road area to Evergreen area is conditioned upon approval of such installation and operation by EGLE. If the pipeline is proposed to be installed on public property, the pipeline installation is conditioned upon approval of such installation by the appropriate local authorities, if required by statute or ordinance, or Order of the Court pursuant to the authority under MCL 324.20135a. Defendant shall design any such pipeline in compliance with all state requirements and install it with monitoring devices to detect any leaks. In the event any leakage is detected, Defendant shall take any measures necessary to repair any leaks and perform any remediation that may be necessary. To reduce the possibility of accidental damage to the pipeline, Defendant shall participate in the notification system provided by MISS DIG and shall comply with the provisions of MCL 460.721, *et seq.*, as may be amended, and with the regulations promulgated thereunder. Defendant shall properly mark its facilities upon notice from MISS DIG.

f. Pipeline from Rose Well. Installation and operation of a proposed pipeline from the Rose Well to the existing Evergreen area infrastructure is conditioned upon approval of such installation and operation by EGLE. If the pipeline is proposed to be installed on public property, the pipeline installation is conditioned upon approval of such installation by the appropriate local authorities, if required by statute or ordinance, or Order of the Court

pursuant to the authority under MCL 324.20135a. Defendant shall design and install any such pipeline in compliance with all state requirements and install it with monitoring devices to detect any leaks. In the event any leakage is detected, Defendant shall take any measures necessary to repair any leaks and perform any remediation that may be necessary. To reduce the possibility of accidental damage to the pipeline, Defendant shall participate in the notification system provided by MISS DIG and shall comply with the provisions of MCL 460.721, *et seq*., as may be amended, and with the regulations promulgated thereunder. Defendant shall properly mark its facilities upon notice from MISS DIG. Defendant may operate such pipeline to, among other things, convey groundwater extracted from the Rose Well to the existing Evergreen Area infrastructure and then to the Wagner Road Treatment Facility, where the purged groundwater shall be treated to reduce 1,4-dioxane concentrations to the level required by NPDES Permit No. MI-0048453, as amended or reissued.

g. Surface Water Discharge to First Sister Lake. Groundwater extracted from the Parklake Well may be discharged to First Sister Lake, conditioned on EGLE's issuance of an NPDES permit with effluent limitations, discharge limits (other than volume), and other conditions no more restrictive than those included in Defendant's 2014 NPDES Permit that authorizes discharge of groundwater to First Sister Lake following treatment with ozone/hydrogen peroxide technology. Defendant shall submit a protocol to EGLE and the appropriate local authority(ies) for their review and approval, a protocol under which the Parklake Well shall be temporarily shut down during storm events or high water levels in First Sister Lake as necessary to avoid flooding. Defendant shall not be under any obligation to operate the Parklake Well unless the protocol for temporary shutdown is approved by all necessary authorities. Following approval of the protocol, Defendant shall operate the Parklake

Well in accordance with the approved protocol.

9. Wagner Road Extraction. The extraction wells currently or in the future located just west of Wagner Road (the "Wagner Road Wells") shall be considered part of the Eastern Area System even though they are located west of Wagner Road. The Defendant shall initially operate the Wagner Road Wells at a combined 200 gpm extraction rate. The Defendant shall continue to operate the Wagner Road Wells in order to reduce the migration of 1,4-dioxane east of Wagner Road at this rate until such time as the Eastern Area Objectives will be met with a lower combined extraction rate or without the need to operate these wells or that reduction of the Wagner Road extraction rate would enhance 1,4-dioxane mass removal from the Parklake Well and/or the Rose Well/IW-2 and Defendant's efforts to reduce the mass of 1,4-dioxane migrating east of Maple Road and/or through the Evergreen Subdivision Area. Before significantly reducing or terminating extraction from the Wagner Road Wells, Defendant shall consult with EGLE and provide a written analysis, together with the data that supports its conclusion that the above-objectives can be met at a reduced extraction rate or without the need to operate these extraction wells. EGLE will review the analysis and data and provide a written response to Defendants within 56 days after receiving Defendant's written analysis and data. If Defendant disagrees with EGLE's conclusion, Defendant may initiate dispute resolution under Section XVI of this Consent Judgment. The Defendant shall not significantly reduce or terminate the Wagner Road extraction during the 56-day review period or while Defendant is disputing EGLE's conclusion.

10. Options Array for Transmission Line Failure/Inadequate Capacity. The Defendant has provided EGLE with documentation regarding the life expectancy of the deep transmission line and an Options Array (attached as Attachment H). The Options Array

describes the various options that may be available if the deep transmission line fails or the 200 gpm capacity of the existing deep transmission line that transports groundwater from the Eastern Area System to the treatment system located on the Gelman Property proves to be insufficient to meet the Prohibition Zone Containment Objective.

B. Western Area

1. Western Area Non-Expansion Cleanup Objective. The Defendant shall prevent the horizontal extent of the Groundwater Contamination in the Western Area, regardless of the depth (as established under Section V.B.3.b and c), from expanding. Compliance with this objective shall be determined as set forth in Section V.B.4, below. Continued migration of Groundwater Contamination into the Prohibition Zone, as may be modified, shall not be considered expansion and is allowed. A change in the horizontal extent of Groundwater Contamination resulting solely from the Court's application of a new cleanup criterion shall not constitute expansion. Nothing in this Section prohibits EGLE from seeking additional response activities pursuant to Section XVIII.E of this Consent Judgment. Compliance with the Non-Expansion Cleanup Objective shall be established and verified by the network of monitoring wells in the Western Area to be selected and/or installed by the Defendant as provided in Sections V.B.3.b and c, below ("Western Area Compliance Well Network") and the Compliance Process set forth in Section V.B.4 ("Western Area Compliance Process"). Except as provided in Section VI.C.1, there is no independent mass removal requirement or a requirement that Defendant operate any particular Western Area extraction well(s) at any particular rate beyond what is necessary to prevent the prohibited expansion, provided that Defendant's ability to terminate all groundwater extraction in the Western Area is subject to Section V.C.1.c and the establishment of property use restrictions as required by Section V.B.3.a. If prohibited

expansion occurs, as determined by the Western Area Compliance Well Network and the Western Area Compliance Process, Defendant shall undertake additional response activities to return the Groundwater Contamination to the boundary established by the Western Area Compliance Well Network (such response activities may include groundwater extraction at particular locations).

As part of the Third Amendment to Consent Judgment, EGLE agreed to modify the remedial objective for the Western Area as provided herein to a no expansion performance objective in reliance on Defendant's agreement to comply with a no expansion performance objective for the Western Area. To ensure compliance with this objective, Defendant acknowledges that in addition to taking further response action to return the horizontal extent of Groundwater Contamination to the boundary established by the Compliance Well Network, Defendant shall be subject to stipulated penalties for violation of the objective as provided in Section XVII. Nothing in this Section shall limit Defendant's ability to contest the assessment of such stipulated penalties as provided in this Consent Judgment.

2. Western Area Groundwater-Surface Water Interface Objective.

a. Defendant shall prevent 1,4-dioxane from venting into surface waters in the Western Area at concentrations above the Generic GSI Cleanup Criterion, except in compliance with Part 201, including MCL 324.20120e ("Groundwater-Surface Water Interface Objective" for the Western Area).

b. GSI Investigation Work Plan. Within 90 days of entry of this Consent Judgment, Defendant shall submit to EGLE for its review and approval a work plan for investigation of the groundwater-surface water interface in the Western Area and a schedule for implementing the work plan. Defendant's work plan shall include:

i. An evaluation of the Western Area and identification of any areas where the GSI pathway is relevant, i.e., any areas where 1,4-dioxane in groundwater is reasonably expected to vent to surface water in concentrations that exceed the Generic GSI Criterion based on evaluation of the factors listed in MCL 324.20120e(3); and

ii. A description of the Response Activities Defendant will take to determine whether 1,4-dioxane in groundwater is venting to surface water in any such areas in concentrations that exceed the Generic GSI Criterion.

c. GSI Response Activity Work Plan. With respect to any areas where the above-described GSI investigation demonstrates that 1,4-dioxane in groundwater is venting to surface water in any such areas in concentrations that exceed the Generic GSI Criterion, Defendant shall submit for EGLE review and approval a work plan and a schedule for implementing the work plan that describes the Response Activities, including any evaluations under MCL 324.20120e, Defendant will undertake to ensure compliance with Groundwater-Surface Water Interface Objective within a reasonable timeframe.

d. Compliance with Groundwater-Surface Water Interface Objective. Defendant shall undertake such Response Activities and/or evaluations as necessary to achieve compliance with the Groundwater-Surface Water Interface Objective. It shall not be a violation of this Consent Judgment nor shall Defendant be subject to stipulated penalties unless and until Defendant fails to achieve compliance with the Groundwater-Surface Water Interface Objective within a reasonable timeframe established by EGLE and then only from that point forward. EGLE's determination of a reasonable timeframe for compliance with the Groundwater-Surface Water Interface Objective is subject to dispute resolution under Section XVI.

3. Western Area Response Activities. Defendant shall implement the

following response activities:

a. Groundwater Extraction. The Western Area Response Activities shall include the operation of groundwater extraction wells as necessary to meet the objectives described in Section V.B.1 and 2, including operation of the Marshy Area groundwater extraction system described in Defendant's May 5, 2000 Final Design and Effectiveness Monitoring Plan, as subsequently modified and approved by EGLE. Defendant shall also install and operate additional groundwater extraction wells at the Gelman Property as described in Section VI, below, in order to reduce the mass of 1,4-dioxane in the groundwater. Purged groundwater from the Western Area shall be treated with ozone/hydrogen peroxide or ultraviolet light and oxidizing agent(s), or such other method approved by EGLE to reduce 1,4-dioxane concentrations to the level required by NPDES Permit No. MI-0048453, as amended or reissued. Discharge to the Honey Creek tributary shall be in accordance with NPDES Permit No. MI-0048453, as amended or reissued. The Defendant shall have property use restrictions that are sufficient to prevent unacceptable exposures in place for any properties affected by Soil Contamination or Groundwater Contamination before completely terminating extraction in the Western Area.

b. Western Area Delineation Investigation. Defendant shall install the following additional groundwater monitoring wells pursuant to a schedule approved by EGLE and subject to the accessibility of the locations and obtaining access and any required approvals under Section VII.D at the approximate locations described below and on the map attached as Attachment G to address gaps in the current definition of the Groundwater Contamination and to further define the horizontal extent of Groundwater Contamination in the Western Area:

i. Commercial area north of Jackson Road (across from April Drive) and south of US-Highway I-94, near MW-40s&d. (Deep well only) (Location "I" on Attachment G);
ii. Commercial area north of Jackson Road (across from Nancy Drive) and south of US-Highway I-94, east of MW-40s&d and west of the MW-133 cluster (Location "J" on Attachment G);
iii. Residential area west of West Delhi, north of Jackson Road and south of US-Highway I-94 (Location "K" on Attachment G);
iv. Residential area southwest of the MW-141 cluster in the vicinity of Kilkenny and Birkdale (Location "L" on Attachment G);
v. Residential area along Myrtle between Jackson Road and Park Road (Shallow Well only) (Location "M" on Attachment G); and
vi. Residential and vacant area within approximately 250 feet of Honey Creek southwest of Dexter Road (Location "N" on Attachment G).

This investigation may be amended by agreement of EGLE and the Defendant to reflect data obtained during the investigation. Defendant shall promptly provide the data/results from the investigation to EGLE so that EGLE receives them prior to Defendant's submission of the Compliance Monitoring Plan described in Subsection V.B.3.c, below. Based on the data obtained from the wells described above, Defendant may propose to install additional monitoring wells to potentially serve as Compliance Wells rather than one or more of the wells identified above. EGLE reserves the right to request the installation of additional borings/monitoring wells, if the totality of the data indicate that the horizontal extent of Groundwater Contamination has not been completely defined.

c. Compliance Well Network and Compliance Monitoring Plan. Within 30 days of completing the investigation described in Subsection V.B.3.b, above, Defendant shall amend its Western Area Monitoring Plan dated April 18, 2011, including Defendant's analysis of the data obtained during the investigation for review and approval by

EGLE, to identify the network of compliance wells that will be used to confirm compliance with the Western Area Non-Expansion Cleanup Objective (hereinafter referred to as the "Compliance Monitoring Plan"). The Compliance Monitoring Plan shall include the collection of data from a compliance well network sufficient to verify the effectiveness of the Western Area System in meeting the Western Area Non-Expansion Cleanup Objective. The locations and/or number of the Compliance Wells for the Compliance Monitoring Plan will be determined based on the data obtained from the investigation Defendant shall conduct pursuant to Section V.B.3.b, and shall be made up of existing monitoring wells. EGLE shall approve the Compliance Monitoring Plan, submit to Defendant changes in the Compliance Monitoring Plan that would result in approval, or deny the Compliance Monitoring Plan within 35 days of receiving the Compliance Monitoring Plan. Defendant shall either implement the EGLE-approved Compliance Monitoring Plan, including any changes required by EGLE, or initiate dispute resolution pursuant to Section XVI of this Consent Judgment. Defendant shall implement the EGLE- (or Court)-approved Compliance Monitoring Plan to verify the effectiveness of the Western Area System in meeting the Western Area Non-Expansion Cleanup Objective. Defendant shall continue to implement the current EGLE-approved monitoring plan(s) until EGLE approves the Compliance Monitoring Plan required by this Section. The monitoring program shall be continued until terminated pursuant to Section V.D.

d. Municipal Water Connection Contingency Plan ("MWCCP"). Defendant shall develop a MWCCP addressing the potential provision of township water to properties using private drinking water wells on Elizabeth Road. The MWCCP will be developed according to a schedule to be approved by EGLE.

4. Compliance Determination for Non-Expansion Objective. The Compliance Monitoring Plan shall include the following steps for verifying sampling results and confirming compliance or noncompliance with the Western Area Non-Expansion Cleanup Objective.

a. Monitoring Frequency/Analytical Method. Defendant will sample groundwater from the Compliance Wells on a quarterly basis unless an alternative schedule is agreed upon on with EGLE. Groundwater samples will be submitted to a laboratory owned, operated or contracted by Defendant for 1,4-dioxane analysis.

b. Verification Process. Defendant shall conduct the Verification Process as defined in Section III.X for each Compliance Well to verify any exceedance of 7.2 ug/L. A verified detection above 7.2 ug/L will be considered a "Verified Compliance Well Exceedance." If a second sample does not exceed 7.2 ug/L, monitoring of the well will increase to monthly until the pattern of exceedances is broken by two successive sampling events below 7.2 ug/L. At that point, a quarterly monitoring frequency will resume.

c. Response Activities. In the event of a Verified Compliance Well Exceedance, Defendant shall take the following Response Activities:

i. Sample selected nearby private drinking water wells. Defendant shall sample select private drinking water wells unless otherwise the Parties otherwise agree. Prior to sampling the selected wells, Defendant shall submit a list of the wells to be sampled and other sampling details to EGLE for approval. In selecting wells to be sampled, Defendant shall consider data collected from monitoring and private drinking water wells within 1,000 feet of the Compliance Well(s) that exceeded 7.2 ug/L, groundwater flow, hydrogeology and well depth. EGLE shall respond within seven days after receipt of Defendant's list of select

private drinking water wells and shall either approve the list or propose alternate or additional wells to be sampled.

ii. If a Verified Compliance Well Exceedance occurs in the same Compliance Well in any two successive monthly sampling events, Defendant shall take the following Response Activities:

(A) Continue to sample the previously selected private drinking water well(s) on a monthly basis unless otherwise agreed upon with EGLE.

(B) Conduct focused hydrogeological investigation to determine whether the Verified Compliance Well Exceedance is a temporary fluctuation or evidence of plume expansion. The investigation shall include the measurement of groundwater levels in relevant monitoring wells in the vicinity of the Compliance Well with the Verified Compliance Well Exceedance. Defendant shall report its findings to EGLE within 30 days of completing the hydrogeological investigation.

(C) Conduct Statistical Analysis. During the eight month period after the second consecutive Verified Compliance Well Exceedance, Defendant shall complete a statistical analysis of the data using a Mann-Kendall Trend Test or other statistical technique approved by EGLE.

(D) Interim Measures Feasibility Study. During the eight month period after the second consecutive Verified Compliance Well Exceedance, Defendant shall evaluate affirmative measures to control expansion of the Groundwater Contamination as necessary to reduce the concentration of 1,4-dioxane in the relevant Compliance Well to below 7.2 ug/L, including adjustments in groundwater extraction rates, the installation of additional groundwater extraction wells or other remedial technologies.

Defendant shall submit to EGLE a feasibility study within 240 days of the Verified Compliance Well Exceedance. The feasibility study shall include an evaluation of the feasibility and effectiveness of all applicable measures to control expansion of the Groundwater Contamination as necessary to reduce the concentration of 1,4-dioxane in the relevant Compliance Well to below 7.2 ug/L in light of the geology and current understanding of the fate and transport of the Groundwater Contamination.

iii. If, after conducting the focused hydrogeological investigation and statistical analysis, the totality of the data evidences a reasonable likelihood that the Western Area Non-Expansion Cleanup Objective is not being met, Defendant shall evaluate and, subject to EGLE approval, implement one or more of the potential response activities identified in the feasibility study, or other response activities, as necessary to achieve compliance with the Western Area Non-Expansion Cleanup Objective. Nothing in this Section shall prevent Defendant from implementing response activities as necessary to achieve the Western Area Non-Expansion Cleanup Objective at an earlier time.

d. Stipulated Penalties/Exacerbation. Defendant shall not be subject to stipulated penalties until concentrations in at least four consecutive monthly samples from a given Compliance Well exceed 7.2 ug/L, at which point Defendant shall be subject to stipulated penalties for violation of the Western Area Non-Expansion Cleanup Objective as provided in Section XVII, provided, however, that Defendant shall not be subject to stipulated penalties with respect to prohibited expansion of the horizontal extent of the Groundwater Contamination if Defendant can demonstrate by a preponderance of the evidence that the migration of the Groundwater Contamination is caused in whole or in part by the actions of an unrelated third party that have contributed to or exacerbated the Groundwater Contamination. In such event,

although Defendant is not subject to stipulated penalties, Defendant shall remain responsible for mitigating the migration of the Groundwater Contamination. Nothing in this Consent Judgment shall preclude Defendant from seeking contribution or cost recovery from other parties responsible for or contributing to exacerbation of the Groundwater Contamination.

e. Private Drinking Water Well Response Activities. If, after conducting the focused hydrogeological investigation and statistical analysis, the totality of the data evidences a reasonable likelihood that 1,4-dioxane will be present at concentrations above 7.2 ug/L in a residential drinking water well and/or at concentrations above 350 ug/L in an active non-residential drinking water well, Defendant shall evaluate and, if appropriate, implement response activities, including, without limitation, the following:

i. Sampling of at risk drinking water well(s) on a monthly basis;

ii. Implementation of affirmative interim measures to mitigate the expansion of 1,4-dioxane at concentrations above the applicable drinking water standard toward the drinking water well(s) as determined in the feasibility study described in Section V.B.4.c.ii.(D);

iii. Evaluation of land use restrictions and/or institutional controls to eliminate drinking water exposures to 1,4-dioxane in the groundwater at concentrations above the applicable drinking water standard; and

iv. Evaluation of water supply alternatives including, but not limited to, providing bottled water, a township water connection, installation of a new drinking water well completed in an uncontaminated portion of the subsurface, and point-of-use treatment systems.

v. If at any time 1,4-dioxane is detected in an active private drinking water well above 3.0 ug/L, Defendant shall promptly at its expense, offer the occupants of the property the option of receiving bottled water and shall sample the well monthly. These obligations shall terminate if either (i) the 1,4-dioxane concentration in the well drops below 3.0 ug/L during two consecutive sampling events or (ii) the property is connected to a permanent alternative water supply. Furthermore, Defendant shall work with EGLE and municipal authorities to evaluate long-term and economically reasonable water supply options.

vi. If 1,4-dioxane is detected at concentrations above 7.2 ug/L in an active residential drinking water well and/or at concentrations above 350 ug/L in an active non-residential drinking water well, Defendant shall conduct the Verification Process as defined in Section III.X for each such private drinking water well. If the detection above 7.2 ug/L is verified, Defendant shall monitor each such private drinking water well on a monthly basis if not already doing so and shall continue monthly monitoring until the well is no longer considered at risk under Section V.B.4.e.i. If 1,4-dioxane is detected at concentrations above 7.2 ug/L in four consecutive monthly samples or any seven monthly samples in any 12 month period, Defendant shall provide at its expense a long-term alternative water supply to the property serviced by the affected well. Such long-term alternative water supply may be in the form of a township water connection, installation of a new drinking water well completed in an uncontaminated portion of the subsurface, or a point-of-use treatment system, or other long-term drinking water supply option approved by EGLE. Defendant shall also provide at its expense bottled water to the property owner until the property is serviced by a long-term alternative water supply.

5. Groundwater Contamination Delineation. Additional delineation of the extent of Groundwater Contamination, including within the plume boundary, and/or

characterization of source areas shall not be required except as provided in Section V.B.3.c. EGLE reserves the right to petition the Court to require additional work if there are findings that EGLE determines warrant additional Groundwater Contamination delineation.

C. Termination of Groundwater Extraction Systems

1. Defendant may only terminate the Groundwater Extraction Systems listed below as provided below:

a. Termination Criteria for Evergreen Wells/Maple Road Wells/Wagner Road Wells. Except as otherwise provided pursuant to Section V.C.2, Defendant may only reduce (below the stated minimum purge rates) or terminate operation of the Evergreen Wells/Maple Road Wells as provided in Section V.A.3.f.i. and of the Wagner Road Wells as provided in Section V.A.9.

b. Termination Criteria for Parklake Well. Except as otherwise provided pursuant to Section V.C.2, Defendant may reduce or terminate operation of the Parklake Well as provided in Section V.A.3.f.ii.

c. Termination Criteria for Western Area. Defendant may terminate the groundwater extraction described in Section VI.C.1 as provided in that Section. Except as otherwise provided pursuant to Section V.C.2, and subject to Section V.B.1., Defendant shall not terminate all groundwater extraction in the Western Area until all of the following are established:

i. Defendant can establish to EGLE's satisfaction that groundwater extraction is no longer necessary to prevent the expansion of Groundwater Contamination prohibited under Section V.B.1;

ii. Defendant's demonstration shall also establish that

groundwater extraction is no longer necessary to satisfy the Groundwater-Surface Water Interface Objective under Section V.B.2; and

iii. Defendant has the land use or resource use restrictions described in Section V.B.3.a in place.

Defendant's request to terminate extraction in the Western Area must be made in writing for review and approval pursuant to Section X of this Consent Judgment. The request must include all supporting documentation demonstrating compliance with the termination criteria. Defendant may initiate dispute resolution pursuant to Section XVI of this Consent Judgment if EGLE does not approve the Defendant's request/demonstration. Defendant may terminate Western Area groundwater extraction upon: (i) receipt of notice of approval from EGLE; or (ii) receipt of notice of a final decision approving termination pursuant to dispute resolution procedures of Section XVI of this Consent Judgment.

2. Modification of Termination Criteria/Cleanup Criteria. The termination criteria provided in Section V.C.1. and/or the definition of "Groundwater Contamination" or "Soil Contamination" may be modified as follows:

a. After entry of this Fourth Amended Consent Judgment, Defendant may propose to EGLE that the termination criteria be modified based upon either or both of the following:

i. a change in legally applicable or relevant and appropriate regulatory criteria since the entry of this Fourth Amended Consent Judgment; for purposes for this Subsection, "regulatory criteria" shall mean any promulgated standard criterion or limitation under federal or state environmental law specifically applicable to 1,4-dioxane; or

ii. scientific evidence newly released since the date of the

United States Environmental Protection Agency's IRIS risk assessment for 1,4-dioxane (August 11, 2010), which, in combination with the existing scientific evidence, establishes that different termination criteria/definitions for 1,4-dioxane are appropriate and will assure protection of public health, safety, welfare, the environment, and natural resources.

b. Defendant shall submit any such proposal in writing, together with supporting documentation, to EGLE for review.

c. If the Defendant and EGLE agree to a proposed modification, the agreement shall be made by written Stipulation filed with the Court pursuant to Section XXIV of this Consent Judgment.

d. If EGLE disapproves the proposed modification, Defendant may invoke the dispute resolution procedures contained in Section XVI of this Consent Judgment. Alternatively, if EGLE disapproves a proposed modification, Defendant may seek to have the dispute resolved pursuant to Subsection V.C.3.

3. If the Defendant invokes the procedures of this Subsection, Defendant and EGLE shall prepare a list of the items of difference to be submitted to a scientific advisory panel for review and recommendations. The scientific advisory panel shall be comprised of three persons with scientific expertise in the discipline(s) relevant to the items of difference. No member of the panel may be a person who has been employed or retained by either Party, except persons compensated solely for providing peer review of the Hartung Report, in connection with the subject of this litigation.

a. If this procedure is invoked, each Party shall, within 14 days, select one member of the panel. Those two members of the panel shall select the third member. Defendant shall, within 28 days after this procedure is invoked, establish a fund of at least

$10,000.00, from which each member of the panel shall be paid reasonable compensation for their services, including actual and necessary expenses. If EGLE and Defendant do not agree concerning the qualifications, eligibility, or compensation of panel members, they may invoke the dispute resolution procedures contained in Section XVI of this Consent Judgment.

b. Within a reasonable period of time after selection of all panel members, the panel shall confer and establish a schedule for acceptance of submissions from EGLE and the Defendant completing review and making recommendations on the items of difference.

c. The scientific advisory panel shall make its recommendations concerning resolution of the items of difference to EGLE and the Defendant. If both EGLE and Defendant accept those recommendations, the termination criteria shall be modified in accordance with such recommendations. If EGLE and the Defendant disagree with the recommendations, EGLE's proposed resolution of the dispute shall be final unless Defendant invokes the procedures for judicial dispute resolution as provided in Section XVI of this Consent Judgment. The recommendation of the scientific advisory panel and any related documents shall be submitted to the Court as part of the record to be considered by the Court in resolving the dispute.

D. Post-Termination Monitoring

1. Eastern Area

a. Prohibition Zone Containment Objective. Except as otherwise provided pursuant to Section V.C.2, Defendant shall continue to monitor the Groundwater Contamination as it migrates within the Prohibition Zone until all approved monitoring wells are below 7.2 ug/L or such other applicable criterion for 1,4-dioxane for six consecutive months, or

Defendant can establish to EGLE's satisfaction that continued monitoring is not necessary to satisfy the Prohibition Zone Containment Objective. Defendant's request to terminate monitoring must be made in writing for review and approval pursuant to Section X of this Consent Judgment. Defendant may initiate dispute resolution pursuant to Section XVI of this Consent Judgment if EGLE does not approve its termination request.

b. Groundwater-Surface Water Interface Objective. Except as provided in Section V.D.1.a, for Prohibition Zone monitoring wells, post-termination monitoring is required for Eastern Area wells for a minimum of ten years after purging is terminated under Section V.C.1.a with cessation subject to EGLE approval. Defendant's request to terminate monitoring must be made in writing for review and approval pursuant to Section X of this Consent Judgment. Defendant may initiate dispute resolution pursuant to Section XVI of this Consent Judgment if EGLE does not approve its termination request.

2. Western Area. Post-termination monitoring will be required for a minimum of ten years after termination of extraction with cessation subject to EGLE approval. Except as otherwise provided pursuant to Section V.C.2, Defendant shall continue to monitor the groundwater in accordance with approved monitoring plan(s), to verify that it remains in compliance with the Non-Expansion Cleanup Objective set forth in Section V.B.1 and the Groundwater-Surface Water Interface Objective set forth in Section V.B.2. If any exceedance is detected, Defendant shall immediately notify EGLE and take whatever steps are necessary to comply with the requirements of Section V.B.1, or V.B.2, as applicable.

E. Quality Assurance Project Plan (QAPP). Defendant previously voluntarily submitted to EGLE for review and approval a QAPP, which is intended to describe the quality control, quality assurance, sampling protocol, and chain of custody procedures that will be used

in carrying out the tasks required by this Consent Judgment. EGLE shall review, and Defendant shall revise accordingly, the QAPP to ensure that it is in general accordance with the United States Environmental Protection Agency's ("U.S. EPA" or "EPA") "Guidance for Quality Assurance Project Plans," EPA QA/G-5, December 2002; and American National Standard ANSI/ASQC E4-2004, "Quality Systems For Environmental Data And Technology Programs – Requirements With Guidance For Use."

## VI. GELMAN PROPERTY RESPONSE ACTIVITIES

A. Gelman Property Objectives. The objectives for the Gelman Property shall be to prevent the migration of 1,4-dioxane from contaminated soils on the Gelman Property into any aquifer at concentrations or locations that cause non-compliance with the Western Area objectives set forth in Sections V.B.1 and V.B.2.

B. Response Activities.

1. Remedial Systems. Defendant shall design and implement remedial systems at the Gelman Property as necessary to achieve the Gelman Property Objectives.

2. Monitoring. Defendant shall implement an EGLE-approved Compliance Monitoring Plan to verify that the Gelman Property Soil Contamination does not cause or contribute to non-compliance with the Western Area objectives set forth in Sections V.B.1 and V.B.2, and to verify the effectiveness of any implemented remedial system.

C. Additional Source Control. Defendant shall implement the following Response Activities to reduce the mass of and/or exposure to 1,4-dioxane present in the soils and/or shallow groundwater on the Gelman Property subject to receipt of any required approvals pursuant to Section VII.D:

1. Additional Groundwater Extraction. Defendant shall install and operate

three "Phase I" extraction wells (one of which was previously installed) at the general locations depicted in the attached Attachment I to enhance control and mass removal of 1,4-dioxane from this area of shallow groundwater contamination. Defendant shall operate these extraction wells at a combined purge rate of approximately 75 gpm, subject to aquifer yield. Defendant shall have the discretion to adjust the individual well purge rates in order to optimize mass removal. Subject to Defendant's ability to adjust individual well purge rates, Defendant shall continue to extract a combined purge rate of approximately 75 gpm, subject to aquifer yield, from this system until the 1,4-dioxane concentration in the groundwater extracted from each of these extraction wells has been reduced below 500 ug/L and, once the concentrations in all three of the wells have been reduced below 500 ug/L, Defendant shall cycle those wells off and on for several periods of time approved by EGLE to demonstrate that significant concentration rebound is not occurring. Before otherwise significantly reducing or terminating extraction from this system, Defendant shall consult with EGLE and provide a written analysis, together with the data that supports its conclusion that the concentration of 1,4-dioxane in the groundwater extracted from each of these wells has been reduced below 500 ug/L, as stated above. EGLE will review the analysis and data and provide a written response to Defendants within 56 days after receiving Defendant's written analysis and data. If Defendant disagrees with EGLE's conclusion, Defendant may initiate dispute resolution under Section XVI of this Consent Judgment. The Defendant shall not significantly reduce or terminate the extraction from this system during the 56-day review period or while Defendant is disputing EGLE's conclusion.

Based on the performance achieved from these extraction wells, the Parties shall evaluate whether installation of up to three additional extraction wells at the general locations indicated on Attachment I would accelerate mass removal to a degree that meaningfully benefits the

Remediation. If EGLE determines that additional mass removal from these locations would be beneficial, Defendant shall, subject to its right to invoke Dispute Resolution under Section XVI, install and operate these additional wells pursuant to a work plan approved by EGLE.

Groundwater extracted from the extraction wells described in this subparagraph will be conveyed to the Wagner Road Treatment Facility for treatment and disposal pursuant to Defendant's NPDES Permit No. MI-0048453, as amended or re-issued.

2. Phytoremediation—Former Pond 1 and 2 Area. Defendant shall apply phytoremediation techniques in the treatment area depicted on Attachment I to reduce the potential mass flux of 1,4-dioxane from vadose zone soils in this area to the groundwater aquifers. Defendant shall plant and maintain trees in the treatment area in order to: (i) remove 1,4-dioxane mass by via biodegradation and transpiration; and (ii) extract and reduce the volume of shallow perched groundwater in this area. Defendant shall install and maintain the trees in a healthy state and replace trees as necessary to assure continued success of the phytoremediation system. Defendant shall continue to operate the phytoremediation system as set forth above until it determines that the further reduction of the mass flux of 1,4-dioxane from the vadose zone soils to the groundwater aquifers is not necessary to achieve compliance with the Gelman Property Objectives. Before significantly reducing or terminating phytoremediation in the Former Pond 1 and 2 area, Defendant shall consult with EGLE and provide a written analysis, together with the data that supports its conclusions. EGLE will review the analysis and data and provide a written response to Defendants within 56 days after receiving Defendant's written analysis and data. If Defendant disagrees with EGLE's conclusion, Defendant may initiate dispute resolution under Section XVI of this Consent Judgment. The Defendant shall not significantly reduce or terminate the phytoremediation during the 56-day review period or while

Defendant is disputing EGLE's conclusion.

3. Phytoremediation—Marshy Area. Defendant will undertake actions to reduce the percolation/infiltration of 1,4-dioxane from Marshy Area to the underlying groundwater through the application of phytoremediation techniques in the area depicted in Attachment I. The initial phase of these Response Activities may include further investigation of the Marshy Area as needed to complete the phytoremediation design regarding methods of enabling roots from trees grown in the Marshy Area to extend into deeper soils containing elevated concentrations of 1,4-dioxane. Defendant shall install and maintain the trees in a healthy state as necessary to assure continued success of the phytoremediation system. Defendant shall continue to operate the phytoremediation system as set forth above until it determines that the further reduction of the percolation/infiltration of 1,4-dioxane from the Marshy Area to the underlying groundwater is not necessary to achieve compliance with the Gelman Property Objectives. Before significantly reducing or terminating phytoremediation in the Marshy Area, Defendant shall consult with EGLE and provide a written analysis, together with the data that supports its conclusions. EGLE will review the analysis and data and provide a written response to Defendants within 56 days after receiving Defendant's written analysis and data. If Defendant disagrees with EGLE's decision to reduce or terminate the phytoremediation in the Marshy Area, Defendant may initiate dispute resolution under Section XVI of this Consent Judgment. The Defendant shall not significantly reduce or terminate the phytoremediation in the Marshy Area during the 56-day review period or while Defendant is disputing EGLE's conclusion.

4. Former Burn Pit Area. Defendant shall undertake the following Response Activities with respect to the former Burn Pit area depicted on Attachments I and J:

a. Install, operate, and maintain a Heated Soil Vapor Extraction System ("HSVE System"). The HSVE System shall be designed to reduce the mass of 1,4-dioxane present in the soils in the portion of the former Burn Pit area identified as "Heated Soil Vapor Extraction" on Attachment J. Defendant shall operate the HSVE system until 1,4-dioxane concentrations in the HSVE System's effluent/exhaust has been reduced to levels that indicate that continued operation of the HVSE system will no longer contribute to meaningful reduction of 1,4-dioxane mass in the Former Burn Pit Area Soils or the Soil Contamination in the treatment area is eliminated, whichever occurs first. Before significantly reducing or terminating operation of the HSVE system, Defendant shall consult with EGLE and provide a written analysis, together with the data that supports its conclusion, that one or both of the above conditions has been satisfied. EGLE will review the analysis and data and provide a written response to Defendant within 56 days after receiving Defendant's written analysis and data. If Defendant disagrees with EGLE's conclusion, Defendant may initiate dispute resolution under Section XVI of this Consent Judgment. The Defendant shall not significantly reduce or terminate operation of the HSVE system during the 56-day review period or while Defendant is disputing EGLE's conclusion.

Following completion of the HSVE treatment, Defendant shall install an impervious barrier over the HSVE Treatment Area to inhibit water from percolating through the soils in the former Burn Pit Area, except with regard to any areas where Defendant can demonstrate to EGLE's satisfaction that Soil Contamination does not exist. Defendant shall maintain the impervious barrier in place until Soil Contamination is no longer present in the underlying soils.

b. Cap the portion of the former Burn Pit area identified as "Capped Area" on Attachment J with an impervious barrier to inhibit water from percolating through the

soils in the former Burn Pit area. Defendant shall maintain the impervious barrier in place until Soil Contamination is no longer present in the underlying soils.

5. After completing installation of the Response Activity systems listed in Sections VI.C.2, VI.C.3 and VI.C.4, the Defendant shall submit a separate installation report (i.e., as-built report) for each of the systems. The reports shall describe the systems as installed including, but not limited to, components of a system, location of components within the specific areas, depths of components of a system, and operational specifications of components of a system.

6. Required Approvals. Notwithstanding the above, Defendant's obligation to implement any of the additional source control Response Activities described in Section VI.C is conditioned upon receipt of any required approvals pursuant to Section VII.D.

## VII. COMPLIANCE WITH OTHER LAWS AND PERMITS

A. Defendant shall undertake all activities pursuant to this Consent Judgment in accordance with the requirements of all applicable laws, regulations, and permits.

B. Defendant shall apply for all permits necessary for implementation of this Consent Judgment including, without limitation, surface water discharge permit(s) and air discharge permit(s).

C. Defendant shall include in all contracts entered into by the Defendant for Remedial Action required under this Consent Judgment (and shall require that any contractor include in all subcontracts), a provision stating that such contractors and subcontractors, including their agents and employees, shall perform all activities required by such contracts or subcontracts in compliance with and all applicable laws, regulations, and permits. Defendant shall provide a copy of relevant approved work plans to any such contractor or subcontractor.

D. The Plaintiffs agree to provide reasonable cooperation and assistance to the Defendant in obtaining necessary approvals and permits for Remedial Action. Plaintiffs shall not unreasonably withhold or delay any required approvals or permits for Defendant's performance of Remedial Action. Plaintiffs expressly acknowledge that one or more of the following permits and approvals may be a necessary prerequisite for one or more of the Response Activities set forth in this Consent Judgment:

1. Renewal of NPDES Permit No. MI-0048453 with respect to the discharge of treated groundwater to the unnamed tributary of Honey Creek.

2. An NPDES Permit that authorizes the discharge of groundwater to First Sister Lake in connection with operation of the Parklake Well following treatment with ozone/hydrogen peroxide technology that has effluent limitations, discharge limits (other than volume), and other conditions no more restrictive than those included in Defendant's 2014 NPDES Permit.

3. Negotiation and execution of an access agreement between Defendant and the City of Ann Arbor providing reasonable and necessary access to the City-owned parcel at Parklake Avenue and Jackson Road with respect to installation and operation of an extraction well, operation and maintenance of a groundwater treatment unit, and disposal of treated groundwater.

4. An Air Permit for discharges of contaminants to the atmosphere for vapor extraction systems, including the HSVE system described in Subsection VI.C.4, under terms reasonably acceptable to Defendant and as necessary if such systems are part of the remedial design.

5. Wetlands Permit(s) from EGLE and/or Scio Township if necessary for the

response activities described in Section VI.C.3 with terms reasonably acceptable to Defendant.

6. An Industrial User's Permit to be issued by the City of Ann Arbor for use of the sewer to dispose of treated or untreated purged groundwater from the Evergreen and/or Maple Road Wells. Plaintiffs have no objection to receipt by the Ann Arbor Wastewater Treatment Plant of the purged groundwater extracted pursuant to the terms and conditions of this Consent Judgment, and acknowledge that receipt of the purged groundwater would not necessitate any change in current and proposed residual management programs of the Ann Arbor Wastewater Treatment Plant.

7. Permit(s) or permit exemptions to be issued by EGLE to authorize the reinjection of purged and treated groundwater in the Eastern Area and Western Area.

8. Surface water discharge permit(s) for discharge into surface waters in the area of Little Lake, if necessary.

9. Approval of the City of Ann Arbor and the Washtenaw County Drain Commissioner to use storm drains or sewers for the remedial programs.

10. Washtenaw County permits as necessary for the installation of extraction wells, monitoring wells, and borings.

## VIII. SAMPLING AND ANALYSIS

Defendant shall make available to EGLE the results of all sampling, tests, and/or other data generated in the performance or monitoring of any requirement under this Consent Judgment. Sampling data generated consistent with this Consent Judgment shall be admissible in evidence in any proceeding related to enforcement of this Consent Judgment without waiver by any Party of any objection as to weight or relevance. EGLE and/or their authorized representatives, at their discretion, may take split or duplicate samples and observe the sampling

event. EGLE shall make available to Defendant the results of all sampling, tests, and/or other data generated in the performance or monitoring of any requirement under this Consent Judgment. Defendant will provide EGLE with reasonable notice of changes in the schedule of data collection activities included in the progress reports submitted pursuant to Section XII.

## IX. ACCESS

A. From the effective date of this Consent Judgment, EGLE, its authorized employees, agents, representatives, contractors, and consultants, upon presentation of proper identification, shall have the right at all reasonable times to enter the Site and any property to which access is required for the implementation of this Consent Judgment, to the extent access to the property is owned, controlled by, or available to the Defendant, for the purpose of conducting any activity authorized by this Consent Judgment, including, but not limited to:

1. Monitoring of the Remedial Action or any other activities taking place pursuant to this Consent Judgment on the property;
2. Verification of any data or information submitted to EGLE;
3. Conduct of investigations related to 1,4-dioxane concentrations at the Site;
4. Collection of samples;
5. Assessment of the need for, or planning and implementing of, Response Activities at the Site; and
6. Inspection and copying of non-privileged documents including records, operating logs, contracts, or other documents required to assess Defendant's compliance with this Consent Judgment.

All Parties with access to the Site or other property pursuant to this Section shall comply with all applicable health and safety laws and regulations.

B. To the extent that the Site or any other area where Remedial Action is to be performed by the Defendant under this Consent Judgment is owned or controlled by persons other than the Defendant, Defendant shall use its best efforts to secure from such persons access for Defendant, EGLE, and their authorized employees, agents, representatives, contractors, and consultants. Defendant shall provide EGLE with a copy of each access agreement secured pursuant to this Section. For purposes of this Section, "best efforts" includes, but is not limited to, seeking judicial assistance to secure such access pursuant to MCL 324.20135a.

## X. APPROVALS OF SUBMISSIONS

Upon receipt of any plan, report, or other item that is required to be submitted for approval pursuant to this Consent Judgment, as soon as practicable, but in no event later than 56 days after receipt of such submission, EGLE will: (1) approve the submission or (2) submit to Defendant changes in the submission that would result in approval of the submission. EGLE will (1) approve a feasibility study or plan that proposes a risk based cleanup or a remedy that requires public comment, or (2) submit to Defendant changes in such submittal that would result in approval in the time provided under Part 201. If EGLE does not respond within 56 days, Defendant may submit the matter to dispute resolution pursuant to Section XVI. Upon receipt of a notice of approval or changes from EGLE, Defendant shall proceed to take any action required by the plan, report, or other item, as approved or as may be modified to address the deficiencies identified by EGLE. If Defendant does not accept the changes proposed by EGLE, Defendant may submit the matter to dispute resolution pursuant to Section XVI.

## XI. PROJECT COORDINATORS

A. Plaintiffs designate Daniel Hamel as EGLE's Project Coordinator. Defendant designates Lawrence Gelb as Defendant's Project Coordinator. Defendant's Project Coordinator

shall have primary responsibility for implementation of the Remedial Action at the Site. EGLE's Project Coordinator will be the primary designated representative for Plaintiffs with respect to implementation of the Remedial Action at the Site. All communication between Defendant and EGLE, including all documents, reports, approvals, other submissions, and correspondence concerning the activities performed pursuant to the terms and conditions of this Consent Judgment, shall be directed through the Project Coordinators. If any Party changes its designated Project Coordinator, that Party shall provide the name, address, email address and telephone number of the successor in writing to the other Party seven days prior to the date on which the change is to be effective. This Section does not relieve Defendant from other reporting obligations under the law.

B. EGLE may designate other authorized representatives, employees, contractors, and consultants to observe and monitor the progress of any activity undertaken pursuant to this Consent Judgment. EGLE's Project Coordinator shall provide Defendant's Project Coordinator with the names, addresses, telephone numbers, positions, and responsibilities of any person designated pursuant to this Section.

## XII. PROGRESS REPORTS

Defendant shall provide to EGLE written quarterly progress reports that shall: (1) describe the actions which have been taken toward achieving compliance with this Consent Judgment during the previous three months; (2) describe data collection and activities scheduled for the next three months; and (3) include all results of sampling and tests and other data received by Defendant, its consultants, engineers, or agents during the previous three months relating to Remedial Action performed pursuant to this Consent Judgment. Defendant shall submit the first quarterly report to EGLE within 120 days after entry of this Consent Judgment,

and by the 30th day of the month following each quarterly period thereafter, as feasible, until termination of this Consent Judgment as provided in Section XXV.

## XIII. RESTRICTIONS ON ALIENATION

A. Defendant shall not sell, lease, or alienate the Gelman Property until: (1) it places an EGLE-approved land use or resource use restrictions on the affected portion(s) of the Gelman Property; and (2) any purchaser, lessee, or grantee provides to EGLE its written agreement providing that the purchaser, lessee, or grantee will not interfere with any term or condition of this Consent Judgment. Notwithstanding any purchase, lease, or grant, Defendant shall remain obligated to comply with all terms and conditions of this Consent Judgment.

B. Any deed, title, or other instrument of conveyance regarding the Gelman Property shall contain a notice that Defendant's Property is the subject of this Consent Judgment, setting forth the caption of the case, the case number, and the court having jurisdiction herein.

## XIV. FORCE MAJEURE

Any delay attributable to a Force Majeure shall not be deemed a violation of Defendant's obligations under this Consent Judgment.

A. "Force Majeure" is defined as an occurrence or nonoccurrence arising from causes beyond the control of Defendant or of any entity controlled by the Defendant performing Remedial Action, such as Defendant's employees, contractors, and subcontractors. Such occurrence or nonoccurrence includes, but is not limited to: (1) an Act of God; (2) untimely review of permit applications or submissions; (3) acts or omissions of third parties for which Defendant is not responsible; (4) insolvency of any vendor, contractor, or subcontractor retained

by Defendant as part of implementation of this Consent Judgment; and (5) delay in obtaining necessary access agreements under Section IX that could not have been avoided or overcome by due diligence. "Force Majeure" does not include unanticipated or increased costs, changed financial circumstances, or nonattainment of the treatment and termination standards set forth in Sections V and VI.

B. When circumstances occur that Defendant believes constitute Force Majeure, Defendant shall notify EGLE by telephone of the circumstances within 48 hours after Defendant first believes those circumstances to apply. Within 14 working days after Defendant first believes those circumstances to apply, Defendant shall supply to EGLE, in writing, an explanation of the cause(s) of any actual or expected delay, the anticipated duration of the delay, the measures taken and the measures to be taken by Defendant to avoid, minimize, or overcome the delay, and the timetable for implementation of such measures. Failure of Defendant to comply with the written notice provisions of this Section shall constitute a waiver of Defendant's right to assert a claim of Force Majeure with respect to the circumstances in question.

C. A determination by EGLE that an event does not constitute Force Majeure, that a delay was not caused by Force Majeure, or that the period of delay was not necessary to compensate for Force Majeure may be subject to dispute resolution under Section XVI of this Consent Judgment.

D. EGLE shall respond, in writing, to any request by Defendant for a Force Majeure extension within 30 days of receipt of the Defendant's request. If EGLE does not respond within that time period, Defendant's request shall be deemed granted. If EGLE agrees that a delay is or was caused by Force Majeure, Defendant's delays shall be excused, stipulated penalties shall not accrue, and EGLE shall provide Defendant such additional time as may be necessary to

compensate for the Force Majeure event.

E. Delay in achievement of any obligation established by this Consent Judgment shall not automatically justify or excuse delay in achievement of any subsequent obligation unless the subsequent obligation automatically follows from the delayed obligation.

## XV. REVOCATION OR MODIFICATION OF LICENSES OR PERMITS

Any delay attributable to the revocation or modification of licenses or permits obtained by Defendant to implement remediation actions as set forth in this Consent Judgment shall not be deemed a violation of Defendant's obligations under this Consent Judgment, provided that such revocation or modification arises from causes beyond the control of Defendant or of any entity controlled by the Defendant performing Remedial Action, such as Defendant's employees, contractors, and subcontractors.

A. Licenses or permits that may need to be obtained or modified by Defendant to implement the Remedial Actions are those specified in Section VII.D. and licenses, easements, and other agreements for access to property or rights of way on property necessary for the installation of remedial systems required by this Consent Judgment.

B. A revocation or modification of a license or permit within the meaning of this Section means withdrawal of permission, denial of permission, a limitation or a change in license or permit conditions that delays the implementation of all or part of a remedial system. Revocation or modification due to Defendant's violation of a license or permit (or any conditions of a license or permit) shall not constitute a revocation or modification covered by this Section.

C. When circumstances occur that Defendant believes constitute revocation or modification of a license or permit, Defendant shall notify EGLE by telephone of the circumstances within 48 hours after Defendant first believes those circumstances to apply.

Within 14 working days after Defendant first believes those circumstances to apply, Defendant shall supply to EGLE, in writing, an explanation of the cause(s) of any actual or expected delay, the anticipated duration of the delay, the measures taken and the measures to be taken by Defendant to avoid, minimize, or overcome the delay, and the timetable for implementation of such measures. Failure of Defendant to comply with the written notice provisions of this Section shall constitute a waiver of Defendant's right to assert a claim of revocation or modification of a license or permit with respect to the circumstances in question.

D. A determination by EGLE that an event does not constitute revocation or modification of a license or permit, that a delay was not caused by revocation or modification of a license or permit, or that the period of delay was not necessary to compensate for revocation or modification of a license or permit may be subject to dispute resolution under Section XVI of this Consent Judgment.

E. EGLE shall respond, in writing, to any request by Defendant for a revocation or modification of a license or permit extension within 30 days of receipt of the Defendant's request. If EGLE does not respond within that time period, Defendant's request shall be deemed granted. If EGLE agrees that a delay is or was caused by revocation or modification of a license or permit, Defendant's delays shall be excused, stipulated penalties shall not accrue, and EGLE shall provide Defendant such additional time as may be necessary to compensate for the revocation or modification of a license or permit.

F. Delay in achievement of any obligation established by this Consent Judgment shall not automatically justify or excuse delay in achievement of any subsequent obligation unless the subsequent obligation automatically follows from the delayed obligation.

## XVI. DISPUTE RESOLUTION

A. The dispute resolution procedures of this Section shall be the exclusive mechanism to resolve disputes arising under this Consent Judgment and shall apply to all provisions of this Consent Judgment except for disputes related to Prohibition Zone boundary modification under Sections V.A.2.f and V.A.6, whether or not particular provisions of this Consent Judgment in question make reference to the dispute resolution provisions of this Section. Any dispute that arises under this Consent Judgment initially shall be the subject of informal negotiations between the Parties. The period of negotiations shall not exceed ten working days from the date of written notice by EGLE or the Defendant that a dispute has arisen. This period may be extended or shortened by agreement of EGLE or the Defendant.

B. Immediately upon expiration of the informal negotiation period (or sooner if upon agreement of the parties), EGLE shall provide to Defendant a written statement setting forth EGLE's proposed resolution of the dispute. Such resolution shall be final unless, within 15 days after receipt of EGLE's proposed resolution (clearly identified as such under this Section), Defendant files a petition for resolution with the Washtenaw County Circuit Court setting forth the matter in dispute, the efforts made by the Parties to resolve it, the relief requested, and the schedule, if any, within which the dispute must be resolved to ensure orderly implementation of this Consent Judgment.

C. Within ten days of the filing of the petition, EGLE may file a response to the petition, and unless a dispute arises from the alleged failure of EGLE to timely make a decision, EGLE will submit to the Court all documents containing information related to the matters in dispute, including documents provided to EGLE by Defendant. In the event of a dispute arising from the alleged failure of EGLE to timely make a decision, within ten days of filing of the

petition, each party shall submit to the Court correspondence, reports, affidavits, maps, diagrams, and other documents setting forth facts pertaining to the matters in dispute. Those documents and this Consent Judgment shall comprise the record upon which the Court shall resolve the dispute. Additional evidence may be taken by the Court on its own motion or at the request of either party if the Court finds that the record is incomplete or inadequate. Review of the petition shall be conducted by the Court and shall be confined to the record. The review shall be independent of any factual or legal conclusions made by the Court prior to the date of entry of this Consent Judgment.

D. The Court shall uphold the decision of EGLE on the issue in dispute unless the Court determines that the decision is any of the following:

1. Inconsistent with this Consent Judgment;
2. Not supported by competent, material, and substantial evidence on the whole record;
3. Arbitrary, capricious, or clearly an abuse or unwarranted exercise of discretion; or
4. Affected by other substantial and material error of law.

E. The filing of a petition for resolution of a dispute shall not by itself extend or postpone any obligation of Defendant under this Consent Judgment, provided, however, that payment of stipulated penalties with respect to the disputed matter shall be stayed pending resolution of the dispute. Notwithstanding the stay of payment, stipulated penalties shall accrue as provided in Section XVII. Stipulated penalties that have accrued with respect to the matter in dispute shall not be assessed by the Court and shall be dissolved if Defendant prevails on the matter. The Court may also direct that stipulated penalties shall not be assessed and paid as

provided in Section XVII upon a determination that there was a substantial basis for Defendant's position on the disputed matter.

## XVII. STIPULATED PENALTIES

A. Except as otherwise provided, if Defendant fails or refuses to comply with any term or condition in Sections IV, V, VI, VII, or VIII, or with any plan, requirement, or schedule established pursuant to those Sections, then Defendant shall pay stipulated penalties in the following amounts for each working day for every failure or refusal to comply or conform:

| Period of Delay | Penalty Per Violation Per Day |
|---|---|
| 1st through 15th Day | $ 1,000 |
| 15th through 30th Day | $ 1,500 |
| Beyond 30 Days | $ 2,000 |

B. Except as otherwise provided if Defendant fails or refuses to comply with any other term or condition of this Consent Judgment, Defendant shall pay to EGLE stipulated penalties of $500.00 per working day for each and every failure to comply.

C. If Defendant is in violation of this Consent Judgment, Defendant shall notify EGLE of any violation no later than five working days after first becoming aware of such violation, and shall describe the violation.

D. Stipulated penalties shall begin to accrue upon the next day after performance was due or other failure or refusal to comply occurred. Penalties shall continue to accrue until the final day of correction of the noncompliance. Separate penalties shall accrue for each separate failure or refusal to comply with the terms and conditions of this Consent Judgment. Penalties may be waived in whole or in part by EGLE or may be dissolved by the Court pursuant to Section XVII.

E. Stipulated penalties shall be paid no later than 14 working days after receipt by

Defendant of a written demand from EGLE. Defendant shall make payment by transmitting a check in the amount due, payable to the "State of Michigan," addressed to the Revenue Control Unit; Finance Section, Administration Division; Michigan Department of Environment, Great Lakes, and Energy; P.O. Box 30657; Lansing, MI 48909-8157. The check shall be transmitted via Courier to the Revenue Control Unit; Finance Section, Administration Division; Michigan Department of Environment, Great Lakes, and Energy; Constitution Hall, 5th Floor South Tower; 525 West Allegan Street; Lansing, MI 48933-2125. To ensure proper credit, Defendant shall include the settlement ID - ERD1902 on the payment.

F. Plaintiffs agree that, in the event that an act or omission of Defendant constitutes a violation of this Consent Judgment subject to stipulated penalties and a violation of other applicable law, Plaintiffs will not impose upon Defendant for that violation both the stipulated penalties provided under this Consent Judgment and the civil penalties permitted under other applicable laws. EGLE reserves the right to pursue any other remedy or remedies to which they may be entitled under this Consent Judgment or any applicable law for any failure or refusal of the Defendant to comply with the requirements of this Consent Judgment.

## XVIII. PLAINTIFFS' COVENANT NOT TO SUE AND RESERVATION OF RIGHTS

A. Except as otherwise provided in this Consent Judgment, Plaintiffs covenant not to sue or take administrative action for Covered Matters against Defendant, its officers, employees, agents, directors, and any persons acting on its behalf or under its control.

B. "Covered Matters" shall mean any and all claims available to Plaintiffs under federal and state law arising out of the subject matter of the Plaintiffs' Complaint with respect to the following:

1. Claims for injunctive relief to address soil, groundwater, and surface water

contamination at or emanating from the Gelman Property;

2. Claims for civil penalties and costs;

3. Claims for natural resource damages;

4. Claims for reimbursement of response costs incurred prior to entry of this Consent Judgment or incurred by Plaintiffs for provision of alternative water supplies in the Evergreen Subdivision; and

5. Claims for reimbursement of costs incurred by Plaintiffs for overseeing the implementation of this Consent Judgment.

C. "Covered Matters" does not include:

1. Claims based upon a failure by Defendant to comply with the requirements of this Consent Judgment;

2. Liability for violations of federal or state law which occur during implementation of the Remedial Action; and

3. Liability arising from the disposal, treatment, or handling of any hazardous substance removed from the Site.

D. With respect to liability for alleged past violations of law, this covenant not to sue shall take effect on the effective date of this Consent Judgment. With respect to future liability for performance of response activities required to be performed under this Consent Judgment, the covenant not to sue shall take effect upon issuance by EGLE of the Certificate of Completion in accordance with Section XXV.

E. Notwithstanding any other provision in this Consent Judgment: (1) EGLE reserves the right to institute proceedings in this action or in a new action seeking to require Defendant to perform any additional response activity at the Site; and (2) EGLE reserves the

right to institute proceedings in this action or in a new action seeking to reimburse EGLE for response costs incurred by the State of Michigan relating to the Site. EGLE's rights in Sections XVIII.E.1 and E.2 apply if the following conditions are met:

1. For proceedings prior to EGLE's certification of completion of the Remedial Action concerning the Site,

a. (i) conditions at the Site, previously unknown to EGLE, are discovered after entry of this Consent Judgment, (ii) new information previously unknown to EGLE is received after entry of this Consent Judgment, or (iii) EGLE adopts one or more new, more restrictive cleanup criteria for 1,4-dioxane pursuant to Part 201 after entry of this Consent Judgment; and

b. these previously unknown conditions, new information, and/or change in criteria indicate that the Remedial Action is not protective of the public health, safety, welfare, and the environment; and

2. For proceedings subsequent to EGLE's certification of completion of the Remedial Action concerning the Site,

a. (i) conditions at the Site, previously unknown to EGLE, are discovered after certification of completion by EGLE, (ii) new information previously unknown to EGLE is received after certification of completion by EGLE, or (iii) EGLE adopts one or more new, more restrictive cleanup criteria for 1,4-dioxane pursuant to Part 201, after certification of completion by EGLE; and

b. these previously unknown conditions, new information, and/or change in criteria indicate that the Remedial Action is not protective of the public health, safety, welfare, and the environment.

If EGLE adopts one or more new, more restrictive, cleanup criteria, EGLE's rights in Sections XVIII.E.1 and E.2 shall also be subject to Defendant's right to seek another site-specific criterion(ia) that is protective of public health, safety, welfare, and the environment and/or to argue that EGLE has not made the demonstration(s) required under this Section.

F. Nothing in this Consent Judgment shall in any manner restrict or limit the nature or scope of Response Activities that may be taken by EGLE in fulfilling its responsibilities under federal and state law, and this Consent Judgment does not release, waive, limit, or impair in any manner the claims, rights, remedies, or defenses of EGLE against a person or entity not a party to this Consent Judgment.

G. Except as expressly provided in this Consent Judgment, EGLE reserves all other rights and defenses that they may have, and this Consent Judgment is without prejudice, and shall not be construed to waive, estop, or otherwise diminish EGLE's right to seek other relief with respect to all matters other than Covered Matters.

## XIX. DEFENDANT'S COVENANT NOT TO SUE AND RESERVATION OF RIGHTS

A. Defendant hereby covenants not to sue and agrees not to assert any claim or cause of action against EGLE or any other agency of the State of Michigan with respect to environmental contamination at the Site or response activities relating to the Site arising from this Consent Judgment.

B. Notwithstanding any other provision in this Consent Judgment, for matters that are not Covered Matters as defined in Section XVIII.B, or in the event that Plaintiffs institute proceedings as allowed under Section XVIII.E., Defendant reserves all other rights, defenses, or counterclaims that it may have with respect to such matters and this Consent Judgment is without prejudice, and shall not be construed to waive, estop, or otherwise diminish Defendant's right to

seek other relief and to assert any other rights and defenses with respect to such other matters.

C. Nothing in this Consent Judgment shall in any way impair Defendant's rights, claims, or defenses with respect to any person not a party to this Consent Judgment.

## XX. INDEMNIFICATION, INSURANCE, AND FINANCIAL ASSURANCE

A. Defendant shall indemnify and save and hold harmless the State of Michigan and its departments, agencies, officials, agents, employees, contractors, and representatives from any and all claims or causes of action arising from, or on account of, acts or omissions of Defendant, its officers, employees, agents, and any persons acting on its behalf or under its control in carrying out Remedial Action pursuant to this Consent Judgment. EGLE shall not be held out as a party to any contract entered into by or on behalf of Defendant in carrying out activities pursuant to this Consent Judgment. Neither the Defendant nor any contractor shall be considered an agent of EGLE. Defendant shall not indemnify or save and hold harmless Plaintiffs from their own negligence pursuant to this Section.

B. Prior to commencing any Remedial Action on the Gelman Property, Defendant shall secure, and shall maintain for the duration of the Remedial Action, comprehensive general liability insurance with limits of $1,000,000.00, combined single limit, naming as an additional insured the State of Michigan. If Defendant demonstrates by evidence satisfactory to EGLE that any contractor or subcontractor maintains insurance equivalent to that described above, or insurance covering the same risks but in a lesser amount, then with respect to that contractor or subcontractor, Defendant need provide only that portion, if any, of the insurance described above that is not maintained by the contractor or subcontractor.

C. Financial Assurance

1. Defendant shall be responsible for providing and maintaining financial assurance in a mechanism approved by EGLE in an amount sufficient to cover the estimated cost to assure performance of the response activities required to meet the remedial objectives of this Consent Judgment including, but not limited to, investigation, monitoring, operation and maintenance, and other costs (collectively referred to as "Long-Term Remedial Action Costs"). Defendant shall continuously maintain a financial assurance mechanism ("FAM") until EGLE's Remediation and Redevelopment Division ("RRD") Chief or his or her authorized representative notifies it in writing that it is no longer required to maintain a FAM.

2. The Letter of Credit provided in Attachment K is the initial FAM approved by EGLE. Defendant shall be responsible for providing and maintaining financial assurance in a mechanism acceptable to EGLE to assure the performance of the Long Term Remedial Action Costs required by Defendant's selected remedial action.

3. The FAM shall remain in an amount sufficient to cover Long Term Remedial Action Costs for a 30-year period. Unless Defendant opts to use and satisfies the Financial Test or Financial Test/Corporate Guarantee as provided in Section XX.C.8, the FAM shall remain in a form that allows EGLE to immediately contract for the response activities for which financial assurance is required in the event Defendant fails to implement the required tasks, subject to Defendant's rights under Sections XIV and XVI.

4. Within 120 days of the Effective Date of this Fourth Amended Consent Judgment, Defendant shall provide EGLE with an estimate of the amount of funds necessary to assure Long Term Remedial Action Costs for the following 30-year period based upon an annual estimate of costs for the response activities required by this Fourth Amended Consent Judgment

as if they were to be conducted by a person under contract to EGLE (the "Updated Long Term Remedial Action Cost Estimate"). The Updated Long Term Remedial Action Cost Estimate shall include all assumptions and calculations used in preparing the cost estimate and shall be signed by an authorized representative of Defendant who shall confirm the validity of the data. Defendant may only use a present worth analysis if an interest accruing FAM is selected. Within 60 days after Defendant's submittal of the Updated Long Term Remedial Action Cost Estimate, Defendant shall capitalize or revise the FAM in a manner acceptable to EGLE to address Long Term Remedial Action Costs unless otherwise notified by EGLE. If EGLE disagrees with the conclusions of the Updated Long Term Remedial Action Cost Estimate, Defendant shall capitalize the FAM to a level acceptable to EGLE within 30 days of EGLE notification, subject to Dispute Resolution under Section XVI.

5. Sixty days prior to the 5-year anniversary of the Effective Date of this Fourth Amended Consent Judgment and each subsequent 5-year anniversary, Defendant shall provide to EGLE a report containing the actual Long Term Remedial Action Costs for the previous 5-year period and an estimate of the amount of funds necessary to assure Long Term Remedial Action Costs for the following 30-year period given the financial trends in existence at the time of preparation of the report ("Long Term Remedial Action Cost Report"). The cost estimate shall be based upon an annual estimate of maximum costs for the response activities required by this Fourth Amended Consent Judgment as if they were to be conducted by a person under contract to EGLE, provided that, if Defendant is using the Financial Test or Corporate Guarantee/Financial Test under Section XX.C.8, below, Defendant may use an estimate on its internal costs to satisfy the Financial Test. The Long Term Remedial Action Cost Report shall also include all assumptions and calculations used in preparing the necessary cost estimate and

shall be signed by an authorized representative of Defendant who shall confirm the validity of the data. Defendant may only use a present worth analysis if an interest accruing FAM is selected.

6. Within 60 days after Defendant's submittal of the Long Term Remedial Action Cost Report to EGLE, Defendant shall capitalize or revise the FAM in a manner acceptable to EGLE to address Long Term Remedial Action Costs consistent with the conclusions of the Long Term Remedial Action Cost Report unless otherwise notified by EGLE. If EGLE disagrees with the conclusions of the Long Term Remedial Action Cost Report, Defendant shall capitalize the FAM to a level acceptable to EGLE within 30 days of EGLE notification, subject to dispute resolution under Section XVI. If, at any time, EGLE determines that the FAM does not secure sufficient funds to address Long Term Remedial Action Costs, Defendant shall capitalize the FAM or provide an alternate FAM to secure any additional costs within 30 days of request by EGLE, subject to dispute resolution under Section XVI.

7. If, pursuant to the Long Term Remedial Action Cost Report, Defendant can demonstrate that the FAM provides funds in excess of those needed for Long Term Remedial Action Costs, Defendant may request a modification in the amount. Any requested FAM modifications must be accompanied by a demonstration that the proposed FAM provides adequate funds to address future Long Term Remedial Action Costs. Upon EGLE approval of the request, Defendant may modify the FAM as approved by EGLE. Modifications to the FAM pursuant to this Section shall be approved by EGLE RRD Chief or his or her authorized representative, subject to dispute resolution under Section XVI.

8. If Defendant chooses to use the Financial Test or Corporate Guarantee/Financial Test attached as Attachment L (hereinafter, the term "Financial Test" refers

to both an independent financial test or a financial test utilized in conjunction with a corporate guarantee), Defendant shall, within 90 days after the end of Defendant's next fiscal year and the end of each succeeding fiscal year, submit to EGLE the necessary forms and supporting documents to demonstrate to the satisfaction of EGLE that Defendant can continue to meet the Financial Test requirements. If Defendant can no longer meet the financial test requirements, Defendant shall submit a proposal for an alternate FAM to satisfy its financial obligations with respect to this Consent Judgment.

9. If the Financial Test is being used as the FAM, EGLE, based on a reasonable belief that Defendant may no longer meet the requirements for the Financial Test, may require reports of financial condition at any time from Defendant, and/or require Defendant to submit updated Financial Test information to determine whether it meets the Financial Test criteria. Defendant shall provide, with reasonable promptness to EGLE, any other data and information that may reasonably be expected to materially adversely affect Defendant's ability to meet the Financial Test requirements. If EGLE finds that Defendant no longer meets the Financial Test requirements, Defendant shall, within 30 days after notification from EGLE, submit a proposal for an alternate FAM to satisfy its financial obligations with respect to this Consent Judgment, subject to dispute resolution under Section XVI.

10. If the Financial Test/Corporate Guarantee is used as the FAM, Defendant shall comply with the terms of the Corporate Guarantee. The Corporate Guarantee shall remain in place until Long-Term Remedial Action Costs are no longer required or Defendant establishes an alternate FAM acceptable to EGLE.

11. If Defendant wishes to change the type of FAM or establish a new FAM, Defendant shall submit a request to EGLE for approval. Upon EGLE approval of the request,

Defendant may change the type of FAM or establish the new FAM as approved by EGLE. Modifications to the FAM pursuant to this Section shall be approved by EGLE RRD Chief or his or her authorized representative, subject to dispute resolution under Section XVI.

12. If Defendant dissolves or otherwise ceases to conduct business and fails to make arrangements acceptable to EGLE for the continued implementation of all activities required by this Consent Judgment, all rights under this Consent Judgment regarding the FAM shall immediately and automatically vest in EGLE in accordance with the FAM.

## XXI. RECORD RETENTION

Defendant, Plaintiffs, and their representatives, consultants, and contractors shall preserve and retain, during the pendency of this Consent Judgment and for a period of ten years after its termination, all records, sampling or test results, charts, and other documents that are maintained or generated pursuant to any requirement of this Consent Judgment, including, but not limited to, documents reflecting the results of any sampling or tests or other data or information generated or acquired by Plaintiffs or Defendant, or on their behalf, with respect to the implementation of this Consent Judgment. After the ten-year period of document retention, the Defendant and its successors shall notify EGLE, in writing, at least 90 days prior to the destruction of such documents or records, and upon request, the Defendant and/or its successor shall relinquish custody of all records and documents to EGLE.

## XXII. ACCESS TO INFORMATION

Upon request, EGLE and Defendant shall provide to each other copies of or access to all non-privileged documents and information within their possession and/or control or that of their employees, contractors, agents, or representatives, relating to activities at the Site or to the implementation of this Consent Judgment, including, but not limited to, sampling, analysis, chain

of custody records, manifests, trucking logs, receipts, reports, sample traffic routing, correspondence, or other documents or information related to the Remedial Action. Upon request, Defendant shall also make available to EGLE, their employees, contractors, agents, or representatives with knowledge or relevant facts concerning the performance of the Remedial Action. The Plaintiffs shall treat as confidential all documents provided to Plaintiffs by the Defendant marked "confidential" or "proprietary."

## XXIII. NOTICES

Whenever under the terms of this Consent Judgment notice is required to be given or a report, sampling data, analysis, or other document is required to be forwarded by one Party to the other, such notice or document shall be directed to the following individuals at the specified addresses or at such other address as may subsequently be designated in writing:

For Plaintiffs:

Daniel Hamel
Project Coordinator
Michigan Department
of Environment, Great
Lakes, and Energy,
Remediation and Redevelopment
Division
301 East Louis Glick Highway
Jackson, MI 49201

For Defendants:

Lawrence Gelb
Gelman Sciences Inc.
642 South Wagner Road
Ann Arbor, MI 48106

and

Michael L. Caldwell
Zausmer, P.C.
32255 Northwestern Hwy., Ste. 225
Farmington Hills, MI 48334

Any party may substitute for those designated to receive such notices by providing prior written notice to the other parties.

## XXIV. MODIFICATION

This Consent Judgment may not be modified unless such modification is in writing, signed by the Plaintiffs and the Defendant, and approved and entered by the Court. Remedial Plans, work plans, or other submissions made pursuant to this Consent Judgment may be modified by mutual agreement of the Defendant and EGLE.

## XXV. CERTIFICATION AND TERMINATION

A. When Defendant determines that it has completed all Remedial Action required by this Consent Judgment, Defendant shall submit to EGLE a Notification of Completion and a draft final report. The draft final report must summarize all Remedial Action performed under this Consent Judgment and the performance levels achieved. The draft final report shall include or refer to any supporting documentation.

B. Upon receipt of the Notification of Completion, EGLE will review the Notification of Completion and the accompanying draft final report, any supporting documentation, and the actual Remedial Action performed pursuant to this Consent Judgment. After conducting this review, and not later than three months after receipt of the Notification of Completion, EGLE shall issue a Certificate of Completion upon a determination by EGLE that Defendant has completed satisfactorily all requirements of this Consent Decree, including, but not limited to, completion of all Remedial Action, achievement of all termination and treatment standards required by this Consent Judgment, compliance with all terms and conditions of this Consent Judgment, and payment of any and all stipulated penalties owed to EGLE. If EGLE does not respond to the Notification of Completion within three months after receipt of the Notification of Completion, Defendant may submit the matter to dispute resolution pursuant to Section XVI. This Consent Judgment shall terminate upon motion and order of this Court after issuance of the Certificate of Completion. Upon issuance, the Certificate of Completion may be

recorded.

## XXVI. EFFECTIVE DATE

The effective date of this Consent Judgment shall be the date upon which this Consent Judgment is entered by the Court.

## XXVII. SEVERABILITY

The provisions of this Consent Judgment shall be severable. Should any provision be declared by a court of competent jurisdiction to be inconsistent with federal or state law, and therefore unenforceable, the remaining provisions of this Consent Judgment shall remain in full force and effect.

## XXVIII. SIGNATORIES

Each undersigned representatives of a Party to this Consent Judgment certifies that he or she is fully authorized by the Party to enter into this Consent Judgment and to legally bind such Party to the respective terms and conditions of this Consent Judgment.

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT A

# GELMAN PROPERTY

## Legal Information for H -08-26-100-001 (234 Nancy Dr.)

COM AT N 1/4 POST OF SEC, TH E 1446.11 FT IN N LINE OF SEC, TH S 1199 FT FOR PL OF BEG, TH S 1479.11 FT, TH W 113.7 FT IN E & W 1/4 LINE. TH N 1478.76 FT. TH E 113.7 FT TO PL OF BEG, BEING PART OF NE 1/4 SEC. 26 T2S R5E 3.86 AC.

## Legal Information for H -08-26-100-002 (Jackson Plaza – vacant)

COM AT N 1/4 POST OF SEC, TH E 886.06 FT IN N LINE OF SEC, TH DEFL 91 DEG RIGHT 1199 FT FOR PL OF BEG, TH DEFL 91 DEG LEFT 446.36 FT, TH DEFL 91 DEG RIGHT 1478.76 FT, TH W 446.36 FT IN E & W 1/4 LINE, TH N 1477.34 FT TO PL OF BEG, BEING PART OF NE 1/4 SEC 26 T2S-R5E 15.14 AC.

## Legal Information for H -08-26-100-020 (April Drive – vacant)

COM AT N 1/4 COR OF SEC 26, TH S 2-6-15 W 1102.76 FT TO POB TH N 69-0 E 71.74 FT, TH S 80-46 E 141.53 FT, TH S 60-22 E 215.47 FT, TH S 83-27 E 366.02 FT, TH S 58-36 E 141.63 FT, TH S 2-6-15 W 1371.36 FT, TH N 88-42-15 W 886.06 FT, TH N 2-6-15 E 1570.79 FT TO POB, PART NE 1/4 SEC 26 T2S R5E 30.43 AC

## Legal Information for H -08-26-110-013 (Jackson Plaza – vacant)

BEG AT SE COR OF LOT 22, TH N 88-42-15 W 344.35 FT TH N 2-06-15 E 348.30 FT, TH N 87-24-40 E 463.07 FT TH 69.56 FT IN ARC OF CURVE LEFT, RADIUS 376.77 FT, CHORD S 55-32-20 E 69.47 FT, TH S 29-10-30 W 386.49 FT TO POB, BEING PART OF LOT 22 JACKSON PLAZA BUSINESS PARK

## Legal Information for H -08-26-400-007 (S. Wagner – vacant)

COM AT E 1/4 COR OF SEC 26, TH S 2-8-15 W 976.97 FT TO POB, TH S 2-8-15 W 326.10 FT, TH N 88-42-15 W 1337.18 FT, TH N 2-8-30 E 326.10 FT, TH S 88-42-15 E 1337.16 FT TO POB, PART E 1/4 SEC 26 T2S R5E 10.01 AC

## Legal Information for H -08-26-400-011 (602 S. Wagner)

COM AT E 1/4 COR SEC 26, T2S-R5E; TH N 88-14-19 W 571.00 FT TO POB; TH S 01-18-41 W 490.00 FT; TH N 88-41-19 W 773.65 FT; TH N 02-07-21 E 490.05 FT; TH S 88-41-19 E 766.72 FT TO POB. 8.664 AC. SPLIT ON 08/16/2007 FROM H -08-26-400-008 INTO H-08-26-400-011 & -012

## Legal Information for H -08-26-400-012 (600 S. Wagner)

BEG AT E 1/4 COR SEC 26, T2S-R5E; TH S 02-08-15 W 976.65 FT; TH N 88-41-19 W 1337.46 FT; TH N 02-07-21 E 486.60 FT; TH S 88-41-19 E 773.65 FT; TH N 01-18-42 E 490.00 FT; TH S 88-41-19 E 571.00 FT TO POB. 21.43 AC. SPLIT ON 08/16/2007 FROM H -08-26-400-008, INTO H-08-26-400-011 & -012

## Legal Information for H -08-26-400-013 (S. Wagner – vacant)

COM AT SE COR SEC 26, T2S, R5E; TH N 02-09-20 E 1144.49 FT TO POB; TH N 88-42-15 W 1219.79 FT; TH N 30-40-35 W 106.07 FT; TH N 88-42-15 W 60 FT; TH N 02-08-30 E 146.10 FT; TH S 88-42-15 E 1337.34 FT; TH S 02-09-20 W 236.09 FT TO POB. 7.19 AC. SPLIT ON 08/20/2007 FROM H -08-26-400-005, H -08-26-400-006; INTO CHILDREN H-08-26-400-013 & -014

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT B

EPA United States Environmental Protection Agency

Office of Water

www.epa.gov 1999

# Method 1624, Revision C: Volatile Organic Compounds by Isotope Dilution GCMS

# Method 1624

*Revision C*

*Volatile Organic Compounds by Isotope Dilution GCMS*

# Method 1624

## *Volatile Organic Compounds by Isotope Dilution GCMS*

## 1. SCOPE AND APPLICATION

**1.1** This method is designed to meet the survey requirements of the USEPA ITD. The method is used to determine the volatile toxic organic pollutants associated with the Clean Water Act (as amended 1987); the Resource Conservation and Recovery Act (as amended in 1986); the Comprehensive Environmental Response, Compensation, and Liability Act (as amended in 1986); and other compounds amenable to purge and trap gas chromatography/mass spectrometry (GCMS).

**1.2** The chemical compounds listed in Tables 1 and 2 may be determined in waters, soils, and municipal sludges by the method.

**1.3** The detection limits of the method are usually dependent on the level of interferences rather than instrumental limitations. The levels in Table 3 typify the minimum quantities that can be detected with no interferences present.

**1.4** The GCMS portions of the method are for use only by analysts experienced with GCMS or under the close supervision of such qualified persons. Laboratories unfamiliar with analysis of environmental samples by GCMS should run the performance tests in Reference 1 before beginning.

## 2. SUMMARY OF METHOD

**2.1** The percent solids content of the sample is determined. If the solids content is known or determined to be less than 1%, stable isotopically labeled analogs of the compounds of interest are added to a 5-mL sample and the sample is purged with an inert gas at 20 to 25°C in a chamber designed for soil or water samples. If the solids content is greater than one, mL of reagent water and the labeled compounds are added to a 5-aliquot of sample and the mixture is purged at 40°C. Compounds that will not purge at 20 to 25°C or at 40°C are purged at 75 to 85°C (see Table 2). In the purging process, the volatile compounds are transferred from the aqueous phase into the gaseous phase where they are passed into a sorbent column and trapped. After purging is completed, the trap is backflushed and heated rapidly to desorb the compounds into a gas chromatograph (GC). The compounds are separated by the GC and detected by a mass spectrometer (MS) (References 2 and 3). The labeled compounds serve to correct the variability of the analytical technique.

**2.2** Identification of a pollutant (qualitative analysis) is performed in one of three ways: (1) For compounds listed in Table 1 and other compounds for which authentic standards are available, the GCMS system is calibrated and the mass spectrum and retention time for each standard are stored in a user created library. A compound is identified when its retention time and mass spectrum agree with the library retention time and spectrum. (2) For compounds listed in Table 2 and other compounds for which standards are not available, a compound is identified when the retention time and mass spectrum agree with those specified in this method. (3) For chromatographic peaks which are not identified by (1) and (2) above, the background corrected spectrum at the peak maximum

is compared with spectra in the EPA/NIH mass spectral file (Reference 4). Tentative identification is established when the spectrum agrees (see Section 12).

**2.3** Quantitative analysis is performed in one of four ways by GCMS using extracted ion current profile (EICP) areas: (1) For compounds listed in Table 1 and other compounds for which standards and labeled analogs are available, the GCMS system iscalibrated and the compound concentration is determined using an isotope dilution technique. (2) For compounds listed in Table 1 and for other compounds for which authentic standards but no labeled compounds are available, the GCMS system is calibrated and the compound concentration is determined using an internal standard technique. (3) For compounds listed in Table 2 and other compounds for which standards are not available, compound concentrations are determined using known response factors. (4) For compounds for which neither standards nor known response factors are available, compound concentration is determined using the sum of the EICP areas relative to the sum of the EICP areas of the nearest eluted internal standard.

**2.4** The quality of the analysis is assured through reproducible calibration and testing of the purge and trap and GCMS systems.

Table 1. Volatile Organic Compounds Determined by GCMS Using Isotope Dilution and Internal Standard Techniques

| | Pollutant | | | | Labeled Compound | | |
|---|---|---|---|---|---|---|---|
| Compound | STORET | CAS Registry | EPA EGD | NPDES | Analog | CAS Registry | EPA EGD |
| Acetone | 81552 | 67-64-1 | 516 V | | $d_6$ | 666-52-4 | 616 V |
| Acrolein | 34210 | 107-02-8 | 002 V | 001 V | $d_4$ | 33984-05-3 | 202 V |
| Acrylonitrile | 34215 | 107-13-1 | 003 V | 002 V | $d_3$ | 53807-26-4 | 203 V |
| Benzene | 34030 | 71-43-2 | 004 V | 003 V | $d_6$ | 1076-43-3 | 204 V |
| Bromodichloromethane | 32101 | 75-27-4 | 048 V | 012 V | $^{13}C$ | 93952-10-4 | 248 V |
| Bromoform | 32104 | 75-25-2 | 047 V | 005 V | $^{13}C$ | 72802-81-4 | 247 V |
| Bromomethane | 34413 | 74-83-9 | 046 V | 020 V | $d_3$ | 1111-88-2 | 246 V |
| Carbon tetrachloride | 32102 | 56-23-5 | 006 V | 006 V | $^{13}C$ | 32488-50-9 | 206 V |
| Chlorobenzene | 34301 | 108-90-7 | 007 V | 007 V | $d_5$ | 3114-55-4 | 207 V |
| Chloroethane | 34311 | 75-00-3 | 016 V | 009 V | $d_5$ | 19199-91-8 | 216 V |
| 2-Chloroethylvinyl ether | 34576 | 110-75-8 | 019 V | 010 V | | | |
| Chloroform | 32106 | 67-66-3 | 023 V | 011 V | $^{13}C$ | 31717-44-9 | 223 V |
| Chloromethane | 34418 | 74-87-3 | 045 V | 021 V | $d_3$ | 1111-89-3 | 245 V |
| Dibromochloromethane | 32105 | 124-48-1 | 051 V | 008 V | $^{13}C$ | 93951-99-6 | 251 V |
| 1,1-Dichloroethane | 34496 | 75-34-3 | 013 V | 014 V | $d_3$ | 56912-77-7 | 213 V |
| 1,2-Dichloroethane | 32103 | 107-06-2 | 010 V | 015 V | $d_4$ | 17070-07-0 | 210 V |
| 1,1-Dichloroethene | 34501 | 75-35-4 | 029 V | 016 V | $d_2$ | 22280-73-5 | 229 V |
| trans-1,2-Dichlorethene | 34546 | 156-60-5 | 030 V | 026 V | $d_3$ | 42366-47-2 | 230 V |
| 1,2-Dichloropropane | 34541 | 78-87-5 | 032 V | 017 V | $d_6$ | 93952-08-0 | 232 V |
| trans-1,3-Dichloropropene | 34699 | 10061-02-6 | 033 V | | $d_4$ | 93951-86-1 | 233 V |
| Diethyl ether | 81576 | 60-29-7 | 515 V | | $d_{10}$ | 2679-89-2 | 615 V |
| *p*-Dioxane | 81582 | 123-91-1 | 527 V | | $d_8$ | 17647-74-4 | 627 V |
| Ethylbenzene | 34371 | 100-41-4 | 038 V | 019 V | $d_{10}$ | 25837-05-2 | 238 V |
| Methylene chloride | 34423 | 75-09-2 | 044 V | 022 V | $d_2$ | 1665-00-5 | 244 V |
| Methyl ethyl ketone | 81595 | 78-93-3 | 514 V | | $d_3$ | 53389-26-7 | 614 V |
| 1,1,2,2-Tetrachloroethane | 34516 | 79-34-5 | 015 V | 023 V | $d_2$ | 33685-54-0 | 215 V |
| Tetrachloroethene | 34475 | 127-18-4 | 085 V | 024 V | $^{13}C_2$ | 32488-49-6 | 285 V |
| Toluene | 34010 | 108-88-3 | 086 V | 025 V | $d_8$ | 2037-26-5 | 286 V |
| 1,1,1-Trichloroethane | 34506 | 71-55-6 | 011 V | 027 V | $d_3$ | 2747-58-2 | 211 V |
| 1,1,2-Trichloroethane | 34511 | 79-00-5 | 014 V | 028 V | $^{13}C_2$ | 93952-09-1 | 214 V |
| Trichloroethene | 39180 | 79-01-6 | 087 V | 029 V | $^{13}C_2$ | 93952-00-2 | 287 V |
| Vinyl chloride | 39175 | 75-01-4 | 088 V | 031 V | $d_3$ | 6745-35-3 | 288 V |

Table 2. Volatile Organic Compounds to be Determined by Reverse Search and Quantitation Using Known Retention Times, Response Factors, Reference Compounds, and Mass Spectra

| EGD No. | Compound | CAS Registry |
|---|---|---|
| 532 | Allyl alcohol [1] | 107-18-6 |
| 533 | Carbon disulfide | 75-15-0 |
| 534 | 2-Chloro-1,3-butadiene (Chloroprene) | 126-99-8 |
| 535 | Chloroacetonitrile[1] | 107-14-2 |
| 536 | 3-Chloropropene | 107-05-1 |
| 537 | Crotonaldehyde[1] | 123-73-9 |
| 538 | 1,2-Dibromoethane (EDB) | 106-93-3 |
| 539 | Dibromomethane | 74-95-3 |
| 540 | trans-1,4-Dichloro-2-butene | 110-57-6 |
| 541 | 1,3-Dichloropropane | 142-28-9 |
| 542 | cis-1,3-Dichloropropene | 10061-01-5 |
| 543 | Ethyl cyanide [1] | 107-12-0 |
| 544 | Ethyl methacrylate | 97-63-2 |
| 545 | 2-Hexanone | 591-78-6 |
| 546 | Iodomethane | 74-88-4 |
| 547 | Isobutyl alcohol[1] | 78-83-1 |
| 548 | Methacrylonitrile | 126-98-7 |
| 549 | Methyl methacrylate | 78-83-1 |
| 550 | 4-Methyl-2-pentanone | 108-10-1 |
| 551 | 1,1,1,2-Tetrachloroethane | 630-20-6 |
| 552 | Trichlorofluoromethane | 75-69-4 |
| 553 | 1,2,3-Trichloropropane | 96-18-4 |
| 554 | Vinyl acetate | 108-05-4 |
| 951 | *m*-Xylene | 108-38-3 |
| 952 | *o*- and *p*-Xylene | |

[1] Determined at a purge temperature of 75–85°C.

## 3. CONTAMINATION AND INTERFERENCES

**3.1** Impurities in the purge gas, organic compounds out-gassing from the plumbing upstream of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system is demonstrated to be free from interferences under conditions of the analysis by analyzing reagent water blanks initially and with each sample batch (samples analyzed on the same 8-hour shift), as described in Section 8.5.

**3.2** Samples can be contaminated by diffusion of volatile organic compounds (particularly methylene chloride) through the bottle seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol may serve as a check on such contamination.

**3.3** Contamination by carry-over can occur when high level and low level samples are analyzed sequentially. To reduce carry-over, the purging device (Figure 1 for samples containing less than one percent solids; Figure 2 for samples containing one percent solids or greater) is cleaned or replaced with a clean purging device after each sample is analyzed. When an unusually concentrated sample is encountered, it is followed by analysis of a reagent water blank to check for carry-over. Purging devices are cleaned by washing with soap solution, rinsing with tap and distilled water, and drying in an oven at 100 to 125°C. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

**3.4** Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled.

Table 3. Gas Chromatography of Purgeable Organic Compounds

| EGD No.[1] | Compound | Retention Time Mean (sec) | EGD Ref | Relative [2] | Minimum Level [3] (µg/L) | Method Detection Limit [4] Low Solids (µg/kg) | High Solids (µg/kg) |
|---|---|---|---|---|---|---|---|
| 245 | Chloromethane-$d_3$ | 147 | 181 | 0.141–0.270 | 50 | | |
| 345 | Chloromethane | 148 | 245 | 0.922–1.210 | 50 | 207 [7] | 13 |
| 246 | Bromomenthane-$d_3$ | 243 | 181 | 0.233–0.423 | 50 | | |
| 346 | Bromomethane | 246 | 246 | 0.898–1.195 | 50 | 148 [7] | 11 |
| 288 | Vinyl chloride-$d_3$ | 301 | 181 | 0.286–0.501 | 50 | | |
| 388 | Vinyl chloride | 304 | 288 | 0.946–1.023 | 10 | 190 [7] | 11 |
| 216 | Chloroethane-$d_5$ | 378 | 181 | 0.373–0.620 | 50 | | |
| 316 | Chloroethane | 386 | 216 | 0.999–1.060 | 50 | 789 [7] | 24 |
| 244 | Methylene chloride-$d_2$ | 512 | 181 | 0.582–0.813 | 10 | | |
| 344 | Methylene chloride | 517 | 244 | 0.999–1.017 | 10 | 566 [7] | 280 [7] |
| 546 | Iodomethane | 498 | 181 | 0.68 | | | |
| 616 | Acetone-$d_6$ | 554 | 181 | 0.628–0.889 | 50 | | |
| 716 | Acetone | 565 | 616 | 0.984–1.019 [7] | 50 | 3561 | 322 [7] |
| 202 | Acrolein-$d_4$ | 564 | 181 | 0.641–0.903 | -- [5] | 50 | |
| 302 | Acrolein | 566 | 202 | 0.984–1.018[5] | 50 | 377 [7] | 18 |
| 203 | Acrylonitrile-$d_3$ | 606 | 181 | 0.735–0.926 | 50 | | |
| 303 | Acrylonitrile | 612 | 203 | 0.985–1.030 | 50 | 360 [7] | 9 |
| 533 | Carbon disulfide | 631 | 181 | 0.86 | | | |
| 552 | Trichlorofluoromethane | 663 | 181 | 0.91 | | | |
| 543 | Ethyl cyanide | 672 | 181 | 0.92 | | | |
| 229 | 1,1-Dichloroethene-$d_2$ | 696 | 181 | 0.903–0.976 | 10 | | |
| 329 | 1,1-Dichloroethene | 696 | 229 | 0.999–1.011 | 10 | 31 | 5 |
| 536 | 3-Chloropropene | 696 | 181 | 0.95 | | | |
| 532 | Allyl alcohol | 703 | 181 | 0.96 | | | |
| 181 | Bromochloromethane (I.S.) | 730 | 181 | 1.000–1.000 | 10 | | |
| 213 | 1,1-Dichloroethane-$d_3$ | 778 | 181 | 1.031–1.119 | 10 | | |
| 313 | 1,1-Dichloroethane | 786 | 213 | 0.999–1.014 | 10 | 16 | 1 |
| 615 | Diethyl ether-$d_{10}$ | 804 | 181 | 1.067–1.254 | 50 | | |
| 715 | Diethyl ether | 820 | 615 | 1.010–1.048 | 50 | 63 | 12 |
| 230 | trans-1,2-Dichloroethene-$d_2$ | 821 | 181 | 1.056–1.228 | 10 | | |
| 330 | trans-1,2-Dichloroethene | 821 | 230 | 0.996–1.011 | 10 | 41 | 3 |
| 614 | Methyl ethyl ketone-$d_3$ | 840 | 181 | 0.646–1.202 | 50 | | |
| 714 | Methyl ethyl ketone | 848 | 614 | 0.992–1.055 | 50 | 241 [7] | 80 [7] |
| 223 | Chloroform-$^{13}C_1$ | 861 | 181 | 1.092–1.322 | 10 | | |
| 323 | Chloroform | 861 | 223 | 0.961–1.009 | 10 | 21 | 2 |

| EGD No.[1] | Compound | Retention Time Mean (sec) | EGD Ref | Relative [2] | Minimum Level [3] (µg/L) | Method Detection Limit [4] Low Solids (µg/kg) | High Solids (µg/kg) |
|---|---|---|---|---|---|---|---|
| 535 | Chloroacetonitrile | 884 | 181 | 1.21 | | | |
| 210 | 1,2-Dichloroethane-$d_4$ | 901 | 181 | 1.187–1.416 | 10 | | |
| 310 | 1,2-Dichloroethane | 910 | 210 | 0.973–1.032 | 10 | 23 | 3 |
| 539 | Dibromomethane | 910 | 181 | 1.25 | | | |
| 548 | Methacrylonitrile | 921 | 181 | 1.26 | | | |
| 547 | Isobutyl alcohol | 962 | 181 | 1.32 | | | |
| 211 | 1,1,1-Trichloroethane-$^{13}C_2$ | 989 | 181 | 1.293–1.598 | 10 | | |
| 311 | 1,1,1-Trichloroethane | 999 | 211 | 0.989–1.044 | 10 | 16 | 4 |
| 627 | *p*-Dioxane-$d_8$ | 982 | 181 | 1.262–1.448[5] | 50 | | |
| 727 | *p*-Dioxane | 1001 | 627 | 1.008–1.040[5] | 50 | -- | 140 [7] |
| 206 | Carbon tetrachloride-$^{13}C_2$ | 1018 | 182 | 0.754–0.805 | 10 | | |
| 306 | Carbon tetrachloride | 1018 | 206 | 0.938–1.005 | 10 | 87 | 9 |
| 554 | Vinyl acetate | 1031 | 182 | 0.79 | | | |
| 248 | Bromodichloromethane-$^{13}C_1$ | 1045 | 182 | 0.766–0.825 | 10 | | |
| 348 | Bromodichloromethane | 1045 | 248 | 0.978–1.013 | 10 | 28 | 3 |
| 534 | 2-Chloro-1,3-butadiene | 1084 | 182 | 0.83 | | | |
| 537 | Crotonaldehyde | 1098 | 182 | 0.84 | | | |
| 232 | 1,2-Dichloropropane-$d_6$ | 1123 | 182 | 0.830–0.880 | 10 | | |
| 332 | 1,2-Dichloropropane | 1134 | 232 | 0.984–1.018 | 10 | 29 | 5 |
| 542 | cis-1,3-Dichloropropene | 1138 | 182 | 0.87 | | | |
| 287 | Trichloroethene-$^{13}C_2$ | 1172 | 182 | 0.897–0.917 | 10 | | |
| 387 | Trichloroethene | 1187 | 287 | 0.991–1.037 | 10 | 41 | 2 |
| 541 | 1,3-Dichloropropane | 1196 | 182 | 0.92 | | | |
| 204 | Benezene-$d_6$ | 1200 | 182 | 0.888–0.952 | 10 | | |
| 304 | Benezene | 1212 | 204 | 1.002–1.026 | 10 | 23 | 8 |
| 251 | Chlorodibromomethane-$^{13}C_1$ | 1222 | 182 | 0.915–0.949 | 10 | | |
| 351 | Chlorodibromomethane | 1222 | 231 | 0.989–1.030 | 10 | 15 | 2 |
| 214 | 1,1,2-Trichloroethane-$^{13}C_2$ | 1224 | 182 | 0.922–0.953 | 10 | | |
| 314 | 1,1,2-Trichloroethane | 1224 | 214 | 0.975–1.027 | 10 | 26 | 1 |
| 233 | trans-1,3-Dichloropropene-$d_4$ | 1226 | 182 | 0.922–0.959 | 10 | | |
| 333 | trans-1,3-Dichloropropene | 1226 | 233 | 0.993–1.016 | 10 | --[6,7] | --[6,7] |
| 019 | 2-Chloroethyvinyl ether | 1278 | 182 | 0.983–1.026 | 10 | 122 | 21 |
| 538 | 1,2-Dibromoethane | 1279 | 182 | 0.98 | | | |
| 182 | 2-bromo-1-chloropropane (I.S.) | 1306 | 182 | 1.000–1.000 | 10 | | |

| EGD No.[1] | Compound | Retention Time Mean (sec) | EGD Ref | Relative [2] | Minimum Level [3] (µg/L) | Method Detection Limit [4] Low Solids (µg/kg) | High Solids (µg/kg) |
|---|---|---|---|---|---|---|---|
| 549 | Methyl methacrylate | 1379 | 182 | 1.06 | | | |
| 247 | Bromoform-$^{13}C_1$ | 1386 | 182 | 1.048–1.087 | 10 | | |
| 347 | Bromoform | 1386 | 247 | 0.992–1.003 | 10 | 91 | 7 |
| 551 | 1,1,1,2-Tetrachloroethane | 1408 | 182 | 1.08 | | | |
| 550 | 4-Methyl-2-pentanone | 1435 | 183 | 0.92 | | | |
| 553 | 1,2,3-Trichloropropane | 1520 | 183 | 0.98 | | | |
| 215 | 1,1,2,2-Tetrachloroethane-$d_2$ | 1525 | 183 | 0.969–0.996 | 10 | | |
| 315 | 1,1,2,2-Tetrachloroethane | 1525 | 215 | 0.890–1.016 | 10 | 20 | 6 |
| 545 | 2-Hexanone | 1525 | 183 | 0.98 | | | |
| 285 | Tetrachloroethene-$^{13}C_2$ | 1528 | 183 | 0.966–0.996 | 10 | | |
| 385 | Tetrachloroethene | 1528 | 285 | 0.997–1.003 | 10 | 106 | 10 |
| 540 | trans-1,4-Dichloro-2-butene | 1551 | 183 | 1.00 | | | |
| 183 | 1,4-Dichlorobutane (int std) | 1555 | 183 | 1.000–1.000 | 10 | | |
| 544 | Ethyl methacrylate | 1594 | 183 | 1.03 | | | |
| 286 | Toluene-$d_8$ | 1603 | 183 | 1.016–1.054 | 10 | | |
| 386 | Toluene | 1619 | 286 | 1.001–1.019 | 10 | 27 | 4 |
| 207 | Chlorobenzene-$d_5$ | 1679 | 183 | 1.066–1.135 | 10 | | |
| 307 | Chlorobenzene | 1679 | 207 | 0.914–1.019 | 10 | 21 | 58 [7] |
| 238 | Ethylbenzene-$d_{10}$ | 1802 | 183 | 1.144–1.293 | 10 | | |
| 338 | Ethylbenzene | 1820 | 238 | 0.981–1.018 | 10 | 28 | 4 |
| 185 | Bromofluorobenzene | 1985 | 183 | 1.255–1.290 | 10 | | |
| 951 | *m*-Xylene | 2348 | 183 | 1.51 | 10 | | |
| 952 | *o*- and *p*-Xylene | 2446 | 183 | 1.57 | 10 | | |

[1] Reference numbers beginning with 0, 1, 5, or 9 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

[2] The retention time limits in this column are based on data from four wastewater laboratories. The single values for retention times in this column are based on data from one wastewater laboratory.

[3] This is a minimum level at which the analytical system shall give recognizable mass spectra (background corrected) and acceptable calibration points when calibrated using reagent water. The concentration in the aqueous or solid phase is determined using the equations in Section 13.

[4] Method detection limits determined in digested sludge (low solids) and in filter cake or compost (high solids).

[5] Specification derived from related compound.

[6] An unknown interference in the particular sludge studied precluded measurement of the method detection limit (MDL) for this compound.

[7] Background levels of these compounds were present in the sludge resulting in higher than expected MDLs. The MDL for these compounds is expected to be approximately 20 µg/kg (100 to 200 µg/kg for the gases and water soluble compounds) for the low solids method and 5 to 10 µg/kg (25 to 50 µg/kg for the gases and water soluble compounds) for the high solids methods, with no interferences present.

Column: 2.4 m (8 ft) × 2 mm I.D. glass, packed with 1% SP-1000 coated on 60/80 Carbopak B.
Carrier gas: Helium at 40 mL/min.
Temperature program: 3 min at 45°C, 8°C/min to 240°C, hold at 240°C for 15 minutes.

## 4. SAFETY

**4.1** The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard.

Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 5 through 7.

**4.2** The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

## 5. APPARATUS AND MATERIALS

**5.1** Sample bottles for discrete sampling.

**5.1.1** Bottle: 25– to 40–mL with screw—cap (Pierce 13075, or equivalent). Detergent —wash, rinse with tap and distilled water, and dry at >105°C for a minimum of 1 hour before use.

**5.1.2** Septum: Teflon-faced silicone (Pierce 12722, or equivalent), cleaned as above and baked at 100 to 200°C for 1 hour minimum.

**5.2** Purge and trap device: Consists of purging device, trap, and desorber.

**5.2.1** Purging devices for water and soil samples.

5.2.1.1 Purging device for water samples Designed to accept 5-mL samples with water column at least 3 cm deep. The volume of the gaseous head space between the water and trap shall be less than 15 mL. The purge gas shall be introduced less than 5 mm from the base of the water column and shall pass through the water as bubbles with a

diameter less than 3 mm. The purging device shown in Figure 1 meets these criteria.

5.2.1.2 Purging device for solid samples: Designed to accept 5 g of solids plus 5 mL of water. The volume of the gaseous head space between the water and trap shall be less than 25 mL. The purge gas shall be introduced less than 5 mm from the base of the sample and shall pass through the water as bubbles with a diameter less than 3 mm. The purging device shall be capable of operating at ambient temperature (20 to 25°C) and of being controlled at temperatures of 40°C (±2°C) and 80°C (±5°C) while the sample is being purged. The purging device shown in Figure 2 meets these criteria.

**5.2.2** Trap: 25 to 30 cm long × 2.5 mm I.D. minimum, containing the following:

5.2.2.1 Methyl silicone packing: 1cm (±0.2cm), 3% OV-1 on 60/80 mesh Chromosorb W, or equivalent.

5.2.2.2 Porous polymer: 15cm (±1.0 cm), Tenax GC (2,6-diphenylene oxide polymer), 60/80 mesh, chromatographic grade, or equivalent.

5.2.2.3 Silica gel: 8cm (±1.0 cm), Davison Chemical, 35/60 mesh, grade 15, or equivalent. The trap shown in Figure 3 meets these specifications.

**5.2.3** Desorber: Shall heat the trap to 175°C (±5°C) in 45 seconds or less. The polymer section of the trap shall not exceed a temperature of 180°C and the remaining sections shall not exceed 220°C during desorb, and no portion of the trap shall exceed 225°C during bakeout. The desorber shown in Figure 3 meets these specifications.

**5.2.4** The purge and trap device may be a separate unit, or coupled to a GC as shown in Figures 4 and 5.

**5.3** Gas chromatograph: Shall be linearly temperature programmable with initial and final holds, shall contain a glass jet separator as the MS interface, and shall produce results which meet the calibration (Section 7), quality assurance (Section 8), and performance tests (Section 11) of this method.

**5.3.1** Column: 2.8 · 0.4 m x 2 · 0.5 mm I.D. glass, packed with 1% SP-1000 on Carbopak B, 60/80 mesh, or equivalent.

**5.4** Mass spectrometer: 70 eV electron impact ionization; shall repetitively scan from 20 to 250 amu every 2 to 3 seconds, and produce a unit resolution (valleys between m/z 174 to 176 less than 10% of the height of the m/z 175 peak), background corrected mass spectrum from 50 ng 4-bromofluorobenzene (BFB) injected into the GC. The BFB spectrum shall meet the mass-intensity criteria in Table 4. All portions of the GC column, transfer lines, and separator which connect the GC column to the ion source shall remain at or above the column temperature during analysis to preclude condensation of less volatile compounds.

**5.5** Data system: Shall collect and record MS data, store mass-intensity data in spectral libraries, process GCMS data and generate reports, and shall calculate and record response factors.

Table 4
BFB Mass-Intensity Specifications

| m/z | Intensity Required |
|---|---|
| 50 | 15 to 40% of m/z 95 |
| 75 | 30 to 60% of m/z 95 |
| 95 | base peak, 100% |
| 96 | 5 to 9% of m/z 95 |
| 173 | less than 2% of m/z 174 |
| 174 | greater than 50% of m/z 95 |
| 175 | 5 to 9% of m/z 174 |
| 176 | 95 to 101% of m/z 174 |
| 177 | 5 to 9% of m/z 176 |

**5.5.1** Data acquisition: Mass spectra shall be collected continuously throughout the analysis and stored on a mass storage device.

**5.5.2** Mass spectral libraries: User-created libraries containing mass spectra obtained from analysis of authentic standards shall be employed to reverse search GCMS runs for the compounds of interest (Section 7.2).

**5.5.3** Data processing: The data system shall be used to search, locate, identify, and quantify the compounds of interest in each GCMS analysis. Software routines shall be employed to compute retention times and EICP areas. Displays of spectra, mass chromatograms, and library comparisons are required to verify results.

**5.5.4** Response factors and multipoint calibrations: The data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and generate multi-point calibration curves (Section 7). Computations of relative standard deviation (coefficient of variation) are useful for testing calibration linearity. Statistics on initial and ongoing performance shall be maintained (Sections 8 and 11).

**5.6** Syringes: 5-mL glass hypodermic, with Luer-lok tips.

**5.7** Micro syringes: 10-, 25-, and 100 µL.

**5.8** Syringe valves: 2-way, with Luer ends (Teflon or Kel-F).

**5.9** Syringe: 5-mL, gas-tight, with shut-off valve.

**5.10** Bottles: 15-mL, screw-cap with Teflon liner.

**5.11** Balances.

**5.11.1** Analytical, capable of weighing 0.1 mg.

**5.11.2** Top-loading, capable of weighing 10 mg.

**5.12** Equipment for determining percent moisture.

**5.12.1** Oven,capable of being temperature-controlled at 110°C (±5°C).

**5.12.2** Dessicator.

**5.12.3** Beakers: 50 to 100-mL.

## 6. REAGENTS AND STANDARDS

**6.1** Reagent water: Water in which the compounds of interest and interfering compounds are not detected by this method (Section 11.7). It may be generated by any of the following methods:

**6.1.1** Activated carbon: pass tap water through a carbon bed (Calgon Filtrasorb-300, or equivalent).

**6.1.2** Water purifier: Pass tap water through a purifier (Millipore Super Q, or equivalent).

**6.1.3** Boil and purge: Heat tap water to between 90 and 100°C and bubble contaminant free inert gas through it for approximately 1 hour. While still hot, transfer the water to screw-cap bottles and seal with a Teflon-lined cap.

**6.2** Sodium thiosulfate: ACS granular.

**6.3** Methanol: Pesticide-quality or equivalent.

**6.4** Standard solutions: Purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96% or greater, the weight may be used without correction to calculate the concentration of the standard.

**6.5** Preparation of stock solutions: Prepare in methanol using liquid or gaseous standards per the steps below. Observe the safety precautions given in Section 4.

**6.5.1** Place approximately 9.8 mL of methanol in a 10-mL ground-glass-stoppered volumetric flask. Allow the flask to stand unstoppered for approximately 10 minutes or until all methanol wetted surfaces have dried. In each case, weigh the flask, immediately add the compound, then immediately reweigh to prevent evaporation losses from affecting the measurement.

6.5.1.1 Liquids: Using a 100 µL syringe, permit 2 drops of liquid to fall into the methanol without contacting the neck of the flask. Alternatively, inject a known volume of the compound into the methanol in the flask using a micro-syringe.

6.5.1.2 Gases (chloromethane, bromomethane, chloroethane, vinyl chloride): Fill a valved 5-mL gas-tight syringe with the compound. Lower the needle to approximately 5 mm above the methanol meniscus. Slowly introduce the compound above the surface of the meniscus. The gas will dissolve rapidly in the methanol.

**6.5.2** Fill the flask to volume, stopper, then mix by inverting several times. Calculate the concentration in mg/mL (µg/µL) from the weight gain (or density if a known volume was injected).

**6.5.3** Transfer the stock solution to a Teflon–sealed screw-cap bottle. Store, with minimal headspace, in the dark at –10 to –20°C.

**6.5.4** Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. All other standards are replaced after one month, or sooner if comparison with check standards indicate a change in concentration. Quality control check standards that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

**6.6** Labeled compound spiking solution: From stock standard solutions prepared as above, or from mixtures, prepare the spiking solution to contain a concentration such that a 5- to 10- µL spike into each 5-mL sample, blank, or aqueous standard analyzed will result in a concentration of 20 ug/L of each labeled compound. For the gases and for the water soluble compounds (acrolein, acrylonitrile, acetone, diethyl ether, p-dioxane, and MEK), a concentration of 100 ug/L may be used. Include the internal standards (Section 7.5) in this solution so that a concentration of 20 ug/L in each sample, blank, or aqueous standard will be produced.

**6.7** Secondary standards: Using stock solutions, prepare a secondary standard in methanol to contain each pollutant at a concentration of 500 µg/mL. For the gases and water soluble compounds (Section 6.6), a concentration of 2.5 mg/mL may be used.

**6.7.1** Aqueous calibration standards: Using a 25-µL syringe, add 20 µL of the secondary standard (Section 6.7) to 50, 100, 200, 500, and 1000 mL of reagent water to produce concentrations of 200, 100, 50, 20, and 10 µg/L, respectively. If the higher concentration standard for the gases and water soluble compounds was chosen (Section 6.6), these compounds will be at concentrations of 1000, 500, 250, 100, and 50 µg/L in the aqueous calibration standards.

**6.7.2** Aqueous performance standard: An aqueous standard containing all pollutants, internal standards, labeled compounds, and BFB is prepared daily, and analyzed each shift to demonstrate performance (Section 11). This standard shall contain either 20 or 100 µg/L of the labeled and pollutant gases and water soluble compounds, 10 µg/L BFB, and 20 µg/L of all other pollutants, labeled compounds, and internal standards. It may be the nominal 20 µg/L aqueous calibration standard (Section 6.7.1).

**6.7.3** A methanolic standard containing all pollutants and internal standards is prepared to demonstrate recovery of these compounds when syringe injection and purge-and-trap analyses are compared. This standard shall contain either 100 µg/mL or 500 µg/mL of the gases and water soluble compounds, and 100 µg/mL of the remaining pollutants and internal standards (consistent with the amounts in the aqueous performance standard in 6.7.2).

**6.7.4** Other standards which may be needed are those for test of BFB performance (Section 7.1) and for collection of mass spectra for storage in spectral libraries (Section 7.2).

## 7. CALIBRATION

Calibration of the GCMS system is performed by purging the compounds of interest and their labeled analogs from reagent water at the temperature to be used for analysis of samples.

**7.1** Assemble the gas chromatographic apparatus and establish operating conditions given in Table 3. By injecting standards into the GC, demonstrate that the analytical system meets the minimum levels in Table 3 for the compounds for which calibration is to be performed, and the mass-intensity criteria in Table 4 for 50 ng BFB.

**7.2** Mass spectral libraries: Detection and identification of the compounds of interest are dependent upon the spectra stored in user created libraries.

**7.2.1** For the compounds in Table 1 and other compounds for which the GCMS is to be calibrated, obtain a mass spectrum of each pollutant and labeled compound and each internal standard by analyzing an authentic standard either singly or as part of a mixture in which there is no interference between closely eluted components. Examine the spectrum to determine that only a single compound is present. Fragments not attributable to the compound under study indicate the presence of an interfering compound. Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at the GC peak maximum. An undistorted spectrum will usually be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to "enhance" the spectrum may eliminate distortion, but may also eliminate authentic m/z's or introduce other distortion.

**7.2.2** The authentic reference spectrum is obtained under BFB tuning conditions (Section 7.1 and Table 4) to normalize it to spectra from other instruments.

**7.2.3** The spectrum is edited by saving the five most intense mass spectral peaks and all other mass spectral peaks greater than 10% of the base peak. The spectrum may be further edited to remove common interfering masses. If five mass spectral peaks cannot be obtained under the scan conditions given in Section 5.4, the mass spectrometer may be scanned to an m/z lower than 20 to gain additional spectral information. The spectrum obtained is stored for reverse search and for compound confirmation.

**7.2.4** For the compounds in Table 2 and other compounds for which the mass spectra, quantitation m/z's, and retention times are known but the instrument is not to be calibrated, add the retention time and reference compound (Table 3); the response factor and the quantitation m/z (Table 5); and spectrum (Appendix A) to the reverse search library. Edit the spectrum per Section 7.2.3, if necessary.

**7.3** Assemble the purge-and-trap device. Pack the trap as shown in Figure 3 and condition overnight at 170 to 180°C by backflushing with an inert gas at a flow rate of 20 to 30 mL/min. Condition traps daily for a minimum of 10 minutes prior to use.

**7.3.1** Analyze the aqueous performance standard (Section 6.7.2) according to the purge–and–trap procedure in Section 10. Compute the area at the primary m/z (Table 5) for each compound. Compare these areas to those obtained by injecting 1 µL of the methanolic standard (Section 6.7.3) to determine compound recovery. The recovery shall be greater than 20% for the water soluble compounds (Section 6.6), and 60 to 110% for all other compounds. This recovery is demonstrated initially for each purge-and-trap GCMS system. The test is repeated only if the

purge-and-trap or GCMS systems are modified in any way that might result in a change in recovery.

**7.3.2** Demonstrate that 100 ng toluene (or toluene-$d_8$) produces an area at m/z 91 (or 99) approximately one-tenth that required to exceed the linear range of the system. The exact value must be determined by experience for each instrument. It is used to match the calibration range of the instrument to the analytical range and detection limits required.

Table 5. Volatile Organic Compound Characteristic M/Z'S

| Compound | labeled Analog | Primary m/z[1] | Reference Compound[2] | Response purge temp. Of: 20 °C | 80 °C |
|---|---|---|---|---|---|
| Acetone | $d_6$ | 58/64 | | | |
| Acrolein | $d_4$ | 56/60 | | | |
| Acrylonitrile | $d_3$ | 53/56 | | | |
| Allyl alcohol | | 57 | 181 | --[3] | 0.20 |
| Benzene | $d_6$ | 78/84 | | | |
| 2-Bromo-1-chloropropane[4] | | 77 | | | |
| Bromochloromethane[4] | | 128 | | | |
| Bromodichloromethane | $13_c$ | 83/86 | | | |
| Bromoform | $13_c$ | 173/176 | | | |
| Bromomethane | $d_3$ | 96/99 | | | |
| Carbon disulfide | | 76 | 181 | 1.93 | 2.02 |
| Carbon tetrachloride | $13_c$ | 47/48 | | | |
| 2-Chloro-1,3-butadiene | | 53 | 182 | 0.29 | 0.50 |
| Chloroacetonitrile | | 75 | 181 | --[3] | 1.12 |
| Chlorobenzene | $d_5$ | 112/117 | | | |
| Chloroethane | $d_5$ | 64/71 | | | |
| 2-Chloroethylvinyl ether | $d_7$ | 106/113 | | | |
| Chloroform | $13_C$ | 85/86 | | | |
| Chloromethane | $d_3$ | 50/53 | | | |
| 3-Chloropropene | | 76 | 181 | 0.43 | 0.63 |
| Crotonaldehyde | | 70 | 182 | --[3] | 0.090 |
| Dibromochloromethane | $13_c$ | 129/130 | | | |
| 1,2-Dibromoethane | | 107 | 182 | 0.86 | 0.68 |
| Dibromomethane | | 93 | 181 | 1.35 | 1.91 |
| 1,4-Dichlorobutane | | 55 | | | |
| trans-1,4-Dichloro-2-butene | | 75 | 183 | 0.093 | 0.014 |
| 1,1-Dichloroethane | $d_3$ | 63/66 | | | |

| Compound | labeled Analog | Primary m/z[1] | Reference Compound[2] | Response purge temp. Of: 20 °C | 80 °C |
|---|---|---|---|---|---|
| 1,2-Dichloroethane | $d_4$ | 62/67 | | | |
| 1,1-Dichloroethene | $d_2$ | 61/65 | | | |
| trans-1,2-Dichlorethene | $d_2$ | 61/65 | | | |
| 1,2-Dichloropropane | $d_6$ | 63/67 | | | |
| 1,3-Dichloropropane | | 76 | 182 | 0.89 | 0.88 |
| cis-1,3-Dichloropropene | | 75 | 182 | 0.29 | 0.41 |
| trans-1,3-Dichloropropene | $d_4$ | 75/79 | | | |
| Diethyl ether | $d_{10}$ | 74/84 | | | |
| *p*-Dioxane | $d_8$ | 88/96 | | | |
| Ethyl cyanide | | 54 | 181 | (3) | 1.26 |
| Ethyl methacrylate | | 69 | 183 | 0.69 | 0.52 |
| Ethylbenzene | $d_{10}$ | 106/116 | | | |
| 2-Hexanone | | 58 | 183 | 0.076 | 0.33 |
| Iodomethane | | 142 | 181 | 4.55 | 2.55 |
| Isobutyl alcohol | | 74 | 181 | (3) | 0.22 |
| Methylene chloride | $d_2$ | 84/88 | | | |
| Methyl ethyl ketone | $d_8$ | 72/80 | | | |
| Methyl methacrylate | | 69 | 182 | 0.23 | 0.79 |
| 4-Methyl-2-pentanone | | 58 | 183 | 0.15 | 0.29 |
| Methacrylonitrile | | 67 | 181 | 0.25 | 0.79 |
| 1,1,1,2-Tetrachloroethane | | 131 | 182 | 0.20 | 0.25 |
| 1,1,2,2-Tetrachloroethane | $d_2$ | 83/84 | | | |
| Tetrachloroethene | $13_C$[2] | 164/172 | | | |
| Toluene | $d_8$ | 92/100 | | | |
| 1,1,1-Trichloroethane | $d_3$ | 97/102 | | | |
| 1,1,2-Trichloroethane | $13_C$[2] | 83/84 | | | |
| Trichloroethene | $13_C$[2] | 95/136 | | | |
| Trichlorofluoromethane | | 101 | 181 | 2.31 | 2.19 |
| 1,2,3-Trichloropropane | | 75 | 183 | 0.89 | 0.72 |
| Vinyl acetate | | 86 | 182 | 0.054 | 0.19 |
| Vinyl chloride | $d_3$ | 62/65 | | | |
| *m*-Xylene | | 106 | 183 | 1.69 | - |
| 0- and *p*-Xylene | | 106 | 183 | 3.33 | - |

[1] Native/labeled

[2] 181 = bromochloromethane
182 = 2-bromo-1-chloropropane
183 = 1,4-dichlorobutane

[3] Not detected at a purge temperature of 20°C

[4] Internal standard

Note: Because the composition and purity of commercially-supplied isotopically labeled standard's may vary, the primary m/z of the labeled analogs given in this table should be used as guidance. The appropriate m/z of the labeled analogs should be determined prior to use for sample analysis. Deviations from the m/z's listed here must be documented by the laboratory and submitted with the data.

**7.4** Calibration by isotope dilution: The isotope dilution approach is used for the purgeable organic compounds when appropriate labeled compounds are available and when interferences do not preclude the analysis. If labeled compounds are not available, or interferences are present, the internal standard method (Section 7.5) is used. A calibration curve encompassing the concentration range of interest is prepared for each compound determined. The relative response (RR) vs. concentration (µg/L) is plotted or computed using a linear regression. An example of a calibration curve for toluene using toluene-$d_8$ is given in Figure 6. Also shown are the ±10% error limits (dotted lines). Relative response is determined according to the procedures described below. A minimum of five data points are required for calibration (Section 7.4.4).

**7.4.1** The relative response (RR) of pollutant to labeled compound is determined from isotope ratio values calculated from acquired data. Three isotope ratios are used in this process:

$R_x$ = *the isotope ratio measured in the pure pollutant (Figure 7A).*
$R_y$ = *the isotope ratio of pure labeled compound (Figure 7B).*
$R_m$ = *the isotope ratio measured in the analytical mixture of the pollutant and labeled compounds (Figure 7C.)*

The correct way to calculate RR is:

$$RR = \frac{(R_y - R_m)(R_x + 1)}{(R_m - R_x)(R_y + 1)}$$

If $R_m$ is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by the internal standard method (Section 7.5).

**7.4.2** In most cases, the retention times of the pollutant and labeled compound are the same, and isotope ratios (R's) can be calculated from the EICP areas, where:

$$R = \frac{(area\ at\ m_1/z)}{(area\ at\ m_2/z)}$$

If either of the areas is zero, it is assigned a value of one in the calculations; that is, if: area of $m_1/z$ = 50721,
area of mz/Z = 0,
then R = 50721/1 = 50720
The data from these analyses are reported to three significant figures (see Section 13.6). In order to prevent rounding errors from affecting the values to be

reported, all calculations performed prior to the final determination of concentrations should be carried out using at least four significant figures. Therefore, the calculation of R above is rounded to four significant figures.
The m/z's are always selected such that $R_x > R_y$. When there is a difference in retention times (RT) between the pollutant and labeled compounds, special precautions are required to determine the isotope ratios.

*$R_x$, $R_y$, and $R_m$ are defined as follows:*

$$R_x = \frac{[area\ m_1/z\ (at\ RT_1)]}{1}$$

$$R_y = \frac{1}{[area\ m_2/z\ (at\ RT_2)]}$$

$$R_m = \frac{[area\ m_1/z\ (at\ RT_1)]}{[area\ m_2/z\ (at\ RT_2)]}$$

**7.4.3** An example of the above calculations can be taken from the data plotted in Figure 7 for toluene and toluene-$d_8$. For these data:

$$R_x = \frac{168920}{1} = 168900$$

$$R_y = \frac{1}{60960} = 0.00001640$$

$$R_m = \frac{96868}{82508} = 1.174$$

The RR for the above data is then calculated using the equation given in Section 7.4.1. For the example, rounded to four significant figures, RR = 1.174. Not all labeled compounds elute before their pollutant analogs.

**7.4.4** To calibrate the analytical system by isotope dilution, analyze a 5-mL aliquot of each of the aqueous calibration standards (Section 6.7.1) spiked with an appropriate constant amount of the labeled compound spiking solution (Section 6.6), using the purge-and-trap procedure in Section 10. Compute the RR at each concentration.

**7.4.5** Linearity: If the ratio of relative response to concentration for any compound is constant (less than 20% coefficient of variation) over the five point calibration range, an averaged relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five point calibration range.

**7.5** Calibration by internal standard: Used when criteria for isotope dilution (Section 7.4) cannot be met. The method is applied to pollutants having no labeled analog and to the labeled compounds. The internal standards used for volatiles analyses are bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Concentrations

of the labeled compounds and pollutants without labeled analogs are computed relative to the nearest eluting internal standard, as shown in Tables 3 and 5.

**7.5.1** Response factors: Calibration requires the determination of response factors (RF) which are defined by the following equation:

$$R = \frac{(A_s \times C_{is}),}{(a_{is} \times C_s)}$$

*Where*:

$A$ = *is the EICP area at the characteristic m/z for the compound in the daily standard.*

$A_{is}$ = *is the EICP area at the characteristic m/z for the internal standard.*

$C_{is}$ = *is the concentration (µg/L) of the internal standard.*

$C_s$ = *is the concentration of the pollutant in the daily standard.*

**7.5.2** The response factor is determined at 10, 20, 50, 100, and 200 µg/L for the pollutants (optionally at five times these concentrations for gases and water soluble pollutants; see Section 6.7), in a way analogous to that for calibration by isotope dilution (Section 7.4.4). The RF is plotted against concentration for each compound in the standard ($C_s$) to produce a calibration curve.

**7.5.3** Linearity: If the response factor (RF) for any compound is constant (less than 35% coefficient of variation) over the five-point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-point range.

**7.6** Combined calibration: By adding the isotopically labeled compounds and internal standards (Section 6.6) to the aqueous calibration standards (Section 6.7.1), a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (Section 11.5) by purging the aqueous performance standard (Section 6.7.2). Recalibration is required only if calibration and ongoing performance (Section 11.5) criteria cannot be met.

**7.7** Elevated purge temperature calibration: Samples containing greater than 1% solids are analyzed at a temperature of 40°C (±2°C) (Section 10). For these samples, the analytical system may be calibrated using a purge temperature of 40°C(±2°C) in order to more closely approximate the behavior of the compounds of interest in high solids samples.

## 8. QUALITY ASSURANCE/QUALITY CONTROL

**8.1** Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 8). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

**8.1.1** The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

**8.1.2** The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance specifications are met. Each time a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2 to demonstrate method performance.

**8.1.3** Analyses of blanks are required to demonstrate freedom from contamination and that the compounds of interest and interfering compounds have not been carried over from a previous analysis (Section 3). The procedures and criteria for analysis of a blank are described in Section 8.5.

**8.1.4** The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in Section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (Section 14.2).

**8.1.5** The laboratory shall, on an ongoing basis, demonstrate through the analysis of the aqueous performance standard (Section 6.7.2) that the analysis system is in control. This procedure is described in Sections 11.1 and 11.5.

**8.1.6** The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Sections 8.4 and 11.5.2.

Table 6. Acceptance Criteria for Performance Tests

| EGD | | Acceptance criteria at 20 µg/L or as noted | | | |
|---|---|---|---|---|---|
| | | Labeled and native compound initial precision and accuracy (Sect. 8.2.3) | | Labeled compound recovery (Sect. 8.3 and 14.2) | Labeled and native compound ongoing accuracy (Sect. 11.5) |
| No.[1] | Compound | s ( µg/L) | X (µg/L) | P (%) | R (µg/L) |
| 516 | acetone* | 51.0 | 77 - 153 | 35 - 165 | 55 - 145 |
| 002 | acrolein* | 72.0 | 32 - 168 | 37 - 163 | 7 - 190 |
| 003 | acrylonitrile* | 16.0 | 70 - 132 | ns - 204 | 58 - 144 |
| 004 | benzene | 9.0 | 13 - 28 | ns - 196 | 4 - 33 |
| 048 | bromodichloro-methane | 8.2 | 7 - 32 | ns - 199 | 4 - 34 |
| 047 | bromoform | 7.0 | 7 - 35 | ns - 214 | 6 - 36 |
| 046 | bromomethane | 25.0 | d - 54 | ns - 414 | d - 61 |
| 006 | carbon tetrachloride | 6.9 | 16 - 25 | 42 - 165 | 12 - 30 |
| 007 | chlorobenzene | 8.2 | 14 - 30 | ns - 205 | 4 - 35 |
| 016 | chloroethane | 15.0 | d - 47 | ns - 308 | d - 51 |
| 019 | 2-chloroethylvinyl ether | 36.0 | d - 70 | ns - 554 | d - 79 |
| 023 | chloroform | 7.9 | 12 - 26 | 18 - 172 | 8 - 30 |
| 045 | chloromethane | 26.0 | d - 56 | ns - 410 | d - 64 |
| 051 | dibromochloro-methane | 7.9 | 11 - 29 | 16 - 185 | 8 - 32 |
| 013 | 1,1-dichloroethane | 6.7 | 11 - 31 | 23 - 191 | 9 - 33 |
| 010 | 1,2-dichloroethane | 7.7 | 12 - 30 | 12 - 192 | 8 - 33 |
| 029 | 1,1-dichloroethene | 12.0 | d - 50 | ns - 315 | d - 52 |
| 030 | trans-1,2-dichloro-ethene | 7.4 | 11 - 32 | 15 - 195 | 8 - 34 |
| 032 | 1,2-dichloropropane | 19.0 | d - 47 | ns - 343 | d - 51 |
| 033 | trans-1,3-dichloro-propene | 15.0 | d - 40 | ns - 284 | d - 44 |
| 515 | diethyl ether* | 44.0 | 75 - 146 | 44 - 156 | 55 - 145 |

| EGD | | Acceptance criteria at 20 µg/L or as noted | | | |
|---|---|---|---|---|---|
| | | Labeled and native compound initial precision and accuracy (Sect. 8.2.3) | | Labeled compound recovery (Sect. 8.3 and 14.2) | Labeled and native compound ongoing accuracy (Sect. 11.5) |
| No.[1] | Compound | s ( µg/L) | X (µg/L) | P (%) | R (µg/L) |
| 527 | p-dioxane* | 7.2 | 13 - 27 | ns - 239 | 11 - 29 |
| 038 | ethylbenzene | 9.6 | 16 - 29 | ns - 203 | 5 - 35 |
| 044 | methylene chloride | 9.7 | d - 50 | ns - 316 | d - 50 |
| 514 | methyl ethyl ketone* | 57.0 | 66 - 159 | 36 - 164 | 42 - 158 |
| 015 | 1,1,2,2-tetrachloroethane | 9.6 | 11 - 30 | 5 - 199 | 7 - 34 |
| 085 | tetrachloroethane | 6.6 | 15 - 29 | 31 - 181 | 11 - 32 |
| 086 | toluene | 6.3 | 15 - 29 | 4 - 193 | 6 - 33 |
| 011 | 1,1,1-trichloroethane | 5.9 | 11 - 33 | 12 - 200 | 8 - 35 |
| 014 | 1,1,2-trichloroethane | 7.1 | 12 - 30 | 21 - 184 | 9 - 32 |
| 087 | trichloroethene | 8.9 | 17 - 30 | 35 - 196 | 12 - 34 |
| 088 | vinyl chloride | 28.0 | d - 59 | ns - 452 | d - 65 |

* acceptance criteria at 100 µg/L
d = detected; result must be greater than zero.
ns = no specification; limit would be below detection limit.

[1] Reference numbers beginning with 0, 1, or 5 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal Standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

**8.2** Initial precision and accuracy: To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations for compounds to be calibrated:

**8.2.1** Analyze two sets of four 5-mL aliquots (8 aliquots total) of the aqueous performance standard (Section 6.7.2) according to the method beginning in Section 10.

**8.2.2** Using results of the first set of four analyses in Section 8.2.1, compute the average recovery (X) in µg/L and the standard deviation of the recovery (s) in µg/L for each compound, by isotope dilution for pollutants with a labeled analog, and by internal standard for labeled compounds and pollutants with no labeled analog.

**8.2.3** For each compound, compare s and X with the corresponding limits for initial precision and accuracy found in Table 6. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound.

---

NOTE: *The large number of compounds in Table 6 present a substantial probability that one or more will fail one of the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure can be attributed to probability, proceed as follows:*

---

**8.2.4** Using the results of the second set of four analyses, compute s and X for only those compounds which failed the test of the first set of four analyses (Section 8.2.3). If these compounds now pass, system performance is acceptable for all compounds and analysis of blanks and samples may begin. If, however, any of the same compounds fail again, the analysis system is not performing properly for the compound (s) in question. In this event, correct the problem and repeat the entire test (Section 8.2.1).

**8.3** The laboratory shall spike all samples with labeled compounds to assess method performance on the sample matrix.

**8.3.1** Spike and analyze each sample according to the method beginning in Section 10.

**8.3.2** Compute the percent recovery (P) of the labeled compounds using the internal standard method (Section 7.5).

**8.3.3** Compare the percent recovery for each compound with the corresponding labeled compound recovery limit in Table 6. If the recovery of any compound falls outside its warning limit, method performance is unacceptable for that compound in that sample. Therefore, the sample matrix is complex and the sample is to be diluted and reanalyzed, per Section 14.2.

**8.4** As part of the QA program for the laboratory, method accuracy for wastewater samples shall be assessed and records shall be maintained. After the analysis of five wastewater samples for which the labeled compounds pass the tests in Section 8.3.3, compute the

average percent recovery (P) and the standard deviation of the percent recovery (sp) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from P - 2sp to P + 2sp. For example, if P = 90% and sp = 10%, the accuracy interval is expressed as 70 to 110%. Update the accuracy assessment for each compound on a regular basis (e.g., after each 5 to 10 new accuracy measurements).

**8.5** Blanks: Reagent water blanks are analyzed to demonstrate freedom from carry-over (Section 3) and contamination.

**8.5.1** The level at which the purge and trap system will carry greater than 5 µg/L of a pollutant of interest (Tables 1 and 2) into a succeeding blank shall be determined by analyzing successively larger concentrations of these compounds. When a sample contains this concentration or more, a blank shall be analyzed immediately following this sample to demonstrate no carry-over at the 5 µg/L level.

**8.5.2** With each sample lot (samples analyzed on the same 8-hour shift), a blank shall be analyzed immediately after analysis of the aqueous performance standard (Section 11.1) to demonstrate freedom from contamination. If any of the compounds of interest (Tables 1 and 2) or any potentially interfering compound is found in a blank at greater than 10 µg/L (assuming a response factor of 1 relative to the nearest eluted internal standard for compounds not listed in Tables 1 and 2), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

**8.6** The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for calibration (Section 7), calibration verification (Section 11.5) and for initial (Section 8.2) and ongoing (Section 11.5) precision and accuracy should be identical, so that the most precise results will be obtained. The GCMS instrument in particular will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of volatiles by this method.

**8.7** Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal method is used.

## 9. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

**9.1** Grab samples are collected in glass containers having a total volume greater than 20 mL. For aqueous samples which pour freely, fill sample bottles so that no air bubbles pass through the sample as the bottle is filled and seal each bottle so that no air bubbles are entrapped. Maintain the hermetic seal on the sample bottle until time of analysis.

**9.2** Samples are maintained at 0 to 4°C from the time of collection until analysis. If an aqueous sample contains residual chlorine, add sodium thiosulfate preservative (10 mg/40 mL) to the empty sample bottles just prior to shipment to the sample site. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine (Reference 9). If preservative has been added, shake the bottle vigorously for one minute immediately after filling.

**9.3** For aqueous samples, experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological

degradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding HCl (1+1) while stirring. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.1. If residual chlorine is present, add sodium thiosulfate to a separate sample container and fill as in Section 9.1.

**9.4** All samples shall be analyzed within 14 days of collection.

## 10. PURGE, TRAP, AND GCMS ANALYSIS

Samples containing less than one percent solids are analyzed directly as aqueous samples (Section 10.4). Samples containing one percent solids or greater are analyzed as solid samples utilizing one of two methods, depending on the levels of pollutants in the sample. Samples containing one percent solids or greater and low to moderate levels of pollutants are analyzed by purging a known weight of sample added to 5 mL of reagent water (Section 10.5). Samples containing 1% solids or greater and high levels of pollutants are extracted with methanol, and an aliquot of the methanol extract is added to reagent water and purged (Section 10.6).

**10.1** Determination of percent solids.

**10.1.1** Weigh 5 to 10 g of sample into a tared beaker.

**10.1.2** Dry overnight (12 hours minimum) at 110°C (±5°C), and cool in a dessicator.

**10.1.3** Determine percent solids as follows:

$$\%\ solids = \frac{weight\ of\ sample\ dry}{weight\ of\ sample\ wet} \times 100$$

**10.2** Remove standards and samples from cold storage and bring to 20 to 25°C.

**10.3** Adjust the purge gas flow rate to 40 (±4mL/min).

**10.4** Samples containing less than 1% solids.

**10.4.1** Mix the sample by shaking vigorously. Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle and carefully pour the sample into the syringe barrel until it overflows. Replace the plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL (±0.1 mL). Because this process of taking an aliquot destroys the validity of the sample for future analysis, fill a second syringe at this time to protect against possible loss of data.

**10.4.2** Add an appropriate amount of the labeled compound spiking solution (Section 6.6) through the valve bore, then close the valve.

**10.4.3** Attach the syringe valve assembly to the syringe valve on the purging device. Open both syringe valves and inject the sample into the purging chamber. Purge the sample per Section 10.7.

**10.5** Samples containing 1% solids or greater and low to moderate levels of pollutants.

**10.5.1** Mix the sample thoroughly using a clean spatula.

**10.5.2** Weigh 5 g (±1 g) of sample into a purging vessel (Figure 2). Record the weight to three significant figures.

**10.5.3** Add 5 mL (±0.1 mL) of reagent water to the vessel.

**10.5.4** Using a metal spatula, break up any lumps of sample to disperse the sample in the water.

**10.5.5** Add an appropriate amount of the labeled compound spiking solution (Section 6.6) to the sample in the purge vessel. Place a cap on the purging vessel and and shake vigorously to further disperse the sample. Attach the purge vessel to the purging device, and purge the sample per Section 10.7.

**10.6** Samples containing 1% solids or greater and high levels of pollutants, or samples requiring dilution by a factor of more than 100 (see Section 13.4).

**10.6.1** Mix the sample thoroughly using a clean spatula.

**10.6.2** Weigh 5g (±1 g) of sample into a calibrated 15- to 25-mL centrifuge tube. Record the weight of the sample to three significant figures.

**10.6.3** Add 10 mL of methanol to the centrifuge tube. Cap the tube and shake it vigorously for 15 to 20 seconds to disperse the sample in the methanol. Allow the sample to settle in the tube. If necessary, centrifuge the sample to settle suspended particles.

**10.6.4** Remove approximately 0.1% of the volume of the supernatant methanol using a 15- to 25- µL syringe. This volume will be in the range of 10 to 15 µL.

**10.6.5** Add this volume of the methanol extract to 5 mL reagent water in a 5 mL syringe, and analyze per Section 10.4.1.

**10.6.6** For further dilutions, dilute 1 mL of the supernatant methanol (Section 10.6.4) to 10 mL, 100 mL, 1000 mL, etc., in reagent water. Remove a volume of this methanol extract/reagent water mixture equivalent to the volume in Section 10.6.4, add it to 5 mL reagent water in a 5 mL syringe, and analyze per Section 10.4.1.

**10.7** Purge the sample for 11 minutes (±0.1 minute) at 20 to 25°C for samples containing less than 1% solids. Purge samples containing one percent solids or greater at 40°(±2°). If the compounds in Table 2 that do not purge at 20 to 40°C are to be determined, a purge temperature of 80°C (±5°C) is used.

**10.8** After the 11 minute purge time, attach the trap to the chromatograph and set the purge-and- trap apparatus to the desorb mode (Figure 5). Desorb the trapped compounds into the GC column by heating the trap to between 170 and 180°C while backflushing with carrier gas at 20 to 60 mL/min for 4 minutes. Start MS data acquisition upon start of the desorb cycle, and start the GC column temperature program 3 minutes later. Table 3 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and minimum levels that can be achieved under these conditions. An example of the separations achieved by the column listed is shown in Figure 9. Other columns may be used provided the requirements in Section 8 are met.

If the priority pollutant gases produce GC peaks so broad that the precision and recovery specifications (Section 8.2) cannot be met, the column may be cooled to ambient or subambient temperatures to sharpen these peaks.

**10.9** After desorbing the sample for four minutes, recondition the trap by purging with purge gas while maintaining the trap temperature at between 170 and 180°C. After approximately 7 minutes, turn off the trap heater to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

**10.10** While analysis of the desorbed compounds proceeds, remove and clean the purge device. Rinse with tap water, clean with detergent and water, rinse with tap and distilled water, and dry for aminimum of 1 hour in an oven at a temperature greater than 150°C.

## 11. SYSTEM PERFORMANCE

**11.1** At the beginning of each 8 hour shift during which analyses are performed, system calibration and performance shall be verified for the pollutants and labeled compounds (Table 1). For these tests, analysis of the aqueous performance standard (Section 6.7.2) shall be used to verify all performance criteria. Adjustment and/or recalibration (per Section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may blanks and samples be analyzed.

**11.2** BFB spectrum validity: The criteria in Table 4 shall be met.

**11.3** Retention times: The absolute retention times of the internal standards shall be as follows: bromochloromethane: 653 to 782 seconds; 2-bromo-1-chloropropane: 1270 to 1369 seconds; 1,4-dichlorobutane: 1510 to 1605 seconds. The relative retention times of all pollutants and labeled compounds shall fall within the limits given in Table 3.

**11.4** GC resolution: The valley height between toluene and toluene-$d_8$ (at m/z 91 and 99 plotted on the same graph) shall be less than 10% of the taller of the two peaks.

**11.5** Calibration verification and ongoing precision and accuracy: Compute the concentration of each pollutant (Table 1) by isotope dilution (Section 7.4) for those compounds which have labeled analogs. Compute the concentration of each pollutant which has no labeled analog by the internal standard method (Section 7.5). Compute the concentrations of the labeled compounds themselves by the internal standard method. These concentrations are computed based on the calibration data determined in Section 7.

**11.5.1** For each pollutant and labeled compound, compare the concentration with the corresponding limit for ongoing accuracy in Table 6. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue. If any individual value falls outside the range given, system performance is unacceptable for that compound.

---

NOTE: *The large number of compounds in Table 6 present a substantial probability that one or more will fail the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure may be attributed to probability, proceed as follows:*

---

11.5.1.1 Analyze a second aliquot of the aqueous performance standard (Section 6.7.2).

11.5.1.2 Compute the concentration for only those compounds which failed the first test (Section 11.5.1). If these compounds now pass, system performance is acceptable for all compounds, and analyses of blanks and samples may proceed. If, however, any of the compounds fail again, the measurement system is not performing properly for these compounds. In this event, locate and correct the problem or recalibrate the system (Section 7), and repeat the entire test (Section 11.1) for all compounds.

**11.5.2** Add results which pass the specification in Section 11.5.1.2 to initial (Section 8.2) and previous on-going data. Update QC charts to form a graphic representation of laboratory performance (Figure 8). Develop a statement of accuracy for each pollutant and labeled compound by calculating the average percent recovery (R) and the standard deviation of percent recovery (sr). Express the accuracy as a recovery interval from R – 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85 to 105%.

## 12. QUALITATIVE DETERMINATION

Identification is accomplished by comparison of data from analysis of a sample or blank with data stored in the mass-spectral libraries. For compounds for which the relative retention times and mass spectra are known, identification is confirmed per Sections 12.1 and 12.2. For unidentified GC peaks, the spectrum is compared to spectra in the EPA/NIH mass spectral file per Section 12.3.

12.1 Labeled compounds and pollutants having no labeled analog (Tables 1 and 2):

**12.1.1** The signals for all characteristic m/z's stored in the spectral library (Section 7.2.3) shall be present and shall maximize within the same two consecutive scans.

**12.1.2** Either (1) the background corrected EICP areas or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of 2 (0.5 to 2 times) for all masses stored in the library.

**12.1.3** In order for the compounds for which the system has been calibrated (Table 1) to be identified, their relative retention times shall be within the retention-time windows specified in Table 3.

**12.1.4** The system has not been calibrated for the compounds listed in Table 2; however, the relative retention times and mass spectra of these compounds are known. Therefore, for a compound in Table 2 to be identified, its relative retention time must fall within a retention-time window of ±60 seconds or ±20 scans (whichever is greater) of the nominal retention time of the compound specified in Table 3.

12.2 Pollutants having a labeled analog (Table 1):

**12.2.1** The signals for all characteristic m/z's stored in the spectral library (Section 7.2.3) shall be present and shall maximize within the same two consecutive scans.

**12.2.2** Either (1) the background corrected EICP areas or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two for all masses stored in the spectral library.

**12.2.3** The relative retention time between the pollutant and its labeled analog shall be within the windows specified in Table 3.

**12.3** Unidentified GC peaks.

**12.3.1** The signals for m/z's specific to a GC peak shall all maximize within the same two consecutive scans.

**12.3.2** Either (1) the background corrected EICP areas or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of 2 with the masses stored in the EPA/NIH mass-spectral file.

**12.4** The m/z's present in the sample mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the sample mass spectrum is contaminated, or if identification is ambiguous, an experienced spectrometrist (Section 1.4) is to determine the presence or absence of the compound.

## 13. QUANTITATIVE DETERMINATION

**13.1** Isotope dilution: Because the pollutant and its labeled analog exhibit the same effects upon purging, desorption, and gas chromatography, correction for recovery of the pollutant can be made by adding a known amount of a labeled compound to every sample prior to purging. Relative response (RR) values for sample mixtures are used in conjunction with the calibration curves described in Section 7.4 to determine concentrations directly, so long as labeled compound spiking levels are constant. For the toluene example given in Figure 7 (Section 7.4.3), RR would be equal to 1.174. For this RR value, the toluene calibration curve given in Figure 6 indicates a concentration of 31.8 µg/L.

**13.2** Internal standard: For the compounds for which the system was calibrated (Table 1) according to Section 7.5, use the response factor determined during the calibration to calculate the concentration from the following equation.

$$Concentration = \frac{(A_s \times C_{is})}{(A_{is} \times RF)}$$

where the terms are as defined in Section 7.5.1. For the compounds for which the system was not calibrated (Table 2), use the response factors in Table 5 to calculate the concentration.

**13.3** The concentration of the pollutant in the solid phase of the sample is computed using the concentration of the pollutant detected in the aqueous solution, as follows:

$$Concentration\ in\ solid\ (\mu g/kg) = \frac{0.005\ L \times aqueous\ conc\ (\mu g/L)}{0.01 \times percent\ solids(g)}$$

*where*
*"percent solids" is from Section* 10.1.3

**13.4** Dilution of samples: If the EICP area at the quantitation m/z exceeds the calibration range of the system, samples are diluted by successive factors of 10 until the area is within the calibration range.

**13.4.1** For aqueous samples, bring 0.50 mL, 0.050 mL, 0.0050 mL, etc., to 5-mL volume with reagent water and analyze per Section 10.4.

**13.4.2** For samples containing high solids, substitute 0.50 or 0.050 g in Section 10.5.2 to achieve a factor of 10 or 100 dilution, respectively.

**13.4.3** If dilution of high solids samples by greater than a factor of 100 is required, then extract the sample with methanol, as described in Section 10.6.

**13.5** Dilution of samples containing high concentrations of compounds not in Table 1: When the EICP area of the quantitation m/z of a compound to be identified per Section 12.3 exceeds the linear range of the GCMS system, or when any peak in the mass spectrum is saturated, dilute the sample per Sections 13.4.1 through 13.4.3.

**13.6** Report results for all pollutants, labeled compounds, and tentatively identified compounds found in all standards, blanks, and samples to three significant figures. For samples containing less than 1% solids, the units are µg/L; and for undiluted samples containing 1% solids or greater, units are µg/kg.

**13.6.1** Results for samples which have been diluted are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 13.4), or at which no m/z in the spectrum is saturated (Section 13.5). For compounds having a labeled analog, results are reported at the least dilute level at which the area at the quantitation m/z is within the calibration range (Section 13.4) and the labeled compound recovery is within the normal range for the method (Section 14.2).

## 14. ANALYSIS OF COMPLEX SAMPLES

**14.1** Some samples may contain high levels (>1000 µg/kg) of the compounds of interest and of interfering compounds. Some samples will foam excessively when purged. Others will overload the trap or the GC column.

**14.2** When the recovery of any labeled compound is outside the range given in Table 6, dilute 0.5 mL of samples containing less than 1% solids, or 0.5 g of samples containing 1% solids or greater, with 4.5 mL of reagent water and analyze this diluted sample. If the recovery remains outside of the range for this diluted sample, the aqueous performance standard shall be analyzed (Section 11) and calibration verified (Section 11.5). If the recovery for the labeled compound in the aqueous performance standard is outside the range given in Table 6, the analytical system is out of control. In this case, the instrument shall be repaired, the performance specifications in Section 11 shall be met, and the analysis of the undiluted sample shall be repeated. If the recovery for the aqueous performance standard is within the range given in Table 6, then the method does not apply to the sample being analyzed, and the result may not be reported for regulatory compliance purposes.

**14.3** When a high level of the pollutant is present, reverse search computer programs may misinterpret the spectrum of chromatographically unresolved pollutant and labeled compound pairs with overlapping spectra. Examine each chromatogram for peaks greater than the height of the internal standard peaks. These peaks can obscure the compounds of interest.

## 15. METHOD PERFORMANCE

**15.1** The specifications for this method were taken from the interlaboratory validation of EPA Method 624 (Reference 10). Method 1624 has been shown to yield slightly better performance on treated effluents than method 624. Results of initial tests of this method at a purge temperature of 80°C can be found in Reference 11 and results of initial tests of this method on municipal sludge can be found in Reference 12.

**15.2** A chromatogram of the 20 µg/L aqueous performance standards (Sections 6.7.2 and 11.1) is shown in Figure 9.

# Reference


1. "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," USEPA, EMSL Cincinnati, OH 45268, EPA-600/4-80-025 (April 1980).
2. Bellar, T. A. and Lichtenberg, J. J., "Journal American Water Works Association," 66, 739 (1974).
3. Bellar, T. A. and Lichtenberg, J. J., "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," in *Measurement of Organic Pollutants in Water and Wastewater*, C. E. VanHall, ed., American Society for Testing Materials, Philadelphia, PA, Special Technical Publication 686, (1978).
4. National Standard Reference Data System, "Mass Spectral Tape Format," U.S. National Bureau of Standards (1979 and later attachments).
5. "Working with Carcinogens," DHEW, PHS, NIOSH, Publication 77-206 (1977).
6. "OSHA Safety and Health Standards, General Industry," 29 *CFR* 1910, OSHA 2206, (1976).
7. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety (1979).
8. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL Cincinnati, OH 45268, EPA-4-79-019 (March 1979).
9. "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL Cincinnati, OH 45268, EPA-4-79-020 (March 1979).
10. "Method 624--Purgeables", 40 *CFR* Part 136 (49 *FR* 43234), 26 October 1984.
11. "Narrative for SAS 106: Development of an Isotope Dilution GC/MS Method for Hot Purge and-Trap Volatiles Analysis," S-CUBED Division of Maxwell Laboratories, Inc., Prepared for W. A. Telliard, Industrial Technology Division (WH-552), USEPA, 401 M St. SW, Washington DC 20460 (July 1986).
12. Colby, Bruce N. and Ryan, Philip W., "Initial Evaluation of Methods 1634 and 1635 for the Analysis of Municipal Wastewater Treatment Sludges by Isotope Dilution GCMS," Pacific Analytical Inc., Prepared for W. A. Telliard, Industrial Technology Division (WH-552), USEPA, 401 M St. SW, Washington DC 20460 (July 1986).

| 532 allyl alcohol | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 42 | 30 | 43 | 39 | 44 | 232 | 45 | 12 | 53 | 13 | 55 | 59 |
| 56 | 58 | 57 | 1000 | 58 | 300 | 61 | 15 | | | | |
| 533 carbon disulfide | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 44 | 282 | 46 | 10 | 64 | 14 | 76 | 1000 | 77 | 27 | 78 | 82 |
| 534 2-chloro-1,3-butadiene (chloroprene) | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 48 | 21 | 49 | 91 | 50 | 223 | 51 | 246 | 52 | 241 | 53 | 1000 |
| 54 | 41 | 61 | 30 | 62 | 54 | 63 | 11 | 64 | 16 | 73 | 21 |
| 87 | 12 | 88 | 452 | 89 | 22 | 90 | 137 | | | | |
| 535 chloroacetonitrile | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 47 | 135 | 48 | 1000 | 49 | 88 | 50 | 294 | 51 | 12 | 73 | 22 |
| 74 | 43 | 75 | 884 | 76 | 39 | 77 | 278 | | | | |
| 536 3-chloropropene | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 35 | 39 | 36 | 40 | 40 | 44 | 42 | 206 | 47 | 40 | 58 | 35 |
| 49 | 176 | 51 | 64 | 52 | 31 | 61 | 29 | 73 | 22 | 75 | 138 |
| 76 | 1000 | 77 | 74 | 78 | 324 | | | | | | |
| 537 crotonaldehyde | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 35 | 26 | 40 | 28 | 42 | 339 | 43 | 48 | 44 | 335 | 49 | 27 |
| 50 | 40 | 51 | 20 | 52 | 21 | 53 | 31 | 55 | 55 | 68 | 24 |
| 69 | 511 | 70 | 1000 | 71 | 43 | | | | | | |

538 1,2-dibromoethane (EDB)

| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 79 | 50 | 80 | 13 | 31 | 51 | 82 | 15 | 93 | 54 | 95 | 42 |
| 105 | 32 | 106 | 29 | 107 | 1000 | 108 | 38 | 109 | 922 | 110 | 19 |
| 186 | 13 | 188 | 27 | 190 | 13 | | | | | | |

539 dibromomethane

| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 43 | 99 | 44 | 101 | 45 | 30 | 79 | 184 | 80 | 35 | 81 | 175 |
| 91 | 142 | 92 | 61 | 93 | 1000 | 94 | 64 | 95 | 875 | 160 | 18 |
| 172 | 375 | 173 | 14 | 174 | 719 | 175 | 12 | 176 | 342 | | |

540 trans-1,4-dichloro-2-butene

| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 49 | 166 | 50 | 171 | 51 | 289 | 52 | 85 | 53 | 878 | 54 | 273 |
| 62 | 286 | 64 | 91 | 75 | 1000 | 77 | 323 | 88 | 246 | 89 | 415 |
| 90 | 93 | 91 | 129 | 124 | 138 | 126 | 86 | 128 | 12 | | |

541 1,3-dichloropropane

| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 15 | 42 | 44 | 47 | 19 | 48 | 20 | 49 | 193 | 51 | 55 |
| 61 | 18 | 62 | 22 | 63 | 131 | 65 | 38 | 75 | 47 | 76 | 1000 |
| 77 | 46 | 78 | 310 | 79 | 12 | | | | | | |

542 cis-1,3-dichloropropene

| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 37 | 262 | 38 | 269 | 39 | 998 | 49 | 596 | 51 | 189 | 75 | 1000 |
| 77 | 328 | 110 | 254 | 112 | 161 | | | | | | |

543 ethyl cyanide

| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 44 | 115 | 50 | 34 | 51 | 166 | 52 | 190 | 53 | 127 | 54 | 1000 |
| 55 | 193 | | | | | | | | | | |

544 ethyl methacrylate

| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 42 | 127 | 43 | 48 | 45 | 155 | 55 | 32 | 58 | 39 | 68 | 60 |
| 69 | 1000 | 70 | 83 | 71 | 25 | 85 | 14 | 86 | 169 | 87 | 21 |
| 96 | 17 | 99 | 93 | 113 | 11 | 114 | 119 | | | | |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 545 2-hexanone (methyl butyl ketone) | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 42 | 61 | 43 | 1000 | 44 | 24 | 55 | 12 | 57 | 130 | 58 | 382 |
| 59 | 21 | 71 | 36 | 85 | 37 | 100 | 56 | | | | |
| 546 iodomethane | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z. | int. | m/z | int. | m/z | int. |
| 44 | 57 | 127 | 328 | 128 | 17 | 139 | 39 | 140 | 34 | 141 | 120 |
| 142 | 1000 | 143 | 12 | | | | | | | | |
| 547 isobutyl alcohol | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 34 | 21 | 35 | 13 | 36 | 13 | 37 | 11 | 39 | 10 | 42 | 575 |
| 43 | 1000 | 44 | 42 | 45 | 21 | 55 | 40 | 56 | 37 | 57 | 21 |
| 59 | 25 | 73 | 12 | 74 | 63 | | | | | | |
| 548 methacrylonitrile | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 38 | 24 | 39 | 21 | 41 | 26 | 42 | 100 | 49 | 19 | 50 | 60 |
| 51 | 214 | 52 | 446 | 53 | 19 | 62 | 24 | 63 | 59 | 64 | 136 |
| 65 | 55 | 66 | 400 | 67 | 1000 | 68 | 51 | | | | |
| 549 methyl methacrylate | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 42 | 127 | 43 | 52 | 45 | 48 | 53 | 30 | 55 | 100 | 56 | 49 |
| 59 | 124 | 68 | 28 | 69 | 1000 | 70 | 51 | 82 | 26 | 85 | 45 |
| 98 | 20 | 99 | 89 | 100 | 442 | 101 | 22 | | | | |
| 550 4-methyl-2-pentanone (methyl isoboutyl ketone; MIBK) | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 42 | 69 | 43 | 1000 | 44 | 54 | 53 | 11 | 55 | 15 | 56 | 13 |
| 57 | 205 | 58 | 346 | 59 | 20 | 67 | 12 | 69 | 10 | 85 | 96 |
| 100 | 94 | | | | | | | | | | |
| 551 1,1,1,2-tetrachloroethane | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 47 | 144 | 49 | 163 | 60 | 303 | 61 | 330 | 62 | 98 | 82 | 45 |
| 84 | 31 | 95 | 416 | 96 | 152 | 97 | 270 | 98 | 84 | 117 | 804 |
| 121 | 236 | 131 | 1000 | 133 | 955 | 135 | 301 | | | | |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 552 trichlorofluoromethane | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 44 | 95 | 47 | 153 | 49 | 43 | 51 | 21 | 52 | 14 | 66 | 162 |
| 68 | 53 | 82 | 40 | 84 | 28 | 101 | 1000 | 102 | 10 | 103 | 671 |
| 105 | 102 | 117 | 16 | 119 | 14 | | | | | | |
| 553 1,2,3-trichloropropane | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 49 | 285 | 51 | 87 | 61 | 300 | 62 | 107 | 63 | 98 | 75 | 1000 |
| 76 | 38 | 77 | 302 | 83 | 23 | 96 | 29 | 97 | 166 | 98 | 20 |
| 99 | 103 | 110 | 265 | 111 | 28 | 112 | 164 | 114 | 25 | | |
| 554 vinyl acetate | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 36 | 5 | 42 | 103 | 43 | 1000 | 44 | 70 | 45 | 8 | 86 | 57 |
| 951 m-xylene | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 65 | 62 | 77 | 124 | 91 | 1000 | 105 | 245 | 106 | 580 | | |
| 951 0- + p-xylene | | | | | | | | | | | |
| m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. | m/z | int. |
| 51 | 88 | 77 | 131 | 91 | 1000 | 105 | 229 | 106 | 515 | | |

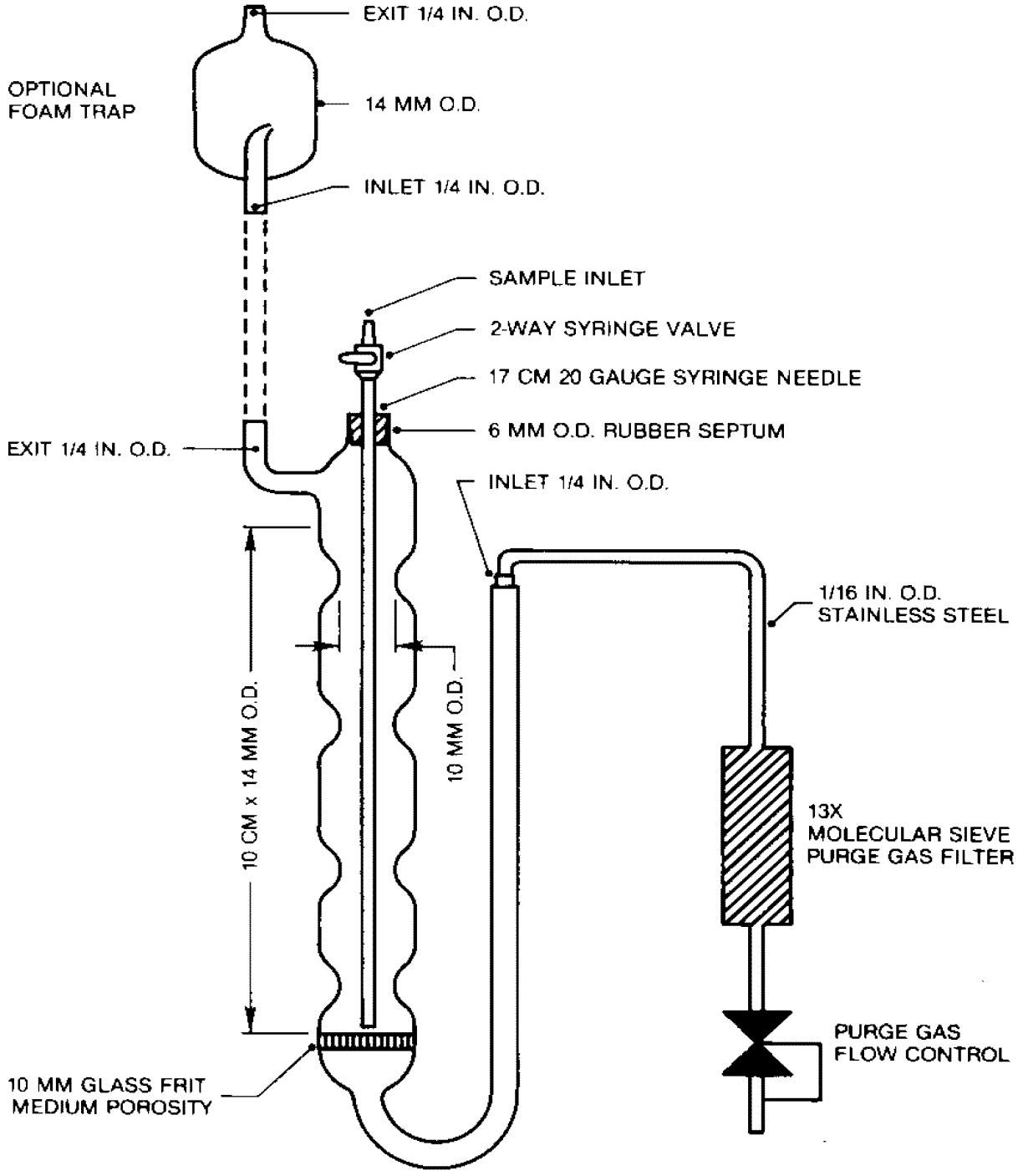



FIGURE 1 Purging Device for Waters

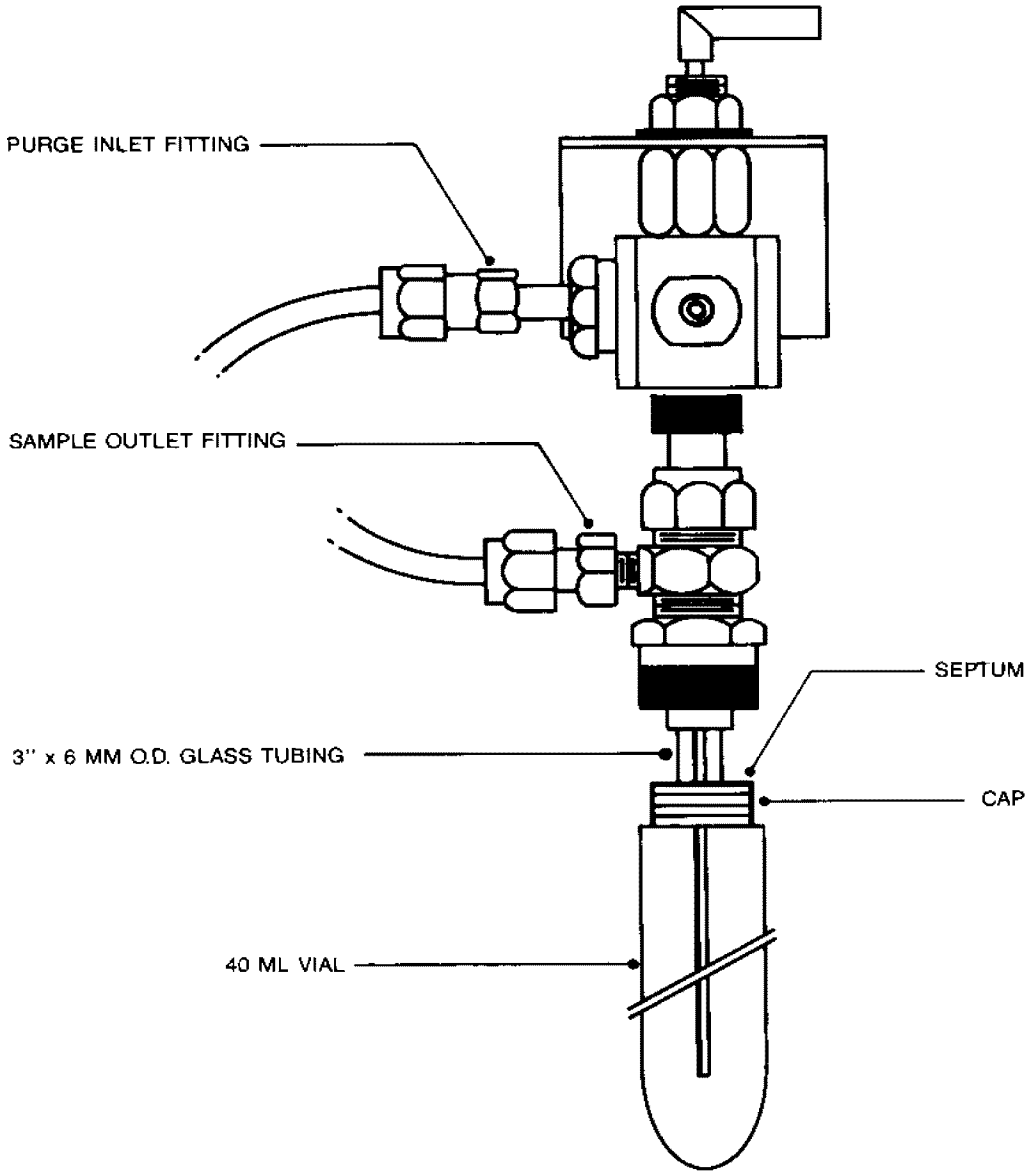



FIGURE 2 Purging Device for Soils or Waters

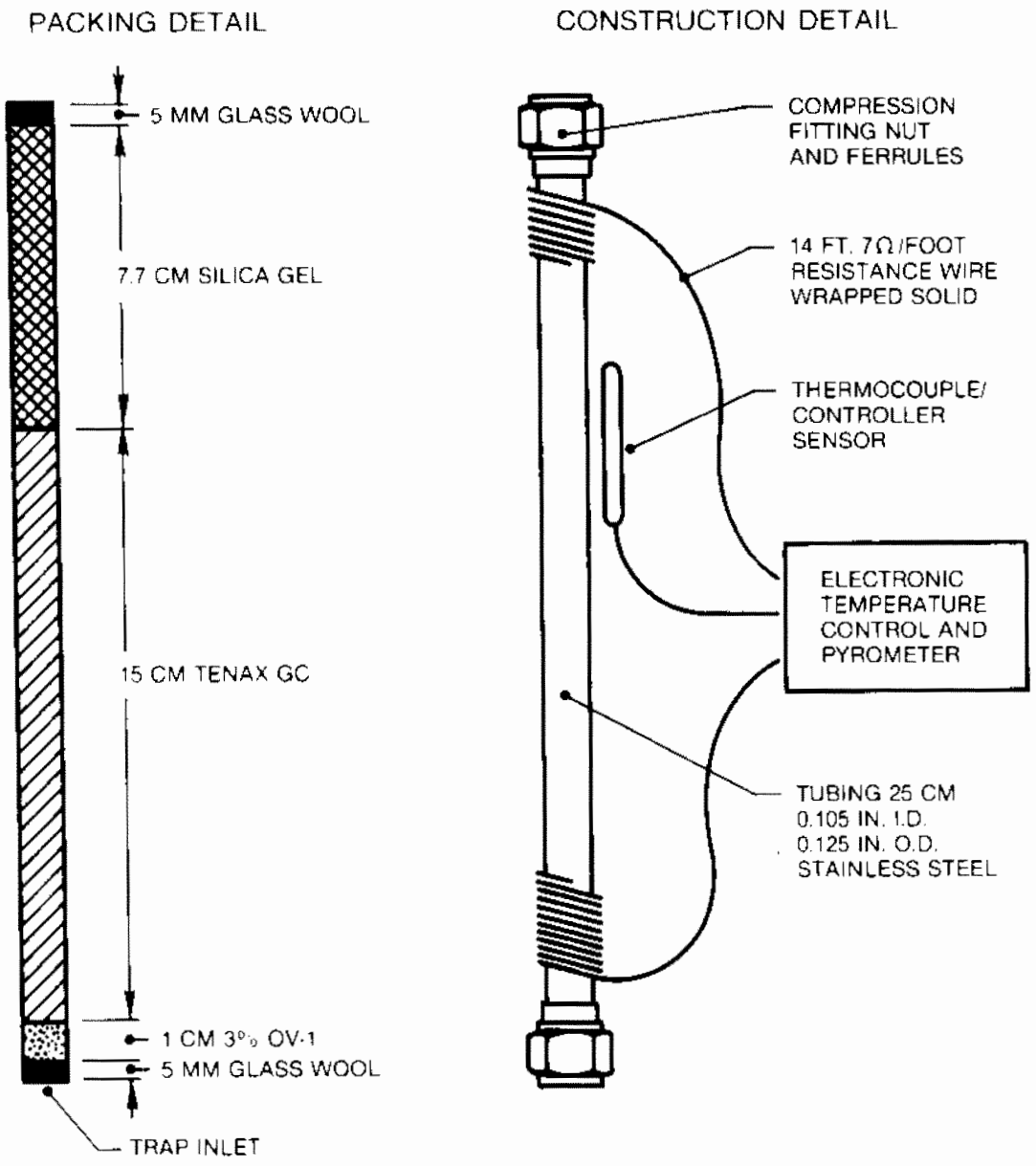
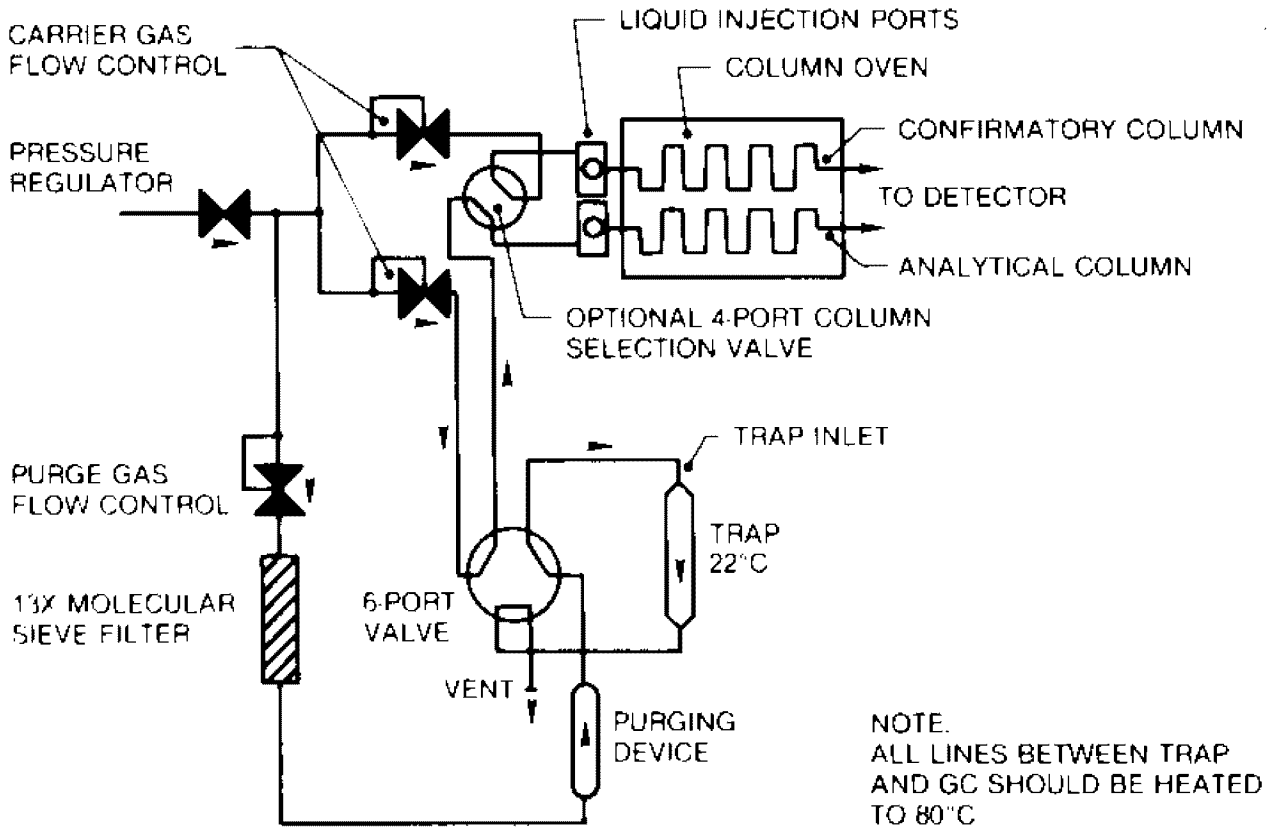



FIGURE 3 Trap Construction and Packings




# FIGURE 4 Schematic of Purge and Trap Device--Purge Mode

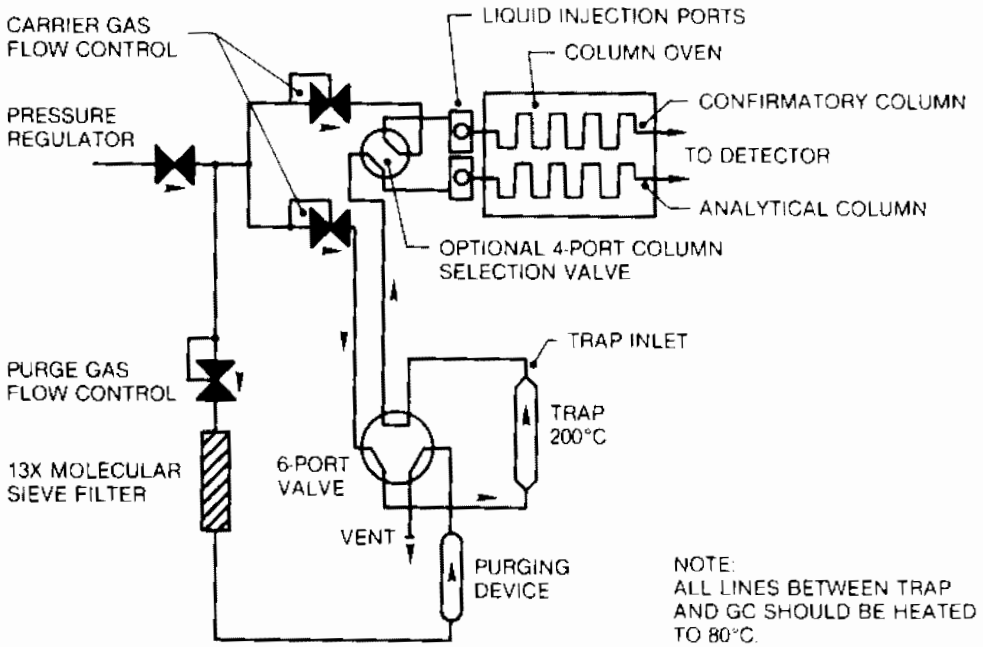



FIGURE 5 Schematic of Purge and Trap Device--Desorb Mode

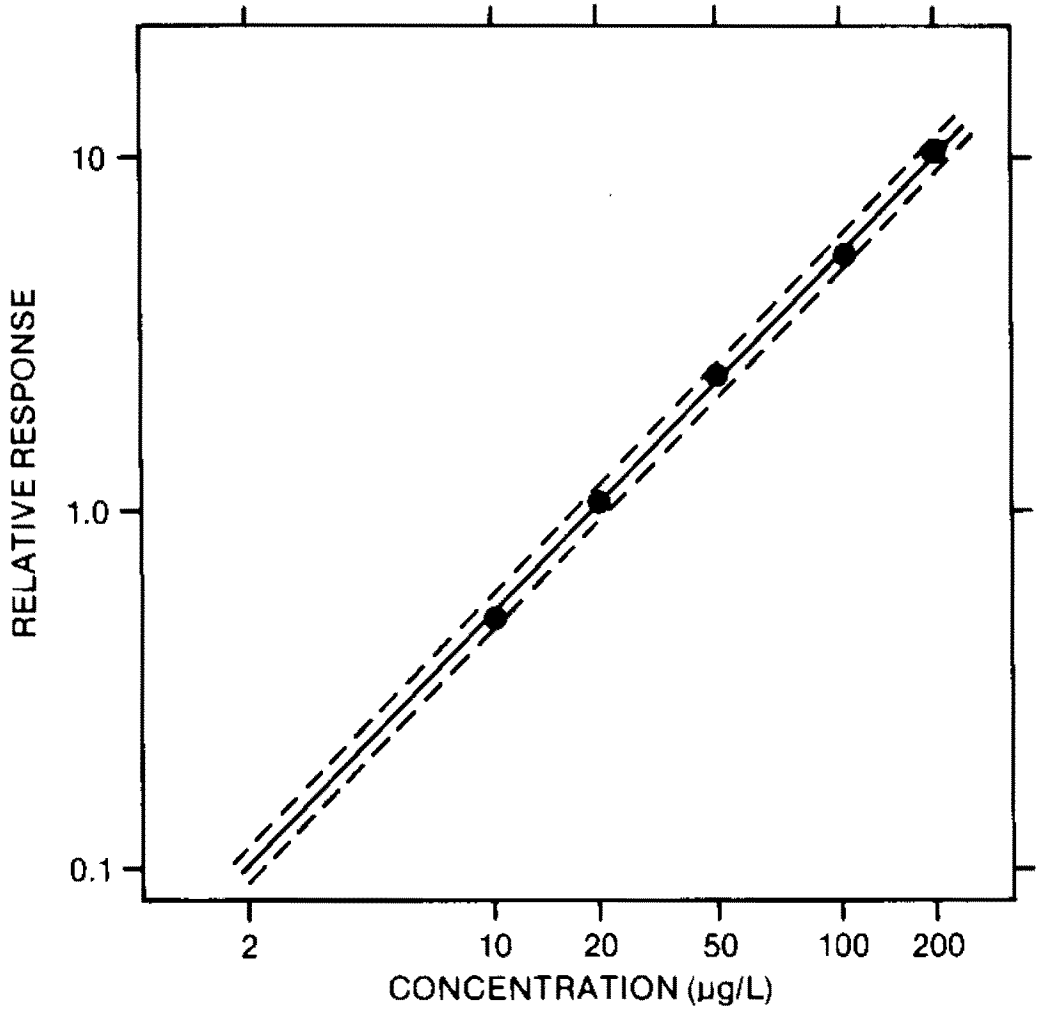



FIGURE 6 Relative Response Calibration Curve for Toluene. The Dotted Lines Enclose a +/- 10 Percent Error Window

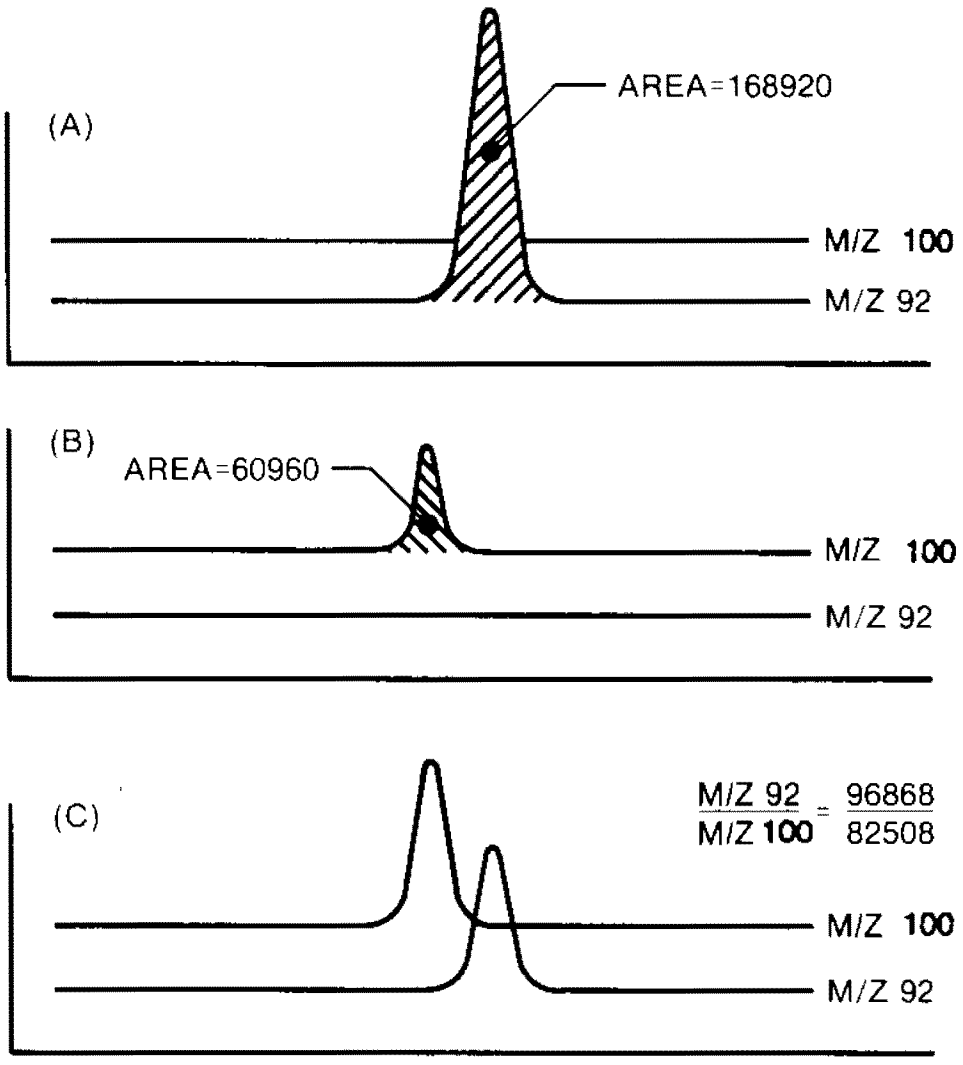



FIGURE 7 Extracted Ion Current Profiles for (A) Toluene, (B) Toluene-$d_8$, and (C) a Mixture of Toluene and Toluene-$d_8$

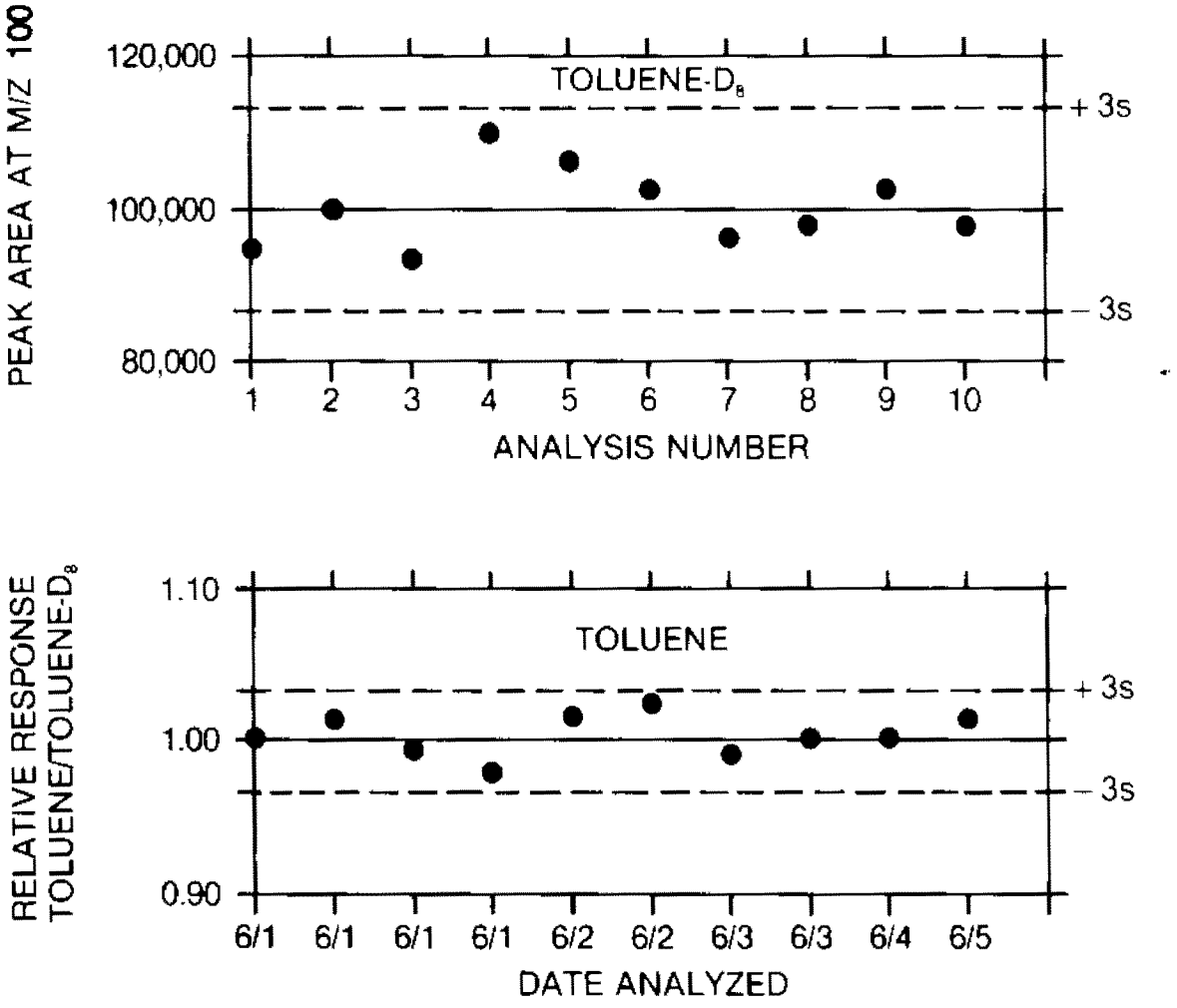



FIGURE 8 Quality Control Charts Showing Area (top graph) and Relative Response of Toluene to Toluene-d8 (lower graph) Plotted as Function of Time or Analysis Number

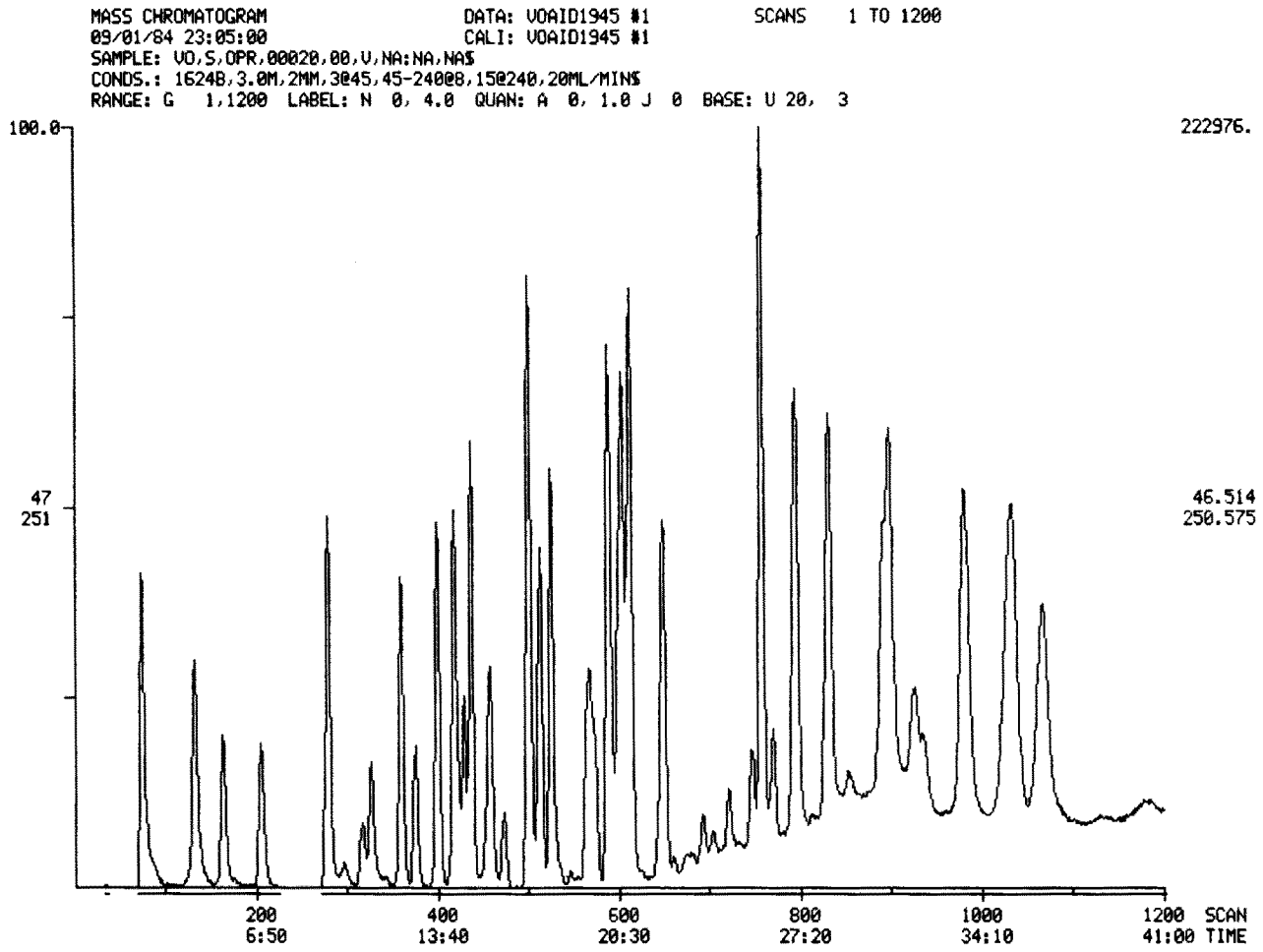



FIGURE 9 Chromatogram of Aqueous Performance Standard

METHOD 8260B
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/
MASS SPECTROMETRY (GC/MS)

## 1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

| | | Appropriate Preparation Technique[a] | | | | | |
|---|---|---|---|---|---|---|---|
| Compound | CAS No.[b] | 5030/ 5035 | 5031 | 5032 | 5021 | 5041 | Direct Inject. |
| Acetone | 67-64-1 | pp | c | c | nd | c | c |
| Acetonitrile | 75-05-8 | pp | c | nd | nd | nd | c |
| Acrolein (Propenal) | 107-02-8 | pp | c | c | nd | nd | c |
| Acrylonitrile | 107-13-1 | pp | c | c | nd | c | c |
| Allyl alcohol | 107-18-6 | ht | c | nd | nd | nd | c |
| Allyl chloride | 107-05-1 | c | nd | nd | nd | nd | c |
| Benzene | 71-43-2 | c | nd | c | c | c | c |
| Benzyl chloride | 100-44-7 | c | nd | nd | nd | nd | c |
| Bis(2-chloroethyl)sulfide | 505-60-2 | pp | nd | nd | nd | nd | c |
| Bromoacetone | 598-31-2 | pp | nd | nd | nd | nd | c |
| Bromochloromethane | 74-97-5 | c | nd | c | c | c | c |
| Bromodichloromethane | 75-27-4 | c | nd | c | c | c | c |
| 4-Bromofluorobenzene (surr) | 460-00-4 | c | nd | c | c | c | c |
| Bromoform | 75-25-2 | c | nd | c | c | c | c |
| Bromomethane | 74-83-9 | c | nd | c | c | c | c |
| n-Butanol | 71-36-3 | ht | c | nd | nd | nd | c |
| 2-Butanone (MEK) | 78-93-3 | pp | c | c | nd | nd | c |
| t-Butyl alcohol | 75-65-0 | pp | c | nd | nd | nd | c |
| Carbon disulfide | 75-15-0 | pp | nd | c | nd | c | c |
| Carbon tetrachloride | 56-23-5 | c | nd | c | c | c | c |
| Chloral hydrate | 302-17-0 | pp | nd | nd | nd | nd | c |
| Chlorobenzene | 108-90-7 | c | nd | c | c | c | c |
| Chlorobenzene-$d_5$ (IS) | | c | nd | c | c | c | c |
| Chlorodibromomethane | 124-48-1 | c | nd | c | nd | c | c |
| Chloroethane | 75-00-3 | c | nd | c | c | c | c |
| 2-Chloroethanol | 107-07-3 | pp | nd | nd | nd | nd | c |
| 2-Chloroethyl vinyl ether | 110-75-8 | c | nd | c | nd | nd | c |
| Chloroform | 67-66-3 | c | nd | c | c | c | c |
| Chloromethane | 74-87-3 | c | nd | c | c | c | c |
| Chloroprene | 126-99-8 | c | nd | nd | nd | nd | c |
| 3-Chloropropionitrile | 542-76-7 | l | nd | nd | nd | nd | pc |

(continued)

| Compound | CAS No.[b] | Appropriate Preparation Technique[a] 5030/ 5035 | 5031 | 5032 | 5021 | 5041 | Direct Inject. |
|---|---|---|---|---|---|---|---|
| Crotonaldehyde | 4170-30-3 | pp | c | nd | nd | nd | c |
| 1,2-Dibromo-3-chloropropane | 96-12-8 | pp | nd | nd | c | nd | c |
| 1,2-Dibromoethane | 106-93-4 | c | nd | nd | c | nd | c |
| Dibromomethane | 74-95-3 | c | nd | c | c | c | c |
| 1,2-Dichlorobenzene | 95-50-1 | c | nd | nd | c | nd | c |
| 1,3-Dichlorobenzene | 541-73-1 | c | nd | nd | c | nd | c |
| 1,4-Dichlorobenzene | 106-46-7 | c | nd | nd | c | nd | c |
| 1,4-Dichlorobenzene-$d_4$ (IS) | | c | nd | nd | c | nd | c |
| cis-1,4-Dichloro-2-butene | 1476-11-5 | c | nd | c | nd | nd | c |
| trans-1,4-Dichloro-2-butene | 110-57-6 | pp | nd | c | nd | nd | c |
| Dichlorodifluoromethane | 75-71-8 | c | nd | c | c | nd | c |
| 1,1-Dichloroethane | 75-34-3 | c | nd | c | c | c | c |
| 1,2-Dichloroethane | 107-06-2 | c | nd | c | c | c | c |
| 1,2-Dichloroethane-$d_4$ (surr) | | c | nd | c | c | c | c |
| 1,1-Dichloroethene | 75-35-4 | c | nd | c | c | c | c |
| trans-1,2-Dichloroethene | 156-60-5 | c | nd | c | c | c | c |
| 1,2-Dichloropropane | 78-87-5 | c | nd | c | c | c | c |
| 1,3-Dichloro-2-propanol | 96-23-1 | pp | nd | nd | nd | nd | c |
| cis-1,3-Dichloropropene | 10061-01-5 | c | nd | c | nd | c | c |
| trans-1,3-Dichloropropene | 10061-02-6 | c | nd | c | nd | c | c |
| 1,2,3,4-Diepoxybutane | 1464-53-5 | c | nd | nd | nd | nd | c |
| Diethyl ether | 60-29-7 | c | nd | nd | nd | nd | c |
| 1,4-Difluorobenzene (IS) | 540-36-3 | nd | nd | nd | nd | c | nd |
| 1,4-Dioxane | 123-91-1 | pp | c | c | nd | nd | c |
| Epichlorohydrin | 106-89-8 | l | nd | nd | nd | nd | c |
| Ethanol | 64-17-5 | l | c | c | nd | nd | c |
| Ethyl acetate | 141-78-6 | l | c | nd | nd | nd | c |
| Ethylbenzene | 100-41-4 | c | nd | c | c | c | c |
| Ethylene oxide | 75-21-8 | pp | c | nd | nd | nd | c |
| Ethyl methacrylate | 97-63-2 | c | nd | c | nd | nd | c |
| Fluorobenzene (IS) | 462-06-6 | c | nd | nd | nd | nd | nd |
| Hexachlorobutadiene | 87-68-3 | c | nd | nd | c | nd | c |
| Hexachloroethane | 67-72-1 | l | nd | nd | nd | nd | c |
| 2-Hexanone | 591-78-6 | pp | nd | c | nd | nd | c |
| 2-Hydroxypropionitrile | 78-97-7 | l | nd | nd | nd | nd | pc |
| Iodomethane | 74-88-4 | c | nd | c | nd | c | c |
| Isobutyl alcohol | 78-83-1 | pp | c | nd | nd | nd | c |
| Isopropylbenzene | 98-82-8 | c | nd | nd | c | nd | c |
| Malononitrile | 109-77-3 | pp | nd | nd | nd | nd | c |
| Methacrylonitrile | 126-98-7 | pp | l | nd | nd | nd | c |
| Methanol | 67-56-1 | l | c | nd | nd | nd | c |
| Methylene chloride | 75-09-2 | c | nd | c | c | c | c |
| Methyl methacrylate | 80-62-6 | c | nd | nd | nd | nd | c |
| 4-Methyl-2-pentanone (MIBK) | 108-10-1 | pp | c | c | nd | nd | c |
| Naphthalene | 91-20-3 | c | nd | nd | c | nd | c |

(continued)

| Compound | CAS No.[b] | Appropriate Preparation Technique[a] 5030/ 5035 | 5031 | 5032 | 5021 | 5041 | Direct Inject. |
|---|---|---|---|---|---|---|---|
| Nitrobenzene | 98-95-3 | c | nd | nd | nd | nd | c |
| 2-Nitropropane | 79-46-9 | c | nd | nd | nd | nd | c |
| N-Nitroso-di-n-butylamine | 924-16-3 | pp | c | nd | nd | nd | c |
| Paraldehyde | 123-63-7 | pp | c | nd | nd | nd | c |
| Pentachloroethane | 76-01-7 | l | nd | nd | nd | nd | c |
| 2-Pentanone | 107-87-9 | pp | c | nd | nd | nd | c |
| 2-Picoline | 109-06-8 | pp | c | nd | nd | nd | c |
| 1-Propanol | 71-23-8 | pp | c | nd | nd | nd | c |
| 2-Propanol | 67-63-0 | pp | c | nd | nd | nd | c |
| Propargyl alcohol | 107-19-7 | pp | l | nd | nd | nd | c |
| β-Propiolactone | 57-57-8 | pp | nd | nd | nd | nd | c |
| Propionitrile (ethyl cyanide) | 107-12-0 | ht | c | nd | nd | nd | pc |
| n-Propylamine | 107-10-8 | c | nd | nd | nd | nd | c |
| Pyridine | 110-86-1 | l | c | nd | nd | nd | c |
| Styrene | 100-42-5 | c | nd | c | c | c | c |
| 1,1,1,2-Tetrachloroethane | 630-20-6 | c | nd | nd | c | c | c |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | c | nd | c | c | c | c |
| Tetrachloroethene | 127-18-4 | c | nd | c | c | c | c |
| Toluene | 108-88-3 | c | nd | c | c | c | c |
| Toluene-$d_8$ (surr) | 2037-26-5 | c | nd | c | c | c | c |
| o-Toluidine | 95-53-4 | pp | c | nd | nd | nd | c |
| 1,2,4-Trichlorobenzene | 120-82-1 | c | nd | nd | c | nd | c |
| 1,1,1-Trichloroethane | 71-55-6 | c | nd | c | c | c | c |
| 1,1,2-Trichloroethane | 79-00-5 | c | nd | c | c | c | c |
| Trichloroethene | 79-01-6 | c | nd | c | c | c | c |
| Trichlorofluoromethane | 75-69-4 | c | nd | c | c | c | c |
| 1,2,3-Trichloropropane | 96-18-4 | c | nd | c | c | c | c |
| Vinyl acetate | 108-05-4 | c | nd | c | nd | nd | c |
| Vinyl chloride | 75-01-4 | c | nd | c | c | c | c |
| o-Xylene | 95-47-6 | c | nd | c | c | c | c |
| m-Xylene | 108-38-3 | c | nd | c | c | c | c |
| p-Xylene | 106-42-3 | c | nd | c | c | c | c |

[a] See Sec. 1.2 for other appropriate sample preparation techniques
[b] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80°C
nd = Not determined
l = Inappropriate technique for this analyte
pc = Poor chromatographic behavior
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
surr = Surrogate
IS = Internal Standard

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Chloroacetonitrile
1-Chlorobutane
1-Chlorohexane
2-Chlorotoluene
4-Chlorotoluene
Dibromofluoromethane
cis-1,2-Dichloroethene
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
p-Isopropyltoluene
Methyl acrylate
Methyl-t-butyl ether
Pentafluorobenzene
n-Propylbenzene
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

1.4 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

## 2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Sec. 1.2). The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

## 3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explained this in text accompanying the uncorrected data.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

3.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

3.7 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.8 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

3.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

## 4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device for aqueous samples - Described in Method 5030.

4.2 Purge-and-trap device for solid samples - Described in Method 5035.

4.3 Automated static headspace device for solid samples - Described in Method 5021.

4.4 Azeotropic distillation apparatus for aqueous and solid samples - Described in Method 5031.

4.5 Vacuum distillation apparatus for aqueous, solid and tissue samples - Described in Method 5032.

4.6 Desorption device for air trapping media for air samples - Described in Method 5041.

4.7 Air sampling loop for sampling from Tedlar® bags for air samples - Described in Method 0040.

4.8 Injection port liners (HP Catalog #18740-80200, or equivalent) - modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven (see illustration below). A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

4.9 Gas chromatography/mass spectrometer/data system

4.9.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.9.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.9.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

4.9.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

4.9.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.9.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.9.2 Gas chromatographic columns

4.9.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5-µm film thickness, or equivalent.

4.9.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), $Rt_x$-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

4.9.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, $Rt_x$-5, SPB-5, or equivalent), 1-µm film thickness.

4.9.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

4.9.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.9.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

4.9.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

4.9.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

4.9.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 8.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.9.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.10 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000-µL.

4.11 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.12 Syringes - 5-, 10-, or 25-mL, gas-tight with shutoff valve.

4.13 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

4.15 Vials - 2-mL, for GC autosampler.

4.16 Disposable pipets - Pasteur.

4.17 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.18 Spatula - Stainless steel.

## 5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, $CH_3OH$ - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to

5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.7.5 Frequency of Standard Preparation

5.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.7.6 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichloro-difluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100-µL or 500-µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

5.7.6.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.9 The concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

| Gas Volume | Calibration Concentration |
|---|---|
| 40 µL | 20 µg/L |
| 100 µL | 50 µg/L |
| 200 µL | 100 µg/L |
| 300 µL | 150 µg/L |
| 400 µL | 200 µg/L |

5.7.6.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

| Gas Volume | Calibration Concentration |
|---|---|
| 10 µL | 1 µg/L |
| 20 µL | 2 µg/L |
| 50 µL | 5 µg/L |
| 100 µL | 10 µg/L |
| 250 µL | 25 µg/L |

5.8 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.9 Surrogate standards - The recommended surrogates are toluene-$d_8$, 4-bromofluorobenzene, 1,2-dichloroethane-$d_4$, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-$d_5$, and 1,4-dichlorobenzene-$d_4$. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

5.12 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

5.12.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.4 for guidance on calibration verification.

5.12.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.12.4 The calibration standards must also contain the internal standards chosen for the analysis.

5.13 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.13.1 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.2 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

5.13.3 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

## 7.0 PROCEDURE

7.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

7.1.1 Direct injection - This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

7.1.2 Purge-and-trap - This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

7.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

7.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

7.1.3 Vacuum distillation - this technique may be used for the introduction of volatile organics from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system.

7.1.4 Automated static headspace - this technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

7.1.5 Cartridge desorption - this technique may be for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

7.2 Recommended chromatographic conditions

7.2.1 General conditions

| | |
|---|---|
| Injector temperature: | 200 - 225°C |
| Transfer line temperature: | 250 - 300°C |

7.2.2 Column 1 and Column 2 with cryogenic cooling (example chromatograms are presented in Figures 1 and 2)

| | |
|---|---|
| Carrier gas (He) flow rate: | 15 mL/min |
| Initial temperature: | 10°C, hold for 5 minutes |
| Temperature program: | 6°C/min to 70°C, then 15°C/min to 145°C |
| Final temperature: | 145°C, hold until all expected compounds have eluted. |

7.2.5 Direct injection - Column 2

| | |
|---|---|
| Carrier gas (He) flow rate: | 4 mL/min |
| Column: | J&W DB-624, 70m x 0.53 mm |
| Initial temperature: | 40°C, hold for 3 minutes |
| Temperature program: | 8°C/min |
| Final temperature: | 260°C, hold until all expected compounds have eluted. |
| Column Bake out: | 75 minutes |
| Injector temperature: | 200-225°C |
| Transfer line temperature: | 250-300°C |

7.2.6 Direct split interface - Column 4

| | |
|---|---|
| Carrier gas (He) flow rate: | 1.5 mL/min |
| Initial temperature: | 35°C, hold for 2 minutes |
| Temperature program: | 4°C/min to 50°C<br>10°C/min to 220°C |
| Final temperature: | 220°C, hold until all expected compounds have eluted |
| Split ratio: | 100:1 |
| Injector temperature: | 125°C |

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

| | |
|---|---|
| Mass range: | 35 - 260 amu |
| Scan time: | 0.6 - 2 sec/scan |
| Source temperature: | According to manufacturer's specifications |
| Ion trap only: | Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations |

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of

BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

7.3.1.2 Use the BFB mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (see Sec. 5.12 and Method 8000). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

7.3.2.2 The internal standards selected in Sec. 5.10 should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion.

7.3.2.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

7.3.3 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 - 2 µL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

7.3.4 Tabulate the area response of the characteristic ions (see Table 5) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured (Sec. 7.6.2).

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

$A_s$ = Peak area (or height) of the analyte or surrogate.
$A_{is}$ = Peak area (or height) of the internal standard.
$C_s$ = Concentration of the analyte or surrogate.
$C_{is}$ = Concentration of the internal standard.

7.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

7.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.5.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

| | |
|---|---|
| Chloromethane | 0.10 |
| 1,1-Dichloroethane | 0.10 |
| Bromoform | 0.10 |
| Chlorobenzene | 0.30 |
| 1,1,2,2-Tetrachloroethane | 0.30 |

7.3.6 Calibration check compounds (CCCs)

7.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of Method 8000.

7.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

$RF_i$ = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

7.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000. The CCCs are:

| | |
|---|---|
| 1,1-Dichloroethene | Toluene |
| Chloroform | Ethylbenzene |
| 1,2-Dichloropropane | Vinyl chloride |

7.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

7.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.8 Linearity of target analytes

7.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Sec. 7.7.2).

7.3.8.2 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 of Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The 20% RSD criteria in Method 8000 pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000 for method blank performance criteria.

7.4.4 System Performance Check Compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 7.3.5.4). This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration Check Compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Sec. 7.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater

than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low detection levels.

7.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

7.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

7.5.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

7.5.6.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

7.5.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.6.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 7.5.5.

7.5.7 Compositing aqueous samples prior to GC/MS analysis

7.5.7.1 Add 5 mL of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

7.5.7.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

7.5.7.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

7.5.7.4 Once all the aliquots have been combined on the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Sec. 7.1).

7.5.7.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

7.5.8 Add 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution to each sample either manually or by autosampler. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of a non-aqueous sample will yield a concentration of 50 µg/kg of each standard.

If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.9 Add 10 µL of the matrix spike solution (Sec. 5.13) to a 5-mL aliquot of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 8.4 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

7.5.9.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

7.5.10 Analyze the sample following the procedure in the introduction method of choice.

7.5.10.1 For direct injection, inject 1 to 2 µL into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

7.5.10.2 The concentration of the internal standards, surrogates, and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2 µL injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

7.5.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.11.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.12 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library

searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

(1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.7.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.3.6). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas $A_x$ and $A_{is}$ should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8260:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria described in Sec. 7.4.4 and the CCC criteria in Sec. 7.4.5, each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The 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 indicate 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.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

## 9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested using purge-and-trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using purge-and-trap (Method 5030) with water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are presented in Tables 10 and 11 for TCLP volatiles in oil. The performance data were developed by spiking and analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, except for the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm, well below the regulatory concentrations. Prior to spiking, the new oil (an SAE 30-weight motor oil) was heated at 80°C overnight to remove volatiles. The used oil (a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of BTEX compounds and isobutanol. These contaminants contributed to the extremely high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

9.5 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand; a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon; and a surface garden soil. Sample preparation was by Method 5035. Each

sample was fortified with the analytes at a concentration of 4 µg/kg. These data are listed in Tables 17, 18, and 19. All data were calculated using fluorobenzene as the internal standard added to the soil sample prior to extraction. This causes some of the results to be greater than 100% recovery because the precision of results is sometimes as great as 28%.

9.5.1 In general, the recoveries of the analytes from the sand matrix are the highest, the C-Horizon soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

9.5.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, are somewhat greater than 100%. This is due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. Also, the garden soil results in Table 19 include some extraordinarily high recoveries for some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection, and to the fact that no background was subtracted.

9.6 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 12 to 16.

9.7 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 20 to 27.

9.8 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in two soil matrices: sand and a surface garden soil. Replicate samples were fortified with the analytes at concentrations of 10 µg/kg. These data are listed in Table 30. All data were calculated using the internal standards listed for each analyte in Table 28. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

9.8.1 If a detector other than an MS is used for analysis, consideration must be given to the choice of internal standards and surrogates. They must not coelute with any other analyte and must have similar properties to the analytes. The recoveries of the analytes are 50% or higher for each matrix studied. The recoveries of the gases or very volatile compounds are greater than 100% in some cases. Also, results include high recoveries of some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection.

9.8.2 The method detection limits using Method 5021 listed in Table 29 were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These MDLs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

9.9 The MDL concentrations listed in Table 31 were determined using Method 5041 in conjunction with Method 8260. They were obtained using cleaned blank VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under the test conditions, the MDLs for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

9.10 The EQL of sample taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 ppm (See Table 33). Matrix effects may cause the individual compound detection limits to be higher.

## 10.0 REFERENCES


1. Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water Method 524.2, U.S. Environmental Protection Agency, Office of Research Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1986.

2. Bellar, T.A., Lichtenberg, J.J, J. Amer. Water Works Assoc., 1974, 66(12), 739-744.

3. Bellar, T.A., Lichtenberg, J.J., "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds"; in Van Hall, Ed.; Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.

4. Budde, W.L., Eichelberger, J.W., "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, April 1980; EPA-600/4-79-020.

5. Eichelberger, J.W., Harris, L.E., Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems"; Analytical Chemistry 1975, 47, 995-1000.

6. Olynyk, P., Budde, W.L., Eichelberger, J.W., "Method Detection Limit for Methods 624 and 625"; Unpublished report, October 1980.

7. Non Cryogenic Temperatures Program and Chromatogram, Private Communications; M. Stephenson and F. Allen, EPA Region IV Laboratory, Athens, GA.

8. Marsden, P.J., Helms, C.L., Colby, B.N., "Analysis of Volatiles in Waste Oil"; Report for B. Lesnik, OSW/EPA under EPA contract 68-W9-001, 6/92.

9. Methods for the Determination of Organic Compounds in Drinking Water, Supplement II Method 524.2; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1992.

10. Flores, P., Bellar, T., "Determination of Volatile Organic Compounds in Soils Using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, December, 1992.

11. Bruce, M.L., Lee, R.P., Stephens, M.W., "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environmental Science and Technology 1992, 26, 160-163.

12. Cramer, P.H., Wilner, J., Stanley, J.S., "Final Report: Method for Polar, Water Soluble, Nonpurgeable Volatile Organics (VOCs)", For U.S. Environmental Protection Agency, Environmental Monitoring Support Laboratory, EPA Contract No. 68-C8-0041.

13. Hiatt, M.H., "Analysis of Fish and Sediment for Volatile Priority Pollutants", Analytical Chemistry 1981, 53, 1541.

14. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.

15. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

| Compound | Retention Time (minutes) | | | MDL[d] |
|---|---|---|---|---|
| | Column 1[a] | Column 2[b] | Column 2'[c] | (µg/L) |
| Dichlorodifluoromethane | 1.35 | 0.70 | 3.13 | 0.10 |
| Chloromethane | 1.49 | 0.73 | 3.40 | 0.13 |
| Vinyl Chloride | 1.56 | 0.79 | 3.93 | 0.17 |
| Bromomethane | 2.19 | 0.96 | 4.80 | 0.11 |
| Chloroethane | 2.21 | 1.02 | -- | 0.10 |
| Trichlorofluoromethane | 2.42 | 1.19 | 6.20 | 0.08 |
| Acrolein | 3.19 | | | |
| Iodomethane | 3.56 | | | |
| Acetonitrile | 4.11 | | | |
| Carbon disulfide | 4.11 | | | |
| Allyl chloride | 4.11 | | | |
| Methylene chloride | 4.40 | 2.06 | 9.27 | 0.03 |
| 1,1-Dichloroethene | 4.57 | 1.57 | 7.83 | 0.12 |
| Acetone | 4.57 | | | |
| trans-1,2-Dichloroethene | 4.57 | 2.36 | 9.90 | 0.06 |
| Acrylonitrile | 5.00 | | | |
| 1,1-Dichloroethane | 6.14 | 2.93 | 10.80 | 0.04 |
| Vinyl acetate | 6.43 | | | |
| 2,2-Dichloropropane | 8.10 | 3.80 | 11.87 | 0.35 |
| 2-Butanone | -- | | | |
| cis-1,2-Dichloroethene | 8.25 | 3.90 | 11.93 | 0.12 |
| Propionitrile | 8.51 | | | |
| Chloroform | 9.01 | 4.80 | 12.60 | 0.03 |
| Bromochloromethane | -- | 4.38 | 12.37 | 0.04 |
| Methacrylonitrile | 9.19 | | | |
| 1,1,1-Trichloroethane | 10.18 | 4.84 | 12.83 | 0.08 |
| Carbon tetrachloride | 11.02 | 5.26 | 13.17 | 0.21 |
| 1,1-Dichloropropene | -- | 5.29 | 13.10 | 0.10 |
| Benzene | 11.50 | 5.67 | 13.50 | 0.04 |
| 1,2-Dichloroethane | 12.09 | 5.83 | 13.63 | 0.06 |
| Trichloroethene | 14.03 | 7.27 | 14.80 | 0.19 |
| 1,2-Dichloropropane | 14.51 | 7.66 | 15.20 | 0.04 |
| Bromodichloromethane | 15.39 | 8.49 | 15.80 | 0.08 |
| Dibromomethane | 15.43 | 7.93 | 5.43 | 0.24 |
| Methyl methacrylate | 15.50 | | | |
| 1,4-Dioxane | 16.17 | | | |
| 2-Chloroethyl vinyl ether | -- | | | |
| 4-Methyl-2-pentanone | 17.32 | | | |
| trans-1,3-Dichloropropene | 17.47 | -- | 16.70 | -- |
| Toluene | 18.29 | 10.00 | 17.40 | 0.11 |
| cis-1,3-Dichloropropene | 19.38 | -- | 17.90 | -- |

TABLE 1 (cont.)

| Compound | Retention Time (minutes) | | | MDL[d] |
|---|---|---|---|---|
| | Column 1[a] | Column 2[b] | Column 2"[c] | (µg/L) |
| 1,1,2-Trichloroethane | 19.59 | 11.05 | 18.30 | 0.10 |
| Ethyl methacrylate | 20.01 | | | |
| 2-Hexanone | 20.30 | | | |
| Tetrachloroethene | 20.26 | 11.15 | 18.60 | 0.14 |
| 1,3-Dichloropropane | 20.51 | 11.31 | 18.70 | 0.04 |
| Dibromochloromethane | 21.19 | 11.85 | 19.20 | 0.05 |
| 1,2-Dibromoethane | 21.52 | 11.83 | 19.40 | 0.06 |
| 1-Chlorohexane | -- | 13.29 | -- | 0.05 |
| Chlorobenzene | 23.17 | 13.01 | 20.67 | 0.04 |
| 1,1,1,2-Tetrachloroethane | 23.36 | 13.33 | 20.87 | 0.05 |
| Ethylbenzene | 23.38 | 13.39 | 21.00 | 0.06 |
| p-Xylene | 23.54 | 13.69 | 21.30 | 0.13 |
| m-Xylene | 23.54 | 13.68 | 21.37 | 0.05 |
| o-Xylene | 25.16 | 14.52 | 22.27 | 0.11 |
| Styrene | 25.30 | 14.60 | 22.40 | 0.04 |
| Bromoform | 26.23 | 14.88 | 22.77 | 0.12 |
| Isopropylbenzene (Cumene) | 26.37 | 15.46 | 23.30 | 0.15 |
| cis-1,4-Dichloro-2-butene | 27.12 | | | |
| 1,1,2,2-Tetrachloroethane | 27.29 | 16.35 | 24.07 | 0.04 |
| Bromobenzene | 27.46 | 15.86 | 24.00 | 0.03 |
| 1,2,3-Trichloropropane | 27.55 | 16.23 | 24.13 | 0.32 |
| n-Propylbenzene | 27.58 | 16.41 | 24.33 | 0.04 |
| 2-Chlorotoluene | 28.19 | 16.42 | 24.53 | 0.04 |
| trans-1,4-Dichloro-2-butene | 28.26 | | | |
| 1,3,5-Trimethylbenzene | 28.31 | 16.90 | 24.83 | 0.05 |
| 4-Chlorotoluene | 28.33 | 16.72 | 24.77 | 0.06 |
| Pentachloroethane | 29.41 | | | |
| 1,2,4-Trimethylbenzene | 29.47 | 17.70 | 31.50 | 0.13 |
| sec-Butylbenzene | 30.25 | 18.09 | 26.13 | 0.13 |
| tert-Butylbenzene | 30.59 | 17.57 | 26.60 | 0.14 |
| p-Isopropyltoluene | 30.59 | 18.52 | 26.50 | 0.12 |
| 1,3-Dichlorobenzene | 30.56 | 18.14 | 26.37 | 0.12 |
| 1,4-Dichlorobenzene | 31.22 | 18.39 | 26.60 | 0.03 |
| Benzyl chloride | 32.00 | | | |
| n-Butylbenzene | 32.23 | 19.49 | 27.32 | 0.11 |
| 1,2-Dichlorobenzene | 32.31 | 19.17 | 27.43 | 0.03 |
| 1,2-Dibromo-3-chloropropane | 35.30 | 21.08 | -- | 0.26 |
| 1,2,4-Trichlorobenzene | 38.19 | 23.08 | 31.50 | 0.04 |
| Hexachlorobutadiene | 38.57 | 23.68 | 32.07 | 0.11 |
| Naphthalene | 39.05 | 23.52 | 32.20 | 0.04 |
| 1,2,3-Trichlorobenzene | 40.01 | 24.18 | 32.97 | 0.03 |

TABLE 1 (cont.)

| Compound | Retention Time (minutes) Column 1[a] | Column 2[b] | Column 2"[c] | MDL[d] (µg/L) |
|---|---|---|---|---|
| INTERNAL STANDARDS/SURROGATES | | | | |
| 1,4-Difluorobenzene | 13.26 | | | |
| Chlorobenzene-$d_5$ | 23.10 | | | |
| 1,4-Dichlorobenzene-$d_4$ | 31.16 | | | |
| 4-Bromofluorobenzene | 27.83 | 15.71 | 23.63 | |
| 1,2-Dichlorobenzene-$d_4$ | 32.30 | 19.08 | 27.25 | |
| Dichloroethane-$d_4$ | 12.08 | | | |
| Dibromofluoromethane | -- | | | |
| Toluene-$d_8$ | 18.27 | | | |
| Pentafluorobenzene | -- | | | |
| Fluorobenzene | 13.00 | 6.27 | 14.06 | |

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.

[c] Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

[d] MDL based on a 25-mL sample volume.

TABLE 2

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

| Compound | Retention Time (minutes) Column 3[a] | MDL[b] (µg/L) |
|---|---|---|
| Dichlorodifluoromethane | 0.88 | 0.11 |
| Chloromethane | 0.97 | 0.05 |
| Vinyl chloride | 1.04 | 0.04 |
| Bromomethane | 1.29 | 0.03 |
| 1,1-Dichloroethane | 4.03 | 0.03 |
| cis-1,2-Dichloroethene | 5.07 | 0.06 |
| 2,2-Dichloropropane | 5.31 | 0.08 |
| Chloroform | 5.55 | 0.04 |
| Bromochloromethane | 5.63 | 0.09 |
| 1,1,1-Trichloroethane | 6.76 | 0.04 |
| 1,2-Dichloroethane | 7.00 | 0.02 |
| 1,1-Dichloropropene | 7.16 | 0.12 |
| Carbon tetrachloride | 7.41 | 0.02 |
| Benzene | 7.41 | 0.03 |
| 1,2-Dichloropropane | 8.94 | 0.02 |
| Trichloroethene | 9.02 | 0.02 |
| Dibromomethane | 9.09 | 0.01 |
| Bromodichloromethane | 9.34 | 0.03 |
| Toluene | 11.51 | 0.08 |
| 1,1,2-Trichloroethane | 11.99 | 0.08 |
| 1,3-Dichloropropane | 12.48 | 0.08 |
| Dibromochloromethane | 12.80 | 0.07 |
| Tetrachloroethene | 13.20 | 0.05 |
| 1,2-Dibromoethane | 13.60 | 0.10 |
| Chlorobenzene | 14.33 | 0.03 |
| 1,1,1,2-Tetrachloroethane | 14.73 | 0.07 |
| Ethylbenzene | 14.73 | 0.03 |
| p-Xylene | 15.30 | 0.06 |
| m-Xylene | 15.30 | 0.03 |
| Bromoform | 15.70 | 0.20 |
| o-Xylene | 15.78 | 0.06 |
| Styrene | 15.78 | 0.27 |
| 1,1,2,2-Tetrachloroethane | 15.78 | 0.20 |
| 1,2,3-Trichloropropane | 16.26 | 0.09 |
| Isopropylbenzene | 16.42 | 0.10 |
| Bromobenzene | 16.42 | 0.11 |
| 2-Chlorotoluene | 16.74 | 0.08 |
| n-Propylbenzene | 16.82 | 0.10 |
| 4-Chlorotoluene | 16.82 | 0.06 |

TABLE 2 (cont.)

| Compound | Retention Time (minutes) Column 3[a] | MDL[b] (µg/L) |
|---|---|---|
| 1,3,5-Trimethylbenzene | 16.99 | 0.06 |
| tert-Butylbenzene | 17.31 | 0.33 |
| 1,2,4-Trimethylbenzene | 17.31 | 0.09 |
| sec-Butylbenzene | 17.47 | 0.12 |
| 1,3-Dichlorobenzene | 17.47 | 0.05 |
| p-Isopropyltoluene | 17.63 | 0.26 |
| 1,4-Dichlorobenzene | 17.63 | 0.04 |
| 1,2-Dichlorobenzene | 17.79 | 0.05 |
| n-Butylbenzene | 17.95 | 0.10 |
| 1,2-Dibromo-3-chloropropane | 18.03 | 0.50 |
| 1,2,4-Trichlorobenzene | 18.84 | 0.20 |
| Naphthalene | 19.07 | 0.10 |
| Hexachlorobutadiene | 19.24 | 0.10 |
| 1,2,3-Trichlorobenzene | 19.24 | 0.14 |

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25-mL sample volume.

TABLE 3

ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

| Estimated Quantitation Limits | | |
|---|---|---|
| 5-mL Ground Water Purge (µg/L) | 25-mL Ground water Purge (µg/L) | Low Soil/Sediment[b] µg/kg |
| 5 | 1 | 5 |

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

| Other Matrices | Factor[c] |
|---|---|
| Water miscible liquid waste | 50 |
| High concentration soil and sludge | 125 |
| Non-water miscible waste | 500 |

[c] EQL = [EQL for low soil sediment (Table 3)] x [Factor].

For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

| m/z | Required Intensity (relative abundance) |
|---|---|
| 50 | 15 to 40% of m/z 95 |
| 75 | 30 to 60% of m/z 95 |
| 95 | Base peak, 100% relative abundance |
| 96 | 5 to 9% of m/z 95 |
| 173 | Less than 2% of m/z 174 |
| 174 | Greater than 50% of m/z 95 |
| 175 | 5 to 9% of m/z 174 |
| 176 | Greater than 95% but less than 101% of m/z 174 |
| 177 | 5 to 9% of m/z 176 |

[a] Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers" instructions), provided that method performance is not adversely affected.

TABLE 5

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

| Compound | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|---|---|---|
| Acetone | 58 | 43 |
| Acetonitrile | 41 | 40, 39 |
| Acrolein | 56 | 55, 58 |
| Acrylonitrile | 53 | 52, 51 |
| Allyl alcohol | 57 | 58, 39 |
| Allyl chloride | 76 | 41, 39, 78 |
| Benzene | 78 | - |
| Benzyl chloride | 91 | 126, 65, 128 |
| Bromoacetone | 136 | 43, 138, 93, 95 |
| Bromobenzene | 156 | 77, 158 |
| Bromochloromethane | 128 | 49, 130 |
| Bromodichloromethane | 83 | 85, 127 |
| Bromoform | 173 | 175, 254 |
| Bromomethane | 94 | 96 |
| iso-Butanol | 74 | 43 |
| n-Butanol | 56 | 41 |
| 2-Butanone | 72 | 43 |
| n-Butylbenzene | 91 | 92, 134 |
| sec-Butylbenzene | 105 | 134 |
| tert-Butylbenzene | 119 | 91, 134 |
| Carbon disulfide | 76 | 78 |
| Carbon tetrachloride | 117 | 119 |
| Chloral hydrate | 82 | 44, 84, 86, 111 |
| Chloroacetonitrile | 48 | 75 |
| Chlorobenzene | 112 | 77, 114 |
| 1-Chlorobutane | 56 | 49 |
| Chlorodibromomethane | 129 | 208, 206 |
| Chloroethane | 64 (49*) | 66 (51*) |
| 2-Chloroethanol | 49 | 44, 43, 51, 80 |
| Bis(2-chloroethyl) sulfide | 109 | 111, 158, 160 |
| 2-Chloroethyl vinyl ether | 63 | 65, 106 |
| Chloroform | 83 | 85 |
| Chloromethane | 50 (49*) | 52 (51*) |
| Chloroprene | 53 | 88, 90, 51 |
| 3-Chloropropionitrile | 54 | 49, 89, 91 |
| 2-Chlorotoluene | 91 | 126 |
| 4-Chlorotoluene | 91 | 126 |
| 1,2-Dibromo-3-chloropropane | 75 | 155, 157 |
| Dibromochloromethane | 129 | 127 |
| 1,2-Dibromoethane | 107 | 109, 188 |
| Dibromomethane | 93 | 95, 174 |

TABLE 5 (cont.)

| Compound | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|---|---|---|
| 1,2-Dichlorobenzene | 146 | 111, 148 |
| 1,2-Dichlorobenzene-$d_4$ | 152 | 115, 150 |
| 1,3-Dichlorobenzene | 146 | 111, 148 |
| 1,4-Dichlorobenzene | 146 | 111, 148 |
| cis-1,4-Dichloro-2-butene | 75 | 53, 77, 124, 89 |
| trans-1,4-Dichloro-2-butene | 53 | 88, 75 |
| Dichlorodifluoromethane | 85 | 87 |
| 1,1-Dichloroethane | 63 | 65, 83 |
| 1,2-Dichloroethane | 62 | 98 |
| 1,1-Dichloroethene | 96 | 61, 63 |
| cis-1,2-Dichloroethene | 96 | 61, 98 |
| trans-1,2-Dichloroethene | 96 | 61, 98 |
| 1,2-Dichloropropane | 63 | 112 |
| 1,3-Dichloropropane | 76 | 78 |
| 2,2-Dichloropropane | 77 | 97 |
| 1,3-Dichloro-2-propanol | 79 | 43, 81, 49 |
| 1,1-Dichloropropene | 75 | 110, 77 |
| cis-1,3-Dichloropropene | 75 | 77, 39 |
| trans-1,3-Dichloropropene | 75 | 77, 39 |
| 1,2,3,4-Diepoxybutane | 55 | 57, 56 |
| Diethyl ether | 74 | 45, 59 |
| 1,4-Dioxane | 88 | 58, 43, 57 |
| Epichlorohydrin | 57 | 49, 62, 51 |
| Ethanol | 31 | 45, 27, 46 |
| Ethyl acetate | 88 | 43, 45, 61 |
| Ethylbenzene | 91 | 106 |
| Ethylene oxide | 44 | 43, 42 |
| Ethyl methacrylate | 69 | 41, 99, 86, 114 |
| Hexachlorobutadiene | 225 | 223, 227 |
| Hexachloroethane | 201 | 166, 199, 203 |
| 2-Hexanone | 43 | 58, 57, 100 |
| 2-Hydroxypropionitrile | 44 | 43, 42, 53 |
| Iodomethane | 142 | 127, 141 |
| Isobutyl alcohol | 43 | 41, 42, 74 |
| Isopropylbenzene | 105 | 120 |
| p-Isopropyltoluene | 119 | 134, 91 |
| Malononitrile | 66 | 39, 65, 38 |
| Methacrylonitrile | 41 | 67, 39, 52, 66 |
| Methyl acrylate | 55 | 85 |
| Methyl-t-butyl ether | 73 | 57 |
| Methylene chloride | 84 | 86, 49 |
| Methyl ethyl ketone | 72 | 43 |
| Methyl iodide | 142 | 127, 141 |

TABLE 5 (cont.)

| Compound | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|---|---|---|
| Methyl methacrylate | 69 | 41, 100, 39 |
| 4-Methyl-2-pentanone | 100 | 43, 58, 85 |
| Naphthalene | 128 | - |
| Nitrobenzene | 123 | 51, 77 |
| 2-Nitropropane | 46 | - |
| 2-Picoline | 93 | 66, 92, 78 |
| Pentachloroethane | 167 | 130, 132, 165, 169 |
| Propargyl alcohol | 55 | 39, 38, 53 |
| β-Propiolactone | 42 | 43, 44 |
| Propionitrile (ethyl cyanide) | 54 | 52, 55, 40 |
| n-Propylamine | 59 | 41, 39 |
| n-Propylbenzene | 91 | 120 |
| Pyridine | 79 | 52 |
| Styrene | 104 | 78 |
| 1,2,3-Trichlorobenzene | 180 | 182, 145 |
| 1,2,4-Trichlorobenzene | 180 | 182, 145 |
| 1,1,1,2-Tetrachloroethane | 131 | 133, 119 |
| 1,1,2,2-Tetrachloroethane | 83 | 131, 85 |
| Tetrachloroethene | 164 | 129, 131, 166 |
| Toluene | 92 | 91 |
| 1,1,1-Trichloroethane | 97 | 99, 61 |
| 1,1,2-Trichloroethane | 83 | 97, 85 |
| Trichloroethene | 95 | 97, 130, 132 |
| Trichlorofluoromethane | 151 | 101, 153 |
| 1,2,3-Trichloropropane | 75 | 77 |
| 1,2,4-Trimethylbenzene | 105 | 120 |
| 1,3,5-Trimethylbenzene | 105 | 120 |
| Vinyl acetate | 43 | 86 |
| Vinyl chloride | 62 | 64 |
| o-Xylene | 106 | 91 |
| m-Xylene | 106 | 91 |
| p-Xylene | 106 | 91 |
| Internal Standards/Surrogates: | | |
| Benzene-$d_6$ | 84 | 83 |
| Bromobenzene-$d_5$ | 82 | 162 |
| Bromochloromethane-$d_2$ | 51 | 131 |
| 1,4-Difluorobenzene | 114 | |
| Chlorobenzene-$d_5$ | 117 | |
| 1,4-Dichlorobenzene-$d_4$ | 152 | 115, 150 |
| 1,1,2-Trichloroethane-$d_3$ | 100 | |
| 4-Bromofluorobenzene | 95 | 174, 176 |
| Chloroform-$d_1$ | 84 | |
| Dibromofluoromethane | 113 | |

TABLE 5 (cont.)

| Compound | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|---|---|---|
| Internal Standards/Surrogates | | |
| Dichloroethane-$d_4$ | 102 | |
| Toluene-$d_8$ | 98 | |
| Pentafluorobenzene | 168 | |
| Fluorobenzene | 96 | 77 |

* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

TABLE 6

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN (METHOD 5030)

| Compound | Conc. Range (µg/L) | Number of Samples | % Recovery[a] | Standard Deviation of Recovery[b] | RSD |
|---|---|---|---|---|---|
| Benzene | 0.1 - 10 | 31 | 97 | 6.5 | 5.7 |
| Bromobenzene | 0.1 - 10 | 30 | 100 | 5.5 | 5.5 |
| Bromochloromethane | 0.5 - 10 | 24 | 90 | 5.7 | 6.4 |
| Bromodichloromethane | 0.1 - 10 | 30 | 95 | 5.7 | 6.1 |
| Bromoform | 0.5 - 10 | 18 | 101 | 6.4 | 6.3 |
| Bromomethane | 0.5 - 10 | 18 | 95 | 7.8 | 8.2 |
| n-Butylbenzene | 0.5 - 10 | 18 | 100 | 7.6 | 7.6 |
| sec-Butylbenzene | 0.5 - 10 | 16 | 100 | 7.6 | 7.6 |
| tert-Butylbenzene | 0.5 - 10 | 18 | 102 | 7.4 | 7.3 |
| Carbon tetrachloride | 0.5 - 10 | 24 | 84 | 7.4 | 8.8 |
| Chlorobenzene | 0.1 - 10 | 31 | 98 | 5.8 | 5.9 |
| Chloroethane | 0.5 - 10 | 24 | 89 | 8.0 | 9.0 |
| Chloroform | 0.5 - 10 | 24 | 90 | 5.5 | 6.1 |
| Chloromethane | 0.5 - 10 | 23 | 93 | 8.3 | 8.9 |
| 2-Chlorotoluene | 0.1 - 10 | 31 | 90 | 5.6 | 6.2 |
| 4-Chlorotoluene | 0.1 - 10 | 31 | 99 | 8.2 | 8.3 |
| 1,2-Dibromo-3-Chloropropane | 0.5 - 10 | 24 | 83 | 16.6 | 19.9 |
| Dibromochloromethane | 0.1 - 10 | 31 | 92 | 6.5 | 7.0 |
| 1,2-Dibromoethane | 0.5 - 10 | 24 | 102 | 4.0 | 3.9 |
| Dibromomethane | 0.5 - 10 | 24 | 100 | 5.6 | 5.6 |
| 1,2-Dichlorobenzene | 0.1 - 10 | 31 | 93 | 5.8 | 6.2 |
| 1,3-Dichlorobenzene | 0.5 - 10 | 24 | 99 | 6.8 | 6.9 |
| 1,4-Dichlorobenzene | 0.2 - 20 | 31 | 103 | 6.6 | 6.4 |
| Dichlorodifluoromethane | 0.5 - 10 | 18 | 90 | 6.9 | 7.7 |
| 1,1-Dichlorobenzene | 0.5 - 10 | 24 | 96 | 5.1 | 5.3 |
| 1,2-Dichlorobenzene | 0.1 - 10 | 31 | 95 | 5.1 | 5.4 |
| 1,1-Dichloroethene | 0.1 - 10 | 34 | 94 | 6.3 | 6.7 |
| cis-1,2-Dichloroethene | 0.5 - 10 | 18 | 101 | 6.7 | 6.7 |
| trans-1,2-Dichloroethene | 0.1 - 10 | 30 | 93 | 5.2 | 5.6 |
| 1,2-Dichloropropane | 0.1 - 10 | 30 | 97 | 5.9 | 6.1 |
| 1,3-Dichloropropane | 0.1 - 10 | 31 | 96 | 5.7 | 6.0 |
| 2,2-Dichloropropane | 0.5 - 10 | 12 | 86 | 14.6 | 16.9 |
| 1,1-Dichloropropene | 0.5 - 10 | 18 | 98 | 8.7 | 8.9 |
| Ethylbenzene | 0.1 - 10 | 31 | 99 | 8.4 | 8.6 |
| Hexachlorobutadiene | 0.5 - 10 | 18 | 100 | 6.8 | 6.8 |
| Isopropylbenzene | 0.5 - 10 | 16 | 101 | 7.7 | 7.6 |
| p-Isopropyltoluene | 0.1 - 10 | 23 | 99 | 6.7 | 6.7 |
| Methylene chloride | 0.1 - 10 | 30 | 95 | 5.0 | 5.3 |

TABLE 6 (cont.)

| Compound | Conc. Range (µg/L) | Number of Samples | % Recovery[a] | Standard Deviation of Recovery[b] | RSD |
|---|---|---|---|---|---|
| Naphthalene | 0.1 -100 | 31 | 104 | 8.6 | 8.2 |
| n-Propylbenzene | 0.1 - 10 | 31 | 100 | 5.8 | 5.8 |
| Styrene | 0.1 -100 | 39 | 102 | 7.3 | 7.2 |
| 1,1,1,2-Tetrachloroethane | 0.5 - 10 | 24 | 90 | 6.1 | 6.8 |
| 1,1,2,2-Tetrachloroethane | 0.1 - 10 | 30 | 91 | 5.7 | 6.3 |
| Tetrachloroethene | 0.5 - 10 | 24 | 89 | 6.0 | 6.8 |
| Toluene | 0.5 - 10 | 18 | 102 | 8.1 | 8.0 |
| 1,2,3-Trichlorobenzene | 0.5 - 10 | 18 | 109 | 9.4 | 8.6 |
| 1,2,4-Trichlorobenzene | 0.5 - 10 | 18 | 108 | 9.0 | 8.3 |
| 1,1,1-Trichloroethane | 0.5 - 10 | 18 | 98 | 7.9 | 8.1 |
| 1,1,2-Trichloroethane | 0.5 - 10 | 18 | 104 | 7.6 | 7.3 |
| Trichloroethene | 0.5 - 10 | 24 | 90 | 6.5 | 7.3 |
| Trichlorofluoromethane | 0.5 - 10 | 24 | 89 | 7.2 | 8.1 |
| 1,2,3-Trichloropropane | 0.5 - 10 | 16 | 108 | 15.6 | 14.4 |
| 1,2,4-Trimethylbenzene | 0.5 - 10 | 18 | 99 | 8.0 | 8.1 |
| 1,3,5-Trimethylbenzene | 0.5 - 10 | 23 | 92 | 6.8 | 7.4 |
| Vinyl chloride | 0.5 - 10 | 18 | 98 | 6.5 | 6.7 |
| o-Xylene | 0.1 - 31 | 18 | 103 | 7.4 | 7.2 |
| m-Xylene | 0.1 - 10 | 31 | 97 | 6.3 | 6.5 |
| p-Xylene | 0.5 - 10 | 18 | 104 | 8.0 | 7.7 |

[a] Recoveries were calculated using internal standard method. The internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data from three concentrations.

TABLE 7

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

| Compound | Conc. (µg/L) | Number of Samples | % Recovery[a] | Standard Deviation of Recovery[b] | RSD |
|---|---|---|---|---|---|
| Benzene | 0.1 | 7 | 99 | 6.2 | 6.3 |
| Bromobenzene | 0.5 | 7 | 97 | 7.4 | 7.6 |
| Bromochloromethane | 0.5 | 7 | 97 | 5.8 | 6.0 |
| Bromodichloromethane | 0.1 | 7 | 100 | 4.6 | 4.6 |
| Bromoform | 0.5 | 7 | 101 | 5.4 | 5.3 |
| Bromomethane | 0.5 | 7 | 99 | 7.1 | 7.2 |
| n-Butylbenzene | 0.5 | 7 | 94 | 6.0 | 6.4 |
| sec-Butylbenzene | 0.5 | 7 | 110 | 7.1 | 6.5 |
| tert-Butylbenzene | 0.5 | 7 | 110 | 2.5 | 2.3 |
| Carbon tetrachloride | 0.1 | 7 | 108 | 6.8 | 6.3 |
| Chlorobenzene | 0.1 | 7 | 91 | 5.8 | 6.4 |
| Chloroethane | 0.1 | 7 | 100 | 5.8 | 5.8 |
| Chloroform | 0.1 | 7 | 105 | 3.2 | 3.0 |
| Chloromethane | 0.5 | 7 | 101 | 4.7 | 4.7 |
| 2-Chlorotoluene | 0.5 | 7 | 99 | 4.6 | 4.6 |
| 4-Chlorotoluene | 0.5 | 7 | 96 | 7.0 | 7.3 |
| 1,2-Dibromo-3-chloropropane | 0.5 | 7 | 92 | 10.0 | 10.9 |
| Dibromochloromethane | 0.1 | 7 | 99 | 5.6 | 5.7 |
| 1,2-Dibromoethane | 0.5 | 7 | 97 | 5.6 | 5.8 |
| Dibromomethane | 0.5 | 7 | 93 | 5.6 | 6.0 |
| 1,2-Dichlorobenzene | 0.1 | 7 | 97 | 3.5 | 3.6 |
| 1,3-Dichlorobenzene | 0.1 | 7 | 101 | 6.0 | 5.9 |
| 1,4-Dichlorobenzene | 0.1 | 7 | 106 | 6.5 | 6.1 |
| Dichlorodifluoromethane | 0.1 | 7 | 99 | 8.8 | 8.9 |
| 1,1-Dichloroethane | 0.5 | 7 | 98 | 6.2 | 6.3 |
| 1,2-Dichloroethane | 0.1 | 7 | 100 | 6.3 | 6.3 |
| 1,1-Dichloroethene | 0.1 | 7 | 95 | 9.0 | 9.5 |
| cis-1,2-Dichloroethene | 0.1 | 7 | 100 | 3.5 | 3.7 |
| trans-1,2-Dichloroethene | 0.1 | 7 | 98 | 7.2 | 7.3 |
| 1,2-Dichloropropane | 0.5 | 7 | 96 | 6.0 | 6.3 |
| 1,3-Dichloropropane | 0.5 | 7 | 99 | 5.8 | 5.9 |
| 2,2-Dichloropropane | 0.5 | 7 | 99 | 4.9 | 4.9 |
| 1,1-Dichloropropene | 0.5 | 7 | 102 | 7.4 | 7.3 |
| Ethylbenzene | 0.5 | 7 | 99 | 5.2 | 5.3 |
| Hexachlorobutadiene | 0.5 | 7 | 100 | 6.7 | 6.7 |
| Isopropylbenzene | 0.5 | 7 | 102 | 6.4 | 6.3 |
| p-Isopropyltoluene | 0.5 | 7 | 113 | 13.0 | 11.5 |
| Methylene chloride | 0.5 | 7 | 97 | 13.0 | 13.4 |
| Naphthalene | 0.5 | 7 | 98 | 7.2 | 7.3 |

TABLE 7 (cont.)

| Compound | Conc. (µg/L) | Number of Samples | % Recovery[a] | Standard Deviation of Recovery[b] | RSD |
|---|---|---|---|---|---|
| n-Propylbenzene | 0.5 | 7 | 99 | 6.6 | 6.7 |
| Styrene | 0.5 | 7 | 96 | 19.0 | 19.8 |
| 1,1,1,2-Tetrachloroethane | 0.5 | 7 | 100 | 4.7 | 4.7 |
| 1,1,2,2-Tetrachloroethane | 0.5 | 7 | 100 | 12.0 | 12.0 |
| Tetrachloroethene | 0.1 | 7 | 96 | 5.0 | 5.2 |
| Toluene | 0.5 | 7 | 100 | 5.9 | 5.9 |
| 1,2,3-Trichlorobenzene | 0.5 | 7 | 102 | 8.9 | 8.7 |
| 1,2,4-Trichlorobenzene | 0.5 | 7 | 91 | 16.0 | 17.6 |
| 1,1,1-Trichloroethane | 0.5 | 7 | 100 | 4.0 | 4.0 |
| 1,1,2-Trichloroethane | 0.5 | 7 | 102 | 4.9 | 4.8 |
| Trichloroethene | 0.1 | 7 | 104 | 2.0 | 1.9 |
| Trichlorofluoromethane | 0.1 | 7 | 97 | 4.6 | 4.7 |
| 1,2,3-Trichloropropane | 0.5 | 7 | 96 | 6.5 | 6.8 |
| 1,2,4-Trimethylbenzene | 0.5 | 7 | 96 | 6.5 | 6.8 |
| 1,3,5-Trimethylbenzene | 0.5 | 7 | 101 | 4.2 | 4.2 |
| Vinyl chloride | 0.1 | 7 | 104 | 0.2 | 0.2 |
| o-Xylene | 0.5 | 7 | 106 | 7.5 | 7.1 |
| m-Xylene | 0.5 | 7 | 106 | 4.6 | 4.3 |
| p-Xylene | 0.5 | 7 | 97 | 6.1 | 6.3 |

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8

SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

| Surrogate Compound | Water | Soil/Sediment |
|---|---|---|
| 4-Bromofluorobenzene[a] | 86-115 | 74-121 |
| Dibromofluoromethane[a] | 86-118 | 80-120 |
| Toluene-$d_8$[a] | 88-110 | 81-117 |
| Dichloroethane-$d_4$[a] | 80-120 | 80-120 |

[a] Single laboratory data, for guidance only.

TABLE 9

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

| Approximate Concentration Range (µg/kg) | Volume of Extract[a] |
|---|---|
| 500 - 10,000 | 100 µL |
| 1,000 - 20,000 | 50 µL |
| 5,000 - 100,000 | 10 µL |
| 25,000 - 500,000 | 100 µL of 1/50 dilution[b] |

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10

DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM (METHOD 3585)

| Compound | Recovery (%) | %RSD | Blank (ppm) | Spike (ppm) |
|---|---|---|---|---|
| Acetone | 91 | 14.8 | 1.9 | 5.0 |
| Benzene | 86 | 21.3 | 0.1 | 0.5 |
| n-Butanol*,** | 107 | 27.8 | 0.5 | 5.0 |
| iso-Butanol*,** | 95 | 19.5 | 0.9 | 5.0 |
| Carbon tetrachloride | 86 | 44.7 | 0.0 | 0.5 |
| Carbon disulfide** | 53 | 22.3 | 0.0 | 5.0 |
| Chlorobenzene | 81 | 29.3 | 0.0 | 5.0 |
| Chloroform | 84 | 29.3 | 0.0 | 6.0 |
| 1,4-Dichlorobenzene | 98 | 24.9 | 0.0 | 7.5 |
| 1,2-Dichloroethane | 101 | 23.1 | 0.0 | 0.5 |
| 1,1-Dichloroethene | 97 | 45.3 | 0.0 | 0.7 |
| Diethyl ether | 76 | 24.3 | 0.0 | 5.0 |
| Ethyl acetate | 113 | 27.4 | 0.0 | 5.0 |
| Ethylbenzene | 83 | 30.1 | 0.2 | 5.0 |
| Hexachloroethane | 71 | 30.3 | 0.0 | 3.0 |
| Methylene chloride | 98 | 45.3 | 0.0 | 5.0 |
| Methyl ethyl ketone | 79 | 24.6 | 0.4 | 5.0 |
| MIBK | 93 | 31.4 | 0.0 | 5.0 |
| Nitrobenzene | 89 | 30.3 | 0.0 | 2.0 |
| Pyridine | 31 | 35.9 | 0.0 | 5.0 |
| Tetrachloroethene | 82 | 27.1 | 0.0 | 0.7 |
| Trichlorofluoromethane | 76 | 27.6 | 0.0 | 5.0 |
| 1,1,2-Trichlorotrifluoroethane | 69 | 29.2 | 0.0 | 5.0 |
| Toluene | 73 | 21.9 | 0.6 | 5.0 |
| Trichloroethene | 66 | 28.0 | 0.0 | 0.5 |
| Vinyl chloride | 63 | 35.2 | 0.0 | 0.2 |
| o-Xylene | 83 | 29.5 | 0.4 | 5.0 |
| m/p-Xylene | 84 | 29.5 | 0.6 | 10.0 |

* Alternate mass employed
** IS quantitation

Data are taken from Reference 9.

TABLE 11

SINGLE LABORATORY PERFORMANCE
DATA FOR THE DIRECT INJECTION METHOD - USED OIL (METHOD 3585)

| Compound | Recovery (%) | %RSD | Blank (ppm) | Spike (ppm) |
|---|---|---|---|---|
| Acetone** | 105 | 54 | 2.0 | 5.0 |
| Benzene | 3135 | 44 | 14 | 0.5 |
| Benzene-$d_6$ | 56 | 44 | 2.9 | 0.5 |
| n-Butanol** | 100 | 71 | 12 | 5.0 |
| iso-Butanol*,** | 132 | 27 | 0 | 5.0 |
| Carbon tetrachloride | 143 | 68 | 0 | 0.5 |
| Carbon tetrachloride-$^{13}C$ | 99 | 44 | 5.1 | 0.5 |
| Carbon disulfide** | 95 | 63 | 0 | 5.0 |
| Chlorobenzene | 148 | 71 | 0 | 5.0 |
| Chlorobenzene-$d_5$ | 60 | 44 | 3.6 | 5.0 |
| Chloroform | 149 | 74 | 0 | 6.0 |
| Chloroform-$d_1$ | 51 | 44 | 2.6 | 6.0 |
| 1,4-Dichlorobenzene | 142 | 72 | 0 | 7.5 |
| 1,4-Dichlorobenzene-$d_4$ | 53 | 44 | 3.4 | 7.5 |
| 1,2-Dichloroethane** | 191 | 54 | 0 | 0.5 |
| 1,1-Dichloroethene* | 155 | 51 | 0 | 0.7 |
| 1,1-Dichloroethene-$d_2$ | 68 | 44 | 3.4 | 0.7 |
| Diethyl ether** | 95 | 66 | 0 | 5.0 |
| Ethyl acetate*,** | 126 | 39 | 0 | 5.0 |
| Ethylbenzene | 1298 | 44 | 54 | 5.0 |
| Ethylbenzene-$d_{10}$ | 63 | 44 | 3.6 | 5.0 |
| Hexachloroethane | 132 | 72 | 0 | 3.0 |
| Hexachloroethane-$^{13}C$ | 54 | 45 | 3.5 | 3.0 |
| Methylene chloride** | 86 | 65 | 0.3 | 5.0 |
| Methyl ethyl ketone** | 107 | 64 | 0 | 5.0 |
| 4-Methyl-2-pentanone (MIBK)** | 100 | 74 | 0.1 | 5.0 |
| Nitrobenzene | 111 | 80 | 0 | 2.0 |
| Nitrobenzene-$d_5$ | 65 | 53 | 4.0 | 2.0 |
| Pyridine** | 68 | 85 | 0 | 5.0 |
| Pyridine-$d_5$ | ND | -- | 0 | 5.0 |
| Tetrachloroethene** | 101 | 73 | 0 | 0.7 |
| Trichlorofluoromethane** | 91 | 70 | 0 | 5.0 |
| 1,1,2-$Cl_3F_3$ethane** | 81 | 70 | 0 | 5.0 |
| Toluene | 2881 | 44 | 128 | 5.0 |
| Toluene-$d_8$ | 63 | 44 | 3.6 | 5.0 |
| Trichloroethene | 152 | 57 | 0 | 0.5 |
| Trichloroethene-$d_1$ | 55 | 44 | 2.8 | 0.5 |

TABLE 11 (cont.)

| Compound | Recovery (%) | %RSD | Blank (ppm) | Spike (ppm) |
|---|---|---|---|---|
| Vinyl chloride** | 100 | 69 | 0 | 0.2 |
| o-Xylene | 2292 | 44 | 105 | 5.0 |
| o-Xylene-$d_{10}$ | 76 | 44 | 4.2 | 5.0 |
| m-/p-Xylene | 2583 | 44 | 253 | 10.0 |
| p-Xylene-$d_{10}$ | 67 | 44 | 3.7 | 10.0 |

* Alternate mass employed
** IS quantitation
ND = Not Detected

Data are based on seven measurements and are taken from Reference 9.

TABLE 12

METHOD DETECTION LIMITS (METHOD 5031)

| Compound | MDL (µg/L) Macro[a] | Concentration Factor Macro | Micro |
|---|---|---|---|
| Acetone | 31 | 25-500 | - |
| Acetonitrile | 57 | 25-500 | 200 |
| Acrolein | - | - | 100 |
| Acrylonitrile | 16 | 25-500 | 100 |
| Allyl Alcohol | 7 | 25-500 | - |
| 1-Butanol | - | - | 250 |
| Crotonaldehyde | 12 | 25-500 | - |
| 1,4-Dioxane | 12 | 25-500 | 150 |
| Ethyl Acetate | - | - | 100 |
| Isobutyl alcohol | 7 | 25-500 | - |
| Methanol | 38 | 25-500 | 140 |
| Methyl Ethyl Ketone | 16 | 25-500 | - |
| 2-Methyl-1-propanol | - | - | 250 |
| n-Nitroso-di-n-butylamine | 14 | 25-500 | - |
| Paraldehyde | 10 | 25-500 | - |
| 2-Picoline | 7 | 25-500 | - |
| 1-Propanol | - | - | 240 |
| Propionitrile | 11 | 25-500 | 200 |
| Pyridine | 4 | 25-500 | - |
| o-Toluidine | 13 | 25-500 | - |

[a] Produced by analysis of seven aliquots of reagent water spiked at 25 ppb at the listed compounds; calculations based on internal standard technique and use of the following equation:

MDL = 3.134 x Std. Dev. of low concentration spike (ppb).

[b] When a 40-mL sample is used, and the first 100 µL of distillate are collected.

TABLE 13

TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS (METHOD 5031)

| Target Compound | Surrogate | Internal Standard |
|---|---|---|
| Acetone | $d_6$-Acetone | $d_8$-Isopropyl alcohol |
| Acetonitrile | $d_3$-Acetonitrile | $d_8$-Isopropyl alcohol |
| Acrylonitrile | $d_8$-Isopropyl alcohol | |
| Allyl alcohol | $d_7$-Dimethyl formamide | |
| Crotonaldehyde | $d_8$-Isopropyl alcohol | |
| 1,4-Dioxane | $d_8$-1,4-Dioxane | $d_7$-Dimethyl formamide |
| Isobutyl alcohol | $d_7$-Dimethyl formamide | |
| Methanol | $d_3$-Methanol | $d_8$-Isopropyl alcohol |
| Methyl ethyl ketone | $d_8$-Isopropyl alcohol | |
| N-Nitroso-di-n-butylamine | $d_7$-Dimethyl formamide | |
| Paraldehyde | $d_7$-Dimethyl formamide | |
| 2-Picoline | $d_7$-Dimethyl formamide | |
| Propionitrile | $d_8$-Isopropyl alcohol | |
| Pyridine | $d_5$-Pyridine | $d_7$-Dimethyl formamide |
| o-Toluidine | $d_7$-Dimethyl formamide | |

TABLE 14

RECOMMENDED CONCENTRATIONS FOR CALIBRATION SOLUTIONS (METHOD 5031)

| Compound | Concentration(s) (ng/µL) |
|---|---|
| Internal Standards | |
| $d_5$-benzyl alcohol | 10.0 |
| $d_{14}$-Diglyme | 10.0 |
| $d_7$-Dimethyl formamide | 10.0 |
| $d_8$-Isopropyl alcohol | 10.0 |
| Surrogates | |
| $d_6$-Acetone | 10.0 |
| $d_3$-Acetonitrile | 10.0 |
| $d_8$-1,4-Dioxane | 10.0 |
| $d_3$-Methanol | 10.0 |
| $d_5$-Pyridine | 10.0 |
| Target Compounds | |
| Acetone | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Acetonitrile | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Acrylonitrile | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Allyl alcohol | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Crotonaldehyde | 1.0, 5.0, 10.0, 25.0, 100.0 |
| 1,4-Dioxane | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Isobutyl alcohol | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Methanol | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Methyl ethyl ketone | 1.0, 5.0, 10.0, 25.0, 100.0 |
| N-Nitroso-di-n-butylamine | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Paraldehyde | 1.0, 5.0, 10.0, 25.0, 100.0 |
| 2-Picoline | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Propionitrile | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Pyridine | 1.0, 5.0, 10.0, 25.0, 100.0 |
| o-Toluidine | 1.0, 5.0, 10.0, 25.0, 100.0 |

TABLE 15

CHARACTERISTIC IONS AND RETENTION TIMES FOR VOCs (METHOD 5031)

| Compound | Quantitation Ion[a] | Secondary Ions | Retention Time (min)[b] |
|---|---|---|---|
| Internal Standards | | | |
| $d_8$-Isopropyl alcohol | 49 | | 1.75 |
| $d_{14}$-Diglyme | 66 | 98,64 | 9.07 |
| $d_7$-Dimethyl formamide | 50 | 80 | 9.20 |
| Surrogates | | | |
| $d_6$-Acetone | 46 | 64,42 | 1.03 |
| $d_3$-Methanol | 33 | 35,30 | 1.75 |
| $d_3$-Acetonitrile | 44 | 42 | 2.63 |
| $d_8$-1,4-Dioxane | 96 | 64,34 | 3.97 |
| $d_5$-Pyridine | 84 | 56,79 | 6.73 |
| $d_5$-Phenol[c] | 99 | 71 | 15.43 |
| Target Compounds | | | |
| Acetone | 43 | 58 | 1.05 |
| Methanol | 31 | 29 | 1.52 |
| Methyl ethyl ketone | 43 | 72,57 | 1.53 |
| Methacrylonitrile[c] | 67 | 41 | 2.38 |
| Acrylonitrile | 53 | 52,51 | 2.53 |
| Acetonitrile | 41 | 40,39 | 2.73 |
| Methyl isobutyl ketone[c] | 85 | 100,58 | 2.78 |
| Propionitrile | 54 | 52,55 | 3.13 |
| Crotonaldehyde | 41 | 70 | 3.43 |
| 1,4-Dioxane | 58 | 88,57 | 4.00 |
| Paraldehyde | 45 | 89 | 4.75 |
| Isobutyl alcohol | 43 | 33,42 | 5.05 |
| Allyl alcohol | 57 | 39 | 5.63 |
| Pyridine | 79 | 50,52 | 6.70 |
| 2-Picoline | 93 | 66 | 7.27 |
| N-Nitroso-di-n-butylamine | 84 | 116 | 12.82 |
| Aniline[c] | 93 | 66,92 | 13.23 |
| o-Toluidine | 106 | 107 | 13.68 |
| Phenol[c] | 94 | 66,65 | 15.43 |

[a] These ions were used for quantitation in selected ion monitoring.
[b] GC column: DB-Wax, 30 meter x 0.53 mm, 1 µm film thickness.
Oven program: 45°C for 4 min, increased to 220°C at 12°C/min.
[c] Compound removed from target analyte list due to poor accuracy and precision.

TABLE 16

METHOD ACCURACY AND PRECISION BY MEAN PERCENT RECOVERY AND PERCENT RELATIVE STANDARD DEVIATION[a] (METHOD 5031 - MACRODISTILLATION TECHNIQUE)
(Single Laboratory and Single Operator)

| Compound | 25 ppb Spike | | 100 ppb Spike | | 500 ppb Spike | |
|---|---|---|---|---|---|---|
| | Mean %R | %RSD | Mean %R | %RSD | Mean %R | %RSD |
| $d_6$-Acetone | 66 | 24 | 69 | 14 | 65 | 16 |
| $d_3$-Acetonitrile | 89 | 18 | 80 | 18 | 70 | 10 |
| $d_8$-1,4-Dioxane | 56 | 34 | 58 | 11 | 61 | 18 |
| $d_3$-Methanol | 43 | 29 | 48 | 19 | 56 | 14 |
| $d_5$-Pyridine | 83 | 6.3 | 84 | 7.8 | 85 | 9.0 |
| Acetone | 67 | 45 | 63 | 14 | 60 | 14 |
| Acetonitrile | 44 | 35 | 52 | 15 | 56 | 15 |
| Acrylonitrile | 49 | 42 | 47 | 27 | 45 | 27 |
| Allyl alcohol | 69 | 13 | 70 | 9.7 | 73 | 10 |
| Crotonaldehyde | 68 | 22 | 68 | 13 | 69 | 13 |
| 1,4-Dioxane | 63 | 25 | 55 | 16 | 54 | 13 |
| Isobutyl alcohol | 66 | 14 | 66 | 5.7 | 65 | 7.9 |
| Methanol | 50 | 36 | 46 | 22 | 49 | 18 |
| Methyl ethyl ketone | 55 | 37 | 56 | 20 | 52 | 19 |
| N-Nitroso-di-n-butylamine | 57 | 21 | 61 | 15 | 72 | 18 |
| Paraldehyde | 65 | 20 | 66 | 11 | 60 | 8.9 |
| Picoline | 81 | 12 | 81 | 6.8 | 84 | 8.0 |
| Propionitrile | 67 | 22 | 69 | 13 | 68 | 13 |
| Pyridine | 74 | 7.4 | 72 | 6.7 | 74 | 7.3 |
| o-Toluidine | 52 | 31 | 54 | 15 | 58 | 12 |

[a] Data from analysis of seven aliquots of reagent water spiked at each concentration, using a quadrapole mass spectrometer in the selected ion monitoring mode.

TABLE 17

RECOVERIES IN SAND SAMPLES FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

| Compound | Recovery per Replicate (ng) 1 | 2 | 3 | 4 | 5 | Mean | RSD | Mean Rec |
|---|---|---|---|---|---|---|---|---|
| Vinyl chloride | 8.0 | 7.5 | 6.7 | 5.4 | 6.6 | 6.8 | 13.0 | 34.2 |
| Trichlorofluoromethane | 13.3 | 16.5 | 14.9 | 13.0 | 10.3 | 13.6 | 15.2 | 68.0 |
| 1,1-Dichloroethene | 17.1 | 16.7 | 15.1 | 14.8 | 15.6 | 15.9 | 5.7 | 79.2 |
| Methylene chloride | 24.5 | 22.7 | 19.7 | 19.4 | 20.6 | 21.4 | 9.1 | 107 |
| trans-1,2-Dichloroethene | 22.7 | 23.6 | 19.4 | 18.3 | 20.1 | 20.8 | 0.7 | 104 |
| 1,2-Dichloroethane | 18.3 | 18.0 | 16.7 | 15.6 | 15.9 | 16.9 | 6.4 | 84.4 |
| cis-1,2-Dichloroethene | 26.1 | 23.1 | 22.6 | 20.3 | 20.8 | 22.6 | 9.0 | 113 |
| Bromochloromethane | 24.5 | 25.4 | 20.9 | 20.1 | 20.1 | 22.2 | 10.2 | 111 |
| Chloroform | 26.5 | 26.0 | 22.1 | 18.9 | 22.1 | 23.1 | 12.2 | 116 |
| 1,1,1-Trichloroethane | 21.5 | 23.0 | 23.9 | 16.7 | 31.2 | 23.4 | 21.2 | 117 |
| Carbon tetrachloride | 23.6 | 24.2 | 22.6 | 18.3 | 23.3 | 22.4 | 9.4 | 112 |
| Benzene | 22.4 | 23.9 | 20.4 | 17.4 | 19.2 | 20.7 | 11.2 | 103 |
| Trichloroethene | 21.5 | 20.5 | 19.2 | 14.4 | 19.1 | 18.9 | 12.7 | 94.6 |
| 1,2-Dichloropropane | 24.9 | 26.3 | 23.1 | 19.0 | 23.3 | 23.3 | 10.5 | 117 |
| Dibromomethane | 25.4 | 26.4 | 21.6 | 20.4 | 23.6 | 23.5 | 9.6 | 117 |
| Bromodichloromethane | 25.7 | 26.7 | 24.1 | 17.9 | 23.0 | 23.5 | 13.1 | 117 |
| Toluene | 28.3 | 25.0 | 24.8 | 16.3 | 23.6 | 23.6 | 16.9 | 118 |
| 1,1,2-Trichloroethane | 25.4 | 24.5 | 21.6 | 17.7 | 22.1 | 22.2 | 12.1 | 111 |
| 1,3-Dichloropropane | 25.4 | 24.2 | 22.7 | 17.0 | 22.2 | 22.3 | 12.8 | 112 |
| Dibromochloromethane | 26.3 | 26.2 | 23.7 | 18.2 | 23.2 | 23.5 | 12.5 | 118 |
| Chlorobenzene | 22.9 | 22.5 | 19.8 | 14.6 | 19.4 | 19.9 | 15.0 | 99.3 |
| 1,1,1,2-Tetrachloroethane | 22.4 | 27.7 | 25.1 | 19.4 | 22.6 | 23.4 | 12.0 | 117 |
| Ethylbenzene | 25.6 | 25.0 | 22.1 | 14.9 | 24.0 | 22.3 | 17.5 | 112 |
| p-Xylene | 22.5 | 22.0 | 19.8 | 13.9 | 20.3 | 19.7 | 15.7 | 98.5 |
| o-Xylene | 24.2 | 23.1 | 21.6 | 14.0 | 20.4 | 20.7 | 17.3 | 103 |
| Styrene | 23.9 | 21.5 | 20.9 | 14.3 | 20.5 | 20.2 | 15.7 | 101 |
| Bromoform | 26.8 | 25.6 | 26.0 | 20.1 | 23.5 | 24.4 | 9.9 | 122 |
| iso-Propylbenzene | 25.3 | 25.1 | 24.2 | 15.4 | 24.6 | 22.9 | 16.6 | 114 |
| Bromobenzene | 19.9 | 21.8 | 20.0 | 15.5 | 19.1 | 19.3 | 10.7 | 96.3 |
| 1,2,3-Trichloropropane | 25.9 | 23.0 | 25.6 | 15.9 | 21.4 | 22.2 | 15.8 | 111 |
| n-Propylbenzene | 26.0 | 23.8 | 22.6 | 13.9 | 21.9 | 21.6 | 19.0 | 106 |
| 2-Chlorotoluene | 23.6 | 23.8 | 21.3 | 13.0 | 21.5 | 20.6 | 19.2 | 103 |
| 4-Chlorotoluene | 21.0 | 19.7 | 18.4 | 12.1 | 18.3 | 17.9 | 17.1 | 89.5 |
| 1,3,5-Trimethylbenzene | 24.0 | 22.1 | 22.5 | 13.8 | 22.9 | 21.1 | 17.6 | 105 |
| sec-Butylbenzene | 25.9 | 25.3 | 27.8 | 16.1 | 28.6 | 24.7 | 18.1 | 124 |
| 1,2,4-Trimethylbenzene | 30.6 | 39.2 | 22.4 | 18.0 | 22.7 | 26.6 | 28.2 | 133 |
| 1,3-Dichlorobenzene | 20.3 | 20.6 | 18.2 | 13.0 | 17.6 | 17.9 | 15.2 | 89.7 |
| p-iso-Propyltoluene | 21.6 | 22.1 | 21.6 | 16.0 | 22.8 | 20.8 | 11.8 | 104 |
| 1,4-Dichlorobenzene | 18.1 | 21.2 | 20.0 | 13.2 | 17.4 | 18.0 | 15.3 | 90.0 |
| 1,2-Dichlorobenzene | 18.4 | 22.5 | 22.5 | 15.2 | 19.9 | 19.7 | 13.9 | 96.6 |
| n-Butylbenzene | 13.1 | 20.3 | 19.5 | 10.8 | 18.7 | 16.5 | 23.1 | 82.4 |
| 1,2,4-Trichlorobenzene | 14.5 | 14.9 | 15.7 | 8.8 | 12.3 | 13.3 | 18.8 | 66.2 |
| Hexachlorobutadiene | 17.6 | 22.5 | 21.6 | 13.2 | 21.6 | 19.3 | 18.2 | 96.3 |
| 1,2,3-Trichlorobenzene | 14.9 | 15.9 | 16.5 | 11.9 | 13.9 | 14.6 | 11.3 | 73.1 |

Data in Tables 17, 18, and 19 are from Reference 15.

TABLE 18
RECOVERIES IN C-HORIZON SOILS FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

| Compound | Recovery per Replicate (ng) 1 | 2 | 3 | 4 | 5 | Mean | RSD | Mean Rec |
|---|---|---|---|---|---|---|---|---|
| Vinyl chloride | 33.4 | 31.0 | 30.9 | 29.7 | 28.6 | 30.8 | 5.2 | 154 |
| Trichlorofluoromethane | 37.7 | 20.8 | 20.0 | 21.8 | 20.5 | 24.1 | 28.2 | 121 |
| 1,1-Dichloroethene | 21.7 | 33.5 | 39.8 | 30.2 | 32.5 | 31.6 | 18.5 | 158 |
| Methylene chloride | 20.9 | 19.4 | 18.7 | 18.3 | 18.4 | 19.1 | 5.1 | 95.7 |
| trans-1,2-Dichloroethene | 21.8 | 18.9 | 20.4 | 17.9 | 17.8 | 19.4 | 7.9 | 96.8 |
| 1,1-Dichloroethane | 23.8 | 21.9 | 21.3 | 21.3 | 20.5 | 21.8 | 5.2 | 109 |
| cis-1,2-Dichloroethene | 21.6 | 18.8 | 18.5 | 18.2 | 18.2 | 19.0 | 6.7 | 95.2 |
| Bromochloromethane | 22.3 | 19.5 | 19.3 | 19.0 | 19.2 | 20.0 | 6.0 | 100 |
| Chloroform | 20.5 | 17.1 | 17.3 | 16.5 | 15.9 | 17.5 | 9.2 | 87.3 |
| 1,1,1-Trichloroethane | 16.4 | 11.9 | 10.7 | 9.5 | 9.4 | 11.6 | 22.4 | 57.8 |
| Carbon tetrachloride | 13.1 | 11.3 | 13.0 | 11.8 | 11.2 | 12.1 | 6.7 | 60.5 |
| Benzene | 21.1 | 19.3 | 18.7 | 18.2 | 16.9 | 18.8 | 7.4 | 94.1 |
| Trichloroethene | 19.6 | 16.4 | 16.5 | 16.5 | 15.5 | 16.9 | 8.3 | 84.5 |
| 1,2-Dichloropropane | 21.8 | 19.0 | 18.3 | 18.8 | 16.5 | 18.9 | 9.0 | 94.4 |
| Dibromomethane | 20.9 | 17.9 | 17.9 | 17.2 | 18.3 | 18.4 | 6.9 | 92.1 |
| Bromodichloromethane | 20.9 | 18.0 | 18.9 | 18.2 | 17.3 | 18.6 | 6.6 | 93.2 |
| Toluene | 22.2 | 17.3 | 18.8 | 17.0 | 15.9 | 18.2 | 12.0 | 91.2 |
| 1,1,2-Trichloroethane | 21.0 | 16.5 | 17.2 | 17.2 | 16.5 | 17.7 | 9.6 | 88.4 |
| 1,3-Dichloropropane | 21.4 | 17.3 | 18.7 | 18.6 | 16.7 | 18.5 | 8.8 | 92.6 |
| Dibromochloromethane | 20.9 | 18.1 | 19.0 | 18.8 | 16.6 | 18.7 | 7.5 | 93.3 |
| Chlorobenzene | 20.8 | 18.4 | 17.6 | 16.8 | 14.8 | 17.7 | 11.2 | 88.4 |
| 1,1,1,2-Tetrachloroethane | 19.5 | 19.0 | 17.8 | 17.2 | 16.5 | 18.0 | 6.2 | 90.0 |
| Ethylbenzene | 21.1 | 18.3 | 18.5 | 16.9 | 15.3 | 18.0 | 10.6 | 90.0 |
| p-Xylene | 20.0 | 17.4 | 18.2 | 16.3 | 14.4 | 17.3 | 10.9 | 86.3 |
| o-Xylene | 20.7 | 17.2 | 16.8 | 16.2 | 14.8 | 17.1 | 11.4 | 85.7 |
| Styrene | 18.3 | 15.9 | 16.2 | 15.3 | 13.7 | 15.9 | 9.3 | 79.3 |
| Bromoform | 20.1 | 15.9 | 17.1 | 17.5 | 16.1 | 17.3 | 8.6 | 86.7 |
| iso-Propylbenzene | 21.0 | 18.1 | 19.2 | 18.4 | 15.6 | 18.4 | 9.6 | 92.2 |
| Bromobenzene | 20.4 | 16.2 | 17.2 | 16.7 | 15.4 | 17.2 | 10.1 | 85.9 |
| 1,1,2,2-Tetrachloroethane | 23.3 | 17.9 | 21.2 | 18.8 | 16.8 | 19.6 | 12.1 | 96.0 |
| 1,2,3-Trichloropropane | 18.4 | 14.6 | 15.6 | 16.1 | 15.6 | 16.1 | 8.0 | 80.3 |
| n-Propylbenzene | 20.4 | 18.9 | 17.9 | 17.0 | 14.3 | 17.7 | 11.6 | 88.4 |
| 2-Chlorotoluene | 19.1 | 17.3 | 16.1 | 16.0 | 14.4 | 16.7 | 9.2 | 83.6 |
| 4-Chlorotoluene | 19.0 | 15.5 | 16.8 | 15.9 | 13.6 | 16.4 | 10.6 | 81.8 |
| 1,3,5-Trimethylbenzene | 20.8 | 18.0 | 17.4 | 16.1 | 14.7 | 17.4 | 11.7 | 86.9 |
| sec-Butylbenzene | 21.4 | 18.3 | 18.9 | 17.0 | 14.9 | 18.1 | 11.8 | 90.5 |
| 1,2,4-Trimethylbenzene | 20.5 | 18.6 | 16.8 | 15.3 | 13.7 | 17.0 | 14.1 | 85.0 |
| 1,3-Dichlorobenzene | 17.6 | 15.9 | 15.6 | 14.2 | 14.4 | 15.6 | 7.9 | 77.8 |
| p-iso-Propyltoluene | 20.5 | 17.0 | 17.1 | 15.6 | 13.4 | 16.7 | 13.9 | 83.6 |
| 1,4-Dichlorobenzene | 18.5 | 13.8 | 14.8 | 16.7 | 14.9 | 15.7 | 10.5 | 78.7 |
| 1,2-Dichlorobenzene | 18.4 | 15.0 | 15.4 | 15.3 | 13.5 | 15.5 | 10.5 | 77.6 |
| n-Butylbenzene | 19.6 | 15.9 | 15.9 | 14.4 | 18.9 | 16.9 | 11.7 | 84.6 |
| 1,2,4-Trichlorobenzene | 15.2 | 17.2 | 17.4 | 13.6 | 12.1 | 15.1 | 13.5 | 75.4 |
| Hexachlorobutadiene | 18.7 | 16.2 | 15.5 | 13.8 | 16.6 | 16.1 | 10.0 | 80.7 |
| Naphthalene | 13.9 | 11.1 | 10.2 | 10.8 | 11.4 | 11.5 | 11.0 | 57.4 |
| 1,2,3-Trichlorobenzene | 14.9 | 15.2 | 16.8 | 13.7 | 12.7 | 14.7 | 9.5 | 73.2 |

TABLE 19
RECOVERIES IN GARDEN SOIL FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

| Compound | Recovery per Replicate (ng) 1 | 2 | 3 | 4 | 5 | Mean | RSD | Mean Rec |
|---|---|---|---|---|---|---|---|---|
| Vinyl chloride | 12.7 | 10.9 | 9.8 | 8.1 | 7.2 | 9.7 | 20.2 | 48.7 |
| Trichlorofluoromethane | 33.7 | 6.4 | 30.3 | 27.8 | 22.9 | 24.2 | 39.6 | 121 |
| 1,1-Dichloroethene | 27.7 | 20.5 | 24.1 | 15.1 | 13.2 | 20.1 | 26.9 | 101 |
| Methylene chloride | 25.4 | 23.9 | 24.7 | 22.2 | 24.2 | 24.1 | 4.4 | 120 |
| trans-1,2-Dichloroethene | 2.8 | 3.0 | 3.3 | 2.2 | 2.4 | 2.7 | 15.0 | 13.6 |
| 1,1-Dichloroethane | 24.1 | 26.3 | 27.0 | 20.5 | 21.2 | 23.8 | 11.0 | 119 |
| cis-1,2-Dichloroethene | 8.3 | 10.2 | 8.7 | 5.8 | 6.4 | 7.9 | 20.1 | 39.4 |
| Bromochloromethane | 11.1 | 11.8 | 10.2 | 8.8 | 9.0 | 10.2 | 11.2 | 50.9 |
| Chloroform | 16.7 | 16.9 | 17.0 | 13.8 | 15.0 | 15.9 | 7.9 | 79.3 |
| 1,1,1-Trichloroethane | 24.6 | 22.8 | 22.1 | 16.2 | 20.9 | 21.3 | 13.4 | 107 |
| Carbon tetrachloride | 19.4 | 20.3 | 22.2 | 20.0 | 20.2 | 20.4 | 4.6 | 102 |
| Benzene | 21.4 | 22.0 | 22.4 | 19.6 | 20.4 | 21.2 | 4.9 | 106 |
| Trichloroethene | 12.4 | 16.5 | 14.9 | 9.0 | 9.9 | 12.5 | 22.9 | 62.7 |
| 1,2-Dichloropropane | 19.0 | 18.8 | 19.7 | 16.0 | 17.6 | 18.2 | 7.1 | 91.0 |
| Dibromomethane | 7.3 | 8.0 | 6.9 | 5.6 | 6.8 | 6.9 | 11.3 | 34.6 |
| Bromodichloromethane | 14.9 | 15.9 | 15.9 | 12.8 | 13.9 | 14.7 | 8.3 | 73.3 |
| Toluene | 42.6 | 39.3 | 45.1 | 39.9 | 45.3 | 42.4 | 5.9 | 212 |
| 1,1,2-Trichloroethane | 13.9 | 15.2 | 1.4 | 21.3 | 14.9 | 15.9 | 17.0 | 79.6 |
| 1,3-Dichloropropane | 13.3 | 16.7 | 11.3 | 10.9 | 9.5 | 12.3 | 20.3 | 61.7 |
| Dibromochloromethane | 14.5 | 13.1 | 14.5 | 11.9 | 14.4 | 13.7 | 7.6 | 68.3 |
| Chlorobenzene | 8.4 | 10.0 | 8.3 | 6.9 | 7.8 | 8.3 | 12.1 | 41.3 |
| 1,1,1,2-Tetrachloroethane | 16.7 | 16.7 | 15.6 | 15.8 | 15.7 | 16.1 | 3.2 | 80.4 |
| Ethylbenzene | 22.1 | 21.4 | 23.1 | 20.1 | 22.6 | 21.9 | 4.8 | 109 |
| p-Xylene | 41.4 | 38.4 | 43.8 | 38.3 | 44.0 | 41.2 | 6.1 | 206 |
| o-Xylene | 31.7 | 30.8 | 34.3 | 30.4 | 33.2 | 32.1 | 4.6 | 160 |
| Styrene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Bromoform | 8.6 | 8.9 | 9.1 | 7.0 | 7.7 | 8.3 | 9.4 | 41.4 |
| iso-Propylbenzene | 18.1 | 18.8 | 9.7 | 18.3 | 19.6 | 18.9 | 3.5 | 94.4 |
| Bromobenzene | 5.1 | 5.4 | 5.3 | 4.4 | 4.0 | 4.8 | 11.6 | 24.1 |
| 1,1,2,2-Tetrachloroethane | 14.0 | 13.5 | 14.7 | 15.3 | 17.1 | 14.9 | 8.5 | 74.5 |
| 1,2,3-Trichloropropane | 11.0 | 12.7 | 11.7 | 11.7 | 11.9 | 11.8 | 4.5 | 59.0 |
| n-Propylbenzene | 13.4 | 13.3 | 14.7 | 12.8 | 13.9 | 13.6 | 4.7 | 68.1 |
| 2-Chlorotoluene | 8.3 | 9.0 | 11.7 | 8.7 | 7.9 | 9.1 | 14.8 | 45.6 |
| 4-Chlorotoluene | 5.1 | 5.4 | 5.5 | 4.8 | 4.5 | 5.0 | 7.9 | 25.2 |
| 1,3,5-Trimethylbenzene | 31.3 | 27.5 | 33.0 | 31.1 | 33.6 | 31.3 | 6.8 | 157 |
| sec-Butylbenzene | 13.5 | 13.4 | 16.4 | 13.8 | 15.4 | 14.5 | 8.3 | 72.5 |
| 1,2,4-Trimethylbenzene | 38.7 | 32.4 | 40.8 | 34.1 | 40.3 | 37.3 | 9.1 | 186 |
| 1,3-Dichlorobenzene | 3.6 | 3.6 | 3.7 | 3.0 | 3.2 | 3.4 | 8.0 | 17.2 |
| p-iso-Propyltoluene | 14.7 | 14.1 | 16.1 | 13.9 | 15.1 | 14.8 | 5.2 | 73.8 |
| 1,4-Dichlorobenzene | 3.0 | 3.5 | 3.3 | 2.6 | 2.8 | 3.0 | 10.2 | 15.0 |
| 1,2-Dichlorobenzene | 3.6 | 4.3 | 4.0 | 3.5 | 3.6 | 3.8 | 8.3 | 19.0 |
| n-Butylbenzene | 17.4 | 13.8 | 14.0 | 18.9 | 24.0 | 17.6 | 21.2 | 88.0 |
| 1,2,4-Trichlorobenzene | 2.8 | 2.9 | 3.3 | 2.6 | 3.2 | 3.0 | 8.5 | 15.0 |
| Hexachlorobutadiene | 4.8 | 4.0 | 6.1 | 5.6 | 6.0 | 5.3 | 15.1 | 26.4 |
| Naphthalene | 5.5 | 5.1 | 5.5 | 4.7 | 5.6 | 5.3 | 6.2 | 26.5 |
| 1,2,3-Trichlorobenzene | 2.2 | 2.3 | 2.4 | 2.2 | 2.3 | 2.3 | 3.5 | 11.4 |

Data in Table 19 are from Reference 15.

TABLE 20

VOLATILE ORGANIC ANALYTE RECOVERY FROM SOIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

| Compound | Soil/$H_2O$[b] Recovery Mean | RSD | Soil/Oil[c] Recovery Mean | RSD | Soil/Oil/$H_2O$ Recovery Mean | RSD |
|---|---|---|---|---|---|---|
| Chloromethane | 61 | 20 | 40 | 18 | 108 | 68 |
| Bromomethane | 58 | 20 | 47 | 13 | 74 | 13 |
| Vinyl chloride | 54 | 12 | 46 | 11 | 72 | 20 |
| Chloroethane | 46 | 10 | 41 | 8 | 52 | 14 |
| Methylene chloride | 60 | 2 | 65 | 8 | 76 | 11 |
| Acetone | INT[e] | INT | 44 | 8 | | |
| Carbon disulfide | 47 | 13 | 53 | 10 | 47 | 4 |
| 1,1-Dichloroethene | 48 | 9 | 47 | 5 | 58 | 3 |
| 1,1-Dichloroethane | 61 | 6 | 58 | 9 | 61 | 6 |
| trans-1,2-Trichloroethane | 54 | 7 | 60 | 7 | 56 | 5 |
| cis-1,2-Dichloroethene | 60 | 4 | 72 | 6 | 63 | 8 |
| Chloroform | 104 | 11 | 93 | 6 | 114 | 15 |
| 1,2-Dichloroethane | 177 | 50 | 117 | 8 | 151 | 22 |
| 2-Butanone | INT | 36 | 38 | INT | | |
| 1,1,1-Trichloroethane | 124 | 13 | 72 | 16 | 134 | 26 |
| Carbon tetrachloride | 172 | 122 | INT | INT | | |
| Vinyl acetate | 88 | 11 | INT | | | |
| Bromodichloromethane | 93 | 4 | 91 | 23 | 104 | 23 |
| 1,1,2,2-Tetrachloroethane | 96 | 13 | 50 | 12 | 104 | 7 |
| 1,2-Dichloropropane | 105 | 8 | 102 | 6 | 111 | 6 |
| trans-1,3-Dichloropropene | 134 | 10 | 84 | 16 | 107 | 8 |
| Trichloroethene | 98 | 9 | 99 | 10 | 100 | 5 |
| Dibromochloromethane | 119 | 8 | 125 | 31 | 142 | 16 |
| 1,1,2-Trichloroethane | 126 | 10 | 72 | 16 | 97 | 4 |
| Benzene | 99 | 7 | CONT[f] | CONT | | |
| cis-1,3-Dichloropropene | 123 | 12 | 94 | 13 | 112 | 9 |
| Bromoform | 131 | 13 | 58 | 18 | 102 | 9 |
| 2-Hexanone | 155 | 18 | 164 | 19 | 173 | 29 |
| 4-Methyl-2-pentanone | 152 | 20 | 185 | 20 | 169 | 18 |
| Tetrachloroethene | 90 | 9 | 123 | 14 | 128 | 7 |
| Toluene | 94 | 3 | CONT | CONT | | |
| Chlorobenzene | 98 | 7 | 93 | 18 | 112 | 5 |
| Ethylbenzene | 114 | 13 | CONT | CONT | | |
| Styrene | 106 | 8 | 93 | 18 | 112 | 5 |
| p-Xylene | 97 | 9 | CONT | CONT | | |
| o-Xylene | 105 | 8 | 112 | 12 | 144 | 13 |

TABLE 20 (cont.)

| Compound | Soil/$H_2O$[b] Recovery Mean | RSD | Soil/Oil[c] Recovery Mean | RSD | Soil/Oil/$H_2O$ Recovery Mean | RSD |
|---|---|---|---|---|---|---|
| Surrogates | | | | | | |
| 1,2-Dichloroethane | 177 | 50 | 117 | 8 | 151 | 22 |
| Toluene-$d_8$ | 96 | 6 | 79 | 12 | 82 | 6 |
| Bromofluorobenzene | 139 | 13 | 37 | 13 | 62 | 5 |

[a] Results are for 10 min. distillations times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision value reflects the propagated errors. Each analyte was spiked at 50 ppb. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may introduce bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Soil samples spiked with 0.2 mL water containing analytes and then 5 mL water added to make slurry.

[c] Soil sample + 1 g cod liver oil, spiked with 0.2 mL water containing analytes.

[d] Soil samples + 1 g cod liver oil, spiked as above with 5 mL of water added to make slurry.

[e] Interference by co-eluting compounds prevented accurate measurement of analyte.

[f] Contamination of sample matrix by analyte prevented assessment of efficiency.

TABLE 21

VACUUM DISTILLATION EFFICIENCIES FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

| Compound | Efficiency Mean (%) | RSD (%) |
|---|---|---|
| Chloromethane | N/A[b] | |
| Bromomethane | N/A[b] | |
| Vinyl chloride | N/A[b] | |
| Chloroethane | N/A[b] | |
| Methylene chloride | CONT[c] | |
| Acetone | CONT[c] | |
| Carbon disulfide | 79 | 36 |
| 1,1-Dichloroethene | 122 | 39 |
| 1,1-Dichloroethane | 126 | 35 |
| trans-1,2-Trichloroethene | 109 | 46 |
| cis-1,2-Dichloroethene | 106 | 22 |
| Chloroform | 111 | 32 |
| 1,2-Dichloroethane | 117 | 27 |
| 2-Butanone | INT[d] | |
| 1,1,1-Trichloroethane | 106 | 30 |
| Carbon tetrachloride | 83 | 34 |
| Vinyl acetate | INT[d] | |
| Bromodichloromethane | 97 | 22 |
| 1,1,2,2-Tetrachloroethane | 67 | 20 |
| 1,2-Dichloropropane | 117 | 23 |
| trans-1,3-Dichloropropene | 92 | 22 |
| Trichloroethene | 98 | 31 |
| Dibromochloromethane | 71 | 19 |
| 1,1,2-Trichloroethane | 92 | 20 |
| Benzene | 129 | 35 |
| cis-1,3-Dichloropropene | 102 | 24 |
| Bromoform | 58 | 19 |
| 2-Hexanone | INT[d] | |
| 4-Methyl-2-pentanone | 113 | 37 |
| Tetrachloroethene | 66 | 20 |
| Toluene | CONT[c] | |
| Chlorobenzene | 65 | 19 |
| Ethylbenzene | 74 | 19 |
| Styrene | 57 | 14 |
| p-Xylene | 46 | 13 |
| o-Xylene | 83 | 20 |

TABLE 21 (cont.)

| Compound | Efficiency Mean (%) | RSD (%) |
|---|---|---|
| Surrogates | | |
| 1,2-Dichloroethane | 115 | 27 |
| Toluene-$d_8$ | 88 | 24 |
| Bromofluorobenzene | 52 | 15 |

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicate 10-g aliquots of fish spiked at 25 ppb were analyzed using GC/MS external standard quantitation. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards were replicated and results reflect 1 sigma propagated standard deviation.

[b] No analyses.

[c] Contamination of sample matrix by analyte prevented accurate assessment of analyte efficiency.

[d] Interfering by co-eluting compounds prevented accurate measurement of analyte.

TABLE 22

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

| Compound | Method Detection Limit (ppb) External Standard Method | Internal Standard Method |
|---|---|---|
| Chloromethane | 7.8 | 7.3 |
| Bromomethane | 9.7 | 9.8 |
| Vinyl chloride | 9.5 | 9.4 |
| Chloroethane | 9.2 | 10.0 |
| Methylene chloride | CONT[b] | CONT[b] |
| Acetone | CONT[b] | CONT[b] |
| Carbon disulfide | 5.4 | 4.9 |
| 1,1-Dichloroethene | 4.0 | 5.7 |
| 1,1-Dichloroethane | 4.0 | 3.5 |
| trans-1,2-Dichloroethene | 4.4 | 4.0 |
| cis-1,2-Dichloroethene | 4.7 | 4.1 |
| Chloroform | 5.6 | 5.0 |
| 1,2-Dichloroethane | 3.3 | 3.2 |
| 2-Butanone | INT[c] | INT[c] |
| 1,1,1-Trichloroethane | 1.1 | 4.2 |
| Carbon tetrachloride | 3.2 | 3.5 |
| Vinyl acetate | INT[c] | INT[c] |
| Bromodichloromethane | 3.2 | 2.8 |
| 1,1,2,2-Tetrachloroethane | 4.4 | 3.8 |
| 1,2-Dichloropropane | 3.8 | 3.7 |
| trans-1,3-Dichloropropene | 3.4 | 3.0 |
| Trichloroethene | 3.1 | 4.0 |
| Dibromochloromethane | 3.5 | 3.2 |
| 1,1,2-Trichloroethane | 4.4 | 3.3 |
| Benzene | 3.6 | 3.2 |
| cis-1,3-Dichloropropene | 3.5 | 3.0 |
| Bromoform | 4.9 | 4.0 |
| 2-Hexanone | 7.7 | 8.0 |
| 4-Methyl-2-pentanone | 7.5 | 8.0 |
| Tetrachloroethene | 4.3 | 4.0 |
| Toluene | 3.0 | 2.5 |
| Chlorobenzene | 3.3 | 2.8 |
| Ethylbenzene | 3.6 | 3.5 |
| Styrene | 3.5 | 3.3 |
| p-Xylene | 3.7 | 3.5 |
| o-Xylene | 3.3 | 4.7 |

Footnotes are on the following page.

[a] Values shown are the average MDLs for studies on three non-consecutive days, involving seven replicate analyses of 10 g of fish tissue spiked a 5 ppb. Daily MDLs were calculated as three times the standard deviation. Quantitation was performed by GC/MS Method 8260 and separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] Contamination of sample by analyte prevented determination.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 23

VOLATILE ORGANIC ANALYTES RECOVERY FOR WATER
USING VACUUM DISTILLATION (METHOD 5032)[a]

| Compound | 5 mL $H_2O$[b] Recovery Mean | RSD | 20 mL $H_2O$[c] Recovery Mean | RSD | 20 mL $H_2O$/Oil Recovery Mean | RSD |
|---|---|---|---|---|---|---|
| Chloromethane | 114 | 27 | 116 | 29 | 176 | 67 |
| Bromomethane | 131 | 14 | 121 | 14 | 113 | 21 |
| Vinyl chloride | 131 | 13 | 120 | 16 | 116 | 23 |
| Chloroethane | 110 | 15 | 99 | 8 | 96 | 16 |
| Methylene chloride | 87 | 16 | 105 | 15 | 77 | 6 |
| Acetone | 83 | 22 | 65 | 34 | 119 | 68 |
| Carbon disulfide | 138 | 17 | 133 | 23 | 99 | 47 |
| 1,1-Dichloroethene | 105 | 11 | 89 | 4 | 96 | 18 |
| 1,1-Dichloroethane | 118 | 10 | 119 | 11 | 103 | 25 |
| trans-1,2-Dichloroethene | 105 | 11 | 107 | 14 | 96 | 18 |
| cis-1,2-Dichloroethene | 106 | 7 | 99 | 5 | 104 | 23 |
| Chloroform | 114 | 6 | 104 | 8 | 107 | 21 |
| 1,2-Dichloroethane | 104 | 6 | 109 | 8 | 144 | 19 |
| 2-Butanone | 83 | 50 | 106 | 31 | INT[c] | |
| 1,1,1-Trichloroethane | 118 | 9 | 109 | 9 | 113 | 23 |
| Carbon tetrachloride | 102 | 6 | 108 | 12 | 109 | 27 |
| Vinyl acetate | 90 | 16 | 99 | 7 | 72 | 36 |
| Bromodichloromethane | 104 | 3 | 110 | 5 | 99 | 5 |
| 1,1,2,2-Tetrachloroethane | 85 | 17 | 81 | 7 | 111 | 43 |
| 1,2-Dichloropropane | 100 | 6 | 103 | 2 | 104 | 7 |
| trans-1,3-Dichloropropene | 105 | 8 | 105 | 4 | 92 | 4 |
| Trichloroethene | 98 | 4 | 99 | 2 | 95 | 5 |
| Dibromochloroethane | 99 | 8 | 99 | 6 | 90 | 25 |
| 1,1,2-Trichloroethane | 98 | 7 | 100 | 4 | 76 | 12 |
| Benzene | 97 | 4 | 100 | 5 | 112 | 10 |
| cis-1,3-Dichloropropene | 106 | 5 | 105 | 4 | 98 | 3 |
| Bromoform | 93 | 16 | 94 | 8 | 57 | 21 |
| 2-Hexanone | 60 | 17 | 63 | 16 | 78 | 23 |
| 4-Methyl-2-pentanone | 79 | 24 | 63 | 14 | 68 | 15 |
| Tetrachloroethene | 101 | 3 | 97 | 7 | 77 | 14 |
| Toluene | 100 | 6 | 97 | 8 | 85 | 5 |
| Chlorobenzene | 98 | 6 | 98 | 4 | 88 | 16 |
| Ethylbenzene | 100 | 3 | 92 | 8 | 73 | 13 |
| Styrene | 98 | 4 | 97 | 9 | 88 | 16 |
| p-Xylene | 96 | 4 | 94 | 8 | 60 | 12 |
| o-Xylene | 96 | 7 | 95 | 6 | 72 | 14 |

TABLE 23 (cont.)

| Compound | 5 mL $H_2O$[b] Recovery Mean | RSD | 20 mL $H_2O$[c] Recovery Mean | RSD | 20 mL $H_2O$/Oil Recovery Mean | RSD |
|---|---|---|---|---|---|---|
| Surrogates | | | | | | |
| 1,2-Dichloroethane | 104 | 6 | 109 | 6 | 144 | 19 |
| Toluene-$d_8$ | 104 | 5 | 102 | 2 | 76 | 7 |
| Bromofluorobenzene | 106 | 6 | 106 | 9 | 40 | 8 |

[a] Results are for 10 min. distillation times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision values reflect the propagated errors. Concentrations of analytes were 50 ppb for 5-mL samples and 25 ppb for 20-mL samples. Recovery data generated with comparison to analyses of standards without the water matrix.

[b] Sample contained 1 gram cod liver oil and 20 mL water. An emulsion was created by adding 0.2 mL of water saturated with lecithin.

[c] Interference by co-eluting compounds prevented accurate assessment of recovery.

TABLE 24

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES USING VACUUM DISTILLATION (METHOD 5032) (INTERNAL STANDARD METHOD)[a]

| Compound | Water[b] (µg/L) | Soil[c] (µg/kg) | Tissue[d] (µg/kg) | Oil[e] (mg/kg) |
|---|---|---|---|---|
| Chloromethane | 3.2 | 8.0 | 7.3 | N/A[f] |
| Bromomethane | 2.8 | 4.9 | 9.8 | N/A[f] |
| Vinyl chloride | 3.5 | 6.0 | 9.4 | N/A[f] |
| Chloroethane | 5.9 | 6.0 | 10.0 | N/A[f] |
| Methylene chloride | 3.1 | 4.0 | CONT[g] | 0.05 |
| Acetone | 5.6 | CONT[g] | CONT[g] | 0.06 |
| Carbon disulfide | 2.5 | 2.0 | 4.9 | 0.18 |
| 1,1-Dichloroethene | 2.9 | 3.2 | 5.7 | 0.18 |
| 1,1-Dichloroethane | 2.2 | 2.0 | 3.5 | 0.14 |
| trans-1,2-Dichloroethene | 2.2 | 1.4 | 4.0 | 0.10 |
| cis-1,2-Dichloroethene | 2.0 | 2.3 | 4.1 | 0.07 |
| Chloroform | 2.4 | 1.8 | 5.0 | 0.07 |
| 1,2-Dichloroethane | 1.7 | 1.5 | 3.2 | 0.06 |
| 2-Butanone | 7.4 | INT[h] | INT[h] | INT[h] |
| 1,1,1-Trichloroethane | 1.8 | 1.7 | 4.2 | 0.10 |
| Carbon tetrachloride | 1.4 | 1.5 | 3.5 | 0.13 |
| Vinyl acetate | 11.8 | INT[h] | INT[h] | INT[h] |
| Bromodichloromethane | 1.6 | 1.4 | 2.8 | 0.06 |
| 1,1,2,2-Tetrachloroethane | 2.5 | 2.1 | 3.8 | 0.02 |
| 1,2-Dichloropropane | 2.2 | 2.1 | 3.7 | 0.15 |
| trans-1,3-Dichloropropene | 1.5 | 1.7 | 3.0 | 0.05 |
| Trichloroethene | 1.6 | 1.7 | 4.0 | 0.04 |
| Dibromochloromethane | 1.7 | 1.5 | 3.2 | 0.07 |
| 1,1,2-Trichloroethane | 2.1 | 1.7 | 3.3 | 0.05 |
| Benzene | 0.5 | 1.5 | 3.2 | 0.05 |
| cis-1,3-Dichloropropene | 1.4 | 1.7 | 3.0 | 0.04 |
| Bromoform | 1.8 | 1.5 | 4.0 | 0.05 |
| 2-Hexanone | 4.6 | 3.6 | 8.0 | INT[h] |
| 4-Methyl-2-pentanone | 3.5 | 4.6 | 8.0 | INT[h] |
| Tetrachloroethene | 1.4 | 1.6 | 4.0 | 0.10 |
| Toluene | 1.0 | 3.3 | 2.5 | 0.05 |
| Chlorobenzene | 1.4 | 1.4 | 2.8 | 0.06 |
| Ethylbenzene | 1.5 | 2.8 | 3.5 | 0.04 |
| Styrene | 1.4 | 1.4 | 3.3 | 0.18 |
| p-Xylene | 1.5 | 2.9 | 3.5 | 0.20 |
| o-Xylene | 1.7 | 3.4 | 4.7 | 0.07 |

Footnotes are found on the following page.

[a] Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Method detection limits are the average MDLs for studies on three non-consecutive days.

[b] Method detection limits are the average MDLs for studies of three non-consecutive days. Daily studies were seven replicated analyses of 5 mL aliquots of 4 ppb soil. Daily MDLs were three times the standard deviation.

[c] Daily studies were seven replicated analyses of 10 g fish tissue spiked at 5 ppb. Daily MDLs were three times the standard deviation. Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[d] Method detection limits are estimated analyzing 1 g of cod liver oil samples spiked at 250 ppm. Five replicates were analyzed using Method 8260.

[e] No analyses.

[f] Contamination of sample by analyte prevented determination.

[g] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 25

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
(METHOD 5032) (EXTERNAL STANDARD METHOD)[a]

| Compound | Water[b] (µg/L) | Soil[c] (µg/kg) | Tissue[d] (µg/kg) | Oil[e] (mg/kg) |
|---|---|---|---|---|
| Chloromethane | 3.1 | 8.6[f] | 7.8 | N/A[g] |
| Bromomethane | 2.5 | 4.9[f] | 9.7 | N/A[g] |
| Vinyl chloride | 4.0 | 7.1[f] | 9.5 | N/A[g] |
| Chloroethane | 6.1 | 7.5[f] | 9.2 | N/A[g] |
| Methylene chloride | 3.1 | 3.3 | CONT[h] | 0.08 |
| Acetone | 33.0[f] | CONT[h] | CONT[h] | 0.12 |
| Carbon disulfide | 2.5 | 3.2 | 5.4 | 0.19 |
| 1,1-Dichloroethene | 3.4 | 3.8 | 4.0 | 0.19 |
| 1,1-Dichloroethane | 2.3 | 1.7 | 4.0 | 0.13 |
| trans-1,2-Dichloroethene | 3.0 | 3.2 | 4.4 | 0.09 |
| cis-1,2-Dichloroethene | 2.4 | 2.7 | 4.7 | 0.08 |
| Chloroform | 2.7 | 2.6 | 5.6 | 0.06 |
| 1,2-Dichloroethane | 1.6 | 1.7 | 3.3 | 0.06 |
| 2-Butanone | 57.0[f] | INT[i] | INT[i] | INT[i] |
| 1,1,1-Trichloroethane | 1.6 | 2.4 | 1.1 | 0.08 |
| Carbon tetrachloride | 1.5 | 1.7 | 3.2 | 0.15 |
| Vinyl acetate | 23.0[f] | INT[i] | INT[i] | INT[i] |
| Bromodichloromethane | 2.0 | 2.3 | 3.2 | 0.05 |
| 1,1,2,2-Tetrachloroethane | 3.6 | 3.2 | 4.4 | 0.09 |
| 1,2-Dichloropropane | 2.9 | 3.7 | 3.8 | 0.12 |
| trans-1,3-Dichloropropene | 2.3 | 2.4 | 3.8 | 0.08 |
| Trichloroethene | 2.5 | 3.0 | 3.1 | 0.06 |
| Dibromochloromethane | 2.1 | 2.9 | 3.5 | 0.04 |
| 1,1,2-Trichloroethane | 2.7 | 2.8 | 4.4 | 0.07 |
| Benzene | 1.7 | 2.9 | 3.6 | 0.03 |
| cis-1,3-Dichloropropene | 2.1 | 2.5 | 3.5 | 0.06 |
| Bromoform | 2.3 | 2.5 | 4.9 | 0.10 |
| 2-Hexanone | 4.6 | 4.6 | 7.7 | INT[i] |
| 4-Methyl-2-pentanone | 3.8 | 3.9 | 7.5 | INT[i] |
| Tetrachloroethene | 1.8 | 2.6 | 4.3 | 0.12 |
| Toluene | 1.8 | 4.4 | 3.0 | 0.09 |
| Chlorobenzene | 2.4 | 2.6 | 3.3 | 0.07 |
| Ethylbenzene | 2.4 | 4.1 | 3.6 | 0.09 |
| Styrene | 2.0 | 2.5 | 3.5 | 0.16 |
| p-Xylene | 2.3 | 3.9 | 3.7 | 0.18 |
| o-Xylene | 2.4 | 4.1 | 3.3 | 0.08 |

[a] Method detection limits are the average MDLs for studies on three non-consecutive days. Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb. Daily MDLs were three times the standard deviation.

[b] Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb.

[c] These studies were seven replicate analyses of 5-g aliquots of soil spiked at 4 ppb.

[d] These studies were seven replicate analyses of 10-g aliquots of fish tissue spiked at 5 ppb.

[e] Method detection limits were estimated by analyzing cod liver oil samples spiked at 250 ppb. Five replicates were analyzed using Method 8260.

[f] Method detection limits were estimated by analyzing replicate 50 ppb standards five times over a single day.

[g] No analyses.

[h] Contamination of sample by analyte prevented determination.

[l] Interference by co-eluting compound prevented accurate quantitation.

TABLE 26

VOLATILE ORGANIC ANALYTE RECOVERY FROM OIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

| Compound | Recovery Mean (%) | RSD (%) |
|---|---|---|
| Chloromethane | N/A[b] | |
| Bromomethane | N/A[b] | |
| Vinyl chloride | N/A[b] | |
| Chloroethane | N/A[b] | |
| Methylene chloride | 62 | 32 |
| Acetone | 108 | 55 |
| Carbon disulfide | 98 | 46 |
| 1,1-Dichloroethene | 97 | 24 |
| 1,1-Dichloroethane | 96 | 22 |
| trans-1,2-Trichloroethene | 86 | 23 |
| cis-1,2-Dichloroethene | 99 | 11 |
| Chloroform | 93 | 14 |
| 1,2-Dichloroethane | 138 | 31 |
| 2-Butanone | INT[c] | |
| 1,1,1-Trichloroethane | 89 | 14 |
| Carbon tetrachloride | 129 | 23 |
| Vinyl acetate | INT[c] | |
| Bromodichloromethane | 106 | 14 |
| 1,1,2,2-Tetrachloroethane | 205 | 46 |
| 1,2-Dichloropropane | 107 | 24 |
| trans-1,3-Dichloropropene | 98 | 13 |
| Trichloroethene | 102 | 8 |
| Dibromochloromethane | 168 | 21 |
| 1,1,2-Trichloroethane | 95 | 7 |
| Benzene | 146 | 10 |
| cis-1,3-Dichloropropene | 98 | 11 |
| Bromoform | 94 | 18 |
| 2-Hexanone | INT[c] | |
| 4-Methyl-2-pentanone | INT[c] | |
| Tetrachloroethene | 117 | 22 |
| Toluene | 108 | 8 |
| Chlorobenzene | 101 | 12 |
| Ethylbenzene | 96 | 10 |
| Styrene | 120 | 46 |
| p-Xylene | 87 | 23 |
| o-Xylene | 90 | 10 |

TABLE 26 (cont.)

| Compound | Recovery Mean (%) | RSD (%) |
|---|---|---|
| Surrogates | | |
| 1,2-Dichloroethane | 137 | 30 |
| Toluene-$d_8$ | 84 | 6 |
| Bromofluorobenzene | 48 | 2 |

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicates of 10-g fish aliquots spiked at 25 ppb were analyzed. Quantitation was performed with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Standards and samples were replicated and precision value reflects the propagated errors. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Not analyzed.

[c] Interference by co-evaluating compounds prevented accurate measurement of analyte.

TABLE 27

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN OIL (METHOD 5032)[a]

| Compound | Method Detection Limit (ppb) External Standard Method | Internal Standard Method |
|---|---|---|
| Chloromethane | N/A[b] | N/A[b] |
| Bromomethane | N/A[b] | N/A[b] |
| Vinyl chloride | N/A[b] | N/A[b] |
| Chloroethane | N/A[b] | N/A[b] |
| Methylene chloride | 80 | 50 |
| Acetone | 120 | 60 |
| Carbon disulfide | 190 | 180 |
| 1,1-Dichloroethene | 190 | 180 |
| 1,1-Dichloroethane | 130 | 140 |
| trans-1,2-Dichloroethene | 90 | 100 |
| cis-1,2-Dichloroethene | 80 | 70 |
| Chloroform | 60 | 70 |
| 1,2-Dichloroethane | 60 | 60 |
| 2-Butanone | INT[c] | INT[c] |
| 1,1,1-Trichloroethane | 80 | 100 |
| Carbon tetrachloride | 150 | 130 |
| Vinyl acetate | INT[c] | INT[c] |
| Bromodichloromethane | 50 | 60 |
| 1,1,2,2-Tetrachloroethane | 90 | 20 |
| 1,2-Dichloropropane | 120 | 150 |
| trans-1,3-Dichloropropene | 80 | 50 |
| Trichloroethene | 60 | 40 |
| Dibromochloromethane | 40 | 70 |
| 1,1,2-Trichloroethane | 70 | 50 |
| Benzene | 30 | 50 |
| cis-1,3-Dichloropropene | 60 | 40 |
| Bromoform | 100 | 50 |
| 2-Hexanone | INT[c] | INT[c] |
| 4-Methyl-2-pentanone | INT[c] | INT[c] |
| Tetrachloroethene | 120 | 100 |
| Toluene | 90 | 50 |
| Chlorobenzene | 70 | 60 |
| Ethylbenzene | 90 | 40 |
| Styrene | 160 | 180 |
| p-Xylene | 180 | 200 |
| o-Xylene | 80 | 70 |

[a] Method detection limits are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MDLs were calculated as three times the standard deviation. Quantitation was performed using a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] No analyses.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 28

INTERNAL STANDARDS FOR ANALYTES AND SURROGATES PREPARED USING EQUILIBRIUM HEADSPACE ANALYSIS (METHOD 5021)

| Chloroform-$d_1$ | 1,1,2-TCA-$d_3$ | Bromobenzene-$d_5$ |
|---|---|---|
| Dichlorodifluoromethane | 1,1,1-Trichloroethane | Chlorobenzene |
| Chloromethane | 1,1-Dichloropropene | Bromoform |
| Vinyl chloride | Carbon tetrachloride | Styrene |
| Bromomethane | Benzene | iso-Propylbenzene |
| Chloroethane | Dibromomethane | Bromobenzene |
| Trichlorofluoromethane | 1,2-Dichloropropane | n-Propylbenzene |
| 1,1-Dichloroethene | Trichloroethene | 2-Chlorotoluene |
| Methylene chloride | Bromodichloromethane | 4-Chlorotoluene |
| trans-1,2-Dichloroethene | cis-1,3-Dichloropropene | 1,3,5-Trimethylbenzene |
| 1,1-Dichloroethane | trans-1,3-Dichloropropene | tert-Butylbenzene |
| cis-1,2-Dichloroethene | 1,1,2-Trichloroethane | 1,2,4-Trimethylbenzene |
| Bromochloromethane | Toluene | sec-Butylbenzene |
| Chloroform | 1,3-Dichloropropane | 1,3-Dichlorobenzene |
| 2,2-Dichloropropane | Dibromochloromethane | 1,4-Dichlorobenzene |
| 1,2-Dichloroethane | 1,2-Dibromoethane | p-iso-Propyltoluene |
| | Tetrachloroethene | 1,2-Dichlorobenzene |
| | 1,1,2-Trichloroethane | n-Butylbenzene |
| | Ethylbenzene | 1,2-Dibromo-3-chloropropane |
| | m-Xylene | 1,2,4-Trichlorobenzene |
| | p-Xylene | Naphthalene |
| | o-Xylene | Hexachlorobutadiene |
| | 1,1,2,2-Tetrachloroethane | 1,2,3-Trichlorobenzene |
| | 1,2,3-Trichloropropane | |

TABLE 29

PRECISION AND MDL DETERMINED FOR ANALYSIS OF FORTIFIED SAND[a] (METHOD 5021)

| Compound | % RSD | MDL (µg/kg) |
|---|---|---|
| Benzene | 3.0 | 0.34 |
| Bromochloromethane | 3.4 | 0.27 |
| Bromodichloromethane | 2.4 | 0.21 |
| Bromoform | 3.9 | 0.30 |
| Bromomethane | 11.6 | 1.3 |
| Carbon tetrachloride | 3.6 | 0.32 |
| Chlorobenzene | 3.2 | 0.24 |
| Chloroethane | 5.6 | 0.51 |
| Chloroform | 3.1 | 0.30 |
| Chloromethane | 4.1 | 3.5[b] |
| 1,2-Dibromo-3-chloropropane | 5.7 | 0.40 |
| 1,2-Dibromoethane | 3.2 | 0.29 |
| Dibromomethane | 2.8 | 0.20 |
| 1,2-Dichlorobenzene | 3.3 | 0.27 |
| 1,3-Dichlorobenzene | 3.4 | 0.24 |
| 1,4-Dichlorobenzene | 3.7 | 0.30 |
| Dichlorodifluoromethane | 3.0 | 0.28 |
| 1,1-Dichloroethane | 4.5 | 0.41 |
| 1,2-Dichloroethane | 3.0 | 0.24 |
| 1,1-Dichloroethene | 3.3 | 0.28 |
| cis-1,2-Dichloroethene | 3.2 | 0.27 |
| trans-1,2-Dichloroethene | 2.6 | 0.22 |
| 1,2-Dichloropropane | 2.6 | 0.21 |
| 1,1-Dichloropropene | 3.2 | 0.30 |
| cis-1,3-Dichloropropene | 3.4 | 0.27 |
| Ethylbenzene | 4.8 | 0.47 |
| Hexachlorobutadiene | 4.1 | 0.38 |
| Methylene chloride | 8.2 | 0.62[c] |
| Naphthalene | 16.8 | 3.4[c] |
| Styrene | 7.9 | 0.62 |
| 1,1,1,2-Tetrachloroethane | 3.6 | 0.27 |
| 1,1,2,2-Tetrachloroethane | 2.6 | 0.20 |
| Tetrachloroethene | 9.8 | 1.2[c] |
| Toluene | 3.5 | 0.38 |
| 1,2,4-Trichlorobenzene | 4.2 | 0.44 |
| 1,1,1-Trichloroethane | 2.7 | 0.27 |
| 1,1,2-Trichloroethane | 2.6 | 0.20 |
| Trichloroethene | 2.3 | 0.19 |

TABLE 29 (cont.)

| Compound | % RSD | MDL (µg/kg) |
|---|---|---|
| Trichlorofluoromethane | 2.7 | 0.31 |
| 1,2,3-Trichloropropane | 1.5 | 0.11 |
| Vinyl chloride | 4.8 | 0.45 |
| m-Xylene/p-Xylene | 3.6 | 0.37 |
| o-Xylene | 3.6 | 0.33 |

[a] Most compounds spiked at 2 ng/g (2 µg/kg)
[b] Incorrect ionization due to methanol
[c] Compound detected in unfortified sand at >1 ng

TABLE 30

RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5021)

| Compound | Recovery per Replicate (ng) Sample 1 | Sample 2 | Sample 3 | Mean (ng) | RSD | Recovery (%) |
|---|---|---|---|---|---|---|
| Benzene | 37.6 | 35.2 | 38.4 | 37.1 | 3.7 | 185[a] |
| Bromochloromethane | 20.5 | 19.4 | 20.0 | 20.0 | 2.3 | 100 |
| Bromodichloromethane | 21.1 | 20.3 | 22.8 | 21.4 | 4.9 | 107 |
| Bromoform | 23.8 | 23.9 | 25.1 | 24.3 | 2.4 | 121 |
| Bromomethane | 21.4 | 19.5 | 19.7 | 20.2 | 4.2 | 101 |
| Carbon tetrachloride | 27.5 | 26.6 | 28.6 | 27.6 | 3.0 | 138 |
| Chlorobenzene | 25.6 | 25.4 | 26.4 | 25.8 | 1.7 | 129 |
| Chloroethane | 25.0 | 24.4 | 25.3 | 24.9 | 1.5 | 125 |
| Chloroform | 21.9 | 20.9 | 21.7 | 21.5 | 2.0 | 108 |
| Chloromethane | 21.0 | 19.9 | 21.3 | 20.7 | 2.9 | 104[a] |
| 1,2-Dibromo-3-chloro-propane | 20.8 | 20.8 | 21.0 | 20.9 | 0.5 | 104 |
| 1,2-Dibromoethane | 20.1 | 19.5 | 20.6 | 20.1 | 2.2 | 100 |
| Dibromomethane | 22.2 | 21.0 | 22.8 | 22.0 | 3.4 | 110 |
| 1,2-Dichlorobenzene | 18.0 | 17.7 | 17.1 | 17.6 | 2.1 | 88.0 |
| 1,3-Dichlorobenzene | 21.2 | 21.0 | 20.1 | 20.8 | 2.3 | 104 |
| 1,4-Dichlorobenzene | 20.1 | 20.9 | 19.9 | 20.3 | 2.1 | 102 |
| Dichlorodifluoromethane | 25.3 | 24.1 | 25.4 | 24.9 | 2.4 | 125 |
| 1,1-Dichloroethane | 23.0 | 22.0 | 22.7 | 22.6 | 1.9 | 113 |
| 1,2-Dichloroethane | 20.6 | 19.5 | 19.8 | 20.0 | 2.3 | 100 |
| 1,1-Dichloroethene | 24.8 | 23.8 | 24.4 | 24.3 | 1.7 | 122 |
| cis-1,2-Dichloroethene | 21.6 | 20.0 | 21.6 | 21.1 | 3.6 | 105 |
| trans-1,2-Dichloroethene | 22.4 | 21.4 | 22.2 | 22.0 | 2.0 | 110 |
| 1,2-Dichloropropane | 22.8 | 22.2 | 23.4 | 22.8 | 2.1 | 114 |
| 1,1-Dichloropropene | 26.3 | 25.7 | 28.0 | 26.7 | 3.7 | 133 |
| cis-1,3-Dichloropropene | 20.3 | 19.5 | 21.1 | 20.3 | 3.2 | 102 |
| Ethylbenzene | 24.7 | 24.5 | 25.5 | 24.9 | 1.7 | 125 |
| Hexachlorobutadiene | 23.0 | 25.3 | 25.2 | 24.5 | 4.3 | 123 |
| Methylene chloride | 26.0 | 25.7 | 26.1 | 25.9 | 0.7 | 130[a] |
| Naphthalene | 13.8 | 12.7 | 11.8 | 12.8 | 6.4 | 63.8[a] |
| Styrene | 24.2 | 23.3 | 23.3 | 23.6 | 1.8 | 118 |
| 1,1,1,2-Tetrachloroethane | 21.4 | 20.2 | 21.3 | 21.0 | 2.6 | 105 |
| 1,1,2,2-Tetrachloroethane | 18.6 | 17.8 | 19.0 | 18.5 | 2.7 | 92.3 |
| Tetrachloroethene | 25.2 | 24.8 | 26.4 | 25.5 | 2.7 | 127 |
| Toluene | 28.6 | 27.9 | 30.9 | 29.1 | 4.4 | 146[a] |
| 1,2,4-Trichlorobenzene | 15.0 | 14.4 | 12.9 | 14.1 | 6.3 | 70.5 |
| 1,1,1-Trichloroethane | 28.1 | 27.2 | 29.9 | 28.4 | 4.0 | 142 |
| 1,1,2-Trichloroethane | 20.8 | 19.6 | 21.7 | 20.7 | 4.2 | 104 |

TABLE 30 (cont.)

| Compound | Recovery per Replicate (ng) Sample 1 | Sample 2 | Sample 3 | Mean (ng) | RSD | Recovery (%) |
|---|---|---|---|---|---|---|
| Trichloroethene | 26.3 | 24.9 | 26.8 | 26.0 | 3.1 | 130 |
| Trichlorofluoromethane | 25.9 | 24.8 | 26.5 | 25.7 | 2.7 | 129 |
| 1,2,3-Trichloropropane | 18.8 | 18.3 | 19.3 | 18.8 | 2.2 | 94.0 |
| Vinyl chloride | 24.8 | 23.2 | 23.9 | 24.0 | 2.7 | 120 |
| m-Xylene/p-Xylene | 24.3 | 23.9 | 25.3 | 24.5 | 2.4 | 123 |
| o-Xylene | 23.1 | 22.3 | 23.4 | 22.9 | 2.0 | 115 |

[a] Compound found in unfortified garden soil matrix at >5 ng.

TABLE 31

METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)[a]

| Compound | Detection Limit (ng) | Boiling Point (°C) |
|---|---|---|
| Chloromethane | 58 | -24 |
| Bromomethane | 26 | 4 |
| Vinyl chloride | 14 | -13 |
| Chloroethane | 21 | 13 |
| Methylene chloride | 9 | 40 |
| Acetone | 35 | 56 |
| Carbon disulfide | 11 | 46 |
| 1,1-Dichloroethene | 14 | 32 |
| 1,1-Dichloroethane | 12 | 57 |
| trans-1,2-Dichloroethene | 11 | 48 |
| Chloroform | 11 | 62 |
| 1,2-Dichloroethane | 13 | 83 |
| 1,1,1-Trichloroethane | 8 | 74 |
| Carbon tetrachloride | 8 | 77 |
| Bromodichloromethane | 11 | 88 |
| 1,1,2,2-Tetrachloroethane** | 23 | 146 |
| 1,2-Dichloropropane | 12 | 95 |
| trans-1,3-Dichloropropene | 17 | 112 |
| Trichloroethene | 11 | 87 |
| Dibromochloromethane | 21 | 122 |
| 1,1,2-Trichloroethane | 26 | 114 |
| Benzene | 26 | 80 |
| cis-1,3-Dichloropropene | 27 | 112 |
| Bromoform** | 26 | 150 |
| Tetrachloroethene | 11 | 121 |
| Toluene | 15 | 111 |
| Chlorobenzene | 15 | 132 |
| Ethylbenzene** | 21 | 136 |
| Styrene** | 46 | 145 |
| Trichlorofluoromethane | 17 | 24 |
| Iodomethane | 9 | 43 |
| Acrylonitrile | 13 | 78 |
| Dibromomethane | 14 | 97 |
| 1,2,3-Trichloropropane** | 37 | 157 |
| total Xylenes** | 22 | 138-144 |

Footnotes are found on the following page.

* The method detection limit (MDL) is defined in Chapter One. The detection limits cited above were determined according to 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Boiling Point greater than 130°C. Not appropriate for quantitative sampling by Method 0030.

TABLE 32

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (METHOD 5041)

| Bromochloromethane | 1,4-Difluorobenzene |
|---|---|
| Acetone | Benzene |
| Acrylonitrile | Bromodichloromethane |
| Bromomethane | Bromoform |
| Carbon disulfide | Carbon tetrachloride |
| Chloroethane | Chlorodibromomethane |
| Chloroform | Dibromomethane |
| Chloromethane | 1,2-Dichloropropane |
| 1,1-Dichloroethane | cis-1,3-Dichloropropene |
| 1,2-Dichloroethane | trans-1,3-Dichloropropene |
| 1,2-Dichloroethane-$d_4$ (surrogate) | 1,1,1-Trichloroethane |
| 1,1-Dichloroethene | 1,1,2-Trichloroethane |
| Trichloroethene | |
| trans-1,2-Dichloroethene | |
| Iodomethane | |
| Methylene chloride | |
| Trichlorofluoromethane | |
| Vinyl chloride | |

Chlorobenzene-$d_5$

4-Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-$d_8$ (surrogate)
1,2,3-Trichloropropane
Xylenes

TABLE 33

METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

| Compound | Boiling Point (°C) | Condensation Point at 20°C (%) | Estimated Detection Limit[a] (ppm) |
|---|---|---|---|
| Dichlorodifluoromethane | -30 | Gas | 0.20 |
| Vinyl chloride | -19 | Gas | 0.11 |
| 1,3-Butadiene | -4 | Gas | 0.90 |
| 1,2-Dichloro-1,1,2,2-tetrafluoroethane | 4 | Gas | 0.14 |
| Methyl bromide | 4 | Gas | 0.14 |
| Trichlorofluoromethane | 24 | 88 | 0.18 |
| 1,1-Dichloroethene | 31 | 22 | 0.07 |
| Methylene chloride | 40 | 44 | 0.05 |
| 1,1,2-Trichloro-trifluoroethane | 48 | 37 | 0.13 |
| Chloroform | 61 | 21 | 0.04 |
| 1,1,1-Trichloroethane | 75 | 13 | 0.03 |
| Carbon tetrachloride | 77 | 11 | 0.03 |
| Benzene | 80 | 10 | 0.16 |
| Trichloroethene | 87 | 8 | 0.04 |
| 1,2-Dichloropropane | 96 | 5 | 0.05 |
| Toluene | 111 | 3 | 0.08 |
| Tetrachloroethene | 121 | 2 | 0.03 |

[a] Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS

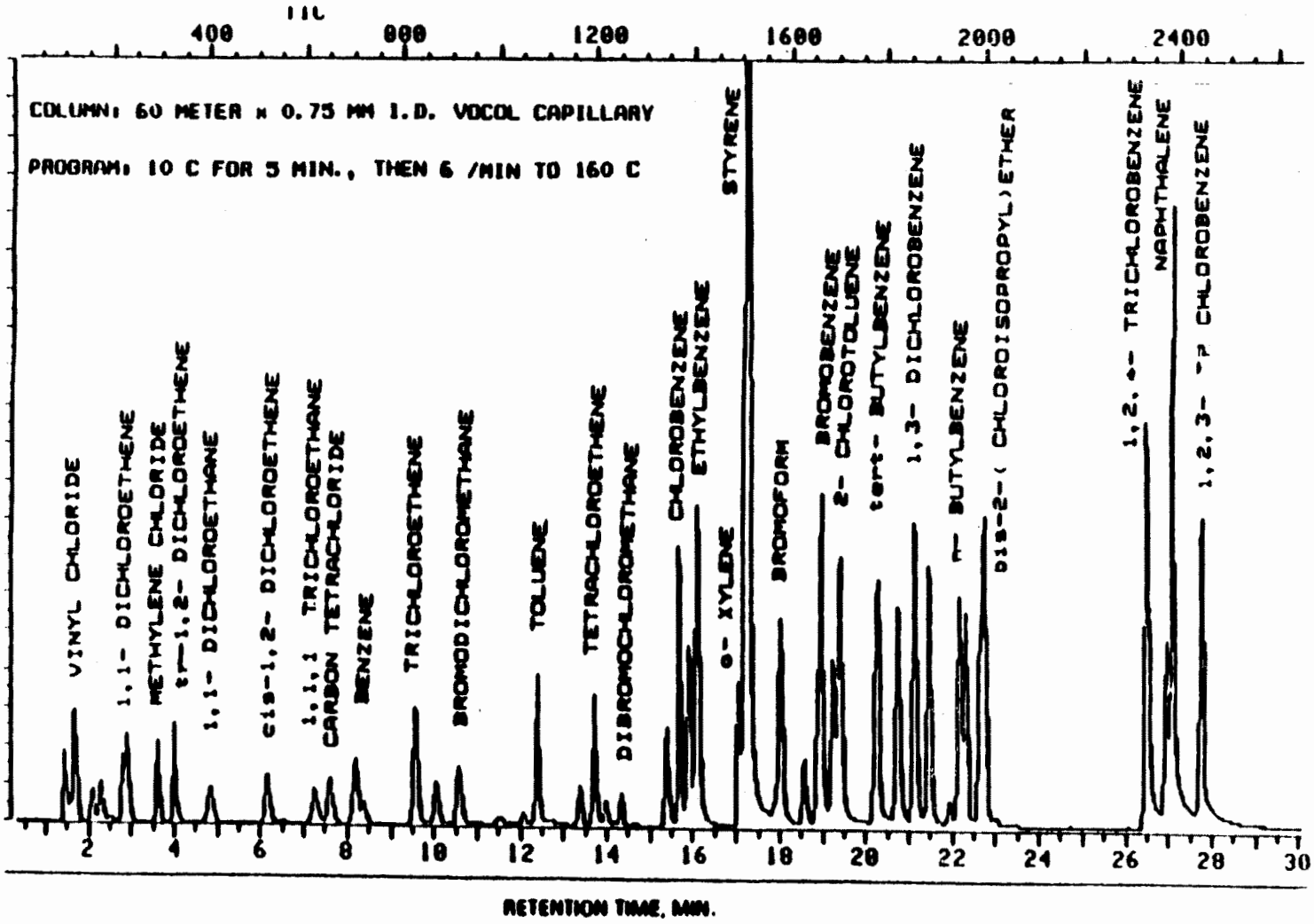


FIGURE 2
GAS CHROMATOGRAM OF VOLATILE ORGANICS

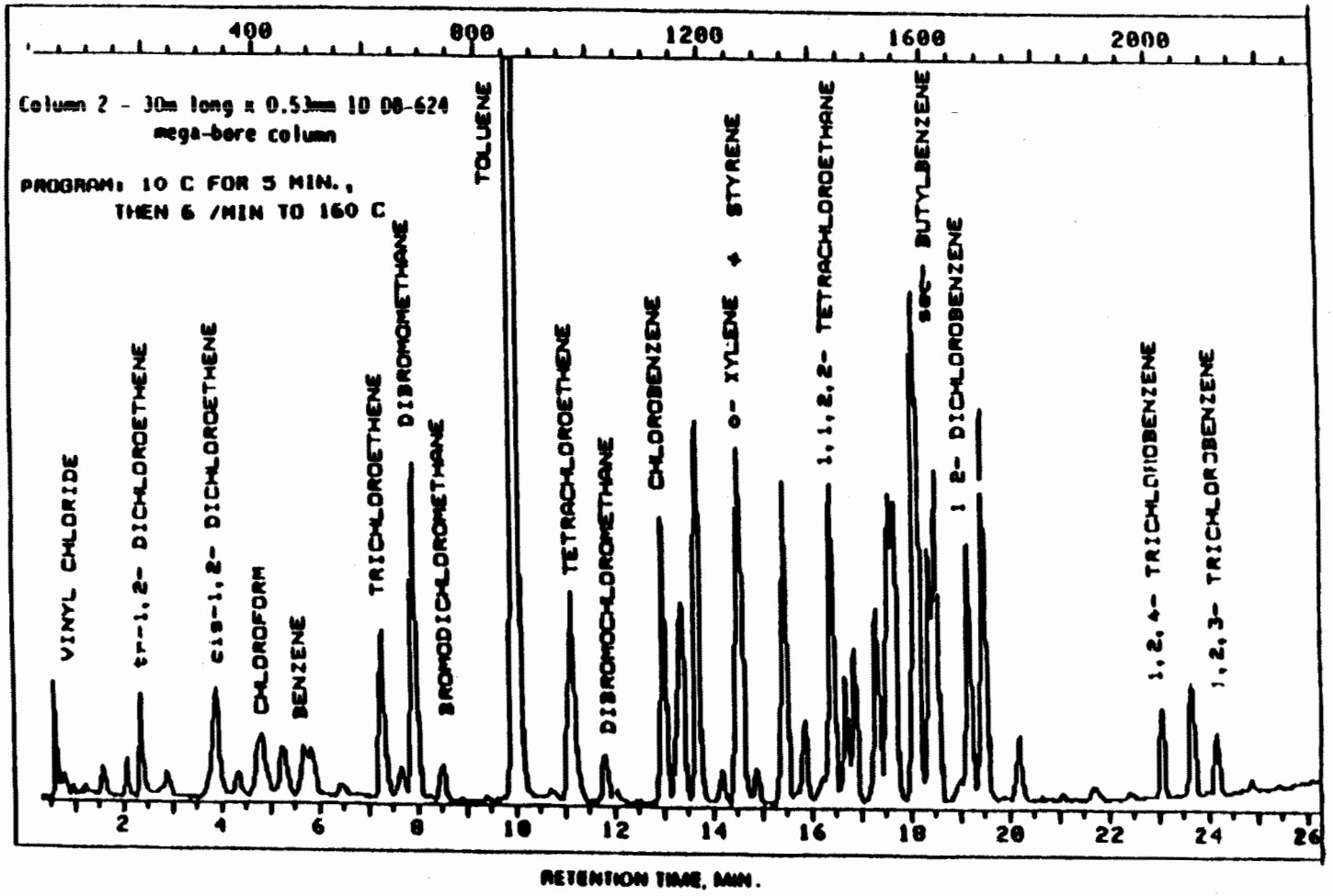


FIGURE 3
GAS CHROMATOGRAM OF VOLATILE ORGANICS

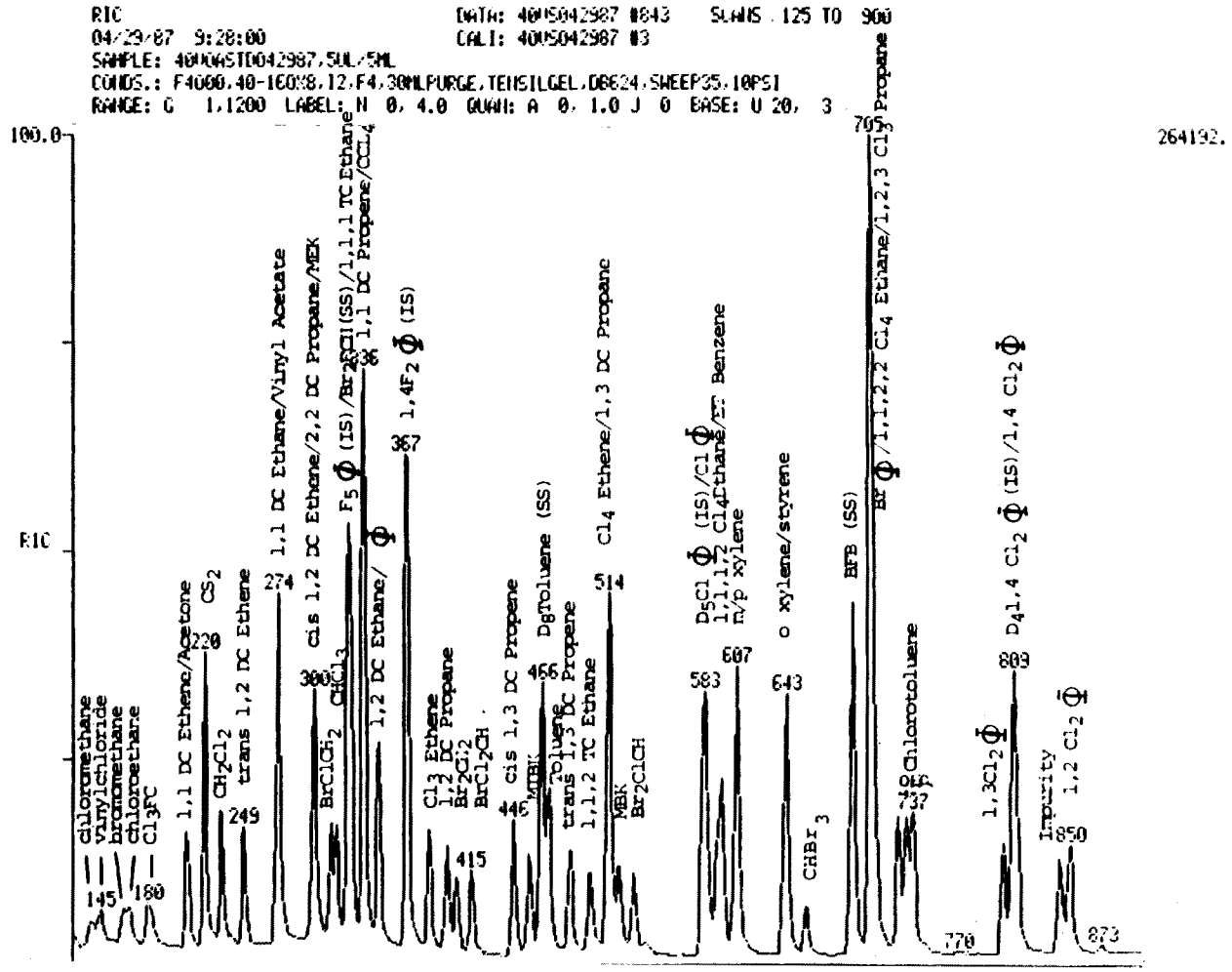
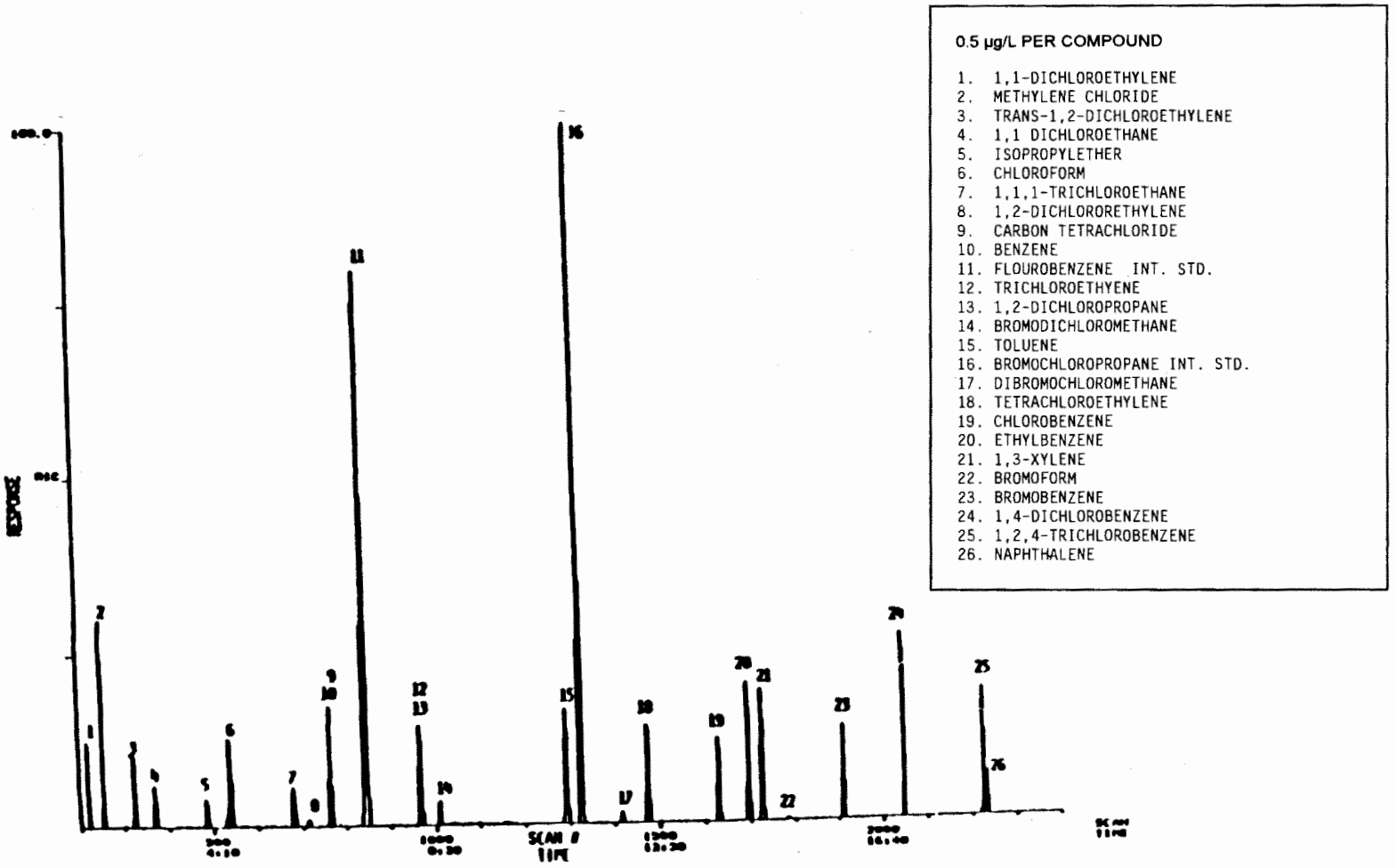
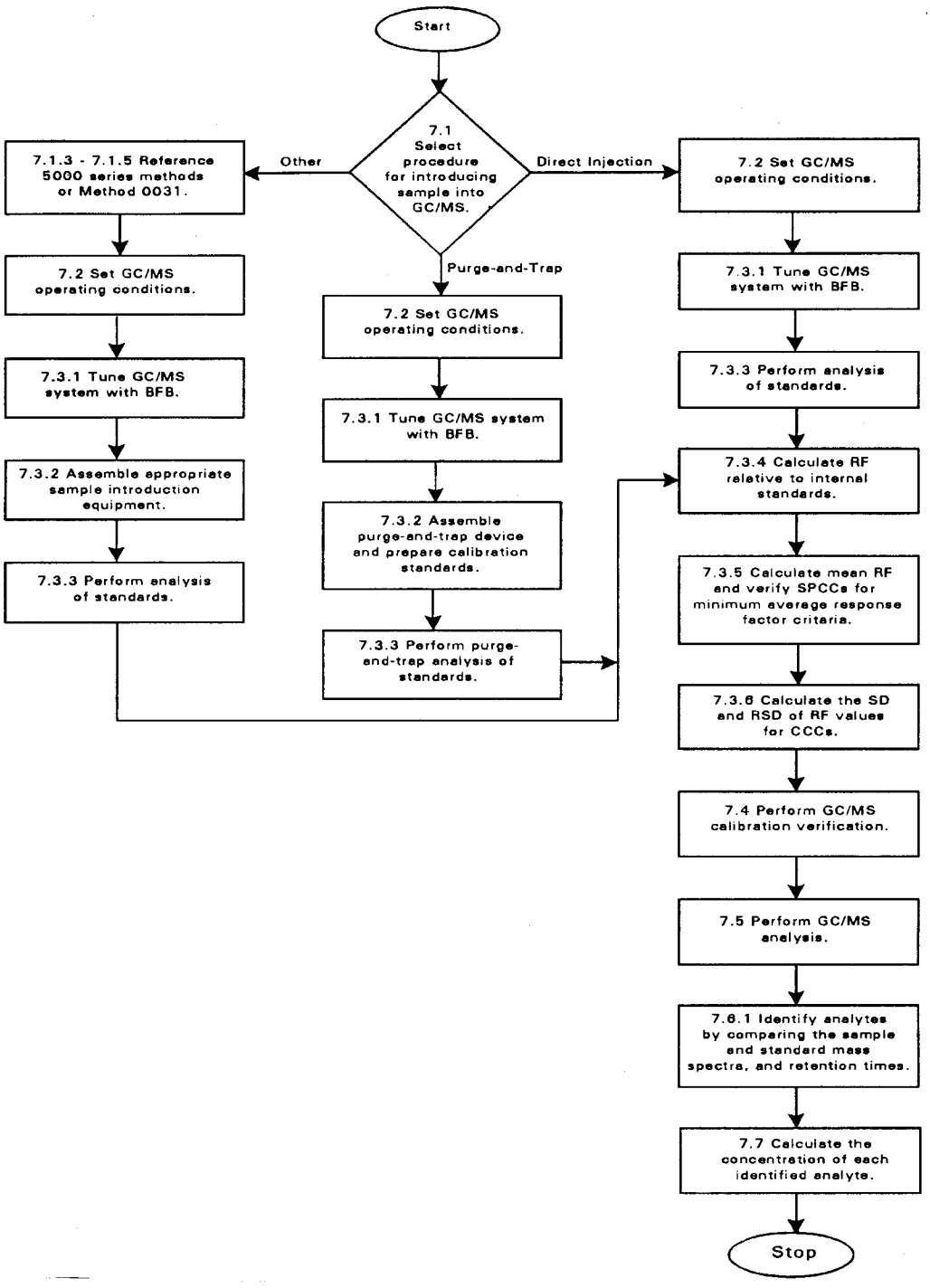


FIGURE 4
GAS CHROMATOGRAM OF TEST MIXTURE




Start
7.1 Select procedure for introducing sample into GC/MS.
Other
Purge-and-Trap
Direct Injection
7.1.3 - 7.1.5 Reference 5000 series methods or Method 0031.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble appropriate sample introduction equipment.
7.3.3 Perform analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble purge-and-trap device and prepare calibration standards.
7.3.3 Perform purge-and-trap analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.3 Perform analysis of standards.
7.3.4 Calculate RF relative to internal standards.
7.3.5 Calculate mean RF and verify SPCCs for minimum average response factor criteria.
7.3.6 Calculate the SD and RSD of RF values for CCCs.
7.4 Perform GC/MS calibration verification.
7.5 Perform GC/MS analysis.
7.6.1 Identify analytes by comparing the sample and standard mass spectra, and retention times.
7.7 Calculate the concentration of each identified analyte.
Stop

METHOD 5035

# CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

## 1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

1.2 The low soil method utilizes a hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 0.5 to 200 µg/kg range.

1.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

1.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030..

1.5 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency.

1.6 Method 5035, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5035 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Method 8021 in series with Method 8015.

1.7 As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.8 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 6.2.2).

1.9 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to and soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains 5 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent.

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol or polyethylene glycol (PEG), a separate aliquot of the sample is spiked with surrogates and diluted in the appropriate solvent. An aliquot of the solution is added to 5 mL of reagent water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) are added to the solution which is then purged using Method 5030 and analyzed by an appropriate determinative method.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585.

## 3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

## 4.0 APPARATUS AND MATERIALS

### 4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other

systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 4.2.2).

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the Disclaimer at the front of this manual for guidance on the use of alternative equipment.

4.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed, it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all the target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocarb 4000), as some degradation has been noted when higher desorption temperatures (especially above 240 - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 The trap used to develop this method was 25 cm long, with an inside diameter of 0.105 inches, and was packed with Carbopack/Carbosieve (Supelco, Inc.).

4.2.2.2 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If

the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

4.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.2.2.2.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.2.2.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.3 Syringe and Syringe Valves

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25-µL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10-, 100-µL.

4.3.5 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

4.4 Miscellaneous

4.4.1 Glass vials

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance - Capable of accurately weighing to 0.01 g.

4.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground-glass stoppers.

4.4.5 2-mL glass vials, for GC autosampler - Used for oily waste samples extracted with methanol or PEG.

4.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

4.5 Field Sampling Equipment

4.5.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.5.2 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.3 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

4.5.4 Portable balance - For field use, capable of weighing to 0.01 g.

4.5.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

## 5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, $CH_3OH$ - purge-and-trap quality or equivalent. Store away from other solvents.

5.3 Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$ - free of interferences at the detection limit of the target analytes.

5.4 Low concentration sample preservative

5.4.1 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

5.4.2 The preservative should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

5.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

### 6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

#### 6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of $\leq 2$.

6.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

6.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the

laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

6.1.2 High concentration soil samples collected without a preservative

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60-mL glass vials with septum seals (see Sec. 4.4).

6.1.3 High concentration soil samples collected and preserved in the field

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.3.1 Add 10 mL of methanol to each vial.

6.1.3.2 Seal the vial with the screw-cap and septum seal.

6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

NOTE: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

6.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the sample after it is returned to the laboratory and prior to analysis.

6.1.4 Oily waste samples

When oily waste samples are known to be soluble in methanol or PEG, sample vials may be prepared as described in Sec. 6.1.3, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 6.1.2.

6.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler ™, and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.2.1 Low concentration soil samples

6.2.1.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

NOTE: Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials that do not contain the preservative solution.

6.2.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

6.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60-mL glass vial or a third 40-mL soil sample vial. However, this third vial must *not* contain the sample preservative solution, as an aliquot will be used to determine dry weight. If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

6.2.1.7 If samples are known or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2 g instead of the 5 g collected in Sec. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

6.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 6.2.2).

6.2.2 High concentration soil samples preserved in the field

The collection of soil samples in vials that contain methanol has been suggested by some as a combined preservation and extraction procedure. However, this procedure is not appropriate for use with the low concentration soil procedure described in this method.

NOTE: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of two potential problems. First, the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure (0.5-200 µg/kg). The exact dilution factor will depend on the masses of solvent and sample, but generally exceeds 1000, and may make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes. Because the analytes of interest are volatile, the methanol extract cannot be concentrated to overcome the dilution problem. Thus, for samples of unknown composition, it may still be necessary to collect an aliquot for analysis by this closed-system procedure and another aliquot preserved in methanol and analyzed by other procedures. The second problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste.

6.2.2.1 When samples are known to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

6.2.2.2 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.2.3 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

6.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight, as described in Sec. 6.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

6.2.3 High concentration soil sample not preserved in the field

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

6.2.4 Oily waste samples

The collection procedures for oily samples depend on knowledge of the waste and its solubility in methanol or other solvents.

6.2.4.1 When an oily waste is known to be soluble in methanol or PEG, the sample may be collected in a vial containing such a solvent (see Sec. 6.1.4), using procedures similar to those described in Sec. 6.2.2.

6.2.4.2 When the solubility of the oily waste is not known, the sample should either be collected in a vial without a preservative, as described in Sec. 6.2.3, or the solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in Sec. 6.2.2. Otherwise, collect an unpreserved sample as described in Sec. 6.2.3.

6.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

6.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at -10°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel. See Sec. 6.2.1.2 for additional information.

## 7.0 PROCEDURE

This section describes procedures for sample screening, the low concentration soil method, the high concentration soil method, and the procedure for oily waste samples. High concentration samples are to be introduced into the GC system using Method 5030. Oily waste samples are to be introduced into the GC system using Method 5030 if they are soluble in a water-miscible solvent, or using Method 3585 if they are not.

7.1 Sample screening

7.1.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system, thereby requiring extensive cleanup and instrument maintenance. The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low concentration closed-system direct purge-and-trap method (Sec. 7.2), the high concentration (methanol extraction) method (Sec. 7.3), or the nonaqueous liquid (oily waste) methanol or PEG dilution procedure (Sec. 7.4).

7.1.2 The analyst may employ any appropriate screening technique. Two suggested screening techniques employing SW-846 methods are:

7.1.2.1 Automated headspace (Method 5021) using a gas chromatograph (GC) equipped with a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series, or,

7.1.2.2 Extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC equipped with a FID and/or an ECD.

7.1.3 The analyst may inject a calibration standard containing the analytes of interest at a concentration equivalent to the upper limit of the calibration range of the low concentration soil method. The results from this standard may be used to determine when the screening results approach the upper limit of the low concentration soil method. There are no linearity or other performance criteria associated with the injection of such a standard, and other approaches may be employed to estimate sample concentrations.

7.1.4 Use the low concentration closed-system purge-and-trap method (Sec. 7.2) if the estimated concentration from the screening procedure falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range of the low concentration soil method, then use either the high concentration soil method (Sec. 7.3), or the oily waste method (Sec. 7.4).

7.2 Low concentration soil method (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.2.1 Initial calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.2.1.2 Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing with an inert gas flow of at least 20 mL/minute. If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.3 If the standard trap in Sec. 4.2.2.2 is employed, prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min, or according to the manufacturer's recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.4 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

7.2.1.5 Prepare a minimum of five initial calibration standards containing all the analytes of interest and surrogates, as described in Method 8000, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL added to the vial before shipping it to the field plus the organic-free reagent water added by the instrument). The calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (e.g., ~1 g), as the presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same fashion as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the surrogates using standards at five concentrations, it may be necessary to disable the automatic addition of surrogates to each vial containing a calibration standard (consult the manufacturer's instructions). Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as recommended by the manufacturer.

7.2.1.6 Carry out the purge-and-trap procedure as outlined in Secs. 7.2.3. to 7.2.5.

7.2.1.7 Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.

7.2.1.8 For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.8.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.2.1.8.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.8.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.9 When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross-contamination and memory effects from a high concentration sample or even the standard are a common problem.

Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification

Refer to Method 8000 for details on calibration verification. A single standard near the mid-point of calibration range is used for verification. This standard should also contain approximately 1 g of sodium bisulfate.

7.2.3 Sample purge-and-trap

This method is designed for a 5-g sample size, but smaller sample sizes may be used. Consult the instrument manufacturer's instructions regarding larger sample sizes, in order to avoid clogging of the purging apparatus. The soil vial is hermetically sealed at the sampling site, and MUST remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01 g, even if the sample weight was determined in the field, and record this weight. This second weighing provides a check on the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant discrepancies between the field and laboratory weights.

7.2.3.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

7.2.3.2 Without disturbing the hermetic seal on the sample vial, add 5 mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

7.2.3.3 For the sample selected for matrix spiking, add the matrix spiking solution described in Sec. 5.0 of Method 5000, either manually, or automatically, following the manufacturer's instructions. The concentration of the spiking solution and the amount added should be established as described in Sec. 8.0 of Method 8000.

7.2.3.4 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

7.2.4 Sample Desorption

7.2.4.1 Non-cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow

of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes (1.5 min is normally adequate for analytes in Method 8015). Begin the temperature program of the gas chromatograph and start data acquisition.

7.2.4.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 245°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Methods 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.5 Trap Reconditioning

After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

7.2.6 Data Interpretation

Perform qualitative and quantitative analysis following the guidance given in the determinative method and Method 8000. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. Such reanalyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method. Alternatively, if a sample aliquot of 1-2 g was also collected (see Sec. 6.2.1.7), it may be practical to analyze that aliquot for the analytes that exceeded the instrument calibration range in the 5-g analysis. If results are to be reported on a dry weight basis, proceed to Sec. 7.5

7.3 High concentration method for soil samples with concentrations generally greater than 200 µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free reagent water containing surrogates and, if applicable, internal and matrix spiking standards, purged according to Method 5030, and analyzed by an appropriate determinative method. Wastes that are insoluble in methanol (i.e., petroleum and coke wastes) are diluted with hexadecane (see Sec. 7.3.8).

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were <u>not</u> preserved in the field are prepared using the steps below, beginning at Sec. 7.3.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.3.4.

7.3.1 When the high concentration sample is <u>not</u> preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Whenever practical, mix the contents of the sample container by shaking or other mechanical means without opening the vial. When shaking is not practical, quickly mix the contents of the vial with a narrow metal spatula and immediately reseal the vial.

7.3.2 If the sample is from an unknown source, perform a solubility test before proceeding. Remove several grams of material from the sample container. Quickly reseal the container to minimize the loss of volatiles. Weigh 1-g aliquots of the sample into several test tubes or other suitable containers. Add 10 mL of methanol to the first tube, 10 mL of PEG to the second, and 10 mL of hexadecane to the third. Swirl the sample and determine if it is soluble in the solvent. Once the solubility has been evaluated, discard these test solutions. If the sample is soluble in either methanol or PEG, proceed with Sec. 7.3.3. If the sample is only soluble in hexadecane, proceed with Sec. 7.3.8.

7.3.3 For soil and solid waste samples that are soluble in methanol, add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution to a tared 20-mL vial. Using a top-loading balance, weigh 5 g (wet weight) of sample into the vial. Quickly cap the vial and reweigh the vial. Record the weight to 0.1 g. Shake the vial for 2 min. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0 mL of PEG in place of the methanol. Proceed with Sec. 7.3.5.

NOTE: The steps in Secs. 7.3.1, 7.3.2, and 7.3.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.4 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 6.2.2), weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum, shake for 2 min, as described above, and proceed with Sec. 7.3.5.

7.3.5 Pipet approximately 1 mL of the extract from either Sec. 7.3.3 or 7.3.4 into a GC vial for storage, using a disposable pipet, and seal the vial. The remainder of the extract may be discarded. Add approximately 1 mL of methanol or PEG to a separate GC vial for use as the method blank for each set of samples extracted with the same solvent.

7.3.6 The extracts must be stored at 4°C in the dark, prior to analysis. Add an appropriate aliquot of the extract (see Table 2) to 5.0 mL of organic-free reagent water and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging high concentration samples.

7.3.7 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the procedure in Sec. 7.5, after the sample extract has been transferred to a GC vial and the vial sealed.

7.3.8 For solids that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste) dilute or extract the sample with hexadecane using the procedures in Sec. 7.0 of Method 3585.

7.4 High concentration method for oily waste samples

This procedure for the analysis of oily waste samples involves the dilution of the sample in methanol or PEG. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. A portion of the diluted sample is then added to 5.0 mL of organic-free reagent water, purged according to Method 5030, and analyzed using an appropriate determinative method.

For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with hexadecane using the procedures in Sec. 7.0 of Method 3585.

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.4.1. If methanol preservation was employed in the field, then the preparation begins with Sec. 7.4.3.

7.4.1 If the waste was not preserved in the field and it is soluble in methanol or PEG, weigh 1 g (wet weight) of the sample into a tared 10-mL volumetric flask, a tared scintillation vial, or a tared culture tube. If a vial or tube is used instead of a volumetric flask, it must be calibrated prior to use. This operation must be performed prior to opening the sample vial and weighing out the aliquot for analysis.

7.4.1.1 To calibrate the vessel, pipet 10.0 mL of methanol or PEG into the vial or tube and mark the bottom of the meniscus.

7.4.1.2 Discard this solvent, and proceed with weighing out the 1-g sample aliquot.

7.4.2 Quickly add 1.0 mL of surrogate spiking solution to the flask, vial, or tube, and dilute to 10.0 mL with the appropriate solvent (methanol or PEG). Swirl the vial to mix the contents and then shake vigorously for 2 minutes.

7.4.3 If the sample was collected in the field in a vial containing methanol or PEG, weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum. Swirl the vial to mix the contents and then shake vigorously for 2 minutes and proceed with Sec. 7.4.4.

7.4.4 Regardless of how the sample was collected, the target analytes are extracted into the solvent along with the majority of the oily waste (i.e., some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

7.4.5 Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis, using Method 5030.

7.4.6 Prepare a matrix spike sample by adding 10 - 50 µL of the matrix spike standard dissolved in methanol to a 1-g aliquot of the oily waste. Shake the vial to disperse the matrix spike solution throughout the oil. Then add 10 mL of extraction solvent and proceed with the extraction and analysis, as described in Secs. 7.4.2 - 7.4.5. Calculate the recovery of the spiked analytes as described in Method 8000. If the recovery is not within the acceptance limits for the application, use the hexadecane dilution technique in Sec. 7.0 of Method 3585.

7.5 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample.

NOTE: It is highly recommended that the dry weight determination only be made after the analyst has determined that no sample aliquots will be taken from the 60-mL vial for high

concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the dry weight determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

7.5.1 Weigh 5-10 g of the sample from the 60-mL VOA vial into a tared crucible.

7.5.2 Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS), and the addition of surrogates to each sample and QC sample.

8.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

## 9.0 METHOD PERFORMANCE

9.1 Single laboratory accuracy and precision data were obtained for the method analytes in three soil matrices, sand, a soil collected 10 feet below the surface of a hazardous landfill, called the

C-Horizon, and a surface garden soil. Each sample was fortified with the analytes at a concentration of 20 ng/5 g, which is equivalent to 4 µg/kg. These data are listed in tables found in Method 8260.

9.2 Single laboratory accuracy and precision data were obtained for certain method analytes when extracting oily liquid using methanol as the extraction solvent. The data are presented in a table in Method 8260. The compounds were spiked into three portions of an oily liquid (taken from a waste site) following the procedure for matrix spiking described in Sec. 7.4. This represents a worst case set of data based on recovery data from many sources of oily liquid.

## 10.0 REFERENCES


1. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

2. Siegrist, R. L., Jenssen, P. D., "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils", Envir Sci Technol, 1990; 24; 1387-92.

3. Hewitt, A. D., Jenkins, T. F., Grant, C. L., "Collection, Handling and Storage: Keys to Improved Data Quality for Volatile Organic Compounds in Soil", Am Environ Lab, 1995; 7(1); 25-8.

4. Liikala, T. L., Olsen, K. B., Teel, S. S., Lanigan, D. C., "Volatile Organic Compounds: Comparison of Two Sample Collection and Preservation Methods", Envir Sci Technol, 1996; 30; 3441-7.

5. Lewis, T. E., Crockett, A. B., Siegrist, R. L., Zarrabi, K., "Soil Sampling and Analysis for Volatile Organic Compounds", Envir Monitoring & Assessment, 1994; 30; 213-46.

6. Hewitt, A. D., "Enhanced Preservation of Volatile Organic Compounds in Soil with Sodium Bisulfate", SR95-26, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

7. Hewitt, A. D., Lukash, N. J. E., "Sampling for In-Vial Analysis of Volatile Organic Compounds in Soil", Am Environ Lab, 1996; Aug; 15-9.

8. Hewitt, A. D., Miyares, P. H., Sletten, R. S., "Determination of Two Chlorinated Volatile Organic Compounds in Soil by Headspace Gas Chromatography and Purge-and-Trap Gas Chromatography/Mass Spectrometry", Hydrocarbon Contaminated Soils, 1993, 3; 135-45, Chelsea, MI, Lewis Publishers.

9. Hewitt, A. D., "Methods of Preparing Soil Samples for Headspace Analysis of Volatile Organic Compounds: Emphasis on Salting Out", 12th Annual Waste Testing and Quality Assurance Symposium, Washington, DC, 1996, 322-9.

10. Hewitt, A. D., Miyares, P. H., Leggett, D. C., Jenkins, T. F., "Comparison of Analytical Methods for Determination of Volatile Organic Compounds", Envir Sci Tech, 1992; 26; 1932-8.

TABLE 1

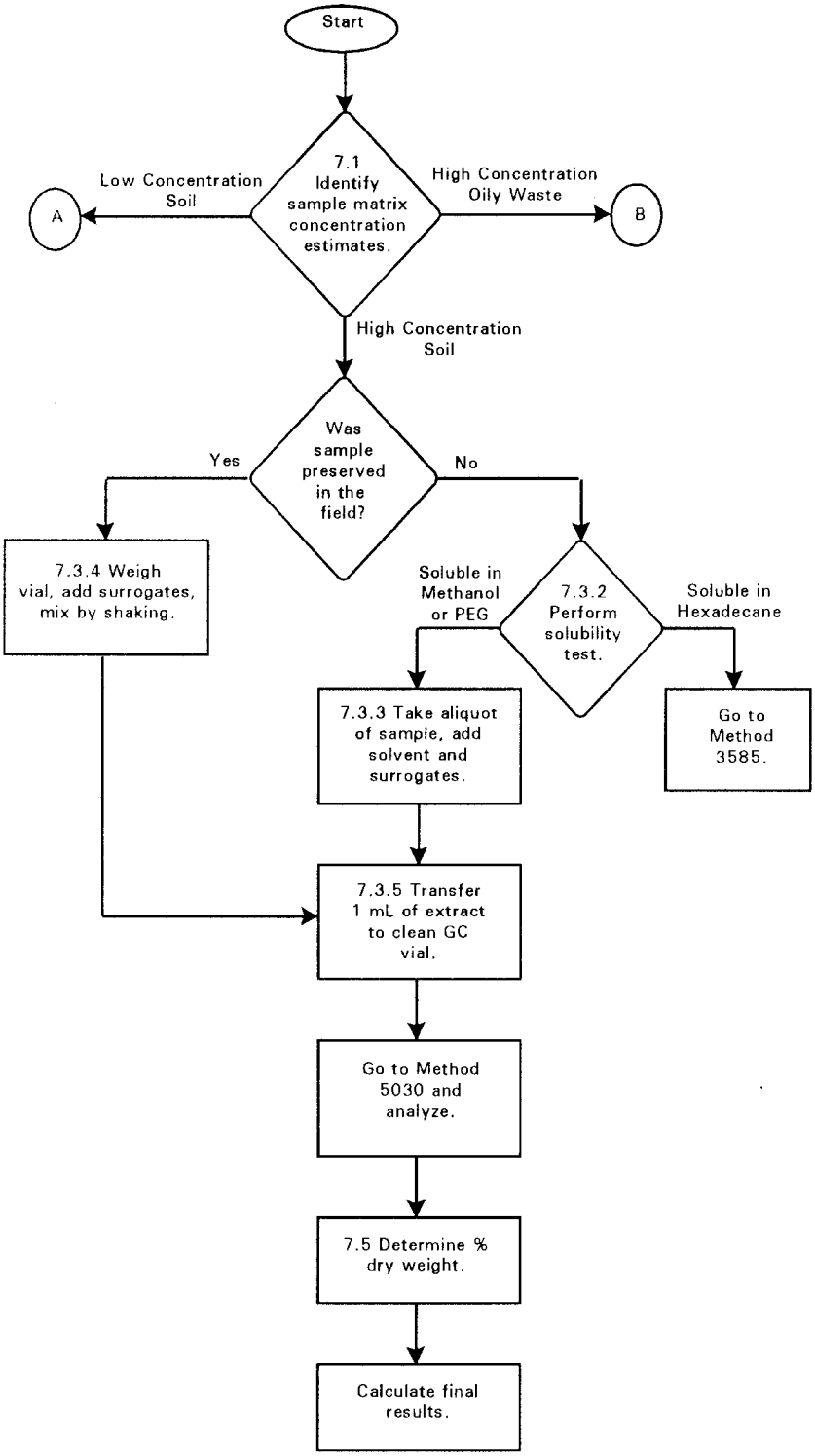
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SOILS/SEDIMENTS

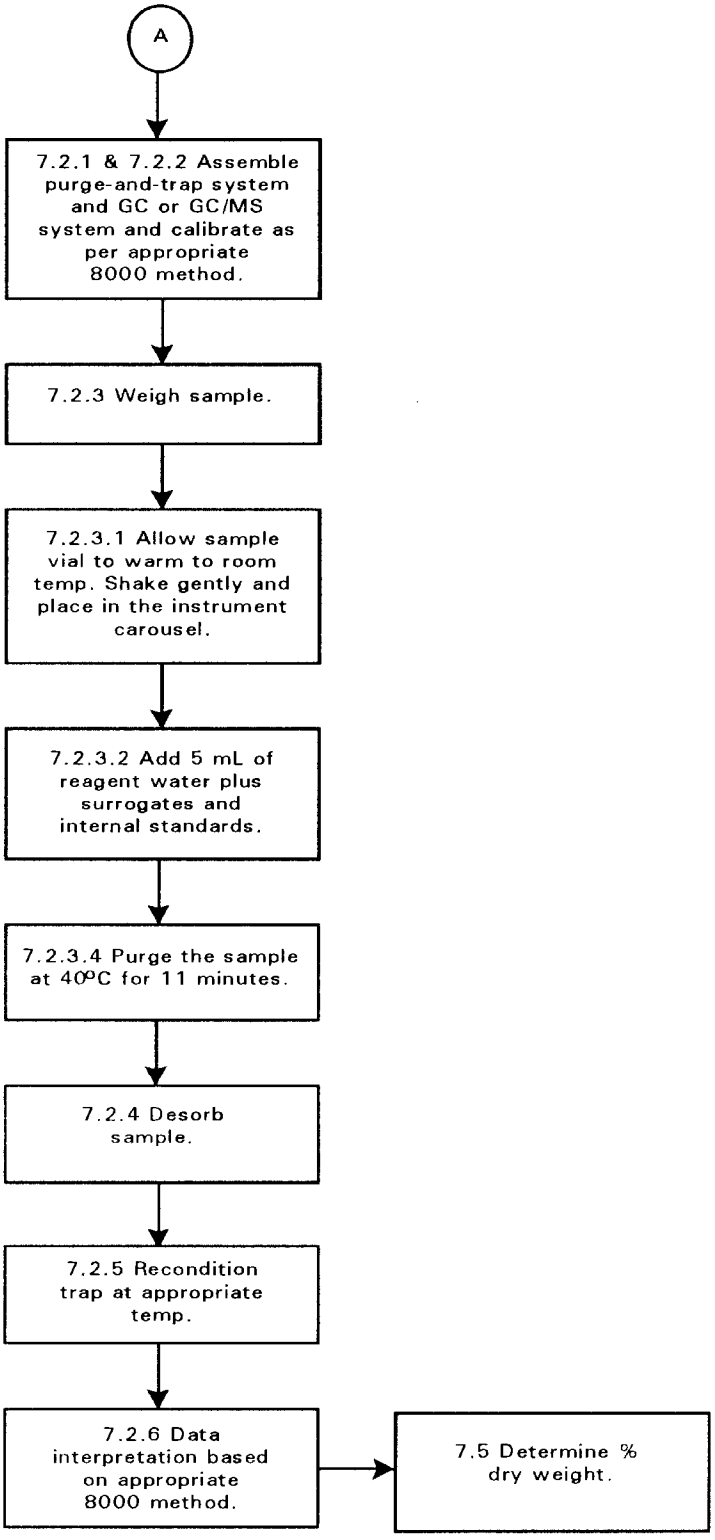
| Approximate Concentration Range | Volume of Methanol Extract[a] |
|---|---|
| 500 - 10,000 µg/kg | 100 µL |
| 1,000 - 20,000 µg/kg | 50 µL |
| 5,000 - 100,000 µg/kg | 10 µL |
| 25,000 - 500,000 µg/kg | 100 µL of 1/50 dilution[b] |

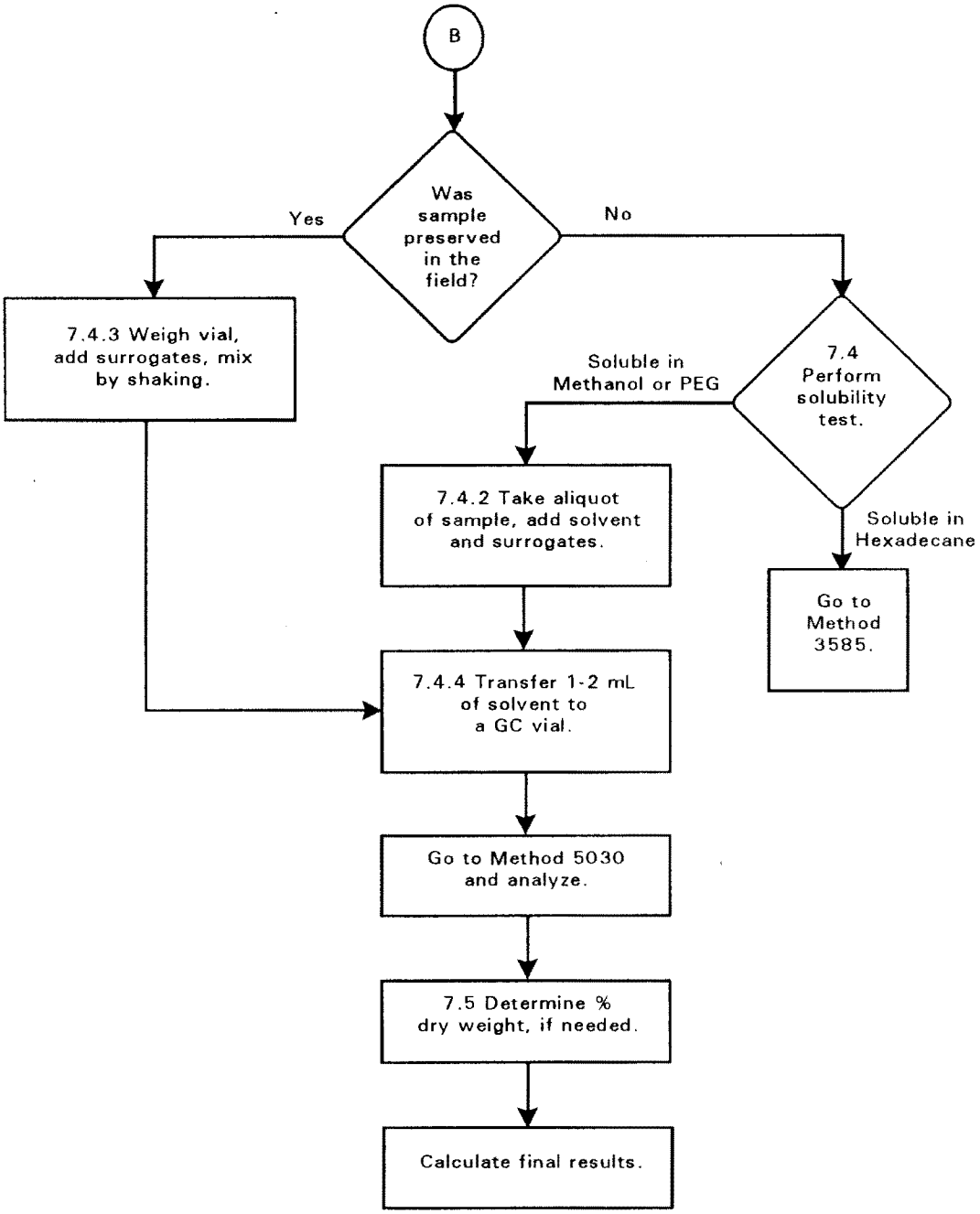
Calculate appropriate dilution factor for concentrations exceeding those in this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100 µL of methanol.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.


Start
7.1 Identify sample matrix concentration estimates.
Low Concentration Soil
A
High Concentration Oily Waste
B
High Concentration Soil
Was sample preserved in the field?
Yes
No
7.3.4 Weigh vial, add surrogates, mix by shaking.
7.3.2 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.3.3 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.3.5 Transfer 1 mL of extract to clean GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight.
Calculate final results.

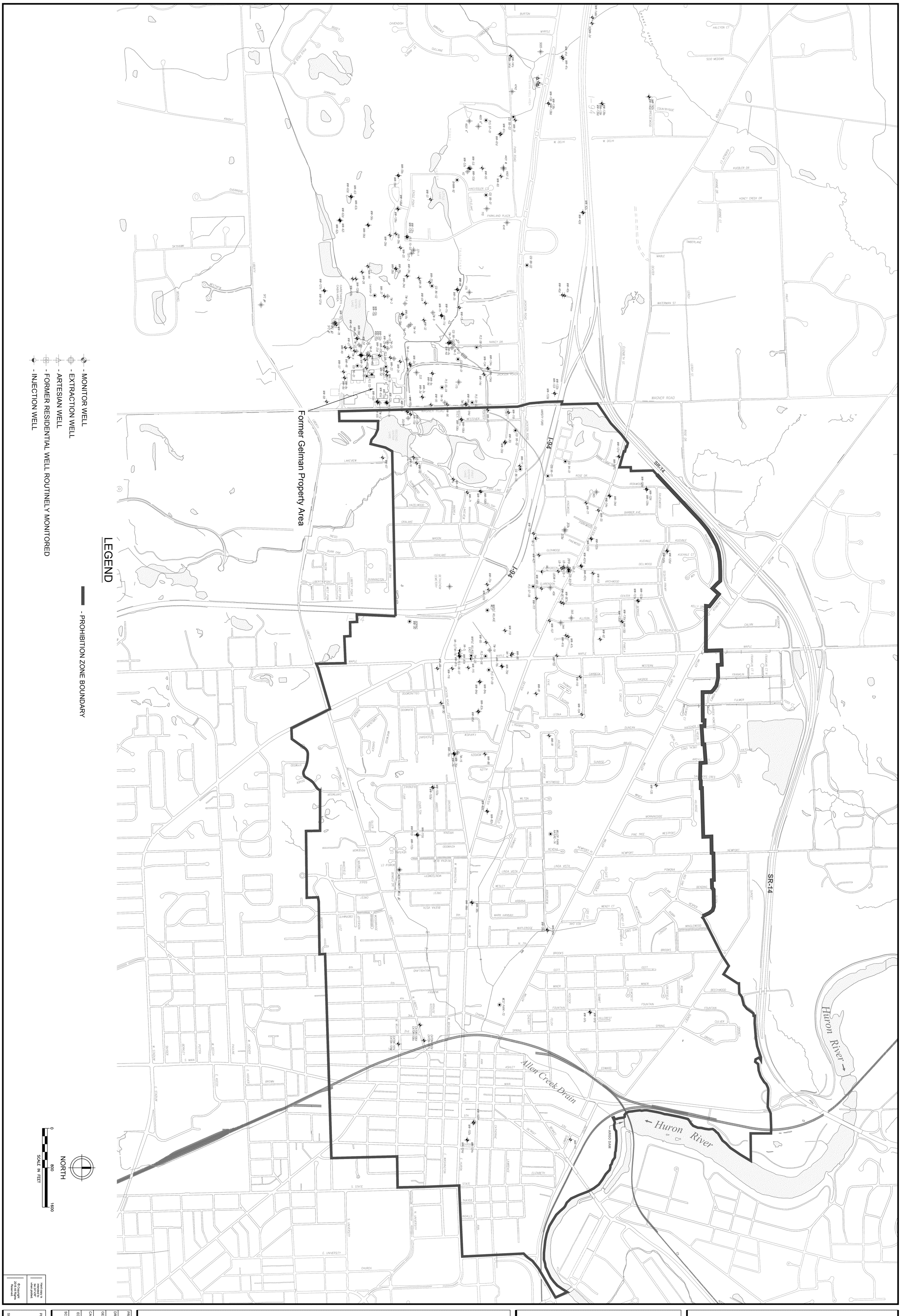

A
7.2.1 & 7.2.2 Assemble purge-and-trap system and GC or GC/MS system and calibrate as per appropriate 8000 method.
7.2.3 Weigh sample.
7.2.3.1 Allow sample vial to warm to room temp. Shake gently and place in the instrument carousel.
7.2.3.2 Add 5 mL of reagent water plus surrogates and internal standards.
7.2.3.4 Purge the sample at 40°C for 11 minutes.
7.2.4 Desorb sample.
7.2.5 Recondition trap at appropriate temp.
7.2.6 Data interpretation based on appropriate 8000 method.
7.5 Determine % dry weight.


B
Was sample preserved in the field?
Yes
No
7.4.3 Weigh vial, add surrogates, mix by shaking.
7.4 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.4.2 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.4.4 Transfer 1-2 mL of solvent to a GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight, if needed.
Calculate final results.

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT C




Hard copy is intended to be 24"x36" when plotted.

© Copyright 2016 All Rights Reserved.

| | |
|---|---|
| PROJECT MGR. | DATE 05/01/20 |
| DRAWN BY | DATE 05/01/20 |
| GEOLOGIST | DATE 05/01/20 |
| CAD FILE | |
| EDIT | |
| SCALE | |
| DRAWING | |
| PROJECT | 806500 |
| SHEET NO. | |

GELMAN SCIENCES

Scio Twp., Washtenaw County, Michigan

FOURTH AMENDED CONSENT JUDGEMENT - ATTACHMENT C

FLEIS&VANDENBRINK

DESIGN. BUILD. OPERATE.

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT D

METHOD 8260B
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/
MASS SPECTROMETRY (GC/MS)

## 1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

| | | Appropriate Preparation Technique[a] | | | | | |
|---|---|---|---|---|---|---|---|
| Compound | CAS No.[b] | 5030/ 5035 | 5031 | 5032 | 5021 | 5041 | Direct Inject. |
| Acetone | 67-64-1 | pp | c | c | nd | c | c |
| Acetonitrile | 75-05-8 | pp | c | nd | nd | nd | c |
| Acrolein (Propenal) | 107-02-8 | pp | c | c | nd | nd | c |
| Acrylonitrile | 107-13-1 | pp | c | c | nd | c | c |
| Allyl alcohol | 107-18-6 | ht | c | nd | nd | nd | c |
| Allyl chloride | 107-05-1 | c | nd | nd | nd | nd | c |
| Benzene | 71-43-2 | c | nd | c | c | c | c |
| Benzyl chloride | 100-44-7 | c | nd | nd | nd | nd | c |
| Bis(2-chloroethyl)sulfide | 505-60-2 | pp | nd | nd | nd | nd | c |
| Bromoacetone | 598-31-2 | pp | nd | nd | nd | nd | c |
| Bromochloromethane | 74-97-5 | c | nd | c | c | c | c |
| Bromodichloromethane | 75-27-4 | c | nd | c | c | c | c |
| 4-Bromofluorobenzene (surr) | 460-00-4 | c | nd | c | c | c | c |
| Bromoform | 75-25-2 | c | nd | c | c | c | c |
| Bromomethane | 74-83-9 | c | nd | c | c | c | c |
| n-Butanol | 71-36-3 | ht | c | nd | nd | nd | c |
| 2-Butanone (MEK) | 78-93-3 | pp | c | c | nd | nd | c |
| t-Butyl alcohol | 75-65-0 | pp | c | nd | nd | nd | c |
| Carbon disulfide | 75-15-0 | pp | nd | c | nd | c | c |
| Carbon tetrachloride | 56-23-5 | c | nd | c | c | c | c |
| Chloral hydrate | 302-17-0 | pp | nd | nd | nd | nd | c |
| Chlorobenzene | 108-90-7 | c | nd | c | c | c | c |
| Chlorobenzene-$d_5$ (IS) | | c | nd | c | c | c | c |
| Chlorodibromomethane | 124-48-1 | c | nd | c | nd | c | c |
| Chloroethane | 75-00-3 | c | nd | c | c | c | c |
| 2-Chloroethanol | 107-07-3 | pp | nd | nd | nd | nd | c |
| 2-Chloroethyl vinyl ether | 110-75-8 | c | nd | c | nd | nd | c |
| Chloroform | 67-66-3 | c | nd | c | c | c | c |
| Chloromethane | 74-87-3 | c | nd | c | c | c | c |
| Chloroprene | 126-99-8 | c | nd | nd | nd | nd | c |
| 3-Chloropropionitrile | 542-76-7 | l | nd | nd | nd | nd | pc |

(continued)

| Compound | CAS No.[b] | Appropriate Preparation Technique[a] 5030/ 5035 | 5031 | 5032 | 5021 | 5041 | Direct Inject. |
|---|---|---|---|---|---|---|---|
| Crotonaldehyde | 4170-30-3 | pp | c | nd | nd | nd | c |
| 1,2-Dibromo-3-chloropropane | 96-12-8 | pp | nd | nd | c | nd | c |
| 1,2-Dibromoethane | 106-93-4 | c | nd | nd | c | nd | c |
| Dibromomethane | 74-95-3 | c | nd | c | c | c | c |
| 1,2-Dichlorobenzene | 95-50-1 | c | nd | nd | c | nd | c |
| 1,3-Dichlorobenzene | 541-73-1 | c | nd | nd | c | nd | c |
| 1,4-Dichlorobenzene | 106-46-7 | c | nd | nd | c | nd | c |
| 1,4-Dichlorobenzene-$d_4$ (IS) | | c | nd | nd | c | nd | c |
| cis-1,4-Dichloro-2-butene | 1476-11-5 | c | nd | c | nd | nd | c |
| trans-1,4-Dichloro-2-butene | 110-57-6 | pp | nd | c | nd | nd | c |
| Dichlorodifluoromethane | 75-71-8 | c | nd | c | c | nd | c |
| 1,1-Dichloroethane | 75-34-3 | c | nd | c | c | c | c |
| 1,2-Dichloroethane | 107-06-2 | c | nd | c | c | c | c |
| 1,2-Dichloroethane-$d_4$ (surr) | | c | nd | c | c | c | c |
| 1,1-Dichloroethene | 75-35-4 | c | nd | c | c | c | c |
| trans-1,2-Dichloroethene | 156-60-5 | c | nd | c | c | c | c |
| 1,2-Dichloropropane | 78-87-5 | c | nd | c | c | c | c |
| 1,3-Dichloro-2-propanol | 96-23-1 | pp | nd | nd | nd | nd | c |
| cis-1,3-Dichloropropene | 10061-01-5 | c | nd | c | nd | c | c |
| trans-1,3-Dichloropropene | 10061-02-6 | c | nd | c | nd | c | c |
| 1,2,3,4-Diepoxybutane | 1464-53-5 | c | nd | nd | nd | nd | c |
| Diethyl ether | 60-29-7 | c | nd | nd | nd | nd | c |
| 1,4-Difluorobenzene (IS) | 540-36-3 | nd | nd | nd | nd | c | nd |
| 1,4-Dioxane | 123-91-1 | pp | c | c | nd | nd | c |
| Epichlorohydrin | 106-89-8 | l | nd | nd | nd | nd | c |
| Ethanol | 64-17-5 | l | c | c | nd | nd | c |
| Ethyl acetate | 141-78-6 | l | c | nd | nd | nd | c |
| Ethylbenzene | 100-41-4 | c | nd | c | c | c | c |
| Ethylene oxide | 75-21-8 | pp | c | nd | nd | nd | c |
| Ethyl methacrylate | 97-63-2 | c | nd | c | nd | nd | c |
| Fluorobenzene (IS) | 462-06-6 | c | nd | nd | nd | nd | nd |
| Hexachlorobutadiene | 87-68-3 | c | nd | nd | c | nd | c |
| Hexachloroethane | 67-72-1 | l | nd | nd | nd | nd | c |
| 2-Hexanone | 591-78-6 | pp | nd | c | nd | nd | c |
| 2-Hydroxypropionitrile | 78-97-7 | l | nd | nd | nd | nd | pc |
| Iodomethane | 74-88-4 | c | nd | c | nd | c | c |
| Isobutyl alcohol | 78-83-1 | pp | c | nd | nd | nd | c |
| Isopropylbenzene | 98-82-8 | c | nd | nd | c | nd | c |
| Malononitrile | 109-77-3 | pp | nd | nd | nd | nd | c |
| Methacrylonitrile | 126-98-7 | pp | l | nd | nd | nd | c |
| Methanol | 67-56-1 | l | c | nd | nd | nd | c |
| Methylene chloride | 75-09-2 | c | nd | c | c | c | c |
| Methyl methacrylate | 80-62-6 | c | nd | nd | nd | nd | c |
| 4-Methyl-2-pentanone (MIBK) | 108-10-1 | pp | c | c | nd | nd | c |
| Naphthalene | 91-20-3 | c | nd | nd | c | nd | c |

(continued)

| Compound | CAS No.[b] | Appropriate Preparation Technique[a] 5030/ 5035 | 5031 | 5032 | 5021 | 5041 | Direct Inject. |
|---|---|---|---|---|---|---|---|
| Nitrobenzene | 98-95-3 | c | nd | nd | nd | nd | c |
| 2-Nitropropane | 79-46-9 | c | nd | nd | nd | nd | c |
| N-Nitroso-di-n-butylamine | 924-16-3 | pp | c | nd | nd | nd | c |
| Paraldehyde | 123-63-7 | pp | c | nd | nd | nd | c |
| Pentachloroethane | 76-01-7 | l | nd | nd | nd | nd | c |
| 2-Pentanone | 107-87-9 | pp | c | nd | nd | nd | c |
| 2-Picoline | 109-06-8 | pp | c | nd | nd | nd | c |
| 1-Propanol | 71-23-8 | pp | c | nd | nd | nd | c |
| 2-Propanol | 67-63-0 | pp | c | nd | nd | nd | c |
| Propargyl alcohol | 107-19-7 | pp | l | nd | nd | nd | c |
| β-Propiolactone | 57-57-8 | pp | nd | nd | nd | nd | c |
| Propionitrile (ethyl cyanide) | 107-12-0 | ht | c | nd | nd | nd | pc |
| n-Propylamine | 107-10-8 | c | nd | nd | nd | nd | c |
| Pyridine | 110-86-1 | l | c | nd | nd | nd | c |
| Styrene | 100-42-5 | c | nd | c | c | c | c |
| 1,1,1,2-Tetrachloroethane | 630-20-6 | c | nd | nd | c | c | c |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | c | nd | c | c | c | c |
| Tetrachloroethene | 127-18-4 | c | nd | c | c | c | c |
| Toluene | 108-88-3 | c | nd | c | c | c | c |
| Toluene-$d_8$ (surr) | 2037-26-5 | c | nd | c | c | c | c |
| o-Toluidine | 95-53-4 | pp | c | nd | nd | nd | c |
| 1,2,4-Trichlorobenzene | 120-82-1 | c | nd | nd | c | nd | c |
| 1,1,1-Trichloroethane | 71-55-6 | c | nd | c | c | c | c |
| 1,1,2-Trichloroethane | 79-00-5 | c | nd | c | c | c | c |
| Trichloroethene | 79-01-6 | c | nd | c | c | c | c |
| Trichlorofluoromethane | 75-69-4 | c | nd | c | c | c | c |
| 1,2,3-Trichloropropane | 96-18-4 | c | nd | c | c | c | c |
| Vinyl acetate | 108-05-4 | c | nd | c | nd | nd | c |
| Vinyl chloride | 75-01-4 | c | nd | c | c | c | c |
| o-Xylene | 95-47-6 | c | nd | c | c | c | c |
| m-Xylene | 108-38-3 | c | nd | c | c | c | c |
| p-Xylene | 106-42-3 | c | nd | c | c | c | c |

[a] See Sec. 1.2 for other appropriate sample preparation techniques
[b] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80°C
nd = Not determined
l = Inappropriate technique for this analyte
pc = Poor chromatographic behavior
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
surr = Surrogate
IS = Internal Standard

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Chloroacetonitrile
1-Chlorobutane
1-Chlorohexane
2-Chlorotoluene
4-Chlorotoluene
Dibromofluoromethane
cis-1,2-Dichloroethene
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
p-Isopropyltoluene
Methyl acrylate
Methyl-t-butyl ether
Pentafluorobenzene
n-Propylbenzene
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

1.4 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

## 2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Sec. 1.2). The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

## 3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explained this in text accompanying the uncorrected data.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

3.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

3.7 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.8 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

3.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

## 4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device for aqueous samples - Described in Method 5030.

4.2 Purge-and-trap device for solid samples - Described in Method 5035.

4.3 Automated static headspace device for solid samples - Described in Method 5021.

4.4 Azeotropic distillation apparatus for aqueous and solid samples - Described in Method 5031.

4.5 Vacuum distillation apparatus for aqueous, solid and tissue samples - Described in Method 5032.

4.6 Desorption device for air trapping media for air samples - Described in Method 5041.

4.7 Air sampling loop for sampling from Tedlar® bags for air samples - Described in Method 0040.

4.8 Injection port liners (HP Catalog #18740-80200, or equivalent) - modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven (see illustration below). A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

4.9 Gas chromatography/mass spectrometer/data system

4.9.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.9.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.9.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

4.9.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

4.9.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.9.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.9.2 Gas chromatographic columns

4.9.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5-µm film thickness, or equivalent.

4.9.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), $Rt_x$-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

4.9.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, $Rt_x$-5, SPB-5, or equivalent), 1-µm film thickness.

4.9.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

4.9.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.9.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

4.9.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

4.9.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

4.9.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 8.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.9.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.10 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000-µL.

4.11 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.12 Syringes - 5-, 10-, or 25-mL, gas-tight with shutoff valve.

4.13 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

4.15 Vials - 2-mL, for GC autosampler.

4.16 Disposable pipets - Pasteur.

4.17 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.18 Spatula - Stainless steel.

## 5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, $CH_3OH$ - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to

5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.7.5 Frequency of Standard Preparation

5.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.7.6 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichloro-difluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100-µL or 500-µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

5.7.6.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.9 The concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

| Gas Volume | Calibration Concentration |
|---|---|
| 40 µL | 20 µg/L |
| 100 µL | 50 µg/L |
| 200 µL | 100 µg/L |
| 300 µL | 150 µg/L |
| 400 µL | 200 µg/L |

5.7.6.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

| Gas Volume | Calibration Concentration |
|---|---|
| 10 µL | 1 µg/L |
| 20 µL | 2 µg/L |
| 50 µL | 5 µg/L |
| 100 µL | 10 µg/L |
| 250 µL | 25 µg/L |

5.8 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.9 Surrogate standards - The recommended surrogates are toluene-$d_8$, 4-bromofluorobenzene, 1,2-dichloroethane-$d_4$, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-$d_5$, and 1,4-dichlorobenzene-$d_4$. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

5.12 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

5.12.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.4 for guidance on calibration verification.

5.12.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.12.4 The calibration standards must also contain the internal standards chosen for the analysis.

5.13 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.13.1 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.2 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

5.13.3 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

## 7.0 PROCEDURE

7.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

7.1.1 Direct injection - This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

7.1.2 Purge-and-trap - This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

7.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

7.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

7.1.3 Vacuum distillation - this technique may be used for the introduction of volatile organics from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system.

7.1.4 Automated static headspace - this technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

7.1.5 Cartridge desorption - this technique may be for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

7.2 Recommended chromatographic conditions

7.2.1 General conditions

| | |
|---|---|
| Injector temperature: | 200 - 225°C |
| Transfer line temperature: | 250 - 300°C |

7.2.2 Column 1 and Column 2 with cryogenic cooling (example chromatograms are presented in Figures 1 and 2)

| | |
|---|---|
| Carrier gas (He) flow rate: | 15 mL/min |
| Initial temperature: | 10°C, hold for 5 minutes |
| Temperature program: | 6°C/min to 70°C, then 15°C/min to 145°C |
| Final temperature: | 145°C, hold until all expected compounds have eluted. |

7.2.5 Direct injection - Column 2

| | |
|---|---|
| Carrier gas (He) flow rate: | 4 mL/min |
| Column: | J&W DB-624, 70m x 0.53 mm |
| Initial temperature: | 40°C, hold for 3 minutes |
| Temperature program: | 8°C/min |
| Final temperature: | 260°C, hold until all expected compounds have eluted. |
| Column Bake out: | 75 minutes |
| Injector temperature: | 200-225°C |
| Transfer line temperature: | 250-300°C |

7.2.6 Direct split interface - Column 4

| | |
|---|---|
| Carrier gas (He) flow rate: | 1.5 mL/min |
| Initial temperature: | 35°C, hold for 2 minutes |
| Temperature program: | 4°C/min to 50°C<br>10°C/min to 220°C |
| Final temperature: | 220°C, hold until all expected compounds have eluted |
| Split ratio: | 100:1 |
| Injector temperature: | 125°C |

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

| | |
|---|---|
| Mass range: | 35 - 260 amu |
| Scan time: | 0.6 - 2 sec/scan |
| Source temperature: | According to manufacturer's specifications |
| Ion trap only: | Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations |

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of

BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

7.3.1.2 Use the BFB mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (see Sec. 5.12 and Method 8000). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

7.3.2.2 The internal standards selected in Sec. 5.10 should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion.

7.3.2.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

7.3.3 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 - 2 µL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

7.3.4 Tabulate the area response of the characteristic ions (see Table 5) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured (Sec. 7.6.2).

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

$A_s$ = Peak area (or height) of the analyte or surrogate.
$A_{is}$ = Peak area (or height) of the internal standard.
$C_s$ = Concentration of the analyte or surrogate.
$C_{is}$ = Concentration of the internal standard.

7.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

7.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.5.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

| | |
|---|---|
| Chloromethane | 0.10 |
| 1,1-Dichloroethane | 0.10 |
| Bromoform | 0.10 |
| Chlorobenzene | 0.30 |
| 1,1,2,2-Tetrachloroethane | 0.30 |

7.3.6 Calibration check compounds (CCCs)

7.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of Method 8000.

7.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

$RF_i$ = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

7.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000. The CCCs are:

| | |
|---|---|
| 1,1-Dichloroethene | Toluene |
| Chloroform | Ethylbenzene |
| 1,2-Dichloropropane | Vinyl chloride |

7.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

7.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.8 Linearity of target analytes

7.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Sec. 7.7.2).

7.3.8.2 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 of Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The 20% RSD criteria in Method 8000 pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000 for method blank performance criteria.

7.4.4 System Performance Check Compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 7.3.5.4). This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration Check Compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Sec. 7.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater

than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low detection levels.

7.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

7.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

7.5.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

7.5.6.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

7.5.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.6.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 7.5.5.

7.5.7 Compositing aqueous samples prior to GC/MS analysis

7.5.7.1 Add 5 mL of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

7.5.7.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

7.5.7.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

7.5.7.4 Once all the aliquots have been combined on the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Sec. 7.1).

7.5.7.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

7.5.8 Add 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution to each sample either manually or by autosampler. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of a non-aqueous sample will yield a concentration of 50 µg/kg of each standard.

If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.9 Add 10 µL of the matrix spike solution (Sec. 5.13) to a 5-mL aliquot of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 8.4 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

7.5.9.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

7.5.10 Analyze the sample following the procedure in the introduction method of choice.

7.5.10.1 For direct injection, inject 1 to 2 µL into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

7.5.10.2 The concentration of the internal standards, surrogates, and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2 µL injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

7.5.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.11.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.12 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library

searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

(1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.7.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.3.6). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas $A_x$ and $A_{is}$ should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8260:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria described in Sec. 7.4.4 and the CCC criteria in Sec. 7.4.5, each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The 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 indicate 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.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

## 9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested using purge-and-trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using purge-and-trap (Method 5030) with water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are presented in Tables 10 and 11 for TCLP volatiles in oil. The performance data were developed by spiking and analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, except for the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm, well below the regulatory concentrations. Prior to spiking, the new oil (an SAE 30-weight motor oil) was heated at 80°C overnight to remove volatiles. The used oil (a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of BTEX compounds and isobutanol. These contaminants contributed to the extremely high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

9.5 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand; a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon; and a surface garden soil. Sample preparation was by Method 5035. Each

sample was fortified with the analytes at a concentration of 4 µg/kg. These data are listed in Tables 17, 18, and 19. All data were calculated using fluorobenzene as the internal standard added to the soil sample prior to extraction. This causes some of the results to be greater than 100% recovery because the precision of results is sometimes as great as 28%.

9.5.1 In general, the recoveries of the analytes from the sand matrix are the highest, the C-Horizon soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

9.5.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, are somewhat greater than 100%. This is due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. Also, the garden soil results in Table 19 include some extraordinarily high recoveries for some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection, and to the fact that no background was subtracted.

9.6 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 12 to 16.

9.7 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 20 to 27.

9.8 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in two soil matrices: sand and a surface garden soil. Replicate samples were fortified with the analytes at concentrations of 10 µg/kg. These data are listed in Table 30. All data were calculated using the internal standards listed for each analyte in Table 28. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

9.8.1 If a detector other than an MS is used for analysis, consideration must be given to the choice of internal standards and surrogates. They must not coelute with any other analyte and must have similar properties to the analytes. The recoveries of the analytes are 50% or higher for each matrix studied. The recoveries of the gases or very volatile compounds are greater than 100% in some cases. Also, results include high recoveries of some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection.

9.8.2 The method detection limits using Method 5021 listed in Table 29 were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These MDLs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

9.9 The MDL concentrations listed in Table 31 were determined using Method 5041 in conjunction with Method 8260. They were obtained using cleaned blank VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under the test conditions, the MDLs for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

9.10 The EQL of sample taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 ppm (See Table 33). Matrix effects may cause the individual compound detection limits to be higher.

## 10.0 REFERENCES


1. Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water Method 524.2, U.S. Environmental Protection Agency, Office of Research Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1986.

2. Bellar, T.A., Lichtenberg, J.J, J. Amer. Water Works Assoc., 1974, 66(12), 739-744.

3. Bellar, T.A., Lichtenberg, J.J., "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds"; in Van Hall, Ed.; Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.

4. Budde, W.L., Eichelberger, J.W., "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, April 1980; EPA-600/4-79-020.

5. Eichelberger, J.W., Harris, L.E., Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems"; Analytical Chemistry 1975, 47, 995-1000.

6. Olynyk, P., Budde, W.L., Eichelberger, J.W., "Method Detection Limit for Methods 624 and 625"; Unpublished report, October 1980.

7. Non Cryogenic Temperatures Program and Chromatogram, Private Communications; M. Stephenson and F. Allen, EPA Region IV Laboratory, Athens, GA.

8. Marsden, P.J., Helms, C.L., Colby, B.N., "Analysis of Volatiles in Waste Oil"; Report for B. Lesnik, OSW/EPA under EPA contract 68-W9-001, 6/92.

9. Methods for the Determination of Organic Compounds in Drinking Water, Supplement II Method 524.2; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1992.

10. Flores, P., Bellar, T., "Determination of Volatile Organic Compounds in Soils Using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, December, 1992.

11. Bruce, M.L., Lee, R.P., Stephens, M.W., "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environmental Science and Technology 1992, 26, 160-163.

12. Cramer, P.H., Wilner, J., Stanley, J.S., "Final Report: Method for Polar, Water Soluble, Nonpurgeable Volatile Organics (VOCs)", For U.S. Environmental Protection Agency, Environmental Monitoring Support Laboratory, EPA Contract No. 68-C8-0041.

13. Hiatt, M.H., "Analysis of Fish and Sediment for Volatile Priority Pollutants", Analytical Chemistry 1981, 53, 1541.

14. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.

15. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

| Compound | Retention Time (minutes) | | | MDL[d] |
|---|---|---|---|---|
| | Column 1[a] | Column 2[b] | Column 2'[c] | (µg/L) |
| Dichlorodifluoromethane | 1.35 | 0.70 | 3.13 | 0.10 |
| Chloromethane | 1.49 | 0.73 | 3.40 | 0.13 |
| Vinyl Chloride | 1.56 | 0.79 | 3.93 | 0.17 |
| Bromomethane | 2.19 | 0.96 | 4.80 | 0.11 |
| Chloroethane | 2.21 | 1.02 | -- | 0.10 |
| Trichlorofluoromethane | 2.42 | 1.19 | 6.20 | 0.08 |
| Acrolein | 3.19 | | | |
| Iodomethane | 3.56 | | | |
| Acetonitrile | 4.11 | | | |
| Carbon disulfide | 4.11 | | | |
| Allyl chloride | 4.11 | | | |
| Methylene chloride | 4.40 | 2.06 | 9.27 | 0.03 |
| 1,1-Dichloroethene | 4.57 | 1.57 | 7.83 | 0.12 |
| Acetone | 4.57 | | | |
| trans-1,2-Dichloroethene | 4.57 | 2.36 | 9.90 | 0.06 |
| Acrylonitrile | 5.00 | | | |
| 1,1-Dichloroethane | 6.14 | 2.93 | 10.80 | 0.04 |
| Vinyl acetate | 6.43 | | | |
| 2,2-Dichloropropane | 8.10 | 3.80 | 11.87 | 0.35 |
| 2-Butanone | -- | | | |
| cis-1,2-Dichloroethene | 8.25 | 3.90 | 11.93 | 0.12 |
| Propionitrile | 8.51 | | | |
| Chloroform | 9.01 | 4.80 | 12.60 | 0.03 |
| Bromochloromethane | -- | 4.38 | 12.37 | 0.04 |
| Methacrylonitrile | 9.19 | | | |
| 1,1,1-Trichloroethane | 10.18 | 4.84 | 12.83 | 0.08 |
| Carbon tetrachloride | 11.02 | 5.26 | 13.17 | 0.21 |
| 1,1-Dichloropropene | -- | 5.29 | 13.10 | 0.10 |
| Benzene | 11.50 | 5.67 | 13.50 | 0.04 |
| 1,2-Dichloroethane | 12.09 | 5.83 | 13.63 | 0.06 |
| Trichloroethene | 14.03 | 7.27 | 14.80 | 0.19 |
| 1,2-Dichloropropane | 14.51 | 7.66 | 15.20 | 0.04 |
| Bromodichloromethane | 15.39 | 8.49 | 15.80 | 0.08 |
| Dibromomethane | 15.43 | 7.93 | 5.43 | 0.24 |
| Methyl methacrylate | 15.50 | | | |
| 1,4-Dioxane | 16.17 | | | |
| 2-Chloroethyl vinyl ether | -- | | | |
| 4-Methyl-2-pentanone | 17.32 | | | |
| trans-1,3-Dichloropropene | 17.47 | -- | 16.70 | -- |
| Toluene | 18.29 | 10.00 | 17.40 | 0.11 |
| cis-1,3-Dichloropropene | 19.38 | -- | 17.90 | -- |

TABLE 1 (cont.)

| Compound | Retention Time (minutes) | | | MDL[d] |
|---|---|---|---|---|
| | Column 1[a] | Column 2[b] | Column 2"[c] | (µg/L) |
| 1,1,2-Trichloroethane | 19.59 | 11.05 | 18.30 | 0.10 |
| Ethyl methacrylate | 20.01 | | | |
| 2-Hexanone | 20.30 | | | |
| Tetrachloroethene | 20.26 | 11.15 | 18.60 | 0.14 |
| 1,3-Dichloropropane | 20.51 | 11.31 | 18.70 | 0.04 |
| Dibromochloromethane | 21.19 | 11.85 | 19.20 | 0.05 |
| 1,2-Dibromoethane | 21.52 | 11.83 | 19.40 | 0.06 |
| 1-Chlorohexane | -- | 13.29 | -- | 0.05 |
| Chlorobenzene | 23.17 | 13.01 | 20.67 | 0.04 |
| 1,1,1,2-Tetrachloroethane | 23.36 | 13.33 | 20.87 | 0.05 |
| Ethylbenzene | 23.38 | 13.39 | 21.00 | 0.06 |
| p-Xylene | 23.54 | 13.69 | 21.30 | 0.13 |
| m-Xylene | 23.54 | 13.68 | 21.37 | 0.05 |
| o-Xylene | 25.16 | 14.52 | 22.27 | 0.11 |
| Styrene | 25.30 | 14.60 | 22.40 | 0.04 |
| Bromoform | 26.23 | 14.88 | 22.77 | 0.12 |
| Isopropylbenzene (Cumene) | 26.37 | 15.46 | 23.30 | 0.15 |
| cis-1,4-Dichloro-2-butene | 27.12 | | | |
| 1,1,2,2-Tetrachloroethane | 27.29 | 16.35 | 24.07 | 0.04 |
| Bromobenzene | 27.46 | 15.86 | 24.00 | 0.03 |
| 1,2,3-Trichloropropane | 27.55 | 16.23 | 24.13 | 0.32 |
| n-Propylbenzene | 27.58 | 16.41 | 24.33 | 0.04 |
| 2-Chlorotoluene | 28.19 | 16.42 | 24.53 | 0.04 |
| trans-1,4-Dichloro-2-butene | 28.26 | | | |
| 1,3,5-Trimethylbenzene | 28.31 | 16.90 | 24.83 | 0.05 |
| 4-Chlorotoluene | 28.33 | 16.72 | 24.77 | 0.06 |
| Pentachloroethane | 29.41 | | | |
| 1,2,4-Trimethylbenzene | 29.47 | 17.70 | 31.50 | 0.13 |
| sec-Butylbenzene | 30.25 | 18.09 | 26.13 | 0.13 |
| tert-Butylbenzene | 30.59 | 17.57 | 26.60 | 0.14 |
| p-Isopropyltoluene | 30.59 | 18.52 | 26.50 | 0.12 |
| 1,3-Dichlorobenzene | 30.56 | 18.14 | 26.37 | 0.12 |
| 1,4-Dichlorobenzene | 31.22 | 18.39 | 26.60 | 0.03 |
| Benzyl chloride | 32.00 | | | |
| n-Butylbenzene | 32.23 | 19.49 | 27.32 | 0.11 |
| 1,2-Dichlorobenzene | 32.31 | 19.17 | 27.43 | 0.03 |
| 1,2-Dibromo-3-chloropropane | 35.30 | 21.08 | -- | 0.26 |
| 1,2,4-Trichlorobenzene | 38.19 | 23.08 | 31.50 | 0.04 |
| Hexachlorobutadiene | 38.57 | 23.68 | 32.07 | 0.11 |
| Naphthalene | 39.05 | 23.52 | 32.20 | 0.04 |
| 1,2,3-Trichlorobenzene | 40.01 | 24.18 | 32.97 | 0.03 |

TABLE 1 (cont.)

| Compound | Retention Time (minutes) Column 1[a] | Column 2[b] | Column 2"[c] | MDL[d] (µg/L) |
|---|---|---|---|---|
| INTERNAL STANDARDS/SURROGATES | | | | |
| 1,4-Difluorobenzene | 13.26 | | | |
| Chlorobenzene-$d_5$ | 23.10 | | | |
| 1,4-Dichlorobenzene-$d_4$ | 31.16 | | | |
| 4-Bromofluorobenzene | 27.83 | 15.71 | 23.63 | |
| 1,2-Dichlorobenzene-$d_4$ | 32.30 | 19.08 | 27.25 | |
| Dichloroethane-$d_4$ | 12.08 | | | |
| Dibromofluoromethane | -- | | | |
| Toluene-$d_8$ | 18.27 | | | |
| Pentafluorobenzene | -- | | | |
| Fluorobenzene | 13.00 | 6.27 | 14.06 | |

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.

[c] Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

[d] MDL based on a 25-mL sample volume.

TABLE 2

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

| Compound | Retention Time (minutes) Column 3[a] | MDL[b] (µg/L) |
|---|---|---|
| Dichlorodifluoromethane | 0.88 | 0.11 |
| Chloromethane | 0.97 | 0.05 |
| Vinyl chloride | 1.04 | 0.04 |
| Bromomethane | 1.29 | 0.03 |
| 1,1-Dichloroethane | 4.03 | 0.03 |
| cis-1,2-Dichloroethene | 5.07 | 0.06 |
| 2,2-Dichloropropane | 5.31 | 0.08 |
| Chloroform | 5.55 | 0.04 |
| Bromochloromethane | 5.63 | 0.09 |
| 1,1,1-Trichloroethane | 6.76 | 0.04 |
| 1,2-Dichloroethane | 7.00 | 0.02 |
| 1,1-Dichloropropene | 7.16 | 0.12 |
| Carbon tetrachloride | 7.41 | 0.02 |
| Benzene | 7.41 | 0.03 |
| 1,2-Dichloropropane | 8.94 | 0.02 |
| Trichloroethene | 9.02 | 0.02 |
| Dibromomethane | 9.09 | 0.01 |
| Bromodichloromethane | 9.34 | 0.03 |
| Toluene | 11.51 | 0.08 |
| 1,1,2-Trichloroethane | 11.99 | 0.08 |
| 1,3-Dichloropropane | 12.48 | 0.08 |
| Dibromochloromethane | 12.80 | 0.07 |
| Tetrachloroethene | 13.20 | 0.05 |
| 1,2-Dibromoethane | 13.60 | 0.10 |
| Chlorobenzene | 14.33 | 0.03 |
| 1,1,1,2-Tetrachloroethane | 14.73 | 0.07 |
| Ethylbenzene | 14.73 | 0.03 |
| p-Xylene | 15.30 | 0.06 |
| m-Xylene | 15.30 | 0.03 |
| Bromoform | 15.70 | 0.20 |
| o-Xylene | 15.78 | 0.06 |
| Styrene | 15.78 | 0.27 |
| 1,1,2,2-Tetrachloroethane | 15.78 | 0.20 |
| 1,2,3-Trichloropropane | 16.26 | 0.09 |
| Isopropylbenzene | 16.42 | 0.10 |
| Bromobenzene | 16.42 | 0.11 |
| 2-Chlorotoluene | 16.74 | 0.08 |
| n-Propylbenzene | 16.82 | 0.10 |
| 4-Chlorotoluene | 16.82 | 0.06 |

TABLE 2 (cont.)

| Compound | Retention Time (minutes) Column 3[a] | MDL[b] (µg/L) |
|---|---|---|
| 1,3,5-Trimethylbenzene | 16.99 | 0.06 |
| tert-Butylbenzene | 17.31 | 0.33 |
| 1,2,4-Trimethylbenzene | 17.31 | 0.09 |
| sec-Butylbenzene | 17.47 | 0.12 |
| 1,3-Dichlorobenzene | 17.47 | 0.05 |
| p-Isopropyltoluene | 17.63 | 0.26 |
| 1,4-Dichlorobenzene | 17.63 | 0.04 |
| 1,2-Dichlorobenzene | 17.79 | 0.05 |
| n-Butylbenzene | 17.95 | 0.10 |
| 1,2-Dibromo-3-chloropropane | 18.03 | 0.50 |
| 1,2,4-Trichlorobenzene | 18.84 | 0.20 |
| Naphthalene | 19.07 | 0.10 |
| Hexachlorobutadiene | 19.24 | 0.10 |
| 1,2,3-Trichlorobenzene | 19.24 | 0.14 |

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25-mL sample volume.

TABLE 3

ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

| Estimated Quantitation Limits | | |
|---|---|---|
| 5-mL Ground Water Purge (µg/L) | 25-mL Ground water Purge (µg/L) | Low Soil/Sediment[b] µg/kg |
| 5 | 1 | 5 |

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

| Other Matrices | Factor[c] |
|---|---|
| Water miscible liquid waste | 50 |
| High concentration soil and sludge | 125 |
| Non-water miscible waste | 500 |

[c] EQL = [EQL for low soil sediment (Table 3)] x [Factor].

For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

| m/z | Required Intensity (relative abundance) |
|---|---|
| 50 | 15 to 40% of m/z 95 |
| 75 | 30 to 60% of m/z 95 |
| 95 | Base peak, 100% relative abundance |
| 96 | 5 to 9% of m/z 95 |
| 173 | Less than 2% of m/z 174 |
| 174 | Greater than 50% of m/z 95 |
| 175 | 5 to 9% of m/z 174 |
| 176 | Greater than 95% but less than 101% of m/z 174 |
| 177 | 5 to 9% of m/z 176 |

[a] Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers" instructions), provided that method performance is not adversely affected.

TABLE 5

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

| Compound | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|---|---|---|
| Acetone | 58 | 43 |
| Acetonitrile | 41 | 40, 39 |
| Acrolein | 56 | 55, 58 |
| Acrylonitrile | 53 | 52, 51 |
| Allyl alcohol | 57 | 58, 39 |
| Allyl chloride | 76 | 41, 39, 78 |
| Benzene | 78 | - |
| Benzyl chloride | 91 | 126, 65, 128 |
| Bromoacetone | 136 | 43, 138, 93, 95 |
| Bromobenzene | 156 | 77, 158 |
| Bromochloromethane | 128 | 49, 130 |
| Bromodichloromethane | 83 | 85, 127 |
| Bromoform | 173 | 175, 254 |
| Bromomethane | 94 | 96 |
| iso-Butanol | 74 | 43 |
| n-Butanol | 56 | 41 |
| 2-Butanone | 72 | 43 |
| n-Butylbenzene | 91 | 92, 134 |
| sec-Butylbenzene | 105 | 134 |
| tert-Butylbenzene | 119 | 91, 134 |
| Carbon disulfide | 76 | 78 |
| Carbon tetrachloride | 117 | 119 |
| Chloral hydrate | 82 | 44, 84, 86, 111 |
| Chloroacetonitrile | 48 | 75 |
| Chlorobenzene | 112 | 77, 114 |
| 1-Chlorobutane | 56 | 49 |
| Chlorodibromomethane | 129 | 208, 206 |
| Chloroethane | 64 (49*) | 66 (51*) |
| 2-Chloroethanol | 49 | 44, 43, 51, 80 |
| Bis(2-chloroethyl) sulfide | 109 | 111, 158, 160 |
| 2-Chloroethyl vinyl ether | 63 | 65, 106 |
| Chloroform | 83 | 85 |
| Chloromethane | 50 (49*) | 52 (51*) |
| Chloroprene | 53 | 88, 90, 51 |
| 3-Chloropropionitrile | 54 | 49, 89, 91 |
| 2-Chlorotoluene | 91 | 126 |
| 4-Chlorotoluene | 91 | 126 |
| 1,2-Dibromo-3-chloropropane | 75 | 155, 157 |
| Dibromochloromethane | 129 | 127 |
| 1,2-Dibromoethane | 107 | 109, 188 |
| Dibromomethane | 93 | 95, 174 |

TABLE 5 (cont.)

| Compound | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|---|---|---|
| 1,2-Dichlorobenzene | 146 | 111, 148 |
| 1,2-Dichlorobenzene-$d_4$ | 152 | 115, 150 |
| 1,3-Dichlorobenzene | 146 | 111, 148 |
| 1,4-Dichlorobenzene | 146 | 111, 148 |
| cis-1,4-Dichloro-2-butene | 75 | 53, 77, 124, 89 |
| trans-1,4-Dichloro-2-butene | 53 | 88, 75 |
| Dichlorodifluoromethane | 85 | 87 |
| 1,1-Dichloroethane | 63 | 65, 83 |
| 1,2-Dichloroethane | 62 | 98 |
| 1,1-Dichloroethene | 96 | 61, 63 |
| cis-1,2-Dichloroethene | 96 | 61, 98 |
| trans-1,2-Dichloroethene | 96 | 61, 98 |
| 1,2-Dichloropropane | 63 | 112 |
| 1,3-Dichloropropane | 76 | 78 |
| 2,2-Dichloropropane | 77 | 97 |
| 1,3-Dichloro-2-propanol | 79 | 43, 81, 49 |
| 1,1-Dichloropropene | 75 | 110, 77 |
| cis-1,3-Dichloropropene | 75 | 77, 39 |
| trans-1,3-Dichloropropene | 75 | 77, 39 |
| 1,2,3,4-Diepoxybutane | 55 | 57, 56 |
| Diethyl ether | 74 | 45, 59 |
| 1,4-Dioxane | 88 | 58, 43, 57 |
| Epichlorohydrin | 57 | 49, 62, 51 |
| Ethanol | 31 | 45, 27, 46 |
| Ethyl acetate | 88 | 43, 45, 61 |
| Ethylbenzene | 91 | 106 |
| Ethylene oxide | 44 | 43, 42 |
| Ethyl methacrylate | 69 | 41, 99, 86, 114 |
| Hexachlorobutadiene | 225 | 223, 227 |
| Hexachloroethane | 201 | 166, 199, 203 |
| 2-Hexanone | 43 | 58, 57, 100 |
| 2-Hydroxypropionitrile | 44 | 43, 42, 53 |
| Iodomethane | 142 | 127, 141 |
| Isobutyl alcohol | 43 | 41, 42, 74 |
| Isopropylbenzene | 105 | 120 |
| p-Isopropyltoluene | 119 | 134, 91 |
| Malononitrile | 66 | 39, 65, 38 |
| Methacrylonitrile | 41 | 67, 39, 52, 66 |
| Methyl acrylate | 55 | 85 |
| Methyl-t-butyl ether | 73 | 57 |
| Methylene chloride | 84 | 86, 49 |
| Methyl ethyl ketone | 72 | 43 |
| Methyl iodide | 142 | 127, 141 |

TABLE 5 (cont.)

| Compound | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|---|---|---|
| Methyl methacrylate | 69 | 41, 100, 39 |
| 4-Methyl-2-pentanone | 100 | 43, 58, 85 |
| Naphthalene | 128 | - |
| Nitrobenzene | 123 | 51, 77 |
| 2-Nitropropane | 46 | - |
| 2-Picoline | 93 | 66, 92, 78 |
| Pentachloroethane | 167 | 130, 132, 165, 169 |
| Propargyl alcohol | 55 | 39, 38, 53 |
| β-Propiolactone | 42 | 43, 44 |
| Propionitrile (ethyl cyanide) | 54 | 52, 55, 40 |
| n-Propylamine | 59 | 41, 39 |
| n-Propylbenzene | 91 | 120 |
| Pyridine | 79 | 52 |
| Styrene | 104 | 78 |
| 1,2,3-Trichlorobenzene | 180 | 182, 145 |
| 1,2,4-Trichlorobenzene | 180 | 182, 145 |
| 1,1,1,2-Tetrachloroethane | 131 | 133, 119 |
| 1,1,2,2-Tetrachloroethane | 83 | 131, 85 |
| Tetrachloroethene | 164 | 129, 131, 166 |
| Toluene | 92 | 91 |
| 1,1,1-Trichloroethane | 97 | 99, 61 |
| 1,1,2-Trichloroethane | 83 | 97, 85 |
| Trichloroethene | 95 | 97, 130, 132 |
| Trichlorofluoromethane | 151 | 101, 153 |
| 1,2,3-Trichloropropane | 75 | 77 |
| 1,2,4-Trimethylbenzene | 105 | 120 |
| 1,3,5-Trimethylbenzene | 105 | 120 |
| Vinyl acetate | 43 | 86 |
| Vinyl chloride | 62 | 64 |
| o-Xylene | 106 | 91 |
| m-Xylene | 106 | 91 |
| p-Xylene | 106 | 91 |
| Internal Standards/Surrogates: | | |
| Benzene-$d_6$ | 84 | 83 |
| Bromobenzene-$d_5$ | 82 | 162 |
| Bromochloromethane-$d_2$ | 51 | 131 |
| 1,4-Difluorobenzene | 114 | |
| Chlorobenzene-$d_5$ | 117 | |
| 1,4-Dichlorobenzene-$d_4$ | 152 | 115, 150 |
| 1,1,2-Trichloroethane-$d_3$ | 100 | |
| 4-Bromofluorobenzene | 95 | 174, 176 |
| Chloroform-$d_1$ | 84 | |
| Dibromofluoromethane | 113 | |

TABLE 5 (cont.)

| Compound | Primary Characteristic Ion | Secondary Characteristic Ion(s) |
|---|---|---|
| Internal Standards/Surrogates | | |
| Dichloroethane-$d_4$ | 102 | |
| Toluene-$d_8$ | 98 | |
| Pentafluorobenzene | 168 | |
| Fluorobenzene | 96 | 77 |

* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

TABLE 6

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN (METHOD 5030)

| Compound | Conc. Range (µg/L) | Number of Samples | % Recovery[a] | Standard Deviation of Recovery[b] | RSD |
|---|---|---|---|---|---|
| Benzene | 0.1 - 10 | 31 | 97 | 6.5 | 5.7 |
| Bromobenzene | 0.1 - 10 | 30 | 100 | 5.5 | 5.5 |
| Bromochloromethane | 0.5 - 10 | 24 | 90 | 5.7 | 6.4 |
| Bromodichloromethane | 0.1 - 10 | 30 | 95 | 5.7 | 6.1 |
| Bromoform | 0.5 - 10 | 18 | 101 | 6.4 | 6.3 |
| Bromomethane | 0.5 - 10 | 18 | 95 | 7.8 | 8.2 |
| n-Butylbenzene | 0.5 - 10 | 18 | 100 | 7.6 | 7.6 |
| sec-Butylbenzene | 0.5 - 10 | 16 | 100 | 7.6 | 7.6 |
| tert-Butylbenzene | 0.5 - 10 | 18 | 102 | 7.4 | 7.3 |
| Carbon tetrachloride | 0.5 - 10 | 24 | 84 | 7.4 | 8.8 |
| Chlorobenzene | 0.1 - 10 | 31 | 98 | 5.8 | 5.9 |
| Chloroethane | 0.5 - 10 | 24 | 89 | 8.0 | 9.0 |
| Chloroform | 0.5 - 10 | 24 | 90 | 5.5 | 6.1 |
| Chloromethane | 0.5 - 10 | 23 | 93 | 8.3 | 8.9 |
| 2-Chlorotoluene | 0.1 - 10 | 31 | 90 | 5.6 | 6.2 |
| 4-Chlorotoluene | 0.1 - 10 | 31 | 99 | 8.2 | 8.3 |
| 1,2-Dibromo-3-Chloropropane | 0.5 - 10 | 24 | 83 | 16.6 | 19.9 |
| Dibromochloromethane | 0.1 - 10 | 31 | 92 | 6.5 | 7.0 |
| 1,2-Dibromoethane | 0.5 - 10 | 24 | 102 | 4.0 | 3.9 |
| Dibromomethane | 0.5 - 10 | 24 | 100 | 5.6 | 5.6 |
| 1,2-Dichlorobenzene | 0.1 - 10 | 31 | 93 | 5.8 | 6.2 |
| 1,3-Dichlorobenzene | 0.5 - 10 | 24 | 99 | 6.8 | 6.9 |
| 1,4-Dichlorobenzene | 0.2 - 20 | 31 | 103 | 6.6 | 6.4 |
| Dichlorodifluoromethane | 0.5 - 10 | 18 | 90 | 6.9 | 7.7 |
| 1,1-Dichlorobenzene | 0.5 - 10 | 24 | 96 | 5.1 | 5.3 |
| 1,2-Dichlorobenzene | 0.1 - 10 | 31 | 95 | 5.1 | 5.4 |
| 1,1-Dichloroethene | 0.1 - 10 | 34 | 94 | 6.3 | 6.7 |
| cis-1,2-Dichloroethene | 0.5 - 10 | 18 | 101 | 6.7 | 6.7 |
| trans-1,2-Dichloroethene | 0.1 - 10 | 30 | 93 | 5.2 | 5.6 |
| 1,2-Dichloropropane | 0.1 - 10 | 30 | 97 | 5.9 | 6.1 |
| 1,3-Dichloropropane | 0.1 - 10 | 31 | 96 | 5.7 | 6.0 |
| 2,2-Dichloropropane | 0.5 - 10 | 12 | 86 | 14.6 | 16.9 |
| 1,1-Dichloropropene | 0.5 - 10 | 18 | 98 | 8.7 | 8.9 |
| Ethylbenzene | 0.1 - 10 | 31 | 99 | 8.4 | 8.6 |
| Hexachlorobutadiene | 0.5 - 10 | 18 | 100 | 6.8 | 6.8 |
| Isopropylbenzene | 0.5 - 10 | 16 | 101 | 7.7 | 7.6 |
| p-Isopropyltoluene | 0.1 - 10 | 23 | 99 | 6.7 | 6.7 |
| Methylene chloride | 0.1 - 10 | 30 | 95 | 5.0 | 5.3 |

TABLE 6 (cont.)

| Compound | Conc. Range (µg/L) | Number of Samples | % Recovery[a] | Standard Deviation of Recovery[b] | RSD |
|---|---|---|---|---|---|
| Naphthalene | 0.1 -100 | 31 | 104 | 8.6 | 8.2 |
| n-Propylbenzene | 0.1 - 10 | 31 | 100 | 5.8 | 5.8 |
| Styrene | 0.1 -100 | 39 | 102 | 7.3 | 7.2 |
| 1,1,1,2-Tetrachloroethane | 0.5 - 10 | 24 | 90 | 6.1 | 6.8 |
| 1,1,2,2-Tetrachloroethane | 0.1 - 10 | 30 | 91 | 5.7 | 6.3 |
| Tetrachloroethene | 0.5 - 10 | 24 | 89 | 6.0 | 6.8 |
| Toluene | 0.5 - 10 | 18 | 102 | 8.1 | 8.0 |
| 1,2,3-Trichlorobenzene | 0.5 - 10 | 18 | 109 | 9.4 | 8.6 |
| 1,2,4-Trichlorobenzene | 0.5 - 10 | 18 | 108 | 9.0 | 8.3 |
| 1,1,1-Trichloroethane | 0.5 - 10 | 18 | 98 | 7.9 | 8.1 |
| 1,1,2-Trichloroethane | 0.5 - 10 | 18 | 104 | 7.6 | 7.3 |
| Trichloroethene | 0.5 - 10 | 24 | 90 | 6.5 | 7.3 |
| Trichlorofluoromethane | 0.5 - 10 | 24 | 89 | 7.2 | 8.1 |
| 1,2,3-Trichloropropane | 0.5 - 10 | 16 | 108 | 15.6 | 14.4 |
| 1,2,4-Trimethylbenzene | 0.5 - 10 | 18 | 99 | 8.0 | 8.1 |
| 1,3,5-Trimethylbenzene | 0.5 - 10 | 23 | 92 | 6.8 | 7.4 |
| Vinyl chloride | 0.5 - 10 | 18 | 98 | 6.5 | 6.7 |
| o-Xylene | 0.1 - 31 | 18 | 103 | 7.4 | 7.2 |
| m-Xylene | 0.1 - 10 | 31 | 97 | 6.3 | 6.5 |
| p-Xylene | 0.5 - 10 | 18 | 104 | 8.0 | 7.7 |

[a] Recoveries were calculated using internal standard method. The internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data from three concentrations.

TABLE 7

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

| Compound | Conc. (µg/L) | Number of Samples | % Recovery[a] | Standard Deviation of Recovery[b] | RSD |
|---|---|---|---|---|---|
| Benzene | 0.1 | 7 | 99 | 6.2 | 6.3 |
| Bromobenzene | 0.5 | 7 | 97 | 7.4 | 7.6 |
| Bromochloromethane | 0.5 | 7 | 97 | 5.8 | 6.0 |
| Bromodichloromethane | 0.1 | 7 | 100 | 4.6 | 4.6 |
| Bromoform | 0.5 | 7 | 101 | 5.4 | 5.3 |
| Bromomethane | 0.5 | 7 | 99 | 7.1 | 7.2 |
| n-Butylbenzene | 0.5 | 7 | 94 | 6.0 | 6.4 |
| sec-Butylbenzene | 0.5 | 7 | 110 | 7.1 | 6.5 |
| tert-Butylbenzene | 0.5 | 7 | 110 | 2.5 | 2.3 |
| Carbon tetrachloride | 0.1 | 7 | 108 | 6.8 | 6.3 |
| Chlorobenzene | 0.1 | 7 | 91 | 5.8 | 6.4 |
| Chloroethane | 0.1 | 7 | 100 | 5.8 | 5.8 |
| Chloroform | 0.1 | 7 | 105 | 3.2 | 3.0 |
| Chloromethane | 0.5 | 7 | 101 | 4.7 | 4.7 |
| 2-Chlorotoluene | 0.5 | 7 | 99 | 4.6 | 4.6 |
| 4-Chlorotoluene | 0.5 | 7 | 96 | 7.0 | 7.3 |
| 1,2-Dibromo-3-chloropropane | 0.5 | 7 | 92 | 10.0 | 10.9 |
| Dibromochloromethane | 0.1 | 7 | 99 | 5.6 | 5.7 |
| 1,2-Dibromoethane | 0.5 | 7 | 97 | 5.6 | 5.8 |
| Dibromomethane | 0.5 | 7 | 93 | 5.6 | 6.0 |
| 1,2-Dichlorobenzene | 0.1 | 7 | 97 | 3.5 | 3.6 |
| 1,3-Dichlorobenzene | 0.1 | 7 | 101 | 6.0 | 5.9 |
| 1,4-Dichlorobenzene | 0.1 | 7 | 106 | 6.5 | 6.1 |
| Dichlorodifluoromethane | 0.1 | 7 | 99 | 8.8 | 8.9 |
| 1,1-Dichloroethane | 0.5 | 7 | 98 | 6.2 | 6.3 |
| 1,2-Dichloroethane | 0.1 | 7 | 100 | 6.3 | 6.3 |
| 1,1-Dichloroethene | 0.1 | 7 | 95 | 9.0 | 9.5 |
| cis-1,2-Dichloroethene | 0.1 | 7 | 100 | 3.5 | 3.7 |
| trans-1,2-Dichloroethene | 0.1 | 7 | 98 | 7.2 | 7.3 |
| 1,2-Dichloropropane | 0.5 | 7 | 96 | 6.0 | 6.3 |
| 1,3-Dichloropropane | 0.5 | 7 | 99 | 5.8 | 5.9 |
| 2,2-Dichloropropane | 0.5 | 7 | 99 | 4.9 | 4.9 |
| 1,1-Dichloropropene | 0.5 | 7 | 102 | 7.4 | 7.3 |
| Ethylbenzene | 0.5 | 7 | 99 | 5.2 | 5.3 |
| Hexachlorobutadiene | 0.5 | 7 | 100 | 6.7 | 6.7 |
| Isopropylbenzene | 0.5 | 7 | 102 | 6.4 | 6.3 |
| p-Isopropyltoluene | 0.5 | 7 | 113 | 13.0 | 11.5 |
| Methylene chloride | 0.5 | 7 | 97 | 13.0 | 13.4 |
| Naphthalene | 0.5 | 7 | 98 | 7.2 | 7.3 |

TABLE 7 (cont.)

| Compound | Conc. (µg/L) | Number of Samples | % Recovery[a] | Standard Deviation of Recovery[b] | RSD |
|---|---|---|---|---|---|
| n-Propylbenzene | 0.5 | 7 | 99 | 6.6 | 6.7 |
| Styrene | 0.5 | 7 | 96 | 19.0 | 19.8 |
| 1,1,1,2-Tetrachloroethane | 0.5 | 7 | 100 | 4.7 | 4.7 |
| 1,1,2,2-Tetrachloroethane | 0.5 | 7 | 100 | 12.0 | 12.0 |
| Tetrachloroethene | 0.1 | 7 | 96 | 5.0 | 5.2 |
| Toluene | 0.5 | 7 | 100 | 5.9 | 5.9 |
| 1,2,3-Trichlorobenzene | 0.5 | 7 | 102 | 8.9 | 8.7 |
| 1,2,4-Trichlorobenzene | 0.5 | 7 | 91 | 16.0 | 17.6 |
| 1,1,1-Trichloroethane | 0.5 | 7 | 100 | 4.0 | 4.0 |
| 1,1,2-Trichloroethane | 0.5 | 7 | 102 | 4.9 | 4.8 |
| Trichloroethene | 0.1 | 7 | 104 | 2.0 | 1.9 |
| Trichlorofluoromethane | 0.1 | 7 | 97 | 4.6 | 4.7 |
| 1,2,3-Trichloropropane | 0.5 | 7 | 96 | 6.5 | 6.8 |
| 1,2,4-Trimethylbenzene | 0.5 | 7 | 96 | 6.5 | 6.8 |
| 1,3,5-Trimethylbenzene | 0.5 | 7 | 101 | 4.2 | 4.2 |
| Vinyl chloride | 0.1 | 7 | 104 | 0.2 | 0.2 |
| o-Xylene | 0.5 | 7 | 106 | 7.5 | 7.1 |
| m-Xylene | 0.5 | 7 | 106 | 4.6 | 4.3 |
| p-Xylene | 0.5 | 7 | 97 | 6.1 | 6.3 |

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8

SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

| Surrogate Compound | Water | Soil/Sediment |
|---|---|---|
| 4-Bromofluorobenzene[a] | 86-115 | 74-121 |
| Dibromofluoromethane[a] | 86-118 | 80-120 |
| Toluene-$d_8$[a] | 88-110 | 81-117 |
| Dichloroethane-$d_4$[a] | 80-120 | 80-120 |

[a] Single laboratory data, for guidance only.

TABLE 9

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

| Approximate Concentration Range (µg/kg) | Volume of Extract[a] |
|---|---|
| 500 - 10,000 | 100 µL |
| 1,000 - 20,000 | 50 µL |
| 5,000 - 100,000 | 10 µL |
| 25,000 - 500,000 | 100 µL of 1/50 dilution[b] |

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10

DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM (METHOD 3585)

| Compound | Recovery (%) | %RSD | Blank (ppm) | Spike (ppm) |
|---|---|---|---|---|
| Acetone | 91 | 14.8 | 1.9 | 5.0 |
| Benzene | 86 | 21.3 | 0.1 | 0.5 |
| n-Butanol*,** | 107 | 27.8 | 0.5 | 5.0 |
| iso-Butanol*,** | 95 | 19.5 | 0.9 | 5.0 |
| Carbon tetrachloride | 86 | 44.7 | 0.0 | 0.5 |
| Carbon disulfide** | 53 | 22.3 | 0.0 | 5.0 |
| Chlorobenzene | 81 | 29.3 | 0.0 | 5.0 |
| Chloroform | 84 | 29.3 | 0.0 | 6.0 |
| 1,4-Dichlorobenzene | 98 | 24.9 | 0.0 | 7.5 |
| 1,2-Dichloroethane | 101 | 23.1 | 0.0 | 0.5 |
| 1,1-Dichloroethene | 97 | 45.3 | 0.0 | 0.7 |
| Diethyl ether | 76 | 24.3 | 0.0 | 5.0 |
| Ethyl acetate | 113 | 27.4 | 0.0 | 5.0 |
| Ethylbenzene | 83 | 30.1 | 0.2 | 5.0 |
| Hexachloroethane | 71 | 30.3 | 0.0 | 3.0 |
| Methylene chloride | 98 | 45.3 | 0.0 | 5.0 |
| Methyl ethyl ketone | 79 | 24.6 | 0.4 | 5.0 |
| MIBK | 93 | 31.4 | 0.0 | 5.0 |
| Nitrobenzene | 89 | 30.3 | 0.0 | 2.0 |
| Pyridine | 31 | 35.9 | 0.0 | 5.0 |
| Tetrachloroethene | 82 | 27.1 | 0.0 | 0.7 |
| Trichlorofluoromethane | 76 | 27.6 | 0.0 | 5.0 |
| 1,1,2-Trichlorotrifluoroethane | 69 | 29.2 | 0.0 | 5.0 |
| Toluene | 73 | 21.9 | 0.6 | 5.0 |
| Trichloroethene | 66 | 28.0 | 0.0 | 0.5 |
| Vinyl chloride | 63 | 35.2 | 0.0 | 0.2 |
| o-Xylene | 83 | 29.5 | 0.4 | 5.0 |
| m/p-Xylene | 84 | 29.5 | 0.6 | 10.0 |

* Alternate mass employed
** IS quantitation

Data are taken from Reference 9.

TABLE 11

SINGLE LABORATORY PERFORMANCE
DATA FOR THE DIRECT INJECTION METHOD - USED OIL (METHOD 3585)

| Compound | Recovery (%) | %RSD | Blank (ppm) | Spike (ppm) |
|---|---|---|---|---|
| Acetone** | 105 | 54 | 2.0 | 5.0 |
| Benzene | 3135 | 44 | 14 | 0.5 |
| Benzene-$d_6$ | 56 | 44 | 2.9 | 0.5 |
| n-Butanol** | 100 | 71 | 12 | 5.0 |
| iso-Butanol*,** | 132 | 27 | 0 | 5.0 |
| Carbon tetrachloride | 143 | 68 | 0 | 0.5 |
| Carbon tetrachloride-$^{13}C$ | 99 | 44 | 5.1 | 0.5 |
| Carbon disulfide** | 95 | 63 | 0 | 5.0 |
| Chlorobenzene | 148 | 71 | 0 | 5.0 |
| Chlorobenzene-$d_5$ | 60 | 44 | 3.6 | 5.0 |
| Chloroform | 149 | 74 | 0 | 6.0 |
| Chloroform-$d_1$ | 51 | 44 | 2.6 | 6.0 |
| 1,4-Dichlorobenzene | 142 | 72 | 0 | 7.5 |
| 1,4-Dichlorobenzene-$d_4$ | 53 | 44 | 3.4 | 7.5 |
| 1,2-Dichloroethane** | 191 | 54 | 0 | 0.5 |
| 1,1-Dichloroethene* | 155 | 51 | 0 | 0.7 |
| 1,1-Dichloroethene-$d_2$ | 68 | 44 | 3.4 | 0.7 |
| Diethyl ether** | 95 | 66 | 0 | 5.0 |
| Ethyl acetate*,** | 126 | 39 | 0 | 5.0 |
| Ethylbenzene | 1298 | 44 | 54 | 5.0 |
| Ethylbenzene-$d_{10}$ | 63 | 44 | 3.6 | 5.0 |
| Hexachloroethane | 132 | 72 | 0 | 3.0 |
| Hexachloroethane-$^{13}C$ | 54 | 45 | 3.5 | 3.0 |
| Methylene chloride** | 86 | 65 | 0.3 | 5.0 |
| Methyl ethyl ketone** | 107 | 64 | 0 | 5.0 |
| 4-Methyl-2-pentanone (MIBK)** | 100 | 74 | 0.1 | 5.0 |
| Nitrobenzene | 111 | 80 | 0 | 2.0 |
| Nitrobenzene-$d_5$ | 65 | 53 | 4.0 | 2.0 |
| Pyridine** | 68 | 85 | 0 | 5.0 |
| Pyridine-$d_5$ | ND | -- | 0 | 5.0 |
| Tetrachloroethene** | 101 | 73 | 0 | 0.7 |
| Trichlorofluoromethane** | 91 | 70 | 0 | 5.0 |
| 1,1,2-$Cl_3F_3$ethane** | 81 | 70 | 0 | 5.0 |
| Toluene | 2881 | 44 | 128 | 5.0 |
| Toluene-$d_8$ | 63 | 44 | 3.6 | 5.0 |
| Trichloroethene | 152 | 57 | 0 | 0.5 |
| Trichloroethene-$d_1$ | 55 | 44 | 2.8 | 0.5 |

TABLE 11 (cont.)

| Compound | Recovery (%) | %RSD | Blank (ppm) | Spike (ppm) |
|---|---|---|---|---|
| Vinyl chloride** | 100 | 69 | 0 | 0.2 |
| o-Xylene | 2292 | 44 | 105 | 5.0 |
| o-Xylene-$d_{10}$ | 76 | 44 | 4.2 | 5.0 |
| m-/p-Xylene | 2583 | 44 | 253 | 10.0 |
| p-Xylene-$d_{10}$ | 67 | 44 | 3.7 | 10.0 |

* Alternate mass employed
** IS quantitation
ND = Not Detected

Data are based on seven measurements and are taken from Reference 9.

TABLE 12

METHOD DETECTION LIMITS (METHOD 5031)

| Compound | MDL (µg/L) Macro[a] | Concentration Factor Macro | Micro |
|---|---|---|---|
| Acetone | 31 | 25-500 | - |
| Acetonitrile | 57 | 25-500 | 200 |
| Acrolein | - | - | 100 |
| Acrylonitrile | 16 | 25-500 | 100 |
| Allyl Alcohol | 7 | 25-500 | - |
| 1-Butanol | - | - | 250 |
| Crotonaldehyde | 12 | 25-500 | - |
| 1,4-Dioxane | 12 | 25-500 | 150 |
| Ethyl Acetate | - | - | 100 |
| Isobutyl alcohol | 7 | 25-500 | - |
| Methanol | 38 | 25-500 | 140 |
| Methyl Ethyl Ketone | 16 | 25-500 | - |
| 2-Methyl-1-propanol | - | - | 250 |
| n-Nitroso-di-n-butylamine | 14 | 25-500 | - |
| Paraldehyde | 10 | 25-500 | - |
| 2-Picoline | 7 | 25-500 | - |
| 1-Propanol | - | - | 240 |
| Propionitrile | 11 | 25-500 | 200 |
| Pyridine | 4 | 25-500 | - |
| o-Toluidine | 13 | 25-500 | - |

[a] Produced by analysis of seven aliquots of reagent water spiked at 25 ppb at the listed compounds; calculations based on internal standard technique and use of the following equation:

MDL = 3.134 x Std. Dev. of low concentration spike (ppb).

[b] When a 40-mL sample is used, and the first 100 µL of distillate are collected.

TABLE 13

TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS (METHOD 5031)

| Target Compound | Surrogate | Internal Standard |
|---|---|---|
| Acetone | $d_6$-Acetone | $d_8$-Isopropyl alcohol |
| Acetonitrile | $d_3$-Acetonitrile | $d_8$-Isopropyl alcohol |
| Acrylonitrile | $d_8$-Isopropyl alcohol | |
| Allyl alcohol | $d_7$-Dimethyl formamide | |
| Crotonaldehyde | $d_8$-Isopropyl alcohol | |
| 1,4-Dioxane | $d_8$-1,4-Dioxane | $d_7$-Dimethyl formamide |
| Isobutyl alcohol | $d_7$-Dimethyl formamide | |
| Methanol | $d_3$-Methanol | $d_8$-Isopropyl alcohol |
| Methyl ethyl ketone | $d_8$-Isopropyl alcohol | |
| N-Nitroso-di-n-butylamine | $d_7$-Dimethyl formamide | |
| Paraldehyde | $d_7$-Dimethyl formamide | |
| 2-Picoline | $d_7$-Dimethyl formamide | |
| Propionitrile | $d_8$-Isopropyl alcohol | |
| Pyridine | $d_5$-Pyridine | $d_7$-Dimethyl formamide |
| o-Toluidine | $d_7$-Dimethyl formamide | |

TABLE 14

RECOMMENDED CONCENTRATIONS FOR CALIBRATION SOLUTIONS (METHOD 5031)

| Compound | Concentration(s) (ng/µL) |
|---|---|
| Internal Standards | |
| $d_5$-benzyl alcohol | 10.0 |
| $d_{14}$-Diglyme | 10.0 |
| $d_7$-Dimethyl formamide | 10.0 |
| $d_8$-Isopropyl alcohol | 10.0 |
| Surrogates | |
| $d_6$-Acetone | 10.0 |
| $d_3$-Acetonitrile | 10.0 |
| $d_8$-1,4-Dioxane | 10.0 |
| $d_3$-Methanol | 10.0 |
| $d_5$-Pyridine | 10.0 |
| Target Compounds | |
| Acetone | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Acetonitrile | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Acrylonitrile | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Allyl alcohol | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Crotonaldehyde | 1.0, 5.0, 10.0, 25.0, 100.0 |
| 1,4-Dioxane | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Isobutyl alcohol | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Methanol | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Methyl ethyl ketone | 1.0, 5.0, 10.0, 25.0, 100.0 |
| N-Nitroso-di-n-butylamine | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Paraldehyde | 1.0, 5.0, 10.0, 25.0, 100.0 |
| 2-Picoline | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Propionitrile | 1.0, 5.0, 10.0, 25.0, 100.0 |
| Pyridine | 1.0, 5.0, 10.0, 25.0, 100.0 |
| o-Toluidine | 1.0, 5.0, 10.0, 25.0, 100.0 |

TABLE 15

CHARACTERISTIC IONS AND RETENTION TIMES FOR VOCs (METHOD 5031)

| Compound | Quantitation Ion[a] | Secondary Ions | Retention Time (min)[b] |
|---|---|---|---|
| Internal Standards | | | |
| $d_8$-Isopropyl alcohol | 49 | | 1.75 |
| $d_{14}$-Diglyme | 66 | 98,64 | 9.07 |
| $d_7$-Dimethyl formamide | 50 | 80 | 9.20 |
| Surrogates | | | |
| $d_6$-Acetone | 46 | 64,42 | 1.03 |
| $d_3$-Methanol | 33 | 35,30 | 1.75 |
| $d_3$-Acetonitrile | 44 | 42 | 2.63 |
| $d_8$-1,4-Dioxane | 96 | 64,34 | 3.97 |
| $d_5$-Pyridine | 84 | 56,79 | 6.73 |
| $d_5$-Phenol[c] | 99 | 71 | 15.43 |
| Target Compounds | | | |
| Acetone | 43 | 58 | 1.05 |
| Methanol | 31 | 29 | 1.52 |
| Methyl ethyl ketone | 43 | 72,57 | 1.53 |
| Methacrylonitrile[c] | 67 | 41 | 2.38 |
| Acrylonitrile | 53 | 52,51 | 2.53 |
| Acetonitrile | 41 | 40,39 | 2.73 |
| Methyl isobutyl ketone[c] | 85 | 100,58 | 2.78 |
| Propionitrile | 54 | 52,55 | 3.13 |
| Crotonaldehyde | 41 | 70 | 3.43 |
| 1,4-Dioxane | 58 | 88,57 | 4.00 |
| Paraldehyde | 45 | 89 | 4.75 |
| Isobutyl alcohol | 43 | 33,42 | 5.05 |
| Allyl alcohol | 57 | 39 | 5.63 |
| Pyridine | 79 | 50,52 | 6.70 |
| 2-Picoline | 93 | 66 | 7.27 |
| N-Nitroso-di-n-butylamine | 84 | 116 | 12.82 |
| Aniline[c] | 93 | 66,92 | 13.23 |
| o-Toluidine | 106 | 107 | 13.68 |
| Phenol[c] | 94 | 66,65 | 15.43 |

[a] These ions were used for quantitation in selected ion monitoring.
[b] GC column: DB-Wax, 30 meter x 0.53 mm, 1 µm film thickness.
Oven program: 45°C for 4 min, increased to 220°C at 12°C/min.
[c] Compound removed from target analyte list due to poor accuracy and precision.

TABLE 16

METHOD ACCURACY AND PRECISION BY MEAN PERCENT RECOVERY AND PERCENT RELATIVE STANDARD DEVIATION[a] (METHOD 5031 - MACRODISTILLATION TECHNIQUE)
(Single Laboratory and Single Operator)

| Compound | 25 ppb Spike | | 100 ppb Spike | | 500 ppb Spike | |
|---|---|---|---|---|---|---|
| | Mean %R | %RSD | Mean %R | %RSD | Mean %R | %RSD |
| $d_6$-Acetone | 66 | 24 | 69 | 14 | 65 | 16 |
| $d_3$-Acetonitrile | 89 | 18 | 80 | 18 | 70 | 10 |
| $d_8$-1,4-Dioxane | 56 | 34 | 58 | 11 | 61 | 18 |
| $d_3$-Methanol | 43 | 29 | 48 | 19 | 56 | 14 |
| $d_5$-Pyridine | 83 | 6.3 | 84 | 7.8 | 85 | 9.0 |
| Acetone | 67 | 45 | 63 | 14 | 60 | 14 |
| Acetonitrile | 44 | 35 | 52 | 15 | 56 | 15 |
| Acrylonitrile | 49 | 42 | 47 | 27 | 45 | 27 |
| Allyl alcohol | 69 | 13 | 70 | 9.7 | 73 | 10 |
| Crotonaldehyde | 68 | 22 | 68 | 13 | 69 | 13 |
| 1,4-Dioxane | 63 | 25 | 55 | 16 | 54 | 13 |
| Isobutyl alcohol | 66 | 14 | 66 | 5.7 | 65 | 7.9 |
| Methanol | 50 | 36 | 46 | 22 | 49 | 18 |
| Methyl ethyl ketone | 55 | 37 | 56 | 20 | 52 | 19 |
| N-Nitroso-di-n-butylamine | 57 | 21 | 61 | 15 | 72 | 18 |
| Paraldehyde | 65 | 20 | 66 | 11 | 60 | 8.9 |
| Picoline | 81 | 12 | 81 | 6.8 | 84 | 8.0 |
| Propionitrile | 67 | 22 | 69 | 13 | 68 | 13 |
| Pyridine | 74 | 7.4 | 72 | 6.7 | 74 | 7.3 |
| o-Toluidine | 52 | 31 | 54 | 15 | 58 | 12 |

[a] Data from analysis of seven aliquots of reagent water spiked at each concentration, using a quadrapole mass spectrometer in the selected ion monitoring mode.

TABLE 17

RECOVERIES IN SAND SAMPLES FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

| Compound | Recovery per Replicate (ng) 1 | 2 | 3 | 4 | 5 | Mean | RSD | Mean Rec |
|---|---|---|---|---|---|---|---|---|
| Vinyl chloride | 8.0 | 7.5 | 6.7 | 5.4 | 6.6 | 6.8 | 13.0 | 34.2 |
| Trichlorofluoromethane | 13.3 | 16.5 | 14.9 | 13.0 | 10.3 | 13.6 | 15.2 | 68.0 |
| 1,1-Dichloroethene | 17.1 | 16.7 | 15.1 | 14.8 | 15.6 | 15.9 | 5.7 | 79.2 |
| Methylene chloride | 24.5 | 22.7 | 19.7 | 19.4 | 20.6 | 21.4 | 9.1 | 107 |
| trans-1,2-Dichloroethene | 22.7 | 23.6 | 19.4 | 18.3 | 20.1 | 20.8 | 0.7 | 104 |
| 1,2-Dichloroethane | 18.3 | 18.0 | 16.7 | 15.6 | 15.9 | 16.9 | 6.4 | 84.4 |
| cis-1,2-Dichloroethene | 26.1 | 23.1 | 22.6 | 20.3 | 20.8 | 22.6 | 9.0 | 113 |
| Bromochloromethane | 24.5 | 25.4 | 20.9 | 20.1 | 20.1 | 22.2 | 10.2 | 111 |
| Chloroform | 26.5 | 26.0 | 22.1 | 18.9 | 22.1 | 23.1 | 12.2 | 116 |
| 1,1,1-Trichloroethane | 21.5 | 23.0 | 23.9 | 16.7 | 31.2 | 23.4 | 21.2 | 117 |
| Carbon tetrachloride | 23.6 | 24.2 | 22.6 | 18.3 | 23.3 | 22.4 | 9.4 | 112 |
| Benzene | 22.4 | 23.9 | 20.4 | 17.4 | 19.2 | 20.7 | 11.2 | 103 |
| Trichloroethene | 21.5 | 20.5 | 19.2 | 14.4 | 19.1 | 18.9 | 12.7 | 94.6 |
| 1,2-Dichloropropane | 24.9 | 26.3 | 23.1 | 19.0 | 23.3 | 23.3 | 10.5 | 117 |
| Dibromomethane | 25.4 | 26.4 | 21.6 | 20.4 | 23.6 | 23.5 | 9.6 | 117 |
| Bromodichloromethane | 25.7 | 26.7 | 24.1 | 17.9 | 23.0 | 23.5 | 13.1 | 117 |
| Toluene | 28.3 | 25.0 | 24.8 | 16.3 | 23.6 | 23.6 | 16.9 | 118 |
| 1,1,2-Trichloroethane | 25.4 | 24.5 | 21.6 | 17.7 | 22.1 | 22.2 | 12.1 | 111 |
| 1,3-Dichloropropane | 25.4 | 24.2 | 22.7 | 17.0 | 22.2 | 22.3 | 12.8 | 112 |
| Dibromochloromethane | 26.3 | 26.2 | 23.7 | 18.2 | 23.2 | 23.5 | 12.5 | 118 |
| Chlorobenzene | 22.9 | 22.5 | 19.8 | 14.6 | 19.4 | 19.9 | 15.0 | 99.3 |
| 1,1,1,2-Tetrachloroethane | 22.4 | 27.7 | 25.1 | 19.4 | 22.6 | 23.4 | 12.0 | 117 |
| Ethylbenzene | 25.6 | 25.0 | 22.1 | 14.9 | 24.0 | 22.3 | 17.5 | 112 |
| p-Xylene | 22.5 | 22.0 | 19.8 | 13.9 | 20.3 | 19.7 | 15.7 | 98.5 |
| o-Xylene | 24.2 | 23.1 | 21.6 | 14.0 | 20.4 | 20.7 | 17.3 | 103 |
| Styrene | 23.9 | 21.5 | 20.9 | 14.3 | 20.5 | 20.2 | 15.7 | 101 |
| Bromoform | 26.8 | 25.6 | 26.0 | 20.1 | 23.5 | 24.4 | 9.9 | 122 |
| iso-Propylbenzene | 25.3 | 25.1 | 24.2 | 15.4 | 24.6 | 22.9 | 16.6 | 114 |
| Bromobenzene | 19.9 | 21.8 | 20.0 | 15.5 | 19.1 | 19.3 | 10.7 | 96.3 |
| 1,2,3-Trichloropropane | 25.9 | 23.0 | 25.6 | 15.9 | 21.4 | 22.2 | 15.8 | 111 |
| n-Propylbenzene | 26.0 | 23.8 | 22.6 | 13.9 | 21.9 | 21.6 | 19.0 | 106 |
| 2-Chlorotoluene | 23.6 | 23.8 | 21.3 | 13.0 | 21.5 | 20.6 | 19.2 | 103 |
| 4-Chlorotoluene | 21.0 | 19.7 | 18.4 | 12.1 | 18.3 | 17.9 | 17.1 | 89.5 |
| 1,3,5-Trimethylbenzene | 24.0 | 22.1 | 22.5 | 13.8 | 22.9 | 21.1 | 17.6 | 105 |
| sec-Butylbenzene | 25.9 | 25.3 | 27.8 | 16.1 | 28.6 | 24.7 | 18.1 | 124 |
| 1,2,4-Trimethylbenzene | 30.6 | 39.2 | 22.4 | 18.0 | 22.7 | 26.6 | 28.2 | 133 |
| 1,3-Dichlorobenzene | 20.3 | 20.6 | 18.2 | 13.0 | 17.6 | 17.9 | 15.2 | 89.7 |
| p-iso-Propyltoluene | 21.6 | 22.1 | 21.6 | 16.0 | 22.8 | 20.8 | 11.8 | 104 |
| 1,4-Dichlorobenzene | 18.1 | 21.2 | 20.0 | 13.2 | 17.4 | 18.0 | 15.3 | 90.0 |
| 1,2-Dichlorobenzene | 18.4 | 22.5 | 22.5 | 15.2 | 19.9 | 19.7 | 13.9 | 96.6 |
| n-Butylbenzene | 13.1 | 20.3 | 19.5 | 10.8 | 18.7 | 16.5 | 23.1 | 82.4 |
| 1,2,4-Trichlorobenzene | 14.5 | 14.9 | 15.7 | 8.8 | 12.3 | 13.3 | 18.8 | 66.2 |
| Hexachlorobutadiene | 17.6 | 22.5 | 21.6 | 13.2 | 21.6 | 19.3 | 18.2 | 96.3 |
| 1,2,3-Trichlorobenzene | 14.9 | 15.9 | 16.5 | 11.9 | 13.9 | 14.6 | 11.3 | 73.1 |

Data in Tables 17, 18, and 19 are from Reference 15.

TABLE 18
RECOVERIES IN C-HORIZON SOILS FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

| Compound | Recovery per Replicate (ng) 1 | 2 | 3 | 4 | 5 | Mean | RSD | Mean Rec |
|---|---|---|---|---|---|---|---|---|
| Vinyl chloride | 33.4 | 31.0 | 30.9 | 29.7 | 28.6 | 30.8 | 5.2 | 154 |
| Trichlorofluoromethane | 37.7 | 20.8 | 20.0 | 21.8 | 20.5 | 24.1 | 28.2 | 121 |
| 1,1-Dichloroethene | 21.7 | 33.5 | 39.8 | 30.2 | 32.5 | 31.6 | 18.5 | 158 |
| Methylene chloride | 20.9 | 19.4 | 18.7 | 18.3 | 18.4 | 19.1 | 5.1 | 95.7 |
| trans-1,2-Dichloroethene | 21.8 | 18.9 | 20.4 | 17.9 | 17.8 | 19.4 | 7.9 | 96.8 |
| 1,1-Dichloroethane | 23.8 | 21.9 | 21.3 | 21.3 | 20.5 | 21.8 | 5.2 | 109 |
| cis-1,2-Dichloroethene | 21.6 | 18.8 | 18.5 | 18.2 | 18.2 | 19.0 | 6.7 | 95.2 |
| Bromochloromethane | 22.3 | 19.5 | 19.3 | 19.0 | 19.2 | 20.0 | 6.0 | 100 |
| Chloroform | 20.5 | 17.1 | 17.3 | 16.5 | 15.9 | 17.5 | 9.2 | 87.3 |
| 1,1,1-Trichloroethane | 16.4 | 11.9 | 10.7 | 9.5 | 9.4 | 11.6 | 22.4 | 57.8 |
| Carbon tetrachloride | 13.1 | 11.3 | 13.0 | 11.8 | 11.2 | 12.1 | 6.7 | 60.5 |
| Benzene | 21.1 | 19.3 | 18.7 | 18.2 | 16.9 | 18.8 | 7.4 | 94.1 |
| Trichloroethene | 19.6 | 16.4 | 16.5 | 16.5 | 15.5 | 16.9 | 8.3 | 84.5 |
| 1,2-Dichloropropane | 21.8 | 19.0 | 18.3 | 18.8 | 16.5 | 18.9 | 9.0 | 94.4 |
| Dibromomethane | 20.9 | 17.9 | 17.9 | 17.2 | 18.3 | 18.4 | 6.9 | 92.1 |
| Bromodichloromethane | 20.9 | 18.0 | 18.9 | 18.2 | 17.3 | 18.6 | 6.6 | 93.2 |
| Toluene | 22.2 | 17.3 | 18.8 | 17.0 | 15.9 | 18.2 | 12.0 | 91.2 |
| 1,1,2-Trichloroethane | 21.0 | 16.5 | 17.2 | 17.2 | 16.5 | 17.7 | 9.6 | 88.4 |
| 1,3-Dichloropropane | 21.4 | 17.3 | 18.7 | 18.6 | 16.7 | 18.5 | 8.8 | 92.6 |
| Dibromochloromethane | 20.9 | 18.1 | 19.0 | 18.8 | 16.6 | 18.7 | 7.5 | 93.3 |
| Chlorobenzene | 20.8 | 18.4 | 17.6 | 16.8 | 14.8 | 17.7 | 11.2 | 88.4 |
| 1,1,1,2-Tetrachloroethane | 19.5 | 19.0 | 17.8 | 17.2 | 16.5 | 18.0 | 6.2 | 90.0 |
| Ethylbenzene | 21.1 | 18.3 | 18.5 | 16.9 | 15.3 | 18.0 | 10.6 | 90.0 |
| p-Xylene | 20.0 | 17.4 | 18.2 | 16.3 | 14.4 | 17.3 | 10.9 | 86.3 |
| o-Xylene | 20.7 | 17.2 | 16.8 | 16.2 | 14.8 | 17.1 | 11.4 | 85.7 |
| Styrene | 18.3 | 15.9 | 16.2 | 15.3 | 13.7 | 15.9 | 9.3 | 79.3 |
| Bromoform | 20.1 | 15.9 | 17.1 | 17.5 | 16.1 | 17.3 | 8.6 | 86.7 |
| iso-Propylbenzene | 21.0 | 18.1 | 19.2 | 18.4 | 15.6 | 18.4 | 9.6 | 92.2 |
| Bromobenzene | 20.4 | 16.2 | 17.2 | 16.7 | 15.4 | 17.2 | 10.1 | 85.9 |
| 1,1,2,2-Tetrachloroethane | 23.3 | 17.9 | 21.2 | 18.8 | 16.8 | 19.6 | 12.1 | 96.0 |
| 1,2,3-Trichloropropane | 18.4 | 14.6 | 15.6 | 16.1 | 15.6 | 16.1 | 8.0 | 80.3 |
| n-Propylbenzene | 20.4 | 18.9 | 17.9 | 17.0 | 14.3 | 17.7 | 11.6 | 88.4 |
| 2-Chlorotoluene | 19.1 | 17.3 | 16.1 | 16.0 | 14.4 | 16.7 | 9.2 | 83.6 |
| 4-Chlorotoluene | 19.0 | 15.5 | 16.8 | 15.9 | 13.6 | 16.4 | 10.6 | 81.8 |
| 1,3,5-Trimethylbenzene | 20.8 | 18.0 | 17.4 | 16.1 | 14.7 | 17.4 | 11.7 | 86.9 |
| sec-Butylbenzene | 21.4 | 18.3 | 18.9 | 17.0 | 14.9 | 18.1 | 11.8 | 90.5 |
| 1,2,4-Trimethylbenzene | 20.5 | 18.6 | 16.8 | 15.3 | 13.7 | 17.0 | 14.1 | 85.0 |
| 1,3-Dichlorobenzene | 17.6 | 15.9 | 15.6 | 14.2 | 14.4 | 15.6 | 7.9 | 77.8 |
| p-iso-Propyltoluene | 20.5 | 17.0 | 17.1 | 15.6 | 13.4 | 16.7 | 13.9 | 83.6 |
| 1,4-Dichlorobenzene | 18.5 | 13.8 | 14.8 | 16.7 | 14.9 | 15.7 | 10.5 | 78.7 |
| 1,2-Dichlorobenzene | 18.4 | 15.0 | 15.4 | 15.3 | 13.5 | 15.5 | 10.5 | 77.6 |
| n-Butylbenzene | 19.6 | 15.9 | 15.9 | 14.4 | 18.9 | 16.9 | 11.7 | 84.6 |
| 1,2,4-Trichlorobenzene | 15.2 | 17.2 | 17.4 | 13.6 | 12.1 | 15.1 | 13.5 | 75.4 |
| Hexachlorobutadiene | 18.7 | 16.2 | 15.5 | 13.8 | 16.6 | 16.1 | 10.0 | 80.7 |
| Naphthalene | 13.9 | 11.1 | 10.2 | 10.8 | 11.4 | 11.5 | 11.0 | 57.4 |
| 1,2,3-Trichlorobenzene | 14.9 | 15.2 | 16.8 | 13.7 | 12.7 | 14.7 | 9.5 | 73.2 |

TABLE 19
RECOVERIES IN GARDEN SOIL FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

| Compound | Recovery per Replicate (ng) 1 | 2 | 3 | 4 | 5 | Mean | RSD | Mean Rec |
|---|---|---|---|---|---|---|---|---|
| Vinyl chloride | 12.7 | 10.9 | 9.8 | 8.1 | 7.2 | 9.7 | 20.2 | 48.7 |
| Trichlorofluoromethane | 33.7 | 6.4 | 30.3 | 27.8 | 22.9 | 24.2 | 39.6 | 121 |
| 1,1-Dichloroethene | 27.7 | 20.5 | 24.1 | 15.1 | 13.2 | 20.1 | 26.9 | 101 |
| Methylene chloride | 25.4 | 23.9 | 24.7 | 22.2 | 24.2 | 24.1 | 4.4 | 120 |
| trans-1,2-Dichloroethene | 2.8 | 3.0 | 3.3 | 2.2 | 2.4 | 2.7 | 15.0 | 13.6 |
| 1,1-Dichloroethane | 24.1 | 26.3 | 27.0 | 20.5 | 21.2 | 23.8 | 11.0 | 119 |
| cis-1,2-Dichloroethene | 8.3 | 10.2 | 8.7 | 5.8 | 6.4 | 7.9 | 20.1 | 39.4 |
| Bromochloromethane | 11.1 | 11.8 | 10.2 | 8.8 | 9.0 | 10.2 | 11.2 | 50.9 |
| Chloroform | 16.7 | 16.9 | 17.0 | 13.8 | 15.0 | 15.9 | 7.9 | 79.3 |
| 1,1,1-Trichloroethane | 24.6 | 22.8 | 22.1 | 16.2 | 20.9 | 21.3 | 13.4 | 107 |
| Carbon tetrachloride | 19.4 | 20.3 | 22.2 | 20.0 | 20.2 | 20.4 | 4.6 | 102 |
| Benzene | 21.4 | 22.0 | 22.4 | 19.6 | 20.4 | 21.2 | 4.9 | 106 |
| Trichloroethene | 12.4 | 16.5 | 14.9 | 9.0 | 9.9 | 12.5 | 22.9 | 62.7 |
| 1,2-Dichloropropane | 19.0 | 18.8 | 19.7 | 16.0 | 17.6 | 18.2 | 7.1 | 91.0 |
| Dibromomethane | 7.3 | 8.0 | 6.9 | 5.6 | 6.8 | 6.9 | 11.3 | 34.6 |
| Bromodichloromethane | 14.9 | 15.9 | 15.9 | 12.8 | 13.9 | 14.7 | 8.3 | 73.3 |
| Toluene | 42.6 | 39.3 | 45.1 | 39.9 | 45.3 | 42.4 | 5.9 | 212 |
| 1,1,2-Trichloroethane | 13.9 | 15.2 | 1.4 | 21.3 | 14.9 | 15.9 | 17.0 | 79.6 |
| 1,3-Dichloropropane | 13.3 | 16.7 | 11.3 | 10.9 | 9.5 | 12.3 | 20.3 | 61.7 |
| Dibromochloromethane | 14.5 | 13.1 | 14.5 | 11.9 | 14.4 | 13.7 | 7.6 | 68.3 |
| Chlorobenzene | 8.4 | 10.0 | 8.3 | 6.9 | 7.8 | 8.3 | 12.1 | 41.3 |
| 1,1,1,2-Tetrachloroethane | 16.7 | 16.7 | 15.6 | 15.8 | 15.7 | 16.1 | 3.2 | 80.4 |
| Ethylbenzene | 22.1 | 21.4 | 23.1 | 20.1 | 22.6 | 21.9 | 4.8 | 109 |
| p-Xylene | 41.4 | 38.4 | 43.8 | 38.3 | 44.0 | 41.2 | 6.1 | 206 |
| o-Xylene | 31.7 | 30.8 | 34.3 | 30.4 | 33.2 | 32.1 | 4.6 | 160 |
| Styrene | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Bromoform | 8.6 | 8.9 | 9.1 | 7.0 | 7.7 | 8.3 | 9.4 | 41.4 |
| iso-Propylbenzene | 18.1 | 18.8 | 9.7 | 18.3 | 19.6 | 18.9 | 3.5 | 94.4 |
| Bromobenzene | 5.1 | 5.4 | 5.3 | 4.4 | 4.0 | 4.8 | 11.6 | 24.1 |
| 1,1,2,2-Tetrachloroethane | 14.0 | 13.5 | 14.7 | 15.3 | 17.1 | 14.9 | 8.5 | 74.5 |
| 1,2,3-Trichloropropane | 11.0 | 12.7 | 11.7 | 11.7 | 11.9 | 11.8 | 4.5 | 59.0 |
| n-Propylbenzene | 13.4 | 13.3 | 14.7 | 12.8 | 13.9 | 13.6 | 4.7 | 68.1 |
| 2-Chlorotoluene | 8.3 | 9.0 | 11.7 | 8.7 | 7.9 | 9.1 | 14.8 | 45.6 |
| 4-Chlorotoluene | 5.1 | 5.4 | 5.5 | 4.8 | 4.5 | 5.0 | 7.9 | 25.2 |
| 1,3,5-Trimethylbenzene | 31.3 | 27.5 | 33.0 | 31.1 | 33.6 | 31.3 | 6.8 | 157 |
| sec-Butylbenzene | 13.5 | 13.4 | 16.4 | 13.8 | 15.4 | 14.5 | 8.3 | 72.5 |
| 1,2,4-Trimethylbenzene | 38.7 | 32.4 | 40.8 | 34.1 | 40.3 | 37.3 | 9.1 | 186 |
| 1,3-Dichlorobenzene | 3.6 | 3.6 | 3.7 | 3.0 | 3.2 | 3.4 | 8.0 | 17.2 |
| p-iso-Propyltoluene | 14.7 | 14.1 | 16.1 | 13.9 | 15.1 | 14.8 | 5.2 | 73.8 |
| 1,4-Dichlorobenzene | 3.0 | 3.5 | 3.3 | 2.6 | 2.8 | 3.0 | 10.2 | 15.0 |
| 1,2-Dichlorobenzene | 3.6 | 4.3 | 4.0 | 3.5 | 3.6 | 3.8 | 8.3 | 19.0 |
| n-Butylbenzene | 17.4 | 13.8 | 14.0 | 18.9 | 24.0 | 17.6 | 21.2 | 88.0 |
| 1,2,4-Trichlorobenzene | 2.8 | 2.9 | 3.3 | 2.6 | 3.2 | 3.0 | 8.5 | 15.0 |
| Hexachlorobutadiene | 4.8 | 4.0 | 6.1 | 5.6 | 6.0 | 5.3 | 15.1 | 26.4 |
| Naphthalene | 5.5 | 5.1 | 5.5 | 4.7 | 5.6 | 5.3 | 6.2 | 26.5 |
| 1,2,3-Trichlorobenzene | 2.2 | 2.3 | 2.4 | 2.2 | 2.3 | 2.3 | 3.5 | 11.4 |

Data in Table 19 are from Reference 15.

TABLE 20

VOLATILE ORGANIC ANALYTE RECOVERY FROM SOIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

| Compound | Soil/$H_2O$[b] Recovery Mean | RSD | Soil/Oil[c] Recovery Mean | RSD | Soil/Oil/$H_2O$ Recovery Mean | RSD |
|---|---|---|---|---|---|---|
| Chloromethane | 61 | 20 | 40 | 18 | 108 | 68 |
| Bromomethane | 58 | 20 | 47 | 13 | 74 | 13 |
| Vinyl chloride | 54 | 12 | 46 | 11 | 72 | 20 |
| Chloroethane | 46 | 10 | 41 | 8 | 52 | 14 |
| Methylene chloride | 60 | 2 | 65 | 8 | 76 | 11 |
| Acetone | INT[e] | INT | 44 | 8 | | |
| Carbon disulfide | 47 | 13 | 53 | 10 | 47 | 4 |
| 1,1-Dichloroethene | 48 | 9 | 47 | 5 | 58 | 3 |
| 1,1-Dichloroethane | 61 | 6 | 58 | 9 | 61 | 6 |
| trans-1,2-Trichloroethane | 54 | 7 | 60 | 7 | 56 | 5 |
| cis-1,2-Dichloroethene | 60 | 4 | 72 | 6 | 63 | 8 |
| Chloroform | 104 | 11 | 93 | 6 | 114 | 15 |
| 1,2-Dichloroethane | 177 | 50 | 117 | 8 | 151 | 22 |
| 2-Butanone | INT | 36 | 38 | INT | | |
| 1,1,1-Trichloroethane | 124 | 13 | 72 | 16 | 134 | 26 |
| Carbon tetrachloride | 172 | 122 | INT | INT | | |
| Vinyl acetate | 88 | 11 | INT | | | |
| Bromodichloromethane | 93 | 4 | 91 | 23 | 104 | 23 |
| 1,1,2,2-Tetrachloroethane | 96 | 13 | 50 | 12 | 104 | 7 |
| 1,2-Dichloropropane | 105 | 8 | 102 | 6 | 111 | 6 |
| trans-1,3-Dichloropropene | 134 | 10 | 84 | 16 | 107 | 8 |
| Trichloroethene | 98 | 9 | 99 | 10 | 100 | 5 |
| Dibromochloromethane | 119 | 8 | 125 | 31 | 142 | 16 |
| 1,1,2-Trichloroethane | 126 | 10 | 72 | 16 | 97 | 4 |
| Benzene | 99 | 7 | CONT[f] | CONT | | |
| cis-1,3-Dichloropropene | 123 | 12 | 94 | 13 | 112 | 9 |
| Bromoform | 131 | 13 | 58 | 18 | 102 | 9 |
| 2-Hexanone | 155 | 18 | 164 | 19 | 173 | 29 |
| 4-Methyl-2-pentanone | 152 | 20 | 185 | 20 | 169 | 18 |
| Tetrachloroethene | 90 | 9 | 123 | 14 | 128 | 7 |
| Toluene | 94 | 3 | CONT | CONT | | |
| Chlorobenzene | 98 | 7 | 93 | 18 | 112 | 5 |
| Ethylbenzene | 114 | 13 | CONT | CONT | | |
| Styrene | 106 | 8 | 93 | 18 | 112 | 5 |
| p-Xylene | 97 | 9 | CONT | CONT | | |
| o-Xylene | 105 | 8 | 112 | 12 | 144 | 13 |

TABLE 20 (cont.)

| Compound | Soil/$H_2O$[b] Recovery Mean | RSD | Soil/Oil[c] Recovery Mean | RSD | Soil/Oil/$H_2O$ Recovery Mean | RSD |
|---|---|---|---|---|---|---|
| Surrogates | | | | | | |
| 1,2-Dichloroethane | 177 | 50 | 117 | 8 | 151 | 22 |
| Toluene-$d_8$ | 96 | 6 | 79 | 12 | 82 | 6 |
| Bromofluorobenzene | 139 | 13 | 37 | 13 | 62 | 5 |

[a] Results are for 10 min. distillations times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision value reflects the propagated errors. Each analyte was spiked at 50 ppb. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may introduce bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Soil samples spiked with 0.2 mL water containing analytes and then 5 mL water added to make slurry.

[c] Soil sample + 1 g cod liver oil, spiked with 0.2 mL water containing analytes.

[d] Soil samples + 1 g cod liver oil, spiked as above with 5 mL of water added to make slurry.

[e] Interference by co-eluting compounds prevented accurate measurement of analyte.

[f] Contamination of sample matrix by analyte prevented assessment of efficiency.

TABLE 21

VACUUM DISTILLATION EFFICIENCIES FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

| Compound | Efficiency Mean (%) | RSD (%) |
|---|---|---|
| Chloromethane | N/A[b] | |
| Bromomethane | N/A[b] | |
| Vinyl chloride | N/A[b] | |
| Chloroethane | N/A[b] | |
| Methylene chloride | CONT[c] | |
| Acetone | CONT[c] | |
| Carbon disulfide | 79 | 36 |
| 1,1-Dichloroethene | 122 | 39 |
| 1,1-Dichloroethane | 126 | 35 |
| trans-1,2-Trichloroethene | 109 | 46 |
| cis-1,2-Dichloroethene | 106 | 22 |
| Chloroform | 111 | 32 |
| 1,2-Dichloroethane | 117 | 27 |
| 2-Butanone | INT[d] | |
| 1,1,1-Trichloroethane | 106 | 30 |
| Carbon tetrachloride | 83 | 34 |
| Vinyl acetate | INT[d] | |
| Bromodichloromethane | 97 | 22 |
| 1,1,2,2-Tetrachloroethane | 67 | 20 |
| 1,2-Dichloropropane | 117 | 23 |
| trans-1,3-Dichloropropene | 92 | 22 |
| Trichloroethene | 98 | 31 |
| Dibromochloromethane | 71 | 19 |
| 1,1,2-Trichloroethane | 92 | 20 |
| Benzene | 129 | 35 |
| cis-1,3-Dichloropropene | 102 | 24 |
| Bromoform | 58 | 19 |
| 2-Hexanone | INT[d] | |
| 4-Methyl-2-pentanone | 113 | 37 |
| Tetrachloroethene | 66 | 20 |
| Toluene | CONT[c] | |
| Chlorobenzene | 65 | 19 |
| Ethylbenzene | 74 | 19 |
| Styrene | 57 | 14 |
| p-Xylene | 46 | 13 |
| o-Xylene | 83 | 20 |

TABLE 21 (cont.)

| Compound | Efficiency Mean (%) | RSD (%) |
|---|---|---|
| Surrogates | | |
| 1,2-Dichloroethane | 115 | 27 |
| Toluene-$d_8$ | 88 | 24 |
| Bromofluorobenzene | 52 | 15 |

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicate 10-g aliquots of fish spiked at 25 ppb were analyzed using GC/MS external standard quantitation. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards were replicated and results reflect 1 sigma propagated standard deviation.

[b] No analyses.

[c] Contamination of sample matrix by analyte prevented accurate assessment of analyte efficiency.

[d] Interfering by co-eluting compounds prevented accurate measurement of analyte.

TABLE 22

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

| Compound | Method Detection Limit (ppb) External Standard Method | Internal Standard Method |
|---|---|---|
| Chloromethane | 7.8 | 7.3 |
| Bromomethane | 9.7 | 9.8 |
| Vinyl chloride | 9.5 | 9.4 |
| Chloroethane | 9.2 | 10.0 |
| Methylene chloride | CONT[b] | CONT[b] |
| Acetone | CONT[b] | CONT[b] |
| Carbon disulfide | 5.4 | 4.9 |
| 1,1-Dichloroethene | 4.0 | 5.7 |
| 1,1-Dichloroethane | 4.0 | 3.5 |
| trans-1,2-Dichloroethene | 4.4 | 4.0 |
| cis-1,2-Dichloroethene | 4.7 | 4.1 |
| Chloroform | 5.6 | 5.0 |
| 1,2-Dichloroethane | 3.3 | 3.2 |
| 2-Butanone | INT[c] | INT[c] |
| 1,1,1-Trichloroethane | 1.1 | 4.2 |
| Carbon tetrachloride | 3.2 | 3.5 |
| Vinyl acetate | INT[c] | INT[c] |
| Bromodichloromethane | 3.2 | 2.8 |
| 1,1,2,2-Tetrachloroethane | 4.4 | 3.8 |
| 1,2-Dichloropropane | 3.8 | 3.7 |
| trans-1,3-Dichloropropene | 3.4 | 3.0 |
| Trichloroethene | 3.1 | 4.0 |
| Dibromochloromethane | 3.5 | 3.2 |
| 1,1,2-Trichloroethane | 4.4 | 3.3 |
| Benzene | 3.6 | 3.2 |
| cis-1,3-Dichloropropene | 3.5 | 3.0 |
| Bromoform | 4.9 | 4.0 |
| 2-Hexanone | 7.7 | 8.0 |
| 4-Methyl-2-pentanone | 7.5 | 8.0 |
| Tetrachloroethene | 4.3 | 4.0 |
| Toluene | 3.0 | 2.5 |
| Chlorobenzene | 3.3 | 2.8 |
| Ethylbenzene | 3.6 | 3.5 |
| Styrene | 3.5 | 3.3 |
| p-Xylene | 3.7 | 3.5 |
| o-Xylene | 3.3 | 4.7 |

Footnotes are on the following page.

[a] Values shown are the average MDLs for studies on three non-consecutive days, involving seven replicate analyses of 10 g of fish tissue spiked a 5 ppb. Daily MDLs were calculated as three times the standard deviation. Quantitation was performed by GC/MS Method 8260 and separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] Contamination of sample by analyte prevented determination.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 23

VOLATILE ORGANIC ANALYTES RECOVERY FOR WATER
USING VACUUM DISTILLATION (METHOD 5032)[a]

| Compound | 5 mL $H_2O$[b] Recovery Mean | RSD | 20 mL $H_2O$[c] Recovery Mean | RSD | 20 mL $H_2O$/Oil Recovery Mean | RSD |
|---|---|---|---|---|---|---|
| Chloromethane | 114 | 27 | 116 | 29 | 176 | 67 |
| Bromomethane | 131 | 14 | 121 | 14 | 113 | 21 |
| Vinyl chloride | 131 | 13 | 120 | 16 | 116 | 23 |
| Chloroethane | 110 | 15 | 99 | 8 | 96 | 16 |
| Methylene chloride | 87 | 16 | 105 | 15 | 77 | 6 |
| Acetone | 83 | 22 | 65 | 34 | 119 | 68 |
| Carbon disulfide | 138 | 17 | 133 | 23 | 99 | 47 |
| 1,1-Dichloroethene | 105 | 11 | 89 | 4 | 96 | 18 |
| 1,1-Dichloroethane | 118 | 10 | 119 | 11 | 103 | 25 |
| trans-1,2-Dichloroethene | 105 | 11 | 107 | 14 | 96 | 18 |
| cis-1,2-Dichloroethene | 106 | 7 | 99 | 5 | 104 | 23 |
| Chloroform | 114 | 6 | 104 | 8 | 107 | 21 |
| 1,2-Dichloroethane | 104 | 6 | 109 | 8 | 144 | 19 |
| 2-Butanone | 83 | 50 | 106 | 31 | INT[c] | |
| 1,1,1-Trichloroethane | 118 | 9 | 109 | 9 | 113 | 23 |
| Carbon tetrachloride | 102 | 6 | 108 | 12 | 109 | 27 |
| Vinyl acetate | 90 | 16 | 99 | 7 | 72 | 36 |
| Bromodichloromethane | 104 | 3 | 110 | 5 | 99 | 5 |
| 1,1,2,2-Tetrachloroethane | 85 | 17 | 81 | 7 | 111 | 43 |
| 1,2-Dichloropropane | 100 | 6 | 103 | 2 | 104 | 7 |
| trans-1,3-Dichloropropene | 105 | 8 | 105 | 4 | 92 | 4 |
| Trichloroethene | 98 | 4 | 99 | 2 | 95 | 5 |
| Dibromochloroethane | 99 | 8 | 99 | 6 | 90 | 25 |
| 1,1,2-Trichloroethane | 98 | 7 | 100 | 4 | 76 | 12 |
| Benzene | 97 | 4 | 100 | 5 | 112 | 10 |
| cis-1,3-Dichloropropene | 106 | 5 | 105 | 4 | 98 | 3 |
| Bromoform | 93 | 16 | 94 | 8 | 57 | 21 |
| 2-Hexanone | 60 | 17 | 63 | 16 | 78 | 23 |
| 4-Methyl-2-pentanone | 79 | 24 | 63 | 14 | 68 | 15 |
| Tetrachloroethene | 101 | 3 | 97 | 7 | 77 | 14 |
| Toluene | 100 | 6 | 97 | 8 | 85 | 5 |
| Chlorobenzene | 98 | 6 | 98 | 4 | 88 | 16 |
| Ethylbenzene | 100 | 3 | 92 | 8 | 73 | 13 |
| Styrene | 98 | 4 | 97 | 9 | 88 | 16 |
| p-Xylene | 96 | 4 | 94 | 8 | 60 | 12 |
| o-Xylene | 96 | 7 | 95 | 6 | 72 | 14 |

TABLE 23 (cont.)

| Compound | 5 mL $H_2O$[b] Recovery Mean | RSD | 20 mL $H_2O$[c] Recovery Mean | RSD | 20 mL $H_2O$/Oil Recovery Mean | RSD |
|---|---|---|---|---|---|---|
| Surrogates | | | | | | |
| 1,2-Dichloroethane | 104 | 6 | 109 | 6 | 144 | 19 |
| Toluene-$d_8$ | 104 | 5 | 102 | 2 | 76 | 7 |
| Bromofluorobenzene | 106 | 6 | 106 | 9 | 40 | 8 |

[a] Results are for 10 min. distillation times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision values reflect the propagated errors. Concentrations of analytes were 50 ppb for 5-mL samples and 25 ppb for 20-mL samples. Recovery data generated with comparison to analyses of standards without the water matrix.

[b] Sample contained 1 gram cod liver oil and 20 mL water. An emulsion was created by adding 0.2 mL of water saturated with lecithin.

[c] Interference by co-eluting compounds prevented accurate assessment of recovery.

TABLE 24

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES USING VACUUM DISTILLATION (METHOD 5032) (INTERNAL STANDARD METHOD)[a]

| Compound | Water[b] (µg/L) | Soil[c] (µg/kg) | Tissue[d] (µg/kg) | Oil[e] (mg/kg) |
|---|---|---|---|---|
| Chloromethane | 3.2 | 8.0 | 7.3 | N/A[f] |
| Bromomethane | 2.8 | 4.9 | 9.8 | N/A[f] |
| Vinyl chloride | 3.5 | 6.0 | 9.4 | N/A[f] |
| Chloroethane | 5.9 | 6.0 | 10.0 | N/A[f] |
| Methylene chloride | 3.1 | 4.0 | CONT[g] | 0.05 |
| Acetone | 5.6 | CONT[g] | CONT[g] | 0.06 |
| Carbon disulfide | 2.5 | 2.0 | 4.9 | 0.18 |
| 1,1-Dichloroethene | 2.9 | 3.2 | 5.7 | 0.18 |
| 1,1-Dichloroethane | 2.2 | 2.0 | 3.5 | 0.14 |
| trans-1,2-Dichloroethene | 2.2 | 1.4 | 4.0 | 0.10 |
| cis-1,2-Dichloroethene | 2.0 | 2.3 | 4.1 | 0.07 |
| Chloroform | 2.4 | 1.8 | 5.0 | 0.07 |
| 1,2-Dichloroethane | 1.7 | 1.5 | 3.2 | 0.06 |
| 2-Butanone | 7.4 | INT[h] | INT[h] | INT[h] |
| 1,1,1-Trichloroethane | 1.8 | 1.7 | 4.2 | 0.10 |
| Carbon tetrachloride | 1.4 | 1.5 | 3.5 | 0.13 |
| Vinyl acetate | 11.8 | INT[h] | INT[h] | INT[h] |
| Bromodichloromethane | 1.6 | 1.4 | 2.8 | 0.06 |
| 1,1,2,2-Tetrachloroethane | 2.5 | 2.1 | 3.8 | 0.02 |
| 1,2-Dichloropropane | 2.2 | 2.1 | 3.7 | 0.15 |
| trans-1,3-Dichloropropene | 1.5 | 1.7 | 3.0 | 0.05 |
| Trichloroethene | 1.6 | 1.7 | 4.0 | 0.04 |
| Dibromochloromethane | 1.7 | 1.5 | 3.2 | 0.07 |
| 1,1,2-Trichloroethane | 2.1 | 1.7 | 3.3 | 0.05 |
| Benzene | 0.5 | 1.5 | 3.2 | 0.05 |
| cis-1,3-Dichloropropene | 1.4 | 1.7 | 3.0 | 0.04 |
| Bromoform | 1.8 | 1.5 | 4.0 | 0.05 |
| 2-Hexanone | 4.6 | 3.6 | 8.0 | INT[h] |
| 4-Methyl-2-pentanone | 3.5 | 4.6 | 8.0 | INT[h] |
| Tetrachloroethene | 1.4 | 1.6 | 4.0 | 0.10 |
| Toluene | 1.0 | 3.3 | 2.5 | 0.05 |
| Chlorobenzene | 1.4 | 1.4 | 2.8 | 0.06 |
| Ethylbenzene | 1.5 | 2.8 | 3.5 | 0.04 |
| Styrene | 1.4 | 1.4 | 3.3 | 0.18 |
| p-Xylene | 1.5 | 2.9 | 3.5 | 0.20 |
| o-Xylene | 1.7 | 3.4 | 4.7 | 0.07 |

Footnotes are found on the following page.

[a] Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Method detection limits are the average MDLs for studies on three non-consecutive days.

[b] Method detection limits are the average MDLs for studies of three non-consecutive days. Daily studies were seven replicated analyses of 5 mL aliquots of 4 ppb soil. Daily MDLs were three times the standard deviation.

[c] Daily studies were seven replicated analyses of 10 g fish tissue spiked at 5 ppb. Daily MDLs were three times the standard deviation. Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[d] Method detection limits are estimated analyzing 1 g of cod liver oil samples spiked at 250 ppm. Five replicates were analyzed using Method 8260.

[e] No analyses.

[f] Contamination of sample by analyte prevented determination.

[g] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 25

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
(METHOD 5032) (EXTERNAL STANDARD METHOD)[a]

| Compound | Water[b] (µg/L) | Soil[c] (µg/kg) | Tissue[d] (µg/kg) | Oil[e] (mg/kg) |
|---|---|---|---|---|
| Chloromethane | 3.1 | 8.6[f] | 7.8 | N/A[g] |
| Bromomethane | 2.5 | 4.9[f] | 9.7 | N/A[g] |
| Vinyl chloride | 4.0 | 7.1[f] | 9.5 | N/A[g] |
| Chloroethane | 6.1 | 7.5[f] | 9.2 | N/A[g] |
| Methylene chloride | 3.1 | 3.3 | CONT[h] | 0.08 |
| Acetone | 33.0[f] | CONT[h] | CONT[h] | 0.12 |
| Carbon disulfide | 2.5 | 3.2 | 5.4 | 0.19 |
| 1,1-Dichloroethene | 3.4 | 3.8 | 4.0 | 0.19 |
| 1,1-Dichloroethane | 2.3 | 1.7 | 4.0 | 0.13 |
| trans-1,2-Dichloroethene | 3.0 | 3.2 | 4.4 | 0.09 |
| cis-1,2-Dichloroethene | 2.4 | 2.7 | 4.7 | 0.08 |
| Chloroform | 2.7 | 2.6 | 5.6 | 0.06 |
| 1,2-Dichloroethane | 1.6 | 1.7 | 3.3 | 0.06 |
| 2-Butanone | 57.0[f] | INT[i] | INT[i] | INT[i] |
| 1,1,1-Trichloroethane | 1.6 | 2.4 | 1.1 | 0.08 |
| Carbon tetrachloride | 1.5 | 1.7 | 3.2 | 0.15 |
| Vinyl acetate | 23.0[f] | INT[i] | INT[i] | INT[i] |
| Bromodichloromethane | 2.0 | 2.3 | 3.2 | 0.05 |
| 1,1,2,2-Tetrachloroethane | 3.6 | 3.2 | 4.4 | 0.09 |
| 1,2-Dichloropropane | 2.9 | 3.7 | 3.8 | 0.12 |
| trans-1,3-Dichloropropene | 2.3 | 2.4 | 3.8 | 0.08 |
| Trichloroethene | 2.5 | 3.0 | 3.1 | 0.06 |
| Dibromochloromethane | 2.1 | 2.9 | 3.5 | 0.04 |
| 1,1,2-Trichloroethane | 2.7 | 2.8 | 4.4 | 0.07 |
| Benzene | 1.7 | 2.9 | 3.6 | 0.03 |
| cis-1,3-Dichloropropene | 2.1 | 2.5 | 3.5 | 0.06 |
| Bromoform | 2.3 | 2.5 | 4.9 | 0.10 |
| 2-Hexanone | 4.6 | 4.6 | 7.7 | INT[i] |
| 4-Methyl-2-pentanone | 3.8 | 3.9 | 7.5 | INT[i] |
| Tetrachloroethene | 1.8 | 2.6 | 4.3 | 0.12 |
| Toluene | 1.8 | 4.4 | 3.0 | 0.09 |
| Chlorobenzene | 2.4 | 2.6 | 3.3 | 0.07 |
| Ethylbenzene | 2.4 | 4.1 | 3.6 | 0.09 |
| Styrene | 2.0 | 2.5 | 3.5 | 0.16 |
| p-Xylene | 2.3 | 3.9 | 3.7 | 0.18 |
| o-Xylene | 2.4 | 4.1 | 3.3 | 0.08 |

[a] Method detection limits are the average MDLs for studies on three non-consecutive days. Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb. Daily MDLs were three times the standard deviation.

[b] Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb.

[c] These studies were seven replicate analyses of 5-g aliquots of soil spiked at 4 ppb.

[d] These studies were seven replicate analyses of 10-g aliquots of fish tissue spiked at 5 ppb.

[e] Method detection limits were estimated by analyzing cod liver oil samples spiked at 250 ppb. Five replicates were analyzed using Method 8260.

[f] Method detection limits were estimated by analyzing replicate 50 ppb standards five times over a single day.

[g] No analyses.

[h] Contamination of sample by analyte prevented determination.

[l] Interference by co-eluting compound prevented accurate quantitation.

TABLE 26

VOLATILE ORGANIC ANALYTE RECOVERY FROM OIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

| Compound | Recovery Mean (%) | RSD (%) |
|---|---|---|
| Chloromethane | N/A[b] | |
| Bromomethane | N/A[b] | |
| Vinyl chloride | N/A[b] | |
| Chloroethane | N/A[b] | |
| Methylene chloride | 62 | 32 |
| Acetone | 108 | 55 |
| Carbon disulfide | 98 | 46 |
| 1,1-Dichloroethene | 97 | 24 |
| 1,1-Dichloroethane | 96 | 22 |
| trans-1,2-Trichloroethene | 86 | 23 |
| cis-1,2-Dichloroethene | 99 | 11 |
| Chloroform | 93 | 14 |
| 1,2-Dichloroethane | 138 | 31 |
| 2-Butanone | INT[c] | |
| 1,1,1-Trichloroethane | 89 | 14 |
| Carbon tetrachloride | 129 | 23 |
| Vinyl acetate | INT[c] | |
| Bromodichloromethane | 106 | 14 |
| 1,1,2,2-Tetrachloroethane | 205 | 46 |
| 1,2-Dichloropropane | 107 | 24 |
| trans-1,3-Dichloropropene | 98 | 13 |
| Trichloroethene | 102 | 8 |
| Dibromochloromethane | 168 | 21 |
| 1,1,2-Trichloroethane | 95 | 7 |
| Benzene | 146 | 10 |
| cis-1,3-Dichloropropene | 98 | 11 |
| Bromoform | 94 | 18 |
| 2-Hexanone | INT[c] | |
| 4-Methyl-2-pentanone | INT[c] | |
| Tetrachloroethene | 117 | 22 |
| Toluene | 108 | 8 |
| Chlorobenzene | 101 | 12 |
| Ethylbenzene | 96 | 10 |
| Styrene | 120 | 46 |
| p-Xylene | 87 | 23 |
| o-Xylene | 90 | 10 |

TABLE 26 (cont.)

| Compound | Recovery Mean (%) | RSD (%) |
|---|---|---|
| Surrogates | | |
| 1,2-Dichloroethane | 137 | 30 |
| Toluene-$d_8$ | 84 | 6 |
| Bromofluorobenzene | 48 | 2 |

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicates of 10-g fish aliquots spiked at 25 ppb were analyzed. Quantitation was performed with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Standards and samples were replicated and precision value reflects the propagated errors. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Not analyzed.

[c] Interference by co-evaluating compounds prevented accurate measurement of analyte.

TABLE 27

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN OIL (METHOD 5032)[a]

| Compound | Method Detection Limit (ppb) External Standard Method | Internal Standard Method |
|---|---|---|
| Chloromethane | N/A[b] | N/A[b] |
| Bromomethane | N/A[b] | N/A[b] |
| Vinyl chloride | N/A[b] | N/A[b] |
| Chloroethane | N/A[b] | N/A[b] |
| Methylene chloride | 80 | 50 |
| Acetone | 120 | 60 |
| Carbon disulfide | 190 | 180 |
| 1,1-Dichloroethene | 190 | 180 |
| 1,1-Dichloroethane | 130 | 140 |
| trans-1,2-Dichloroethene | 90 | 100 |
| cis-1,2-Dichloroethene | 80 | 70 |
| Chloroform | 60 | 70 |
| 1,2-Dichloroethane | 60 | 60 |
| 2-Butanone | INT[c] | INT[c] |
| 1,1,1-Trichloroethane | 80 | 100 |
| Carbon tetrachloride | 150 | 130 |
| Vinyl acetate | INT[c] | INT[c] |
| Bromodichloromethane | 50 | 60 |
| 1,1,2,2-Tetrachloroethane | 90 | 20 |
| 1,2-Dichloropropane | 120 | 150 |
| trans-1,3-Dichloropropene | 80 | 50 |
| Trichloroethene | 60 | 40 |
| Dibromochloromethane | 40 | 70 |
| 1,1,2-Trichloroethane | 70 | 50 |
| Benzene | 30 | 50 |
| cis-1,3-Dichloropropene | 60 | 40 |
| Bromoform | 100 | 50 |
| 2-Hexanone | INT[c] | INT[c] |
| 4-Methyl-2-pentanone | INT[c] | INT[c] |
| Tetrachloroethene | 120 | 100 |
| Toluene | 90 | 50 |
| Chlorobenzene | 70 | 60 |
| Ethylbenzene | 90 | 40 |
| Styrene | 160 | 180 |
| p-Xylene | 180 | 200 |
| o-Xylene | 80 | 70 |

[a] Method detection limits are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MDLs were calculated as three times the standard deviation. Quantitation was performed using a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] No analyses.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 28

INTERNAL STANDARDS FOR ANALYTES AND SURROGATES PREPARED USING EQUILIBRIUM HEADSPACE ANALYSIS (METHOD 5021)

| Chloroform-$d_1$ | 1,1,2-TCA-$d_3$ | Bromobenzene-$d_5$ |
|---|---|---|
| Dichlorodifluoromethane | 1,1,1-Trichloroethane | Chlorobenzene |
| Chloromethane | 1,1-Dichloropropene | Bromoform |
| Vinyl chloride | Carbon tetrachloride | Styrene |
| Bromomethane | Benzene | iso-Propylbenzene |
| Chloroethane | Dibromomethane | Bromobenzene |
| Trichlorofluoromethane | 1,2-Dichloropropane | n-Propylbenzene |
| 1,1-Dichloroethene | Trichloroethene | 2-Chlorotoluene |
| Methylene chloride | Bromodichloromethane | 4-Chlorotoluene |
| trans-1,2-Dichloroethene | cis-1,3-Dichloropropene | 1,3,5-Trimethylbenzene |
| 1,1-Dichloroethane | trans-1,3-Dichloropropene | tert-Butylbenzene |
| cis-1,2-Dichloroethene | 1,1,2-Trichloroethane | 1,2,4-Trimethylbenzene |
| Bromochloromethane | Toluene | sec-Butylbenzene |
| Chloroform | 1,3-Dichloropropane | 1,3-Dichlorobenzene |
| 2,2-Dichloropropane | Dibromochloromethane | 1,4-Dichlorobenzene |
| 1,2-Dichloroethane | 1,2-Dibromoethane | p-iso-Propyltoluene |
| | Tetrachloroethene | 1,2-Dichlorobenzene |
| | 1,1,2-Trichloroethane | n-Butylbenzene |
| | Ethylbenzene | 1,2-Dibromo-3-chloropropane |
| | m-Xylene | 1,2,4-Trichlorobenzene |
| | p-Xylene | Naphthalene |
| | o-Xylene | Hexachlorobutadiene |
| | 1,1,2,2-Tetrachloroethane | 1,2,3-Trichlorobenzene |
| | 1,2,3-Trichloropropane | |

TABLE 29

PRECISION AND MDL DETERMINED FOR ANALYSIS OF FORTIFIED SAND[a] (METHOD 5021)

| Compound | % RSD | MDL (µg/kg) |
|---|---|---|
| Benzene | 3.0 | 0.34 |
| Bromochloromethane | 3.4 | 0.27 |
| Bromodichloromethane | 2.4 | 0.21 |
| Bromoform | 3.9 | 0.30 |
| Bromomethane | 11.6 | 1.3 |
| Carbon tetrachloride | 3.6 | 0.32 |
| Chlorobenzene | 3.2 | 0.24 |
| Chloroethane | 5.6 | 0.51 |
| Chloroform | 3.1 | 0.30 |
| Chloromethane | 4.1 | 3.5[b] |
| 1,2-Dibromo-3-chloropropane | 5.7 | 0.40 |
| 1,2-Dibromoethane | 3.2 | 0.29 |
| Dibromomethane | 2.8 | 0.20 |
| 1,2-Dichlorobenzene | 3.3 | 0.27 |
| 1,3-Dichlorobenzene | 3.4 | 0.24 |
| 1,4-Dichlorobenzene | 3.7 | 0.30 |
| Dichlorodifluoromethane | 3.0 | 0.28 |
| 1,1-Dichloroethane | 4.5 | 0.41 |
| 1,2-Dichloroethane | 3.0 | 0.24 |
| 1,1-Dichloroethene | 3.3 | 0.28 |
| cis-1,2-Dichloroethene | 3.2 | 0.27 |
| trans-1,2-Dichloroethene | 2.6 | 0.22 |
| 1,2-Dichloropropane | 2.6 | 0.21 |
| 1,1-Dichloropropene | 3.2 | 0.30 |
| cis-1,3-Dichloropropene | 3.4 | 0.27 |
| Ethylbenzene | 4.8 | 0.47 |
| Hexachlorobutadiene | 4.1 | 0.38 |
| Methylene chloride | 8.2 | 0.62[c] |
| Naphthalene | 16.8 | 3.4[c] |
| Styrene | 7.9 | 0.62 |
| 1,1,1,2-Tetrachloroethane | 3.6 | 0.27 |
| 1,1,2,2-Tetrachloroethane | 2.6 | 0.20 |
| Tetrachloroethene | 9.8 | 1.2[c] |
| Toluene | 3.5 | 0.38 |
| 1,2,4-Trichlorobenzene | 4.2 | 0.44 |
| 1,1,1-Trichloroethane | 2.7 | 0.27 |
| 1,1,2-Trichloroethane | 2.6 | 0.20 |
| Trichloroethene | 2.3 | 0.19 |

TABLE 29 (cont.)

| Compound | % RSD | MDL (µg/kg) |
|---|---|---|
| Trichlorofluoromethane | 2.7 | 0.31 |
| 1,2,3-Trichloropropane | 1.5 | 0.11 |
| Vinyl chloride | 4.8 | 0.45 |
| m-Xylene/p-Xylene | 3.6 | 0.37 |
| o-Xylene | 3.6 | 0.33 |

[a] Most compounds spiked at 2 ng/g (2 µg/kg)
[b] Incorrect ionization due to methanol
[c] Compound detected in unfortified sand at >1 ng

TABLE 30

RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5021)

| Compound | Recovery per Replicate (ng) Sample 1 | Sample 2 | Sample 3 | Mean (ng) | RSD | Recovery (%) |
|---|---|---|---|---|---|---|
| Benzene | 37.6 | 35.2 | 38.4 | 37.1 | 3.7 | 185[a] |
| Bromochloromethane | 20.5 | 19.4 | 20.0 | 20.0 | 2.3 | 100 |
| Bromodichloromethane | 21.1 | 20.3 | 22.8 | 21.4 | 4.9 | 107 |
| Bromoform | 23.8 | 23.9 | 25.1 | 24.3 | 2.4 | 121 |
| Bromomethane | 21.4 | 19.5 | 19.7 | 20.2 | 4.2 | 101 |
| Carbon tetrachloride | 27.5 | 26.6 | 28.6 | 27.6 | 3.0 | 138 |
| Chlorobenzene | 25.6 | 25.4 | 26.4 | 25.8 | 1.7 | 129 |
| Chloroethane | 25.0 | 24.4 | 25.3 | 24.9 | 1.5 | 125 |
| Chloroform | 21.9 | 20.9 | 21.7 | 21.5 | 2.0 | 108 |
| Chloromethane | 21.0 | 19.9 | 21.3 | 20.7 | 2.9 | 104[a] |
| 1,2-Dibromo-3-chloro-propane | 20.8 | 20.8 | 21.0 | 20.9 | 0.5 | 104 |
| 1,2-Dibromoethane | 20.1 | 19.5 | 20.6 | 20.1 | 2.2 | 100 |
| Dibromomethane | 22.2 | 21.0 | 22.8 | 22.0 | 3.4 | 110 |
| 1,2-Dichlorobenzene | 18.0 | 17.7 | 17.1 | 17.6 | 2.1 | 88.0 |
| 1,3-Dichlorobenzene | 21.2 | 21.0 | 20.1 | 20.8 | 2.3 | 104 |
| 1,4-Dichlorobenzene | 20.1 | 20.9 | 19.9 | 20.3 | 2.1 | 102 |
| Dichlorodifluoromethane | 25.3 | 24.1 | 25.4 | 24.9 | 2.4 | 125 |
| 1,1-Dichloroethane | 23.0 | 22.0 | 22.7 | 22.6 | 1.9 | 113 |
| 1,2-Dichloroethane | 20.6 | 19.5 | 19.8 | 20.0 | 2.3 | 100 |
| 1,1-Dichloroethene | 24.8 | 23.8 | 24.4 | 24.3 | 1.7 | 122 |
| cis-1,2-Dichloroethene | 21.6 | 20.0 | 21.6 | 21.1 | 3.6 | 105 |
| trans-1,2-Dichloroethene | 22.4 | 21.4 | 22.2 | 22.0 | 2.0 | 110 |
| 1,2-Dichloropropane | 22.8 | 22.2 | 23.4 | 22.8 | 2.1 | 114 |
| 1,1-Dichloropropene | 26.3 | 25.7 | 28.0 | 26.7 | 3.7 | 133 |
| cis-1,3-Dichloropropene | 20.3 | 19.5 | 21.1 | 20.3 | 3.2 | 102 |
| Ethylbenzene | 24.7 | 24.5 | 25.5 | 24.9 | 1.7 | 125 |
| Hexachlorobutadiene | 23.0 | 25.3 | 25.2 | 24.5 | 4.3 | 123 |
| Methylene chloride | 26.0 | 25.7 | 26.1 | 25.9 | 0.7 | 130[a] |
| Naphthalene | 13.8 | 12.7 | 11.8 | 12.8 | 6.4 | 63.8[a] |
| Styrene | 24.2 | 23.3 | 23.3 | 23.6 | 1.8 | 118 |
| 1,1,1,2-Tetrachloroethane | 21.4 | 20.2 | 21.3 | 21.0 | 2.6 | 105 |
| 1,1,2,2-Tetrachloroethane | 18.6 | 17.8 | 19.0 | 18.5 | 2.7 | 92.3 |
| Tetrachloroethene | 25.2 | 24.8 | 26.4 | 25.5 | 2.7 | 127 |
| Toluene | 28.6 | 27.9 | 30.9 | 29.1 | 4.4 | 146[a] |
| 1,2,4-Trichlorobenzene | 15.0 | 14.4 | 12.9 | 14.1 | 6.3 | 70.5 |
| 1,1,1-Trichloroethane | 28.1 | 27.2 | 29.9 | 28.4 | 4.0 | 142 |
| 1,1,2-Trichloroethane | 20.8 | 19.6 | 21.7 | 20.7 | 4.2 | 104 |

TABLE 30 (cont.)

| Compound | Recovery per Replicate (ng) Sample 1 | Sample 2 | Sample 3 | Mean (ng) | RSD | Recovery (%) |
|---|---|---|---|---|---|---|
| Trichloroethene | 26.3 | 24.9 | 26.8 | 26.0 | 3.1 | 130 |
| Trichlorofluoromethane | 25.9 | 24.8 | 26.5 | 25.7 | 2.7 | 129 |
| 1,2,3-Trichloropropane | 18.8 | 18.3 | 19.3 | 18.8 | 2.2 | 94.0 |
| Vinyl chloride | 24.8 | 23.2 | 23.9 | 24.0 | 2.7 | 120 |
| m-Xylene/p-Xylene | 24.3 | 23.9 | 25.3 | 24.5 | 2.4 | 123 |
| o-Xylene | 23.1 | 22.3 | 23.4 | 22.9 | 2.0 | 115 |

[a] Compound found in unfortified garden soil matrix at >5 ng.

TABLE 31

METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)[a]

| Compound | Detection Limit (ng) | Boiling Point (°C) |
|---|---|---|
| Chloromethane | 58 | -24 |
| Bromomethane | 26 | 4 |
| Vinyl chloride | 14 | -13 |
| Chloroethane | 21 | 13 |
| Methylene chloride | 9 | 40 |
| Acetone | 35 | 56 |
| Carbon disulfide | 11 | 46 |
| 1,1-Dichloroethene | 14 | 32 |
| 1,1-Dichloroethane | 12 | 57 |
| trans-1,2-Dichloroethene | 11 | 48 |
| Chloroform | 11 | 62 |
| 1,2-Dichloroethane | 13 | 83 |
| 1,1,1-Trichloroethane | 8 | 74 |
| Carbon tetrachloride | 8 | 77 |
| Bromodichloromethane | 11 | 88 |
| 1,1,2,2-Tetrachloroethane** | 23 | 146 |
| 1,2-Dichloropropane | 12 | 95 |
| trans-1,3-Dichloropropene | 17 | 112 |
| Trichloroethene | 11 | 87 |
| Dibromochloromethane | 21 | 122 |
| 1,1,2-Trichloroethane | 26 | 114 |
| Benzene | 26 | 80 |
| cis-1,3-Dichloropropene | 27 | 112 |
| Bromoform** | 26 | 150 |
| Tetrachloroethene | 11 | 121 |
| Toluene | 15 | 111 |
| Chlorobenzene | 15 | 132 |
| Ethylbenzene** | 21 | 136 |
| Styrene** | 46 | 145 |
| Trichlorofluoromethane | 17 | 24 |
| Iodomethane | 9 | 43 |
| Acrylonitrile | 13 | 78 |
| Dibromomethane | 14 | 97 |
| 1,2,3-Trichloropropane** | 37 | 157 |
| total Xylenes** | 22 | 138-144 |

Footnotes are found on the following page.

* The method detection limit (MDL) is defined in Chapter One. The detection limits cited above were determined according to 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Boiling Point greater than 130°C. Not appropriate for quantitative sampling by Method 0030.

TABLE 32

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (METHOD 5041)

| Bromochloromethane | 1,4-Difluorobenzene |
|---|---|
| Acetone | Benzene |
| Acrylonitrile | Bromodichloromethane |
| Bromomethane | Bromoform |
| Carbon disulfide | Carbon tetrachloride |
| Chloroethane | Chlorodibromomethane |
| Chloroform | Dibromomethane |
| Chloromethane | 1,2-Dichloropropane |
| 1,1-Dichloroethane | cis-1,3-Dichloropropene |
| 1,2-Dichloroethane | trans-1,3-Dichloropropene |
| 1,2-Dichloroethane-$d_4$ (surrogate) | 1,1,1-Trichloroethane |
| 1,1-Dichloroethene | 1,1,2-Trichloroethane |
| Trichloroethene | |
| trans-1,2-Dichloroethene | |
| Iodomethane | |
| Methylene chloride | |
| Trichlorofluoromethane | |
| Vinyl chloride | |

Chlorobenzene-$d_5$

4-Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-$d_8$ (surrogate)
1,2,3-Trichloropropane
Xylenes

TABLE 33

METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

| Compound | Boiling Point (°C) | Condensation Point at 20°C (%) | Estimated Detection Limit[a] (ppm) |
|---|---|---|---|
| Dichlorodifluoromethane | -30 | Gas | 0.20 |
| Vinyl chloride | -19 | Gas | 0.11 |
| 1,3-Butadiene | -4 | Gas | 0.90 |
| 1,2-Dichloro-1,1,2,2-tetrafluoroethane | 4 | Gas | 0.14 |
| Methyl bromide | 4 | Gas | 0.14 |
| Trichlorofluoromethane | 24 | 88 | 0.18 |
| 1,1-Dichloroethene | 31 | 22 | 0.07 |
| Methylene chloride | 40 | 44 | 0.05 |
| 1,1,2-Trichloro-trifluoroethane | 48 | 37 | 0.13 |
| Chloroform | 61 | 21 | 0.04 |
| 1,1,1-Trichloroethane | 75 | 13 | 0.03 |
| Carbon tetrachloride | 77 | 11 | 0.03 |
| Benzene | 80 | 10 | 0.16 |
| Trichloroethene | 87 | 8 | 0.04 |
| 1,2-Dichloropropane | 96 | 5 | 0.05 |
| Toluene | 111 | 3 | 0.08 |
| Tetrachloroethene | 121 | 2 | 0.03 |

[a] Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS

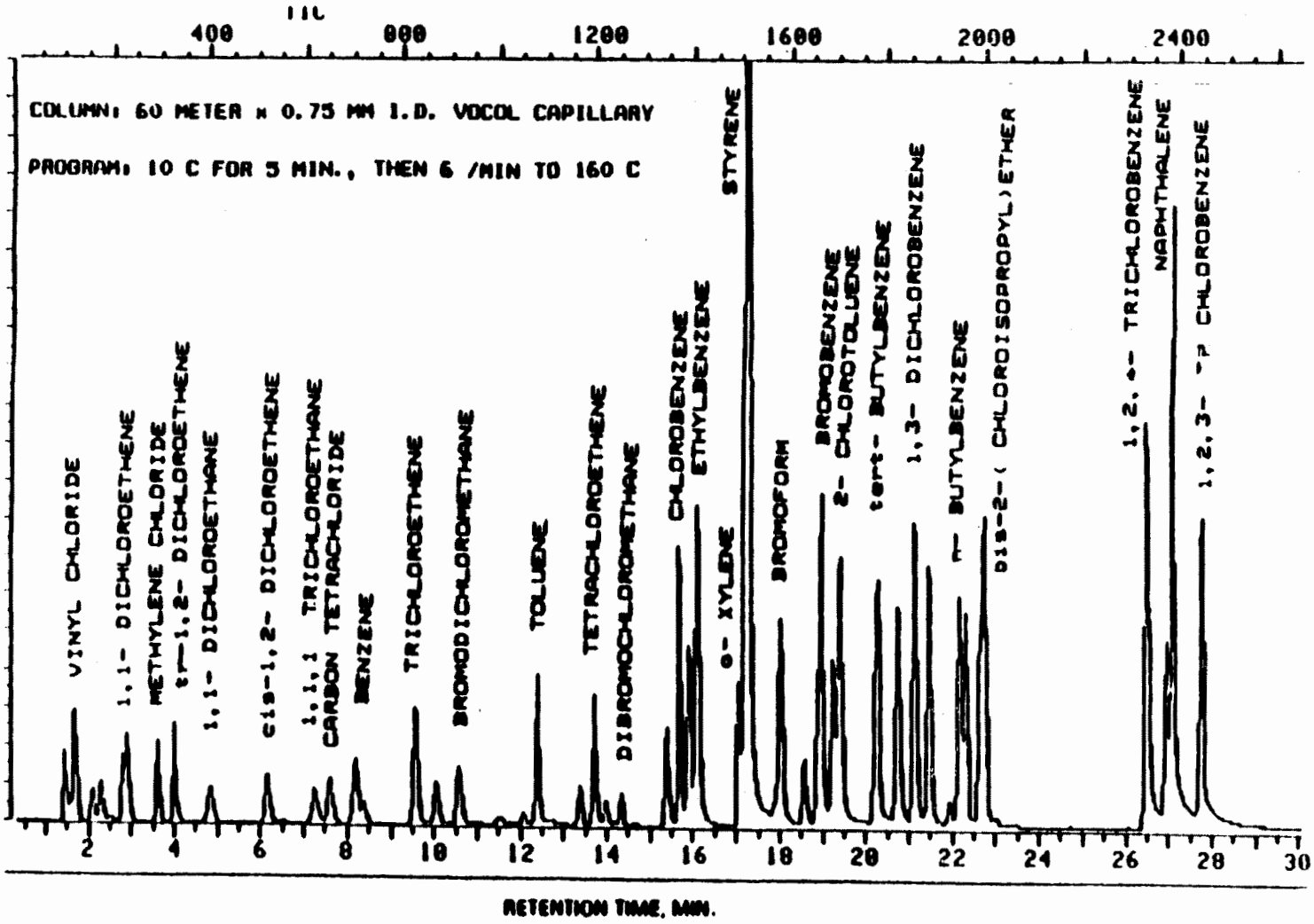


FIGURE 2
GAS CHROMATOGRAM OF VOLATILE ORGANICS

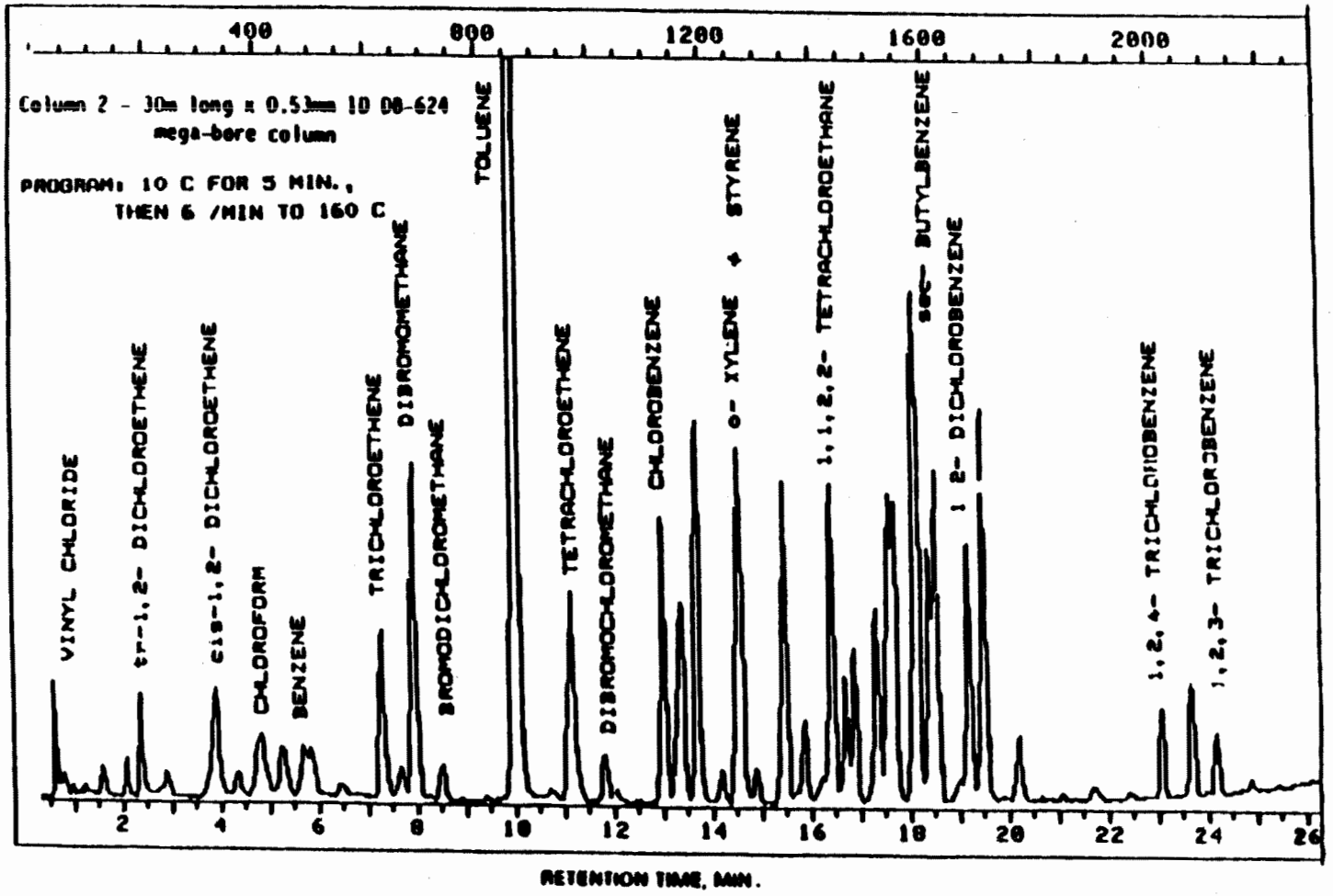


FIGURE 3
GAS CHROMATOGRAM OF VOLATILE ORGANICS

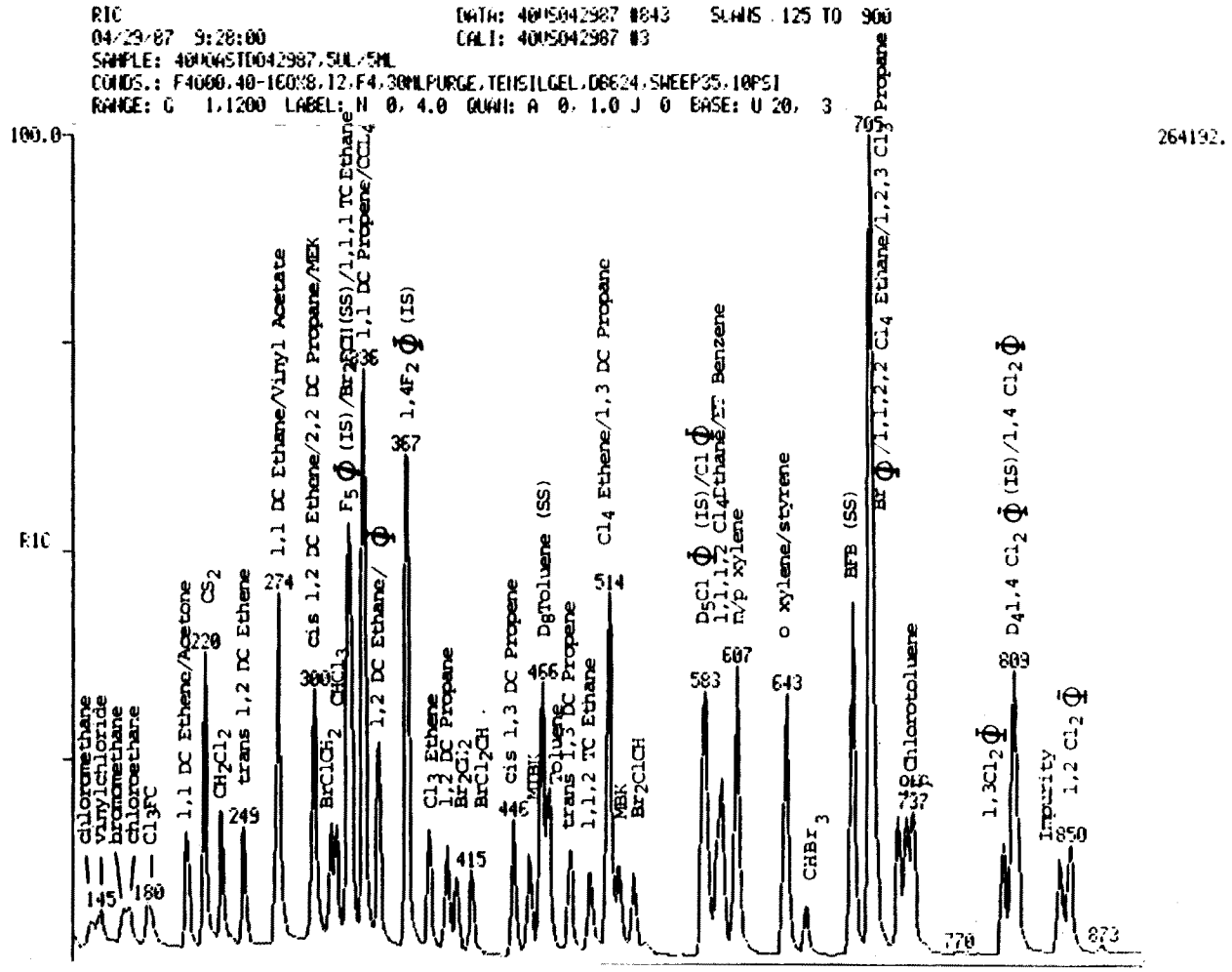
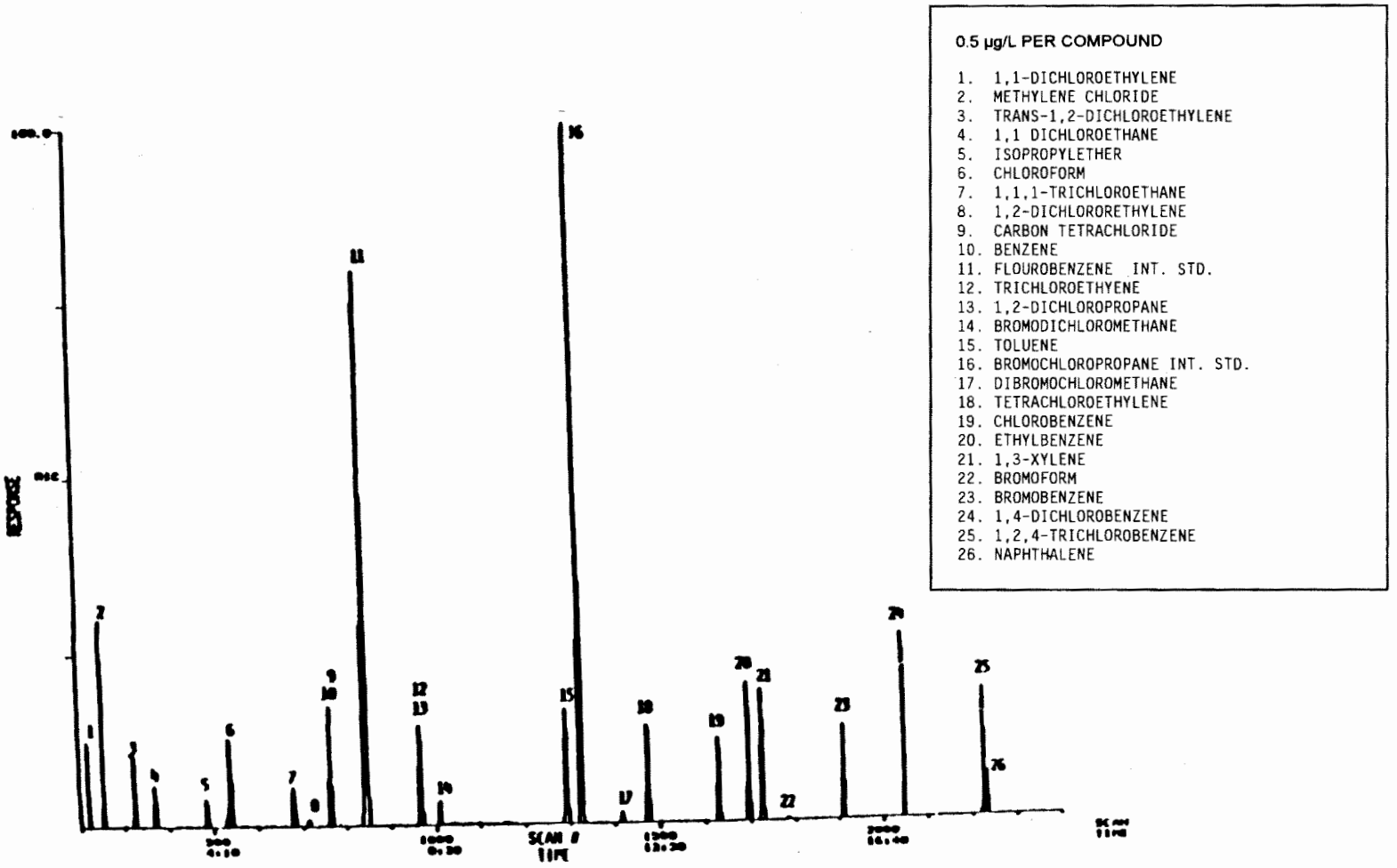
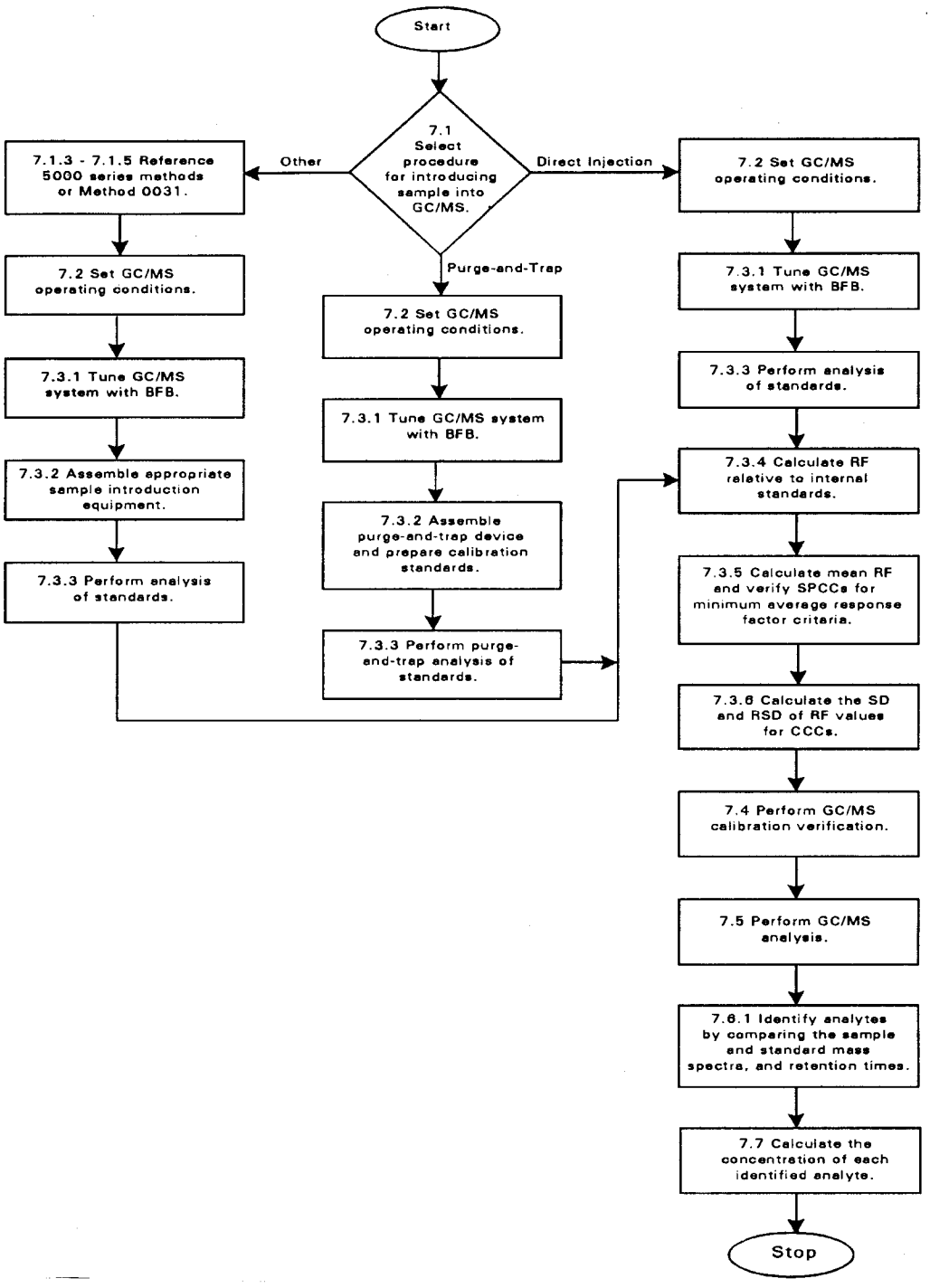


FIGURE 4
GAS CHROMATOGRAM OF TEST MIXTURE




Start
7.1 Select procedure for introducing sample into GC/MS.
Other
Purge-and-Trap
Direct Injection
7.1.3 - 7.1.5 Reference 5000 series methods or Method 0031.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble appropriate sample introduction equipment.
7.3.3 Perform analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble purge-and-trap device and prepare calibration standards.
7.3.3 Perform purge-and-trap analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.3 Perform analysis of standards.
7.3.4 Calculate RF relative to internal standards.
7.3.5 Calculate mean RF and verify SPCCs for minimum average response factor criteria.
7.3.6 Calculate the SD and RSD of RF values for CCCs.
7.4 Perform GC/MS calibration verification.
7.5 Perform GC/MS analysis.
7.6.1 Identify analytes by comparing the sample and standard mass spectra, and retention times.
7.7 Calculate the concentration of each identified analyte.
Stop

METHOD 5035

# CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

## 1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

1.2 The low soil method utilizes a hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 0.5 to 200 µg/kg range.

1.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

1.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030..

1.5 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency.

1.6 Method 5035, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5035 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Method 8021 in series with Method 8015.

1.7 As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.8 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 6.2.2).

1.9 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to and soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains 5 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent.

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol or polyethylene glycol (PEG), a separate aliquot of the sample is spiked with surrogates and diluted in the appropriate solvent. An aliquot of the solution is added to 5 mL of reagent water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) are added to the solution which is then purged using Method 5030 and analyzed by an appropriate determinative method.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585.

## 3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

## 4.0 APPARATUS AND MATERIALS

### 4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other

systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 4.2.2).

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the Disclaimer at the front of this manual for guidance on the use of alternative equipment.

4.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed, it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all the target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocarb 4000), as some degradation has been noted when higher desorption temperatures (especially above 240 - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 The trap used to develop this method was 25 cm long, with an inside diameter of 0.105 inches, and was packed with Carbopack/Carbosieve (Supelco, Inc.).

4.2.2.2 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If

the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

4.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.2.2.2.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.2.2.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.3 Syringe and Syringe Valves

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25-µL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10-, 100-µL.

4.3.5 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

4.4 Miscellaneous

4.4.1 Glass vials

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance - Capable of accurately weighing to 0.01 g.

4.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground-glass stoppers.

4.4.5 2-mL glass vials, for GC autosampler - Used for oily waste samples extracted with methanol or PEG.

4.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

4.5 Field Sampling Equipment

4.5.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.5.2 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.3 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

4.5.4 Portable balance - For field use, capable of weighing to 0.01 g.

4.5.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

## 5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, $CH_3OH$ - purge-and-trap quality or equivalent. Store away from other solvents.

5.3 Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$ - free of interferences at the detection limit of the target analytes.

5.4 Low concentration sample preservative

5.4.1 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

5.4.2 The preservative should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

5.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

### 6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

#### 6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of $\leq 2$.

6.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

6.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the

laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

6.1.2 High concentration soil samples collected without a preservative

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60-mL glass vials with septum seals (see Sec. 4.4).

6.1.3 High concentration soil samples collected and preserved in the field

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.3.1 Add 10 mL of methanol to each vial.

6.1.3.2 Seal the vial with the screw-cap and septum seal.

6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

NOTE: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

6.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the sample after it is returned to the laboratory and prior to analysis.

6.1.4 Oily waste samples

When oily waste samples are known to be soluble in methanol or PEG, sample vials may be prepared as described in Sec. 6.1.3, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 6.1.2.

6.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler ™, and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.2.1 Low concentration soil samples

6.2.1.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

NOTE: Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials that do not contain the preservative solution.

6.2.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

6.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60-mL glass vial or a third 40-mL soil sample vial. However, this third vial must *not* contain the sample preservative solution, as an aliquot will be used to determine dry weight. If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

6.2.1.7 If samples are known or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2 g instead of the 5 g collected in Sec. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

6.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 6.2.2).

6.2.2 High concentration soil samples preserved in the field

The collection of soil samples in vials that contain methanol has been suggested by some as a combined preservation and extraction procedure. However, this procedure is not appropriate for use with the low concentration soil procedure described in this method.

NOTE: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of two potential problems. First, the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure (0.5-200 µg/kg). The exact dilution factor will depend on the masses of solvent and sample, but generally exceeds 1000, and may make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes. Because the analytes of interest are volatile, the methanol extract cannot be concentrated to overcome the dilution problem. Thus, for samples of unknown composition, it may still be necessary to collect an aliquot for analysis by this closed-system procedure and another aliquot preserved in methanol and analyzed by other procedures. The second problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste.

6.2.2.1 When samples are known to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

6.2.2.2 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.2.3 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

6.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight, as described in Sec. 6.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

6.2.3 High concentration soil sample not preserved in the field

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

6.2.4 Oily waste samples

The collection procedures for oily samples depend on knowledge of the waste and its solubility in methanol or other solvents.

6.2.4.1 When an oily waste is known to be soluble in methanol or PEG, the sample may be collected in a vial containing such a solvent (see Sec. 6.1.4), using procedures similar to those described in Sec. 6.2.2.

6.2.4.2 When the solubility of the oily waste is not known, the sample should either be collected in a vial without a preservative, as described in Sec. 6.2.3, or the solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in Sec. 6.2.2. Otherwise, collect an unpreserved sample as described in Sec. 6.2.3.

6.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

6.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at -10°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel. See Sec. 6.2.1.2 for additional information.

## 7.0 PROCEDURE

This section describes procedures for sample screening, the low concentration soil method, the high concentration soil method, and the procedure for oily waste samples. High concentration samples are to be introduced into the GC system using Method 5030. Oily waste samples are to be introduced into the GC system using Method 5030 if they are soluble in a water-miscible solvent, or using Method 3585 if they are not.

7.1 Sample screening

7.1.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system, thereby requiring extensive cleanup and instrument maintenance. The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low concentration closed-system direct purge-and-trap method (Sec. 7.2), the high concentration (methanol extraction) method (Sec. 7.3), or the nonaqueous liquid (oily waste) methanol or PEG dilution procedure (Sec. 7.4).

7.1.2 The analyst may employ any appropriate screening technique. Two suggested screening techniques employing SW-846 methods are:

7.1.2.1 Automated headspace (Method 5021) using a gas chromatograph (GC) equipped with a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series, or,

7.1.2.2 Extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC equipped with a FID and/or an ECD.

7.1.3 The analyst may inject a calibration standard containing the analytes of interest at a concentration equivalent to the upper limit of the calibration range of the low concentration soil method. The results from this standard may be used to determine when the screening results approach the upper limit of the low concentration soil method. There are no linearity or other performance criteria associated with the injection of such a standard, and other approaches may be employed to estimate sample concentrations.

7.1.4 Use the low concentration closed-system purge-and-trap method (Sec. 7.2) if the estimated concentration from the screening procedure falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range of the low concentration soil method, then use either the high concentration soil method (Sec. 7.3), or the oily waste method (Sec. 7.4).

7.2 Low concentration soil method (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.2.1 Initial calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.2.1.2 Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing with an inert gas flow of at least 20 mL/minute. If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.3 If the standard trap in Sec. 4.2.2.2 is employed, prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min, or according to the manufacturer's recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.4 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

7.2.1.5 Prepare a minimum of five initial calibration standards containing all the analytes of interest and surrogates, as described in Method 8000, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL added to the vial before shipping it to the field plus the organic-free reagent water added by the instrument). The calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (e.g., ~1 g), as the presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same fashion as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the surrogates using standards at five concentrations, it may be necessary to disable the automatic addition of surrogates to each vial containing a calibration standard (consult the manufacturer's instructions). Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as recommended by the manufacturer.

7.2.1.6 Carry out the purge-and-trap procedure as outlined in Secs. 7.2.3. to 7.2.5.

7.2.1.7 Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.

7.2.1.8 For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.8.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.2.1.8.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.8.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.9 When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross-contamination and memory effects from a high concentration sample or even the standard are a common problem.

Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification

Refer to Method 8000 for details on calibration verification. A single standard near the mid-point of calibration range is used for verification. This standard should also contain approximately 1 g of sodium bisulfate.

7.2.3 Sample purge-and-trap

This method is designed for a 5-g sample size, but smaller sample sizes may be used. Consult the instrument manufacturer's instructions regarding larger sample sizes, in order to avoid clogging of the purging apparatus. The soil vial is hermetically sealed at the sampling site, and MUST remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01 g, even if the sample weight was determined in the field, and record this weight. This second weighing provides a check on the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant discrepancies between the field and laboratory weights.

7.2.3.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

7.2.3.2 Without disturbing the hermetic seal on the sample vial, add 5 mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

7.2.3.3 For the sample selected for matrix spiking, add the matrix spiking solution described in Sec. 5.0 of Method 5000, either manually, or automatically, following the manufacturer's instructions. The concentration of the spiking solution and the amount added should be established as described in Sec. 8.0 of Method 8000.

7.2.3.4 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

7.2.4 Sample Desorption

7.2.4.1 Non-cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow

of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes (1.5 min is normally adequate for analytes in Method 8015). Begin the temperature program of the gas chromatograph and start data acquisition.

7.2.4.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 245°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Methods 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.5 Trap Reconditioning

After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

7.2.6 Data Interpretation

Perform qualitative and quantitative analysis following the guidance given in the determinative method and Method 8000. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. Such reanalyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method. Alternatively, if a sample aliquot of 1-2 g was also collected (see Sec. 6.2.1.7), it may be practical to analyze that aliquot for the analytes that exceeded the instrument calibration range in the 5-g analysis. If results are to be reported on a dry weight basis, proceed to Sec. 7.5

7.3 High concentration method for soil samples with concentrations generally greater than 200 µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free reagent water containing surrogates and, if applicable, internal and matrix spiking standards, purged according to Method 5030, and analyzed by an appropriate determinative method. Wastes that are insoluble in methanol (i.e., petroleum and coke wastes) are diluted with hexadecane (see Sec. 7.3.8).

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were <u>not</u> preserved in the field are prepared using the steps below, beginning at Sec. 7.3.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.3.4.

7.3.1 When the high concentration sample is <u>not</u> preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Whenever practical, mix the contents of the sample container by shaking or other mechanical means without opening the vial. When shaking is not practical, quickly mix the contents of the vial with a narrow metal spatula and immediately reseal the vial.

7.3.2 If the sample is from an unknown source, perform a solubility test before proceeding. Remove several grams of material from the sample container. Quickly reseal the container to minimize the loss of volatiles. Weigh 1-g aliquots of the sample into several test tubes or other suitable containers. Add 10 mL of methanol to the first tube, 10 mL of PEG to the second, and 10 mL of hexadecane to the third. Swirl the sample and determine if it is soluble in the solvent. Once the solubility has been evaluated, discard these test solutions. If the sample is soluble in either methanol or PEG, proceed with Sec. 7.3.3. If the sample is only soluble in hexadecane, proceed with Sec. 7.3.8.

7.3.3 For soil and solid waste samples that are soluble in methanol, add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution to a tared 20-mL vial. Using a top-loading balance, weigh 5 g (wet weight) of sample into the vial. Quickly cap the vial and reweigh the vial. Record the weight to 0.1 g. Shake the vial for 2 min. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0 mL of PEG in place of the methanol. Proceed with Sec. 7.3.5.

NOTE: The steps in Secs. 7.3.1, 7.3.2, and 7.3.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.4 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 6.2.2), weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum, shake for 2 min, as described above, and proceed with Sec. 7.3.5.

7.3.5 Pipet approximately 1 mL of the extract from either Sec. 7.3.3 or 7.3.4 into a GC vial for storage, using a disposable pipet, and seal the vial. The remainder of the extract may be discarded. Add approximately 1 mL of methanol or PEG to a separate GC vial for use as the method blank for each set of samples extracted with the same solvent.

7.3.6 The extracts must be stored at 4°C in the dark, prior to analysis. Add an appropriate aliquot of the extract (see Table 2) to 5.0 mL of organic-free reagent water and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging high concentration samples.

7.3.7 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the procedure in Sec. 7.5, after the sample extract has been transferred to a GC vial and the vial sealed.

7.3.8 For solids that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste) dilute or extract the sample with hexadecane using the procedures in Sec. 7.0 of Method 3585.

7.4 High concentration method for oily waste samples

This procedure for the analysis of oily waste samples involves the dilution of the sample in methanol or PEG. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. A portion of the diluted sample is then added to 5.0 mL of organic-free reagent water, purged according to Method 5030, and analyzed using an appropriate determinative method.

For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with hexadecane using the procedures in Sec. 7.0 of Method 3585.

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.4.1. If methanol preservation was employed in the field, then the preparation begins with Sec. 7.4.3.

7.4.1 If the waste was not preserved in the field and it is soluble in methanol or PEG, weigh 1 g (wet weight) of the sample into a tared 10-mL volumetric flask, a tared scintillation vial, or a tared culture tube. If a vial or tube is used instead of a volumetric flask, it must be calibrated prior to use. This operation must be performed prior to opening the sample vial and weighing out the aliquot for analysis.

7.4.1.1 To calibrate the vessel, pipet 10.0 mL of methanol or PEG into the vial or tube and mark the bottom of the meniscus.

7.4.1.2 Discard this solvent, and proceed with weighing out the 1-g sample aliquot.

7.4.2 Quickly add 1.0 mL of surrogate spiking solution to the flask, vial, or tube, and dilute to 10.0 mL with the appropriate solvent (methanol or PEG). Swirl the vial to mix the contents and then shake vigorously for 2 minutes.

7.4.3 If the sample was collected in the field in a vial containing methanol or PEG, weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum. Swirl the vial to mix the contents and then shake vigorously for 2 minutes and proceed with Sec. 7.4.4.

7.4.4 Regardless of how the sample was collected, the target analytes are extracted into the solvent along with the majority of the oily waste (i.e., some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

7.4.5 Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis, using Method 5030.

7.4.6 Prepare a matrix spike sample by adding 10 - 50 µL of the matrix spike standard dissolved in methanol to a 1-g aliquot of the oily waste. Shake the vial to disperse the matrix spike solution throughout the oil. Then add 10 mL of extraction solvent and proceed with the extraction and analysis, as described in Secs. 7.4.2 - 7.4.5. Calculate the recovery of the spiked analytes as described in Method 8000. If the recovery is not within the acceptance limits for the application, use the hexadecane dilution technique in Sec. 7.0 of Method 3585.

7.5 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample.

NOTE: It is highly recommended that the dry weight determination only be made after the analyst has determined that no sample aliquots will be taken from the 60-mL vial for high

concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the dry weight determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

7.5.1 Weigh 5-10 g of the sample from the 60-mL VOA vial into a tared crucible.

7.5.2 Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

## 8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS), and the addition of surrogates to each sample and QC sample.

8.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

## 9.0 METHOD PERFORMANCE

9.1 Single laboratory accuracy and precision data were obtained for the method analytes in three soil matrices, sand, a soil collected 10 feet below the surface of a hazardous landfill, called the

C-Horizon, and a surface garden soil. Each sample was fortified with the analytes at a concentration of 20 ng/5 g, which is equivalent to 4 µg/kg. These data are listed in tables found in Method 8260.

9.2 Single laboratory accuracy and precision data were obtained for certain method analytes when extracting oily liquid using methanol as the extraction solvent. The data are presented in a table in Method 8260. The compounds were spiked into three portions of an oily liquid (taken from a waste site) following the procedure for matrix spiking described in Sec. 7.4. This represents a worst case set of data based on recovery data from many sources of oily liquid.

## 10.0 REFERENCES


1. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

2. Siegrist, R. L., Jenssen, P. D., "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils", Envir Sci Technol, 1990; 24; 1387-92.

3. Hewitt, A. D., Jenkins, T. F., Grant, C. L., "Collection, Handling and Storage: Keys to Improved Data Quality for Volatile Organic Compounds in Soil", Am Environ Lab, 1995; 7(1); 25-8.

4. Liikala, T. L., Olsen, K. B., Teel, S. S., Lanigan, D. C., "Volatile Organic Compounds: Comparison of Two Sample Collection and Preservation Methods", Envir Sci Technol, 1996; 30; 3441-7.

5. Lewis, T. E., Crockett, A. B., Siegrist, R. L., Zarrabi, K., "Soil Sampling and Analysis for Volatile Organic Compounds", Envir Monitoring & Assessment, 1994; 30; 213-46.

6. Hewitt, A. D., "Enhanced Preservation of Volatile Organic Compounds in Soil with Sodium Bisulfate", SR95-26, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

7. Hewitt, A. D., Lukash, N. J. E., "Sampling for In-Vial Analysis of Volatile Organic Compounds in Soil", Am Environ Lab, 1996; Aug; 15-9.

8. Hewitt, A. D., Miyares, P. H., Sletten, R. S., "Determination of Two Chlorinated Volatile Organic Compounds in Soil by Headspace Gas Chromatography and Purge-and-Trap Gas Chromatography/Mass Spectrometry", Hydrocarbon Contaminated Soils, 1993, 3; 135-45, Chelsea, MI, Lewis Publishers.

9. Hewitt, A. D., "Methods of Preparing Soil Samples for Headspace Analysis of Volatile Organic Compounds: Emphasis on Salting Out", 12th Annual Waste Testing and Quality Assurance Symposium, Washington, DC, 1996, 322-9.

10. Hewitt, A. D., Miyares, P. H., Leggett, D. C., Jenkins, T. F., "Comparison of Analytical Methods for Determination of Volatile Organic Compounds", Envir Sci Tech, 1992; 26; 1932-8.

TABLE 1

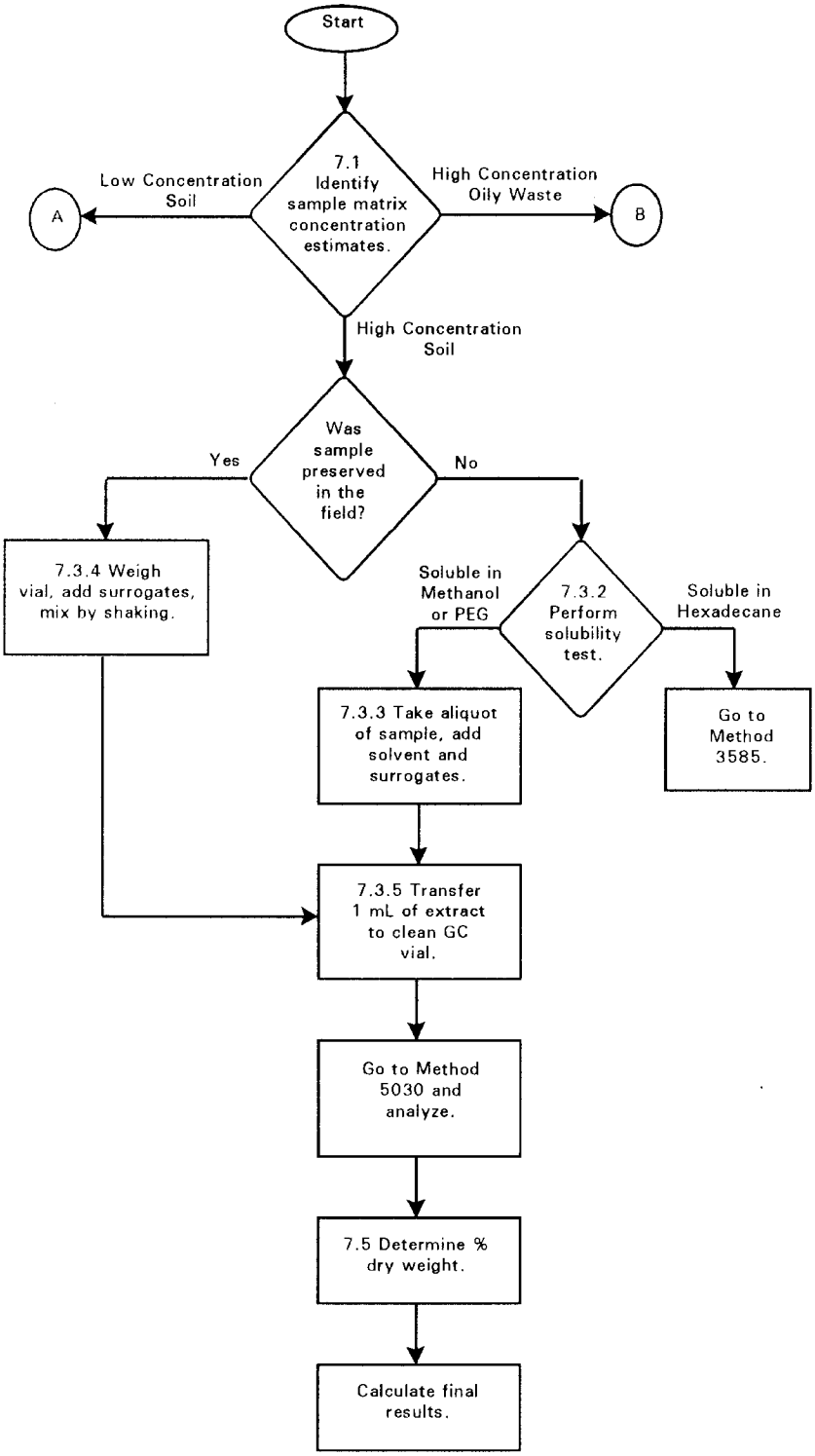
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SOILS/SEDIMENTS

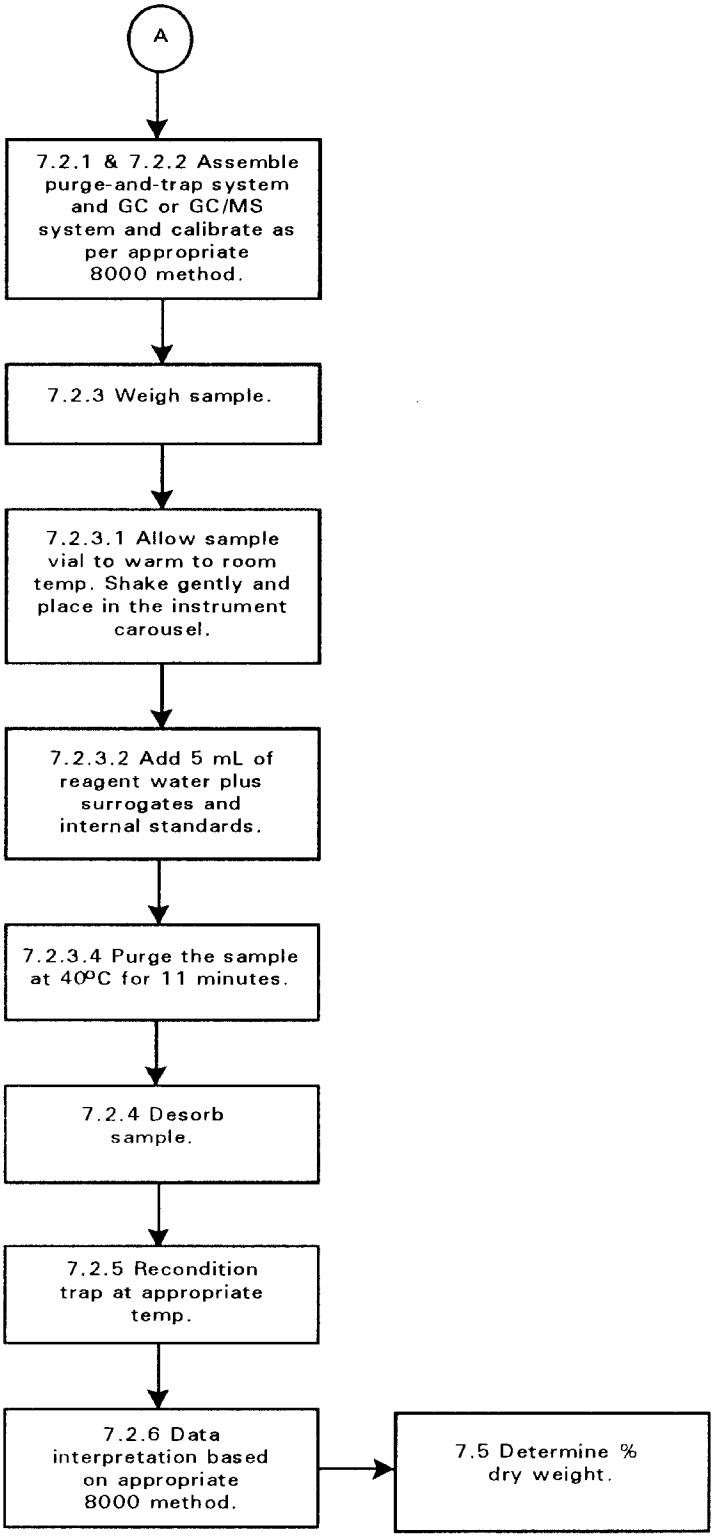
| Approximate Concentration Range | Volume of Methanol Extract[a] |
|---|---|
| 500 - 10,000 µg/kg | 100 µL |
| 1,000 - 20,000 µg/kg | 50 µL |
| 5,000 - 100,000 µg/kg | 10 µL |
| 25,000 - 500,000 µg/kg | 100 µL of 1/50 dilution[b] |

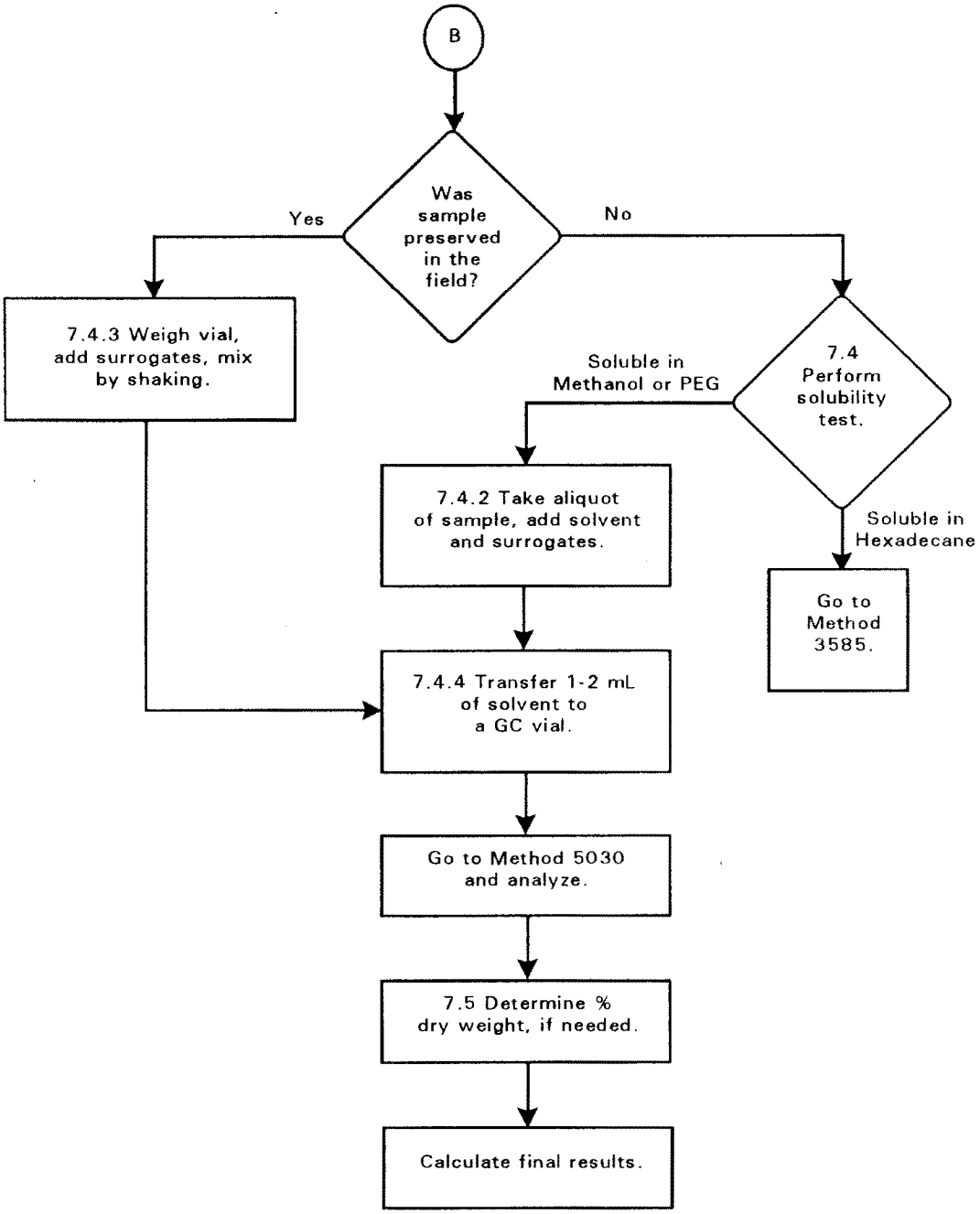
Calculate appropriate dilution factor for concentrations exceeding those in this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100 µL of methanol.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.


Start
7.1 Identify sample matrix concentration estimates.
Low Concentration Soil
A
High Concentration Oily Waste
B
High Concentration Soil
Was sample preserved in the field?
Yes
No
7.3.4 Weigh vial, add surrogates, mix by shaking.
7.3.2 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.3.3 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.3.5 Transfer 1 mL of extract to clean GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight.
Calculate final results.


A
7.2.1 & 7.2.2 Assemble purge-and-trap system and GC or GC/MS system and calibrate as per appropriate 8000 method.
7.2.3 Weigh sample.
7.2.3.1 Allow sample vial to warm to room temp. Shake gently and place in the instrument carousel.
7.2.3.2 Add 5 mL of reagent water plus surrogates and internal standards.
7.2.3.4 Purge the sample at 40°C for 11 minutes.
7.2.4 Desorb sample.
7.2.5 Recondition trap at appropriate temp.
7.2.6 Data interpretation based on appropriate 8000 method.
7.5 Determine % dry weight.


B
Was sample preserved in the field?
Yes
No
7.4.3 Weigh vial, add surrogates, mix by shaking.
7.4 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.4.2 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.4.4 Transfer 1-2 mL of solvent to a GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight, if needed.
Calculate final results.

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT E

**Prohibition Zone Institutional Control**
**Restrictions on Groundwater Use**

Pursuant to MCL 324.20121(8) and the Fourth Amended and Restated Consent Judgment, entered in *Attorney General v Gelman Sciences, Inc.,* Washtenaw County Circuit Court Case No. 88-34734-CE, the following land and resource use restrictions shall apply to the "Prohibition Zone" depicted on the map attached hereto:

a. The installation by any person of a new water supply well in the Prohibition Zone for drinking, irrigation, commercial, or industrial use is prohibited.

b. The Washtenaw County Health Officer or any other entity authorized to issue well construction permits shall not issue a well construction permit for any well in the Prohibition Zone.

c. The consumption or use by any person of groundwater from the Prohibition Zone is prohibited.

d. The prohibitions listed in Subsections a–c, above, do not apply to the installation and use of:

i. Groundwater extraction and monitoring wells as part of Response Activities approved by EGLE or otherwise authorized under Parts 201 or 213 of the Natural Resources and Environmental Protection Act ("NREPA"), or other legal authority;

ii. Dewatering wells for lawful construction or maintenance activities, provided that appropriate measures are taken to prevent unacceptable human or environmental exposures to hazardous substances and comply with MCL 324.20107a;

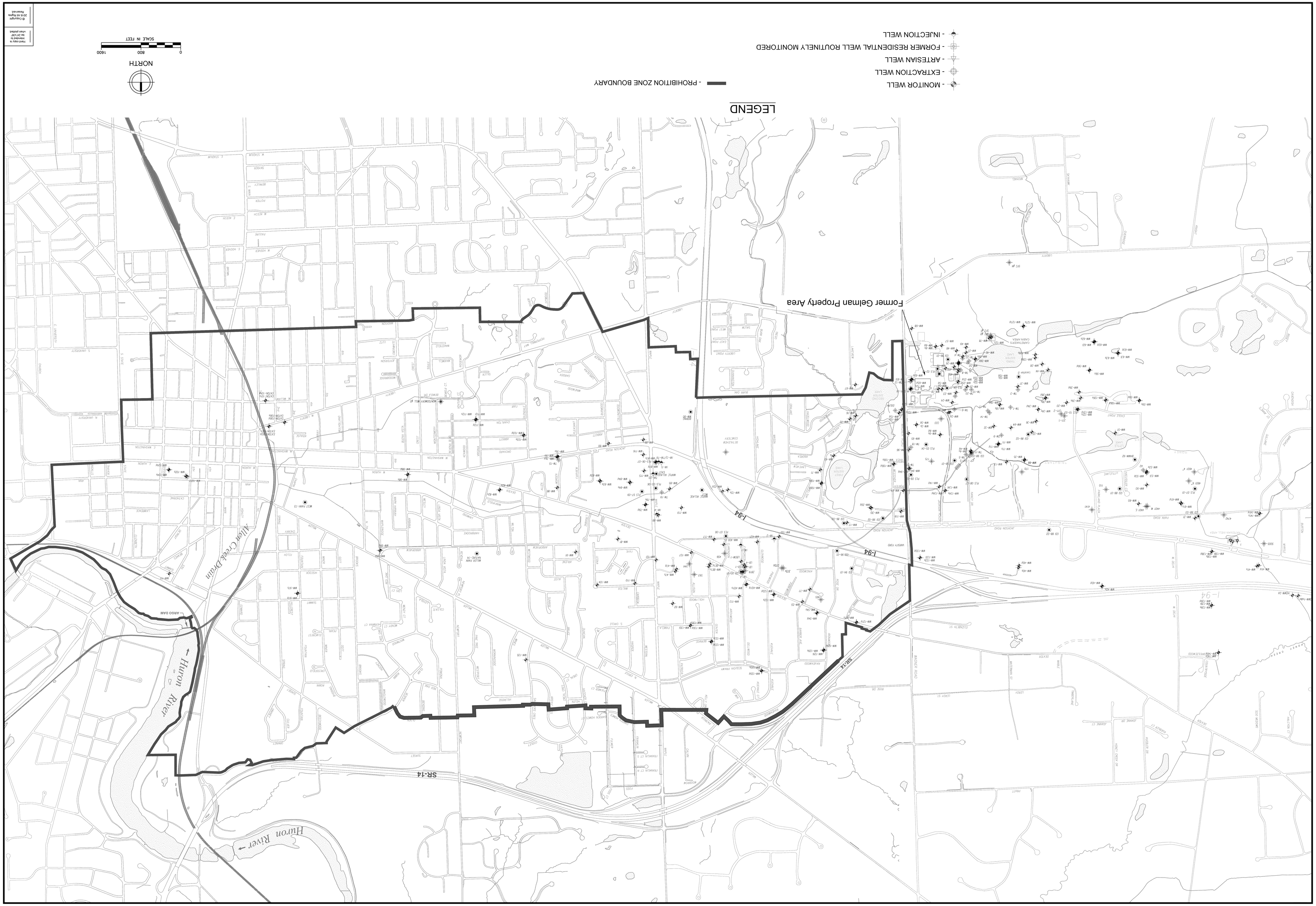
iii. Wells supplying heat pump systems that either operate in a closed loop system or if not, are demonstrated to operate in a manner sufficient to prevent unacceptable human or environmental exposures to hazardous substances and comply with

MCL 324.20107a;

iv. Emergency measures necessary to protect public health, safety, welfare or the environment;

v. Any existing water supply well that has been demonstrated, on a case-by-case basis and with the written approval of EGLE, to draw water from a formation that is not likely to become contaminated with 1,4-dioxane emanating from the Gelman Property. Such wells shall be monitored for 1,4-dioxane by Defendant at a frequency determined by EGLE; and

vi. The City of Ann Arbor's Northwest Supply Well, provided that the City of Ann Arbor operates the Northwest Supply Well in a manner that does not prevent its municipal water supply system from complying with all applicable state and federal laws and regulations.




GELMAN SCIENCES
Scio Twp., Washtenaw County, Michigan
FOURTH AMENDED CONSENT JUDGEMENT

FLEIS&VANDENBRINK
DESIGN. BUILD. OPERATE.

| | |
|---|---|
| PROJECT MGR. | DATE 05/01/20 |
| DRAWN BY | DATE 05/01/20 |
| GEOLOGIST | DATE 05/01/20 |
| CAD FILE | |
| EDIT | |
| SCALE | |
| DRAWING | |

PROJECT 806500

SHEET NO.

© Copyright 2016 All Rights Reserved

Hard copy is intended to be 24"x36" when printed

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT F

On _____, 20__, the Washtenaw County Circuit Court (Court) entered the Fourth Amended and Restated Amendment to Consent Judgment (4th Amended CJ) in the matter of State of Michigan v Gelman Sciences Inc., case number 88-34734-CE (Hon. Timothy P. Connors). The 4th Amended CJ, among other things, provides for an expansion of the area covered by the "Prohibition Zone" previously established by the Third Amendment to Consent Judgment in connection with the groundwater cleanup project being undertaken by Gelman Sciences, Inc., ("Gelman"). The 4th Amended CJ, with limited exceptions, continues to prohibit the consumption or use of groundwater within the "Prohibition Zone" depicted on the map set forth below. The restrictions on groundwater use with in the Prohibition Zone and the map depicting the Prohibition Zone are also set forth at [LINK]. Gelman will provide, at its expense, connection to the City of Ann Arbor municipal water supply to replace any private drinking water wells within the newly established boundaries of the Prohibition Zone that must be abandoned. Such well abandonment and replacement will be performed in accordance with all applicable regulations and procedures at the expense of Gelman. Any private property owner within the Prohibition Zone that is aware of the existence of a water supply well on her or his property should contact Dan Hamel using the contact information listed below to arrange for well abandonment and if applicable, replacement, as provided in the 4th Amended CJ.

Dan Hamel
Project Coordinator
Michigan Department
of Environment, Great
Lakes, and Energy,
Remediation and Redevelopment
Division
301 East Louis Glick Highway
Jackson, MI 49201-1556
517-745-6595
HamelD@michigan.gov

You may contact Gelman at:

Lawrence Gelb
Project Coordinator
Gelman Sciences, Inc.
642 S. Wagner Road
Ann Arbor, MI 48106

**Prohibition Zone Institutional Control**
**Restrictions on Groundwater Use**

Pursuant to MCL 324.20121(8) and the Fourth Amended and Restated Consent Judgment, entered in *Attorney General v Gelman Sciences, Inc.,* Washtenaw County Circuit Court Case No. 88-34734-CE, the following land and resource use restrictions shall apply to the "Prohibition Zone" depicted on the map below:

a. The installation by any person of a new water supply well in the Prohibition Zone for drinking, irrigation, commercial, or industrial use is prohibited.

b. The Washtenaw County Health Officer or any other entity authorized to issue well construction permits shall not issue a well construction permit for any well in the Prohibition Zone.

c. The consumption or use by any person of groundwater from the Prohibition Zone is prohibited.

d. The prohibitions listed in Subsections a–c, above, do not apply to the installation and use of:

    i. Groundwater extraction and monitoring wells as part of Response Activities approved by EGLE or otherwise authorized under Parts 201 or 213 of the Natural Resources and Environmental Protection Act ("NREPA"), or other legal authority;

    ii. Dewatering wells for lawful construction or maintenance activities, provided that appropriate measures are taken to prevent unacceptable human or environmental exposures to hazardous substances and comply with MCL 324.20107a;

    iii. Wells supplying heat pump systems that either operate in a closed loop system or if not, are demonstrated to operate in a manner sufficient to prevent unacceptable human or environmental exposures to hazardous substances and comply with MCL 324.20107a;

    iv. Emergency measures necessary to protect public health, safety, welfare or the environment;

    v. Any existing water supply well that has been demonstrated, on a case-by-case basis and with the written approval of EGLE, to draw water from a formation that is not likely to become contaminated with 1,4-dioxane emanating from the Gelman Property. Such wells shall be monitored for 1,4-dioxane by Defendant at a frequency determined by EGLE; and

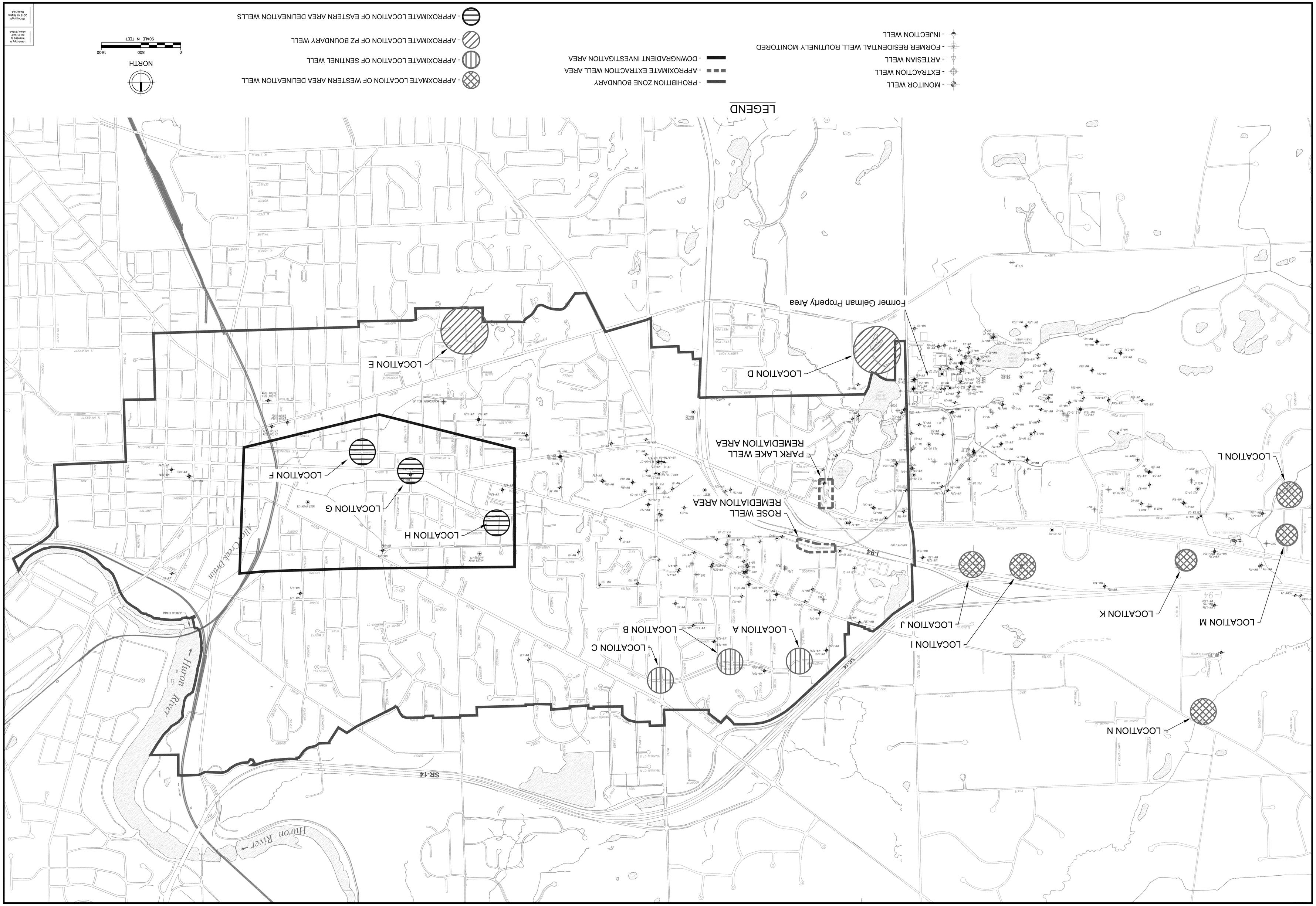
    vi. The City of Ann Arbor's Northwest Supply Well, provided that the City of Ann Arbor operates the Northwest Supply Well in a manner that does not prevent its municipal water supply system from complying with all applicable state and federal laws and regulations.

[Insert Prohibition Zone Map]

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT G




GELMAN SCIENCES
Scio Twp., Washtenaw County, Michigan
FOURTH AMENDED CONSENT JUDGEMENT - ATTACHMENT G

FLEIS&VANDENBRINK
DESIGN. BUILD. OPERATE.

| PROJECT MGR. | DATE | DRAWN BY | DATE | GEOLOGIST | DATE | CAD FILE | EDIT | SCALE | DRAWING |
|---|---|---|---|---|---|---|---|---|---|
| | 05/01/20 | | 05/01/20 | | 05/01/20 | | | | |

PROJECT 806500
SHEET NO.

© Copyright 2016 All Rights Reserved
Hard copy is intended to be 24"x36" when printed

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT H

# OPTIONS ARRAY

Pursuant to Section V.A.10 of the Consent Judgment, as amended, Gelman is submitting this Options Array, which sets forth various options for addressing the potential, if unlikely, risks that:

1. Gelman requires more extraction/treatment capacity to maintain compliance with the Eastern Area objectives than the 200 gpm provided by the current infrastructure; and

2. The northern portion of the deep transmission line fails.[1]

Gelman believes that each of the options discussed below is "implementable" within the identified limitations and subject to obtaining the necessary approvals and/or Court-ordered access. Obviously, the necessary approvals and access rights can only be sought if and when there is an actual set of circumstances that gives rise to the need for such approvals/access. Gelman reserves the right to identify additional alternatives if and when such a specific situation arises.

## SCENARIO 1 MORE THAN THE CURRENTLY AVAILABLE 200 GALLONS PER MINUTE IS NEEDED TO MEET EASTERN AREA OBJECTIVES

The deep transmission line currently allows Gelman to convey up to 200 gallons per minute (gpm) from the Evergreen Subdivision and Maple Road areas back to the Wagner Road facility for treatment and then disposal via Gelman's permitted surface water discharge. The following alternatives are options for addressing the possibility that Gelman will need to extract more than a total of 200 gpm to meet its Eastern Area cleanup objectives, excluding groundwater extracted from the proposed Parklake Well.

### Alternative A: Treatment and Groundwater Injection in Maple Road or Alternative Area

Description. Gelman could utilize a mobile treatment unit similar to that previously used in the Maple Village area along with injection wells to treat and dispose of water. This process was employed previously in the Evergreen and Maple Village areas.

Limitations: This option will take time to implement. Injection locations will need to be identified and necessary permits obtained, infrastructure would need to be installed and, if the existing mobile treatment unit was still in use in connection with the Parklake Well, an additional unit would need to be constructed.

### Alternative B: Treatment and Discharge to Ann Arbor Sanitary Sewer System

[1] Gelman already has in place a redundant near-surface pipeline that could replace the capacity of the Southern transmission line (the portion that begins at the Porter Lot) in the event that part of the transmission line fails.

Description: Discharge of treated water into the sanitary sewer is a possible method of handling additional water beyond the 200 gpm capacity of the deep transmission line. This alternative would involve treatment of the groundwater by a mobile unit and then disposal of the treated groundwater into the City's sanitary sewer. The location of the sewer connection would depend on where the groundwater was extracted and the availability of the necessary City infrastructure.

Limitations: This disposal method would have to be authorized by the City of Ann Arbor. The City Council has previously adopted a resolution that would require Gelman to treat the groundwater to below 3 ppb of 1,4-dioxane before discharging to the sanitary sewer. A mobile unit would utilize ozone to treat 1,4-dioxane contaminated groundwater, which would generate low levels of bromate as a bi-product, particularly if required to treat to such a low level for 1,4-dioxane. Gelman cannot predict how the City would react to a request for such a discharge. In addition, when this discharge option was evaluated in connection with the Unit E Feasibility Analysis, the City informed Gelman that there was insufficient capacity in the sewer system for the high volume of water that would be needed to address that plume. The City would need to confirm what, if any, capacity would exist for this alternative to be feasible. Moreover, costs for this alternative are expected to be high because of the need to operate a mobile treatment system and the cost of sewer fees. This alternative will likely not be implementable due to likely treatment requirements and/or capacity limitations except for low flow and/or temporary situations.

**Alternative C Treatment and Discharge to Ann Arbor Storm Sewer**

Description: Discharge of treated water into the City's storm sewer is also a possible alternative. This alternative would involve treatment of the groundwater by a mobile treatment unit and then disposal of the treated groundwater into the City's storm sewer. The location of the sewer connection and discharge point would depend on where the groundwater was extracted and the availability of the necessary City infrastructure.

Limitations: The storm sewer system has well-documented capacity limitations. This alternative would require approval from the City of Ann Arbor, the Washtenaw County Drain Commissioner and the State of Michigan, and the installation of the necessary infrastructure to connect to the system. It is likely that this alternative would require flow (discharge) into the storm to be temporally suspended during times when the storm sewer is at or near capacity, such as during storm events. Given the capacity concerns and the governmental approvals that would be needed, this alternative may only be implementable in low flow and/or temporary situations.

**Alternative D New Pipeline from Maple Road or Evergreen Area - Treatment at Wagner Road Facility**

Description: A new, near-surface, pipeline could be installed to connect the Evergreen Subdivision or Maple Road areas to the Wagner Road facility for treatment. Approximately 600 gpm of treatment capacity would be available to treat water from the Eastern Area (not including groundwater from the Parklake area). It is anticipated that this treatment capacity would be sufficient to accommodate any foreseeable necessary flow from these areas and the pipeline could be sized appropriately. A feasibility study would need to be conducted to determine the best route for the line.

Limitations: This option may be cost effective if additional capacity needs are relatively high (greater than 100 gpm) and the need for the capacity is long term. This option would require right-of-way access from the City and potentially, Scio Township and MDOT or court-ordered access. This option would require significant construction time before it could be implemented.

**Future Alternatives**

Gelman reserves the right to identify additional alternatives if and when a specific situation requiring capacity beyond that provided by the current infrastructure arises.

## SCENARIO 2 NORTH HORIZONTAL TRANSMISSION PIPELINE FAILS

The northern portion of the deep horizontal transmission line is a HDPE pipeline that Gelman inserted into the original northern horizontal well after the original steel transmission pipeline failed in 2008. Gelman has supplied documentation of the HDPE pipeline's 50 year life expectancy. To supplement this information, Gelman has identified the following alternatives, which are options for addressing the possibility that the pipeline fails despite its expected reliability.

### Alternative A: Treatment and Groundwater Injection in Maple Road or Alternative Area

Description. Gelman could utilize a mobile treatment unit similar to that previously used in the Maple Village area along with injection wells to treat and dispose of water. This process was employed previously in the Evergreen and Maple Village areas.

Limitations: This option will take time to implement. Injection locations will need to be identified and necessary permits obtained, and infrastructure would need to be installed.

### Alternative B: Treatment and Discharge to Ann Arbor Sanitary Sewer System

Description: Discharge of treated water into the sanitary sewer is a possible method of handling additional water beyond the 200 gpm capacity of the deep transmission line. This alternative would involve treatment of the groundwater by a mobile unit and then disposal of the treated groundwater into the City's sanitary sewer. The location of the sewer connection would depend on where the groundwater was extracted and the availability of the necessary City infrastructure.

Limitations: This disposal method would have to be authorized by the City of Ann Arbor. The City Council has previously adopted a resolution that would require Gelman to treat the groundwater to below 3 ppb of 1,4-dioxane before discharging to the sanitary sewer. A mobile unit would utilize ozone to treat 1,4-dioxane contaminated groundwater, which would generate low levels of bromate as a bi-product, particularly if required to treat to such a low level for 1,4-dioxane. Gelman cannot predict how the City would react to a request for such a discharge. In addition, when this discharge option was evaluated in connection with the Unit E Feasibility Analysis, the City informed Gelman that there was insufficient capacity in the sewer

system for the high volume of water that would be needed to address that plume. The City would need to confirm what, if any, capacity would exist for this alternative to be feasible. Moreover, costs for this alternative are expected to be high because of the need to operate the mobile treatment system and the cost of sewer fees. This alternative will likely not be implementable due to likely treatment requirements and/or capacity limitations except for low flow and/or temporary situations.

**Alternative C Treatment and Discharge to Ann Arbor Storm Sewer**

Description: Discharge of treated water into the City's storm sewer is also a possible alternative. This alternative would involve treatment of the groundwater by a mobile treatment unit and then disposal of the treated groundwater into the City's storm sewer. The location of the sewer connection and discharge point would depend on where the groundwater was extracted and the availability of the necessary City infrastructure.

Limitations: The storm sewer system has well-documented capacity limitations. This alternative would require approval from the City of Ann Arbor, the Washtenaw County Drain Commissioner and the State of Michigan, and the installation of the necessary infrastructure to connect to the system. It is likely that this alternative would require flow (discharge) into the storm to be temporally suspended during times when the storm sewer is at or near capacity, such as during storm events. Given the capacity concerns and the governmental approvals that would be needed, this alternative may only be implementable in low flow and/or temporary situations.

**Alternative D New Pipeline from Maple Road or Evergreen Area - Treatment at Wagner Road Facility**

Description: A new, near-surface, pipeline could be installed to connect the Evergreen Subdivision or Maple Road areas to the Wagner Road facility for treatment. Approximately 600 gpm of treatment capacity would be available to treat water from the Eastern Area (not including groundwater from the Parklake area). It is anticipated that this treatment capacity would be sufficient to accommodate any foreseeable necessary flow from these areas and the pipeline could be sized appropriately. A feasibility study would need to be conducted to determine the best route for the line.

Limitations: This option may be cost effective if additional capacity needs are relatively high (greater than 100 gpm) and the need for the capacity is long term. This option would require right-of-way access from the City and potentially, Scio Township and MDOT or court-ordered access. This option would require significant construction time before it could be implemented.

**Future Alternatives**

As noted above, Gelman reserves the right to identify additional alternatives if and when a specific situation affecting the availability of the transmission line arises. For example, when the original transmission line failed, the parties determined that it was leaking in an already contaminated portion of the aquifer and agreed that it could continue to operate while repairs were made, with appropriate monitoring. Similar fact-specific alternatives will likely be identified if and when such a contingency arises.

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT I



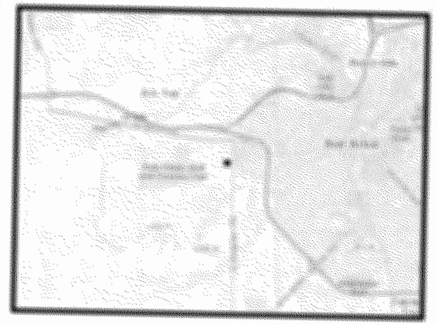

**Attachment I**: Target Treatment Areas
Gelman Sciences
Washtenaw County
Michigan

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

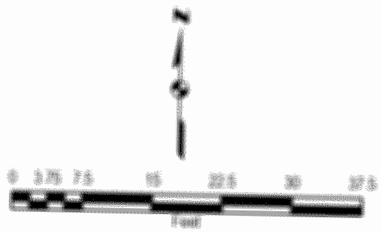
# ATTACHMENT J



**Legend**

- Gelman Property Boundary
- Heated Soil Vapor Extraction
- Capped Area




**Attachment J:** Former Burn Pit Target Treatment Area
Gelman Sciences
Washtenaw County
Michigan

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT K



**BNP PARIBAS**
**CORPORATE & INVESTMENT BANKING**

BNP PARIBAS
TRADE FINANCE OPERATIONS
787 SEVENTH AVENUE
NEW YORK, NY 10019

AUGUST 5, 2014

APPLICANT:
GELMAN SCIENCES INC
600 WAGNER ROAD
ANN ARBOR, MI 48103-9002 USA

BENEFICIARY:
CHIEF, REMEDIATION DIVISION, MICHIGAN DEPARTMENT
OF NATURAL RESOURCES AND ENVIRONMENT, PO BOX
30426, LANSING, MICHIGAN 48909-7926, FEDERAL TAX
IDENTIFICATION NO. 38-6000134 (STATE OF MICHIGAN)
PO BOX 30426, LANSING
MICHIGAN 48909-7926, USA

WE HEREBY AMEND OUR IRREVOCABLE STANDBY LETTER OF CREDIT NO. 04126179
DATED DECEMBER 5, 2013, IN YOUR FAVOR AS FOLLOWS:

1) REPLACE BENEFICIARY NAME AND ADDRESS :
DELETE : BENEFICIARY:
CHIEF, REMEDIATION DIVISION, MICHIGAN DEPARTMENT
OF NATURAL RESOURCES AND ENVIRONMENT, PO BOX
30426, LANSING, MICHIGAN 48909-7926, FEDERAL TAX
IDENTIFICATION NO. 38-6000134 (STATE OF MICHIGAN)
PO BOX 30426, LANSING
MICHIGAN 48909-7926, USA
.
INSERT : BENEFICIARY:
CHIEF, REMEDIATION AND REDEVELOPMENT DIVISION, MICHIGAN
DEPARTMENT OF ENVIRONMENTAL QUALITY
P O BOX 30426
LANSING, MICHIGAN 48909-7926
FEDERAL TAX IDENTIFICATION NO. 38-6000134 (STATE OF MICHIGAN)
.
2) IN SUBJECT HEADING LINE THREE REPLACE SITE ID NUMBER:
DELETE : SITE ID NO. MID005341813
INSERT : SITE ID NO. 81000018
.
3) IN PARAGRAPH 1 REPLACE BENEFICIARY NAME:
DELETE : 'MICHIGAN DEPARTMENT OF NATURAL RESOURCES AND
ENVIRONMENT (DEPARTMENT) ON BEHALF OF GELMAN SCIENCES INC.'
INSERT: 'MICHIGAN DEPARTMENT OF ENVIRONMENTAL

QUALITY(DEPARTMENT)' ON BEHALF OF GELMAN SCIENCES INC.

.

4) IN PARAGRAPH 2 REPLACE SITE ID NUMBER :
DELETE : MID00534818138
INSERT : 81000018

.

5) REPLACE PARAGRAPH 3 :
DELETE : THE LOC SHALL BE AUTOMATICALLY EXTENDED ..... AS EVIDENCED BY THE RETURN CERTIFIED MAIL RECEIPTS.

.

INSERT : THIS LOC IS EFFECTIVE AS OF DECEMBER 5, 2013, AND SHALL EXPIRE ON DECEMBER 5, 2014, BUT SUCH LOC SHALL BE AUTOMATICALLY EXTENDED FOR A PERIOD OF ONE YEAR EACH AND EVERY SUBSEQUENT YEAR UNLESS, NOT LESS THAN ONE HUNDRED AND TWENTY (120) DAYS BEFORE THE EXTENDED EXPIRATION DATE, WE NOTIFY THE DESIGNATED PARTY AND THE DEPARTMENT AUTHORIZED REPRESENTATIVE AS INDICATED ABOVE. WE AGREE THAT THE ONE HUNDRED AND TWENTY (120) DAY PERIOD SHALL BEGIN ON THE DATE WHEN BOTH THE DESIGNATED PARTY AND THE DEPARTMENT AUTHORIZED REPRESENTATIVE HAVE RECEIVED THE NOTICE, AS EVIDENCED BY THE RETURN CERTIFIED MAIL RECEIPTS.

.

6) IN PARAGRAPH 6 READ THE WORD 'UTOMATICALLY' AS ''AUTOMATICALLY''

.

ALL OTHER TERMS AND CONDITIONS REMAIN UNCHANGED.

PLEASE SIGN BELOW TO SIGNIFY YOUR ACCEPTANCE TO THIS AMENDMENT AND FAX RETURN IT TO US TO ATTN: TRADE FINANCE SERVICES AT FAX NO.: (201) 616-7913.

AMENDMENT ACCEPTED:

_____
AUTHORIZED SIGNATURE

CERTAIN ADMINISTRATIVE SERVICES FOR BNP PARIBAS MAY BE PROVIDED BY BNP PARIBAS RCC, INC., BNP PARIBAS, THROUGH ITS CANADA BRANCH, OR ANY DIRECT OR INDIRECT MAJORITY OWNED SUBSIDIARY OF BNP PARIBAS.

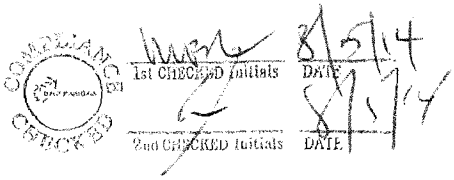
BNP PARIBAS
BY: BNP PARIBAS RCC, INC., AS AUTHORIZED AGENT

AUTHORIZED SIGNATURE

AUTHORIZED SIGNATURE

---------- Instance Type and Transmission ----------
Copy received from SWIFT
Priority : Normal
Message Output Reference : 1100 140801BNPAUS3NCXXX0109389933
Correspondent Input Reference : 1600 140801BNPAGB22CXXX5823667961
---------- Message Header ----------
Swift Output : FIN 767 Guar/Stdby Letter Cred Amendnt
Sender : BNPAGB22XXX
BNP PARIBAS LONDON BRANCH
LONDON GB
Receiver : BNPAUS3NXXX
BNP PARIBAS USA- NEW YORK
NEW YORK US
MUR : 1919F8213A730000
---------- Message Text ----------
27: Sequence of Total
1/1
20: Transaction Reference Number
LAD/GTEE/13/1030
21: Related Reference
04126179
23: Further Identification
REQUEST
30: Date
140801
26E: Number of Amendment
1
31C: Date of Issue / Request to Issue
131204
77C: Amendment Details
APPLICANT. GELMAN SCIENCES INC
BENEFICIARY. CHIEF, REMEDIATION DIVISION, MICHIGAN DEPARTMENT OF NATURAL RESOURCES AND ENVIRONMENT
AMOUNT. USD28,431,846.00
.
KINDLY AMEND THE ABOVE-MENTIONED STANDBY LETTER OF CREDIT AS FOLLOWS:
.
1) REPLACE BENEFICIARY NAME AND ADDRESS :
DELETE : BENEFICIARY:
CHIEF, REMEDIATION DIVISION, MICHIGAN DEPARTMENT
OF NATURAL RESOURCES AND ENVIRONMENT, PO BOX
30426, LANSING, MICHIGAN 48909-7926, FEDERAL TAX
IDENTIFICATION NO. 38-6000134 (STATE OF MICHIGAN)
PO BOX 30426, LANSING
MICHIGAN 48909-7926, USA
.
INSERT : BENEFICIARY:
CHIEF, REMEDIATION AND REDEVELOPMENT DIVISION, MICHIGAN
DEPARTMENT OF ENVIRONMENTAL QUALITY
P O BOX 30426
LANSING, MICHIGAN 48909-7926
FEDERAL TAX IDENTIFICATION NO. 38-6000134 (STATE OF MICHIGAN)
.
2) IN SUBJECT HEADING LINE THREE REPLACE SITE ID NUMBER :
DELETE : SITE ID NO. MID005341813
INSERT : SITE ID NO. 81000018

ORIGINAL
SWIFT MESSAGE



.
3) IN PARAGRAPH 1 REPLACE BENEFICIARY NAME:
DELETE : 'MICHIGAN DEPARTMENT OF NATURAL RESOURCES AND ENVIRONMENT (DEPARTMENT) ON BEHALF OF GELMAN SCIENCES INC.'
INSERT: 'MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY(DEPARTMENT)' ON BEHALF OF GELMAN SCIENCES INC.
.
4) IN PARAGRAPH 2 REPLACE SITE ID NUMBER :
DELETE : MID00534818138
INSERT : 81000018
.
5) REPLACE PARAGRAPH 3 :
DELETE : THE LOC SHALL BE AUTOMATICALLY EXTENDED ..... AS EVIDENCED BY THE RETURN CERTIFIED MAIL RECEIPTS.
.
INSERT : THIS LOC IS EFFECTIVE AS OF DECEMBER 5, 2013, AND SHALL EXPIRE ON DECEMBER 5, 2014, BUT SUCH LOC SHALL BE AUTOMATICALLY EXTENDED FOR A PERIOD OF ONE YEAR EACH AND EVERY SUBSEQUENT YEAR UNLESS, NOT LESS THAN ONE HUNDRED AND TWENTY (120) DAYS BEFORE THE EXTENDED EXPIRATION DATE, WE NOTIFY THE DESIGNATED PARTY AND THE DEPARTMENT AUTHORIZED REPRESENTATIVE AS INDICATED ABOVE. WE AGREE THAT THE ONE HUNDRED AND TWENTY (120) DAY PERIOD SHALL BEGIN ON THE DATE WHEN BOTH THE DESIGNATED PARTY AND THE DEPARTMENT AUTHORIZED REPRESENTATIVE HAVE RECEIVED THE NOTICE, AS EVIDENCED BY THE RETURN CERTIFIED MAIL RECEIPTS.
.
6) IN PARAGRAPH 6 READ THE WORD 'UTOMATICALLY' AS ''AUTOMATICALLY''
.
ALL OTHER TERMS AND CONDITIONS REMAIN UNCHANGED.
.
KINDLY DELIVER THE ORIGINAL AMENDMENT BY COURIER TO :
.
PALL CORPORATION
25 HARBOR PARK DRIVE
PORT WASHINGTON
NY 11050
USA
ATTN. JOHN GRUBER, TREASURY DIRECTOR
PHONE. +15168019494
.
PLEASE FORWARD A COPY OF THE AMENDMENT TO BNP PARIBAS,
10 HAREWEOOD AVENUE, LONDON NW1 6AA, ATTN.LOANS ADMIN/GUARANTEES

ORIGINAL SWIFT MESSAGE

---------- Message Trailer ----------
{CHK:7178F9C913A8}

ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

# ATTACHMENT L

## FINANCIAL TEST AND FINANCIAL TEST/CORPORATE GUARANTEE PART 201

**Prior to use contact Mr. Brad Ermisch, Compliance and Enforcement Section, Remediation and Redevelopment Division (RRD), at ermischb@michigan.gov or 517-275-1173 for any questions relating to this document or the attached model document; or you may call the RRD main number at 517-284-5087 for assistance.

This document provides instructions on the use of the Financial Test (FT) or Financial Test/Corporate Guarantee (FT/CG) to fulfill the requirements for financial assurance pursuant to Section 20114d(4)(b) of Part 201, Environmental Remediation, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (NREPA), MCL 324.20101 *et seq*. This document and attached model documents are provided to the public as preliminary guidance as to the content, format, and terms of the Financial Assurance Mechanism and are not intended, nor can they be relied upon to create any substantive or procedural rights by any other party.

Pursuant to Section 20114d of the NREPA, upon completion of remedial actions that satisfy the requirements of Part 201, a person may submit a No Further Action Report (NFA Report) to the Michigan Department of Environment, Great Lakes, and Energy (EGLE). If a postclosure agreement (Agreement) is required as part of the NFA Report, Section 20114d(4)(b) requires financial assurance to pay for monitoring, operation and maintenance, oversight, and other costs determined by EGLE to be necessary to assure the effectiveness and integrity of the remedial action unless the financial assurance is de minimis. The de minimis threshold is $2,500 per year in 2001 dollars. A link to a Consumer Price Index Inflation Calculator is provided to determine if the current annual costs exceed the 2001 dollar value: CPI Inflation Calculator. Section 20101(u) of the NREPA, defines financial assurance as a performance bond, escrow, cash, certificate of deposit, irrevocable letter of credit, corporate guarantee, or other equivalent security, or combination thereof. EGLE has determined that the FT and the FT/CG are acceptable FAMs. The FT allows for the financial strength of a company to be used as a FAM. If a company cannot meet the requirements for the FT and is a subsidiary, it may rely on its parent company's financial strength to meet the FT requirements; however, the parent company must agree to assume responsibility for the FAM on behalf of its subsidiary.

If a person elects to use the FT to meet its financial assurance obligations (Designated Party), the Designated Party must meet the following requirements:

1. Pass the Standard Financial Test using either Alternative I or II (See Appendix A).

2. Provide a letter signed by the Designated Party's chief financial officer (CFO) that is worded in accordance with the language in Appendix B and include the documents referenced therein.

If a person elects to use the FT/CG, the parent company must:

1. Pass the Standard Financial Test using either Alternative I or II (See Appendix A).

2 Provide a letter signed by the CFO of the parent company that is worded in accordance with the language provided in Appendix B and include the documents referenced therein.

3. Submit a Corporate Guarantee in accordance with Appendix D.

Drafting Instructions: Copy and paste the text portion of the model documents onto appropriate letterhead. Drafting notes and examples appear as ***italicized bold font***, insertion directions appear as **[*italicized bold font within bold brackets*]**, and word choices appear as **[regular bold font within bold brackets]**.

--END OF GUIDANCE AND INSTRUCTIONS--

***Appendix A***
***STANDARD FINANANCIAL TEST MODEL***

## STANDARD FINANCIAL TEST

The figures for the following items marked with an (*) are to be identified as to the source of the information for the company. The preferred source is the independently audited year-end financial statements from the latest fiscal year. Also create a header for this document identifying the purpose and parties represented by the standard financial test. And this test must be renewed thirty days following the close and publication of financial information or an alternative financial assurance document is to be provided to EGLE.

### ALTERNATIVE I

1. Sum of the current cost estimates for response activities needed at Michigan facilities, including the cost for operation and maintenance of remedial actions for the next 30-year time period. $_____

2. Sum of the current cost estimates for response activities needed at non-Michigan facilities, including the cost for operation and maintenance of remedial actions. $_____

3. Sum of lines 1 and 2. $_____

*4. Total liabilities [if any portion of the cost estimates for response activities (lines 1 or 2) is included in total liabilities, you may deduct that amount from this line and add that amount to lines 5 and 6]. $_____

*5. Tangible net worth. $_____

*6. Net worth. $_____

*7. Current assets. $_____

*8. Current liabilities. $_____

9. Net working capital [line 7 minus line 8]. $_____

*10. The sum of net income plus depreciation, depletion and amortization. $_____

*11. Total assets in the United States. $_____

*12. Total assets in Michigan, excluding the value of all real property on which response activities are necessary. $_____

*13. Total assets in Michigan, including the value of all real property on which response activities are necessary. $_____

| | YES | NO |
|---|---|---|
| 14. Is line 5 at least $10 million? | ___ | ___ |
| 15. Is line 5 at least 6 times line 3? | ___ | ___ |
| 16. Is line 9 at least 6 times line 3? | ___ | ___ |
| *17. Are at least 90% of the company's assets located in the United States? If not, complete line 18. | ___ | ___ |
| 18. Is line 11 at least 6 times line 3? | ___ | ___ |
| 19. Is line 4 divided by line 6 less than 2.0? | ___ | ___ |
| 20. Is line 10 divided by line 4 greater than 0.1? | ___ | ___ |
| 21. Is line 7 divided by line 8 greater than 1.5? | ___ | ___ |
| *22. Is line 12 at least $50 million? | ___ | ___ |
| 23. Is line 13 at least 6 times line 1? | ___ | ___ |

To “pass” Alternative I of the standard financial test, the company must meet two out of three of the ratios listed in lines 19, 20, and 21; meet the criterion of either line 17 or line 18; meet the criteria listed in lines 14, 15, and 16; and meet the criterion of either line 22 or 23.

## ALTERNATIVE II

1. Sum of the current cost estimates for response activities needed at Michigan facilities, including the cost for operation and maintenance of remedial actions for the next 30-year time period. $_____

2. Sum of the current cost estimates for response activities needed at non-Michigan facilities, including the cost for operation and maintenance of remedial actions. $_____

3. Sum of lines 1 and 2. $_____

4. Current bond rating of most recent issuance for this company and name of rating service. _____

5. Date of issuance of bond. _____

6. Date of maturity of bond. _____

*7. Tangible net worth (if any portion of the cost estimates for response activities (lines 1 and 2) is included in "total liabilities" on your financial statements, you may add that portion to this line). $_____

*8. Total assets in the United States. $_____

*9. Total assets in Michigan, excluding the value of all real property on which response activities are necessary. $_____

*10. Total assets in Michigan, including the value of all real property on which response activities are necessary. $_____

| | YES | NO |
|---|---|---|
| 11. Is line 7 at least $10 million? | ___ | ___ |
| 12. Is line 7 at least 6 times line 3? | ___ | ___ |
| *13. Are at least 90% of company's assets located in the United States? If not, complete line 14. | ___ | ___ |
| 14. Is line 8 at least 6 times line 3? | ___ | ___ |
| *15. Is line 9 at least $50 million? | ___ | ___ |
| 16. Is line 10 at least 6 times line 1? | ___ | ___ |

To "pass" Alternative II of the standard financial test, the company must have a current rating for the most recent bond issuance of AAA, AA, A, or BBB for Standard and Poor's or Aaa, Aa, A, or Baa for Moody's; meet the criterion of either line 13 or line 14; meet the criteria listed in lines 11 and 12; and meet the criterion of either line 15 or 16.

**[*Insert the following at the end of the Standard Financial Test that you chose to use*]**

I hereby certify that the wording of this form is a true copy of the model financial test provided by the Michigan Department of Environment, Great Lakes, and Energy (EGLE), with the exception of any changes made and agreed to by representatives of EGLE and **[*insert name of company*]**.

_____
Chief Financial Officer

_____
Name of Company

Date: _____

Signed and sealed
in the presence of:

_____
NOTARY PUBLIC

Notary Public _____ County
My Commission Expires _____

## *Appendix B*
## *LETTER FROM CHIEF FINANCIAL OFFICER*
## *FOR FINANCIAL TEST or FINANCIAL TEST/CORPORATE GUARANTEE MODEL*

**[*Insert name of Remediation and Redevelopment Division (RRD) Director*]**, Director
Remediation and Redevelopment Division
Michigan Department of Environment, Great Lakes, and Energy
P.O. Box 30426
Lansing, MI 48909-76115

Dear **[*Insert name of RRD Director*]**:

I am the chief financial officer of **[*insert name of company or name of parent company if Financial Test/Corporate Guarantee (FT/CG)*]**, **[*insert address*]**.

The **[*insert name of company or, for FT/CG, name of subsidiary*]** is liable under Part 201, Environmental Remediation, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (NREPA), for the **[*insert name of facility*]** located at **[*insert address of facility*]** that is the subject of a postclosure agreement submitted as part of a no further action report to the Michigan Department of Environment, Great Lakes, and Energy (EGLE) on **[*insert date of no further action report*]**. Pursuant to the postclosure agreement, **[*insert name of company*]** has agreed to **[*briefly describe response activities required by the Order/Decree/Agreement and any other obligations as necessary*]** at the **[*insert name of facility*]**.

In order for EGLE to approve implementation of these response activities, EGLE requires that **[*insert name of company*]** provide financial assurance to assure performance of the necessary and appropriate response activities to protect public health, safety, and welfare, and to assure the effectiveness and integrity of the remedial action at the facility.

***For a company that is providing its own financial test, insert the following paragraph***

This letter is in support of **[*insert name of company*]**'s use of the financial test to satisfy the financial assurance requirements of Part 201 for the **[*insert name of facility*]**.

***For a parent company that is providing a FT/CG for its subsidiary, insert the following paragraph***

This company is the parent corporation of **[*insert name of subsidiary that is the beneficiary of the FT/CG*]**. This letter is in support of **[*insert name of parent company*]**'s use of the financial test and financial test/corporate guarantee to satisfy the financial assurance requirements of Part 201 for the **[*insert name of facility*]**.

This company has prepared a Standard Financial Test-Alternative **[*insert as appropriate:* I *or* II]** (SFT) using EGLE model SFT and has passed that test as shown in the attached SFT document. The estimated annual cost of response activities to be performed at this facility as reflected in the SFT is **[*insert estimated annual cost amount*]**.

With this letter, I also am submitting the following items to demonstrate to EGLE that **[*insert name of company*]** meets the requirements for using the **[*Insert as appropriate:* financial test *or* financial test and corporate guarantee]** as its financial assurance mechanism:

1. A copy of an independent certified public accountant's report for the latest fiscal year for **[*insert as appropriate: name of company or parent company*]**. The fiscal year of this firm ends on **[*insert date of end of company's fiscal year*]**.

   ***NOTE: Please provide a footnote explaining line items in the financial test that deviate from the amounts given in the audited year-end financial statements.***

   and

2. A letter from an independent certified public accountant certifying its review of this letter and this company's financial statements. ***See Appendix C***

This company **[*insert as appropriate:* is *or* is not]** required to file Form 10K with the Securities and Exchange Commission for the latest completed fiscal year which ended **[*insert date*]**.

I hereby certify that the wording of this letter is identical to the model letter provided by EGLE, with the exception of any changes that have been made with the concurrence of representatives of EGLE and **[*insert as appropriate: name of company or parent company*]**.

_____
Chief Financial Officer

_____
**[*Name of Company or Parent Company*]**

Date: _____

Attachments

Signed and sealed
in the presence of:

_____
NOTARY PUBLIC

Notary public _____ County
My commission expires: _____

## *Appendix C*
## *FINANCIAL TEST or FINANCIAL TEST/CORPORATE GUARANTEE*
## *REPORT OF THE INDEPENDENT CERTIFIED PUBLIC ACCOUNTANT MODEL*

**[*Insert name of Chief Financial Officer* (CFO)]**
**[*Insert name and address of Company*]**

Dear **[*insert name of CFO*]**:

We have audited, in accordance with generally accepted auditing standards, the financial statements of **[*insert as appropriate: name of company or parent company*]** for its fiscal year ending **[*insert fiscal year end date*]** and have issued our report thereon dated **[*insert date*].**

We have not performed any auditing procedures since that date.

At your request, I have read your letter to the Michigan Department of Environment, Great Lakes, and Energy (EGLE) dated **[*insert date of letter to EGLE*]**, that provided a standard Financial Test and have compared the data in that letter, which are specified as having been derived from the **[*insert name of company*]**'s audited financial statements for its fiscal year ending **[*insert fiscal year end date*]**, to the **[*insert name of company*]**'s financial statements for its most recent fiscal year. In connection with that review, no matters came to my attention that caused me to believe that the specified data should be adjusted or corrected.

This letter is furnished solely for the use of **[*insert name of company*]** and EGLE and is not to be used for any other purpose.

_____
**[*Name and address of Accounting Firm*]**

## *Appendix D*
## *CORPORATE GUARANTEE MODEL*

## CORPORATE GUARANTEE

This Corporate Guarantee (Guarantee) is made this **[*insert date*]** to the State of Michigan by **[*insert name of Parent Company or other guaranteeing entity*]** (Guarantor), a business corporation organized under the laws of the State of **[*insert name of state*]**, **[*insert address*]**, on behalf of our subsidiary **[*insert name of subsidiary company*]**, **[*insert subsidiary business address*]**.

## RECITALS

Whereas, Guarantor is the parent corporation of **[*insert name of subsidiary company*]**, is a majority shareholder of **[*insert name of subsidiary company*]**, and will benefit from the operation and activities of **[*insert name of subsidiary company*]**.

Whereas, **[*insert name of subsidiary company*]** is liable pursuant to Part 201, Environmental Remediation, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (NREPA), MCL 324.20101 *et seq.* for the **[*insert name of Facility*]** facility (Facility) located at **[*insert street address, or township, county, and state]*** with Site ID No. **[*insert number*]** which is covered by this Guarantee.

Whereas Section 20114d of the NREPA states that upon completion of remedial actions that satisfy the requirements of Part 201, a person may submit a No Further Action Report (NFA Report) to the Michigan Department of Environment, Great Lakes, and Energy (EGLE).

Whereas Section 20114d(4)(b) requires financial assurance to pay for monitoring, operation and maintenance, oversight and other costs determined by EGLE to be necessary to assure the effectiveness and integrity of the remedial action if a postclosure agreement is required as part of the NFA Report.

Whereas **[*insert name of subsidiary company*]** is required to submit a postclosure agreement as part of their NFA Report.

Whereas Section 20101(u) of the NREPA, defines financial assurance as a performance bond, escrow, cash, certificate of deposit, irrevocable letter of credit, corporate guarantee, or other equivalent security, or combination thereof.

Whereas, EGLE has determined that the Financial Test/Corporate Guarantee (FT/CG) is an acceptable FAM.

Whereas, the Guarantor has met the Financial Test (FT) criteria and provided other financial information to EGLE (Attachment **[*xx*]**) ***NOTE: this attachment must contain the documents included in Appendices A, B, and C*** and EGLE has determined that **[*insert name of subsidiary company*]** may use this Guarantee to fulfill its financial obligations pursuant to Part 201 of the NREPA.

In consideration of the foregoing, it is hereby agreed by and between EGLE and the Guarantor that this Guarantee will provide the required financial assurance for the Facility described above.

## I. REPRESENTATIONS AND WARRANTIES OF GUARANTOR

Guarantor hereby represents and warrants as follows:

1.1 Corporate Authority

A. Guarantor is a corporation duly organized, validly existing and in good standing under the laws of the State of **[*insert name of state where* Guarantor *is incorporated*]**. Guarantor has the requisite corporate powers and authority to own its property and assets, to carry on its business as it is now conducting it, and to execute, deliver, and perform this Guarantee. Guarantor is duly qualified to do business in every jurisdiction, to which such qualification is necessary, including the State of Michigan.

B. The execution, delivery, and performance of this Guarantee and the consummation of the transactions herein contemplated have been duly authorized by all requisite corporate action on the part of the Guarantor and will not violate any provision of law, any order of any court or other agency of government, the articles of incorporation or bylaws of Guarantor, or any indenture, agreement or other instrument to which it is a party or by which it or any of its property is bound; and will not conflict with, result in a breach of, or constitute (with due notice and/or lapse of time) a default under any such indenture, agreement or other instrument.

## II. GUARANTOR'S BUSINESS COVENANTS

The Guarantor covenants that, during such time as this Guarantee is in effect, it will comply with the following:

2.1 Financial Records - Guarantor will:

A. Maintain a system of accounting, which is established and administered in accordance with generally accepted accounting principles;

B. Keep adequate records and books of account in which true, accurate, and complete entries are made and which reflect all transactions that are required to be reflected by such accounting principles; and

C. Keep accurate and complete records of any property owned by it.

2.2 Corporate Existence and Rights - Guarantor will perform or cause to be performed all things necessary to preserve and keep in full force and effect its existence, rights and franchises, provided that this covenant shall not apply so as to prevent the Guarantor from entering into any transaction whereby all or substantially all of its assets and liabilities (including its obligations in respect of this Guarantee) are acquired and assumed by another corporation, whether by, merger or otherwise, as long as such other successor corporation meets the FT criteria set forth in Section III and assumes the obligations of this Guarantee.

2.3 Compliance with Law - Guarantor will not violate any laws, ordinances or governmental rules and regulations to which it is subject and will not fail to obtain any licenses, permits, franchises or other governmental authorizations that are necessary to the ownership of its property or the conduct of its business, if such violation or failure to obtain might materially and adversely affect Guarantor's ability to perform its obligations under this Guarantee.

## III. INFORMATION AS TO GUARANTOR

Guarantor shall provide the following financial and business information to EGLE during the time period that this Guarantee is in effect.

3.1 Financial Information:

A. Except as otherwise provided by Paragraph 3.1.B., within 90 days after the close of each succeeding fiscal year that this Guarantee is in effect, Guarantor shall prepare and submit to EGLE the following:

(1) A letter signed by Guarantor's chief financial officer, which is worded as specified by EGLE, and includes Guarantor's demonstration that it has passed the standard FT using the EGLE model for the FT. ***NOTE: This is Appendix B***

(2) A copy of an independent certified public accountant's report regarding his/her examination of Guarantor's year-end financial statements for the last 5 years.

(3) A letter from an independent certified public accountant to Guarantor which states both of the following: ***NOTE: This letter is Appendix C***

(a) That the independent certified public accountant has compared the data referenced in the letter from the chief financial officer in Paragraph 3.1.A(1) as having been derived from the independently audited, year-end financial statements for the latest fiscal year with the amounts in such financial statements; and

(b) That, in connection with Paragraph 3.1.A(3)(a), no matters came to the attention of the independent certified public accountant that caused the accountant to believe the specified data was incorrect or should be adjusted.

(4) A certificate from the President or a Vice President and the Treasurer or an Assistant Treasurer of Guarantor setting forth that the signers have reviewed the relevant terms of this Guarantee and have made, or caused to be made, under their supervision, a review of the transactions and conditions of the Guarantor from the beginning of the accounting period covered by the financial statements being delivered therewith to the date of the certificate, and that such review has not disclosed the existence during such period of any condition which constitutes an event of noncompliance under this Guarantee. If during such period any such condition or event of noncompliance existed or exists, the certificate shall specify the nature and period of existence thereof and the actions Guarantor has taken or proposes to take with respect thereto.

B. Pursuant to the terms of the postclosure agreement, within 30 days after each succeeding 5-year anniversary date of the end of the fiscal year that the postclosure agreement is in effect, **[*insert name of subsidiary company*]** is required to submit to EGLE and Guarantor an updated cost estimate for implementing the **[*describe the general nature of response activities, including, if appropriate oversight, monitoring and other costs*]** for the next **[*insert* 30-year period, *or if appropriate, other period of time*]**. Within 60 days of Guarantor's receipt of this information from **[*insert name of subsidiary company*]**, Guarantor shall re-evaluate whether it meets the FT criteria set forth in Paragraph 3.1.A(1) and submit the information required in Paragraph 3.1.A(1)-(4) to EGLE.

3.2 Requested Information – In addition to the information specified in Paragraph 3.1.A, EGLE, based on a reasonable belief that the Guarantor may no longer be able to pass

the FT specified in Paragraph 3.1.A(1), may require Guarantor, at any time, to submit reports of its financial condition to EGLE. Guarantor shall provide with reasonable promptness to EGLE any other data and information that may reasonably be expected to materially adversely affect the Guarantor's ability to perform its obligations under the Guarantee.

3.3 Notice of Breach of Covenants or Noncompliance Events - Immediately upon becoming aware of the existence of any condition or event that constitutes either a noncompliance with the pertinent requirements of the postclosure agreement or a Breach of any Covenants under this Guarantee (with the exception of breaches or notices of breach that EGLE sends to Guarantor), Guarantor shall provide written notice to EGLE. Such notice shall specify the nature and duration of the condition or event and the actions the Guarantor is taking or proposes to take to address the condition or event.

## IV. GUARANTEE OF OBLIGATIONS

4.1 Guarantor hereby irrevocably guarantees the full and prompt performance of all obligations of **[*insert name of subsidiary company*]** under the postclosure agreement including, without limitation, payment of all amounts including any interest or stipulated penalties, which are or may become due thereunder.

4.2 Guarantor guarantees that in the event **[*insert name of subsidiary company*]** fails to perform **[*describe the general nature of response activities required under the postclosure agreement*]** for the Facility in accordance with EGLE approved plans, Guarantor will do so.

4.3 Guarantor guarantees that if, at the end of any fiscal year before termination of this Guarantee, Guarantor fails to meet the FT criteria as set forth in Paragraph 3.1.A(1), Guarantor will send within 90 days, by certified mail, notice to EGLE and **[*insert name of subsidiary company*]** that it will provide alternate financial assurance, in a FAM acceptable to EGLE, in the name of **[*insert name of subsidiary company*]**.

4.4 If an alternate FAM must be secured by Guarantor, within 30 days of providing the notice required by Paragraph 4.3, Guarantor shall submit for review and approval to EGLE, the necessary forms and documents for implementing the alternate FAM. Such forms and documents shall be in a form acceptable to EGLE and shall include the type of FAM, the amount of funds to be secured, and a procedure for the continued review and approval of that FAM by the parties, if appropriate. Submittals provided to EGLE pursuant to this paragraph shall be reviewed and approved and/or disapproved in accordance with the postclosure agreement. Upon receipt of approval by the Remediation and Redevelopment Division Director, Guarantor shall implement the alternate FAM within 15 days.

4.5 Pursuant to the postclosure agreement, if at any time **[*insert name of subsidiary company*]** or EGLE identifies the need for additional response activity as provided for in the postclosure agreement, **[*insert name of subsidiary company*]** is required to submit to EGLE for review and approval a proposed plan and schedule for these response activities and is required to provide to EGLE and Guarantor, an estimate of the cost for implementing these response activities. **[*insert name of subsidiary company*]** is required to submit these items to the designated parties within 30 days of identification of the need for the additional response activities. If requested by EGLE, Guarantor shall then re-evaluate whether it meets the FT criteria as set forth in Paragraph 3.1.A(1) in view of the additional cost that will be incurred to implement these response activities and Guarantor shall submit the FT information to EGLE.

4.6 EGLE, based on a reasonable belief that Guarantor may no longer be able to meet the FT requirements specified in Paragraph 3.1.A(1), may require Guarantor to submit updated FT information to determine whether it can continue to meet the FT requirements. If based on that updated information EGLE determines that the Guarantor no longer meets the requirements for the FT, Guarantor shall provide an alternate FAM in accordance with Paragraphs 4.3 and 4.4 of this Guarantee.

4.7 Guarantor agrees to remain bound under this Guarantee notwithstanding any amendment or modification of:

(1) The response activities or other obligations, including **[*generally describe response activities or obligations, for example: plans for monitoring, operation and maintenance, and oversight*]**; or

(2) Plans for additional response activities that are necessary to protect public health, safety, or welfare, or the environment.

4.8 Guarantor agrees to remain bound under this Guarantee for so long as **[*insert name of subsidiary company*]** must comply with the applicable financial assurance requirements of the postclosure agreement for the Facility.

4.9 Guarantor agrees to notify EGLE by certified mail within 10 days of commencement of a voluntary or involuntary proceeding under Title 11 (Bankruptcy), United States Code that names Guarantor as debtor.

4.10 If **[*insert name of subsidiary company*]** and Guarantor fail at any time to adequately implement the response activities required under the postclosure agreement or any response activities provided in a plan approved by EGLE, EGLE, at its discretion, may choose to implement those response activities that have not been performed or may seek other available remedies as specified by the postclosure agreement If **[*insert name of subsidiary company*]** has not reimbursed EGLE its costs within the 30-day time frame or alternate time frame specified in the postclosure agreement, Guarantor shall reimburse EGLE its costs for implementing those response activities as set forth in the postclosure agreement.

4.11 Guarantor further agrees that it shall irrevocably guarantee performance of the obligations of **[*insert name of subsidiary company*]** under the postclosure agreement whether or not it continues to be the holder, directly or indirectly, of the stock of **[*insert name of subsidiary company*]** and whether or not the Facility, or any part of it, is sold, transferred or otherwise alienated. However, this Guarantee may be assigned to a purchaser of Guarantor's interests in **[*insert name of subsidiary company*]** or to a purchaser of all or substantially all of the assets of **[*insert name of subsidiary company*]**, if the following terms and conditions are met in advance of such transaction:

(1) The purchaser demonstrates to EGLE that it can meet the FT set forth in Paragraph 3.1.A(1);

(2) Guarantor and the purchaser enter into an assumption agreement in which the purchaser agrees to assume all of the obligations set forth in this Guarantee and which sets forth the terms and conditions of the transaction;

(3) EGLE agrees in writing to the assumption agreement; and

(4) The postclosure agreement is modified, in accordance with the applicable procedures therein, to reflect this modification.

Upon compliance with the foregoing requirements of this paragraph, Guarantor shall be discharged from its obligations under this Guarantee.

## V. NOTICE TO GUARANTOR/OPPORTUNITY TO CURE

Any obligations of **[*insert name of subsidiary company*]**, which are contained in the postclosure agreement and guaranteed by Guarantor under this Guarantee, shall be enforceable against Guarantor only after EGLE has first made demand of **[*insert name of subsidiary company*]** for performance of such obligations pursuant to the terms of the postclosure agreement. EGLE demand to **[*insert name of subsidiary company*]** for performance shall set forth a detailed description of the nature of the violation of the postclosure agreement and the specific performance required to cure the violation. EGLE shall also provide a copy of the demand for performance to the Guarantor. If **[*insert name of subsidiary company*]** has not complied with EGLE demand for performance within 15 days of receipt of such demand, Guarantor shall either:

(1) Cure the violation within 15 days; or

(2) Commence and diligently pursue the cure and, if the cure cannot be completely performed within 15 days, provide a proposed schedule for approval by EGLE for completion of the cure. Guarantor shall then complete the cure within the time frame approved by EGLE. Under either scenario, within 15 days of completing the cure, Guarantor shall notify EGLE of the date the violation was cured and the actions that were taken to cure the violation.

## VI. TERMS OF GUARANTEE

6.1 This Guarantee shall be fully enforceable by EGLE from the effective date of the Guarantee until EGLE **[*specify the conditions that must be met for the FAM to be released*]** pursuant to the postclosure agreement.

6.2 Except as provided in Paragraph 4.11 of this Guarantee, Guarantor may be excused from its obligations as set forth in this Guarantee only if all of the following conditions are met:

(1) **[*insert name of subsidiary company*]** is willing and financially able to provide an alternate FAM;

(2) **[*insert name of subsidiary company*]** submits and EGLE approves an alternate FAM that meets EGLE requirements;

(3) Such a FAM is in place prior to the termination of this Guarantee; and

(4) The postclosure agreement is modified, in accordance with the applicable procedures stated therein, to reflect this modification.

## VII. NOTICE

Any notifications required under this Guarantee shall be directed to the following individuals at the addresses specified below, unless any of these individuals, their successors,

or their attorneys provide notification of a change to the other party in writing.

As to Guarantor:

**[*Insert Guarantor Name*]**
**[*Title*]**
**[*insert Address*]**

As to EGLE:

**[*insert Name of Division Director*]**, Director
Remediation and Redevelopment Division
Michigan Department of Environment, Great Lakes, and Energy
P.O. Box 30426
Lansing, MI 48909-7926

## VIII. REMEDIES

No failure on the part of EGLE to exercise, nor any delay in exercising, any right hereunder shall operate as a waiver hereof. Neither the single or partial exercise of this Guarantee, nor the exercise of any other right, shall operate as a waiver hereof.

## IX. GOVERNING LAW/CONSENT TO JURISDICTION

This Guarantee shall be governed by and construed in accordance with the laws of the State of Michigan. For the sole and exclusive purpose of enforcing the terms of this Guarantee, Guarantor consents to jurisdiction over it and the subject matter of this Guarantee in the appropriate state or federal courts within the State of Michigan.

## X. SUCCESSORS AND ASSIGNS

This Guarantee shall be binding upon, and shall inure to the benefit of, the successors and assigns of the parties.

## XI. INTEGRATION

This Guarantee constitutes the entire obligation of Guarantor insofar as it concerns the postclosure agreement between **[*insert name of subsidiary company*]** and EGLE.

## XII. EFFECTIVE DATE

This Guarantee shall become effective on the date that it is executed by the Guarantor and EGLE.

## XIII. AUTHORITY

The undersigned representative of Guarantor certifies that he/she is fully authorized to execute and legally bind Guarantor to the obligations undertaken in this Guarantee. The undersigned representative of the State of Michigan certifies that he/she is fully authorized to accept this Guarantee.

EXECUTED THIS _____ day of _____, [***insert year***].

| | |
|---|---|
| **[*insert name of Guarantor*]**<br>ACCEPTANCE OF GUARANTEE | Michigan Department of<br>Environment, Great Lakes, and Energy |
| By: _____ | By: _____ |
| Name: _____<br>(type name) | Name: _____<br>(type name) |
| Title: _____ | Title: Director, Remediation and Redevelopment Division |