

Michigan's Inland Lake Water Quality Assessment Monitoring Program

Quality Assurance Project Plan

Supported By:

**Michigan Department of Environmental Quality
Water Bureau**

and the

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Michigan Water Science Center**

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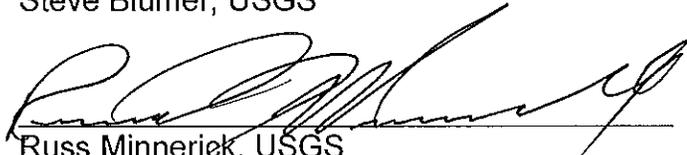
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This Quality Assurance Project Plan (QAPP) for Michigan's Inland Lake Water Quality Assessment (LWQA) Monitoring Program was originally written by Russel Minnerick, U.S. Geological Survey (USGS) and Ralph Bednarz of the Water Bureau, Michigan Department of Environmental Quality (MDEQ). It is intended to be a comprehensive documentation of the program's planning, implementation and assessment including the elements of program management, data generation and acquisition, assessment and oversight as well as data validation and usability. The original QAPP was developed over a three month time period in 2001 with input from all project participants. Since the LWQA Monitoring Program is a long-term, ongoing program the QAPP is intended to be a living document, reviewed and updated periodically.

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TABLE OF CONTENTS	Page
1.0 PROJECT PLANNING AND MANAGEMENT	5
1.1 Introduction	5
1.2 LWQA Monitoring Program Goal	5
1.3 LWQA Monitoring Program Organization	6
1.4 LWQA Monitoring Program Description	7
1.4.1 Overview of Lake Selection	8
1.4.2 Overview of Field Operations	8
1.4.3 Overview of Laboratory Operations	9
1.4.4 Data Analysis and Reporting	9
2.0 DATA QUALITY OBJECTIVES	11
2.1 Laboratory Reporting Level (Sensitivity)	11
3.0 SAMPLING DESIGN AND SITE SELECTION	12
3.1 Network Design	12
3.2 Sampling Methods	12
3.2 Sampling Methods	12
3.3 Sample Handling and Custody	13
3.4 Analytical Methods	13
3.5 Quality Control	13
3.6 Instrument and Equipment Testing	13
3.7 Training	13
4.0 INFORMATION MANAGEMENT	13
4.1 Monitoring Site Information Files	14
4.2 Sample Collection and Field Data Recording	14
4.3 Laboratory Analyses and Data Recording	14
4.4 Data Review, Verification, and Validation Activities	15
4.5 Data Analysis	15
4.6 Data Transfer and Data Management	15
5.0 ASSESSMENT AND OVERSIGHT	16
5.1 Assessment and Response Actions	16
6.0 REFERENCES	17
 ATTACHMENTS	 18
Attachment 1: Lake Water Quality Assessment Monitoring Program Lake Sampling Schedule (2001-2015)	
Attachment 2: Lake Water Quality Assessment Monitoring Program for Michigan Inland Lakes Baseline Water Quality and Trophic Status Monitoring Protocol	
Attachment 3: MDEQ Laboratory Services Standard Operating Procedure Documents	
SOP 304.2 Determination of Total Phosphorus in Water	
SOP 318.1 Nitrate Plus Nitrite as Nitrogen in Water	
SOP 316.1 Ammonia As Nitrogen in Water	
SOP 303.2 Determination of Total Kjeldahl Nitrogen in Water	

- SOP 340.2 Calcium, Magnesium, Potassium, and Sodium Atomic Absorption, Direct Aspiration
- SOP 302.1 Sulfate (Colorimetric, Automated Methylthymol Blue, TRAACS 800) Total in Water
- SOP 300.1 Chloride (Colorimetric, Automated Methylthymol Blue, TRAACS 800) Total in Water
- SOP 310.3 Chlorophyll A
- SOP 361.0 Absorbance (Color) Measurement by Spectrophotometry

1.0 PROJECT PLANNING AND MANAGEMENT

1.1 Introduction

Effective environmental monitoring is an essential component of the Michigan's Department of Environmental Quality's (MDEQ) and the U.S. Geological Survey's (USGS) missions. The MDEQ and USGS recognize that comprehensive water quality monitoring is necessary to improve natural resource management and to maintain sustainable ecosystems (MDEQ 1997).

Comprehensive, viable monitoring programs require long-term funding commitments. However, during the 1990's Federal Clean Water Act (CWA) Clean Lakes Program (Section 314) funds devoted to inland lakes monitoring were eliminated. These funds were MDEQ's primary support for water quality monitoring and assessment programs for Michigan's inland lakes.

In November 1998 the citizens of Michigan passed a general obligation bond, the Clean Michigan Initiative (CMI), to protect and enhance Michigan's environmental quality, natural resources, and infrastructure. The Governor and Legislature supported this initiative. The bond legislation called for a portion of the CMI funds, known as the Clean Water Fund (CWF), to implement the "Strategic Environmental Quality Monitoring Program for Michigan's Surface Waters" (Strategy), which was developed by the MDEQ in January 1997 (MDEQ, 1997). This Strategy identifies a number of monitoring activities necessary for a comprehensive assessment of water quality in Michigan surface waters. One component of the Strategy is to re-establish a lake water quality assessment monitoring program for Michigan's inland lakes.

With CMI-CWF support a cooperative project was undertaken in July 2000 by the MDEQ and the USGS to re-design and re-establish Michigan's inland lakes water quality monitoring program. A Lake Water Quality Assessment (LWQA) Monitoring Program Plan (MDEQ/USGS 2001) was developed to provide current data on baseline water quality and trophic status for Michigan's inland lakes. The LWQA Monitoring Program was implemented during the spring of 2001.

The CMI-CWF rules require that all monitoring activities funded through the CWF have an approved Quality Assurance Project Plan (QAPP). This document fulfills that requirement for the LWQA Monitoring Program. The QAPP includes an overview of the LWQA Monitoring Program, the goals and data quality objectives, sampling and analytical procedures, and quality assurance (QA) and quality control (QC) activities.

1.2 LWQA Monitoring Program Goal

The LWQA Monitoring Program provides current data on baseline water quality and trophic status for Michigan's inland lakes through field observations, water-

column measurements and sampling, and use of Landsat satellite imagery. The data is used to update lake trophic classification and to assess nutrient enrichment and water quality changes and impacts in Michigan's public access lakes statewide.

1.3 LWQA Monitoring Program Organization

- U.S. Geological Survey (Michigan Water Science Center) - Monitor major basins in selected public access lakes within targeted watershed management units. Approximately 60-80 lakes are monitored in a given year. Oversee data management and data storage and develop interpretive products and reports for the project. Develop and test regression models using remote sensing for statewide lake trophic assessment for Michigan's inland lakes.
- MDEQ Water Bureau - Manage project. Conduct trophic assessment for Michigan's inland lakes.
- MDEQ Environmental Laboratory and its overflow laboratories - Perform all specified analyses on lake water quality samples collected for the project. Provide all sample bottles, filters and preservatives.

Table 1 provides specific names and contact information for each participating agency.

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1.4 LWQA Monitoring Program Description

Michigan has nearly 3,500 lakes over 25 acres in size and many thousands of smaller lakes and ponds. . This project targets all public access lakes (i.e. lakes with public boat access sites) greater than 25 acres for lake water quality assessment monitoring by year 2015. The monitoring strategy incorporates the watershed management units and five-year rotational monitoring and assessment cycle currently being used by MDEQ Surface Water Quality Division for ambient surface water quality monitoring programs and management activities. Lakes targeted for monitoring each year are chosen on a random basis within the watershed management units following the five-year rotational cycle (MDEQ/USGS 2001). Approximately 60-80 lakes are monitored and assessed each year.

The deepest basin (primary station) on each lake and secondary basins on some lakes are sampled twice (spring turnover and late summer thermal stratification) in their respective years. Secchi disk transparency measurements, observed color, and vertical profiles for water temperature, dissolved oxygen, pH, and specific conductance are made at each major basin. Water samples are collected and analyzed for major nutrients (total phosphorus, ammonia, nitrate/nitrite, Kjeldahl nitrogen), chlorophyll *a*, true color, and selected ions. Macrophyte observations are made on each lake. Total phosphorus, chlorophyll *a*, and Secchi disk transparency results are used to calculate a Carlson's Trophic State Index TSI (Carlson 1977) and to update the lake trophic status classification for each lake. Apparent macrophyte density is used as an adjustment factor for the lake trophic state classifications. Current data will be compared to historical data to assess nutrient enrichment and baseline water quality changes. Apparent threatened and impaired lakes are noted and reported to the MDEQ Water Bureau.

Remote Sensing using Landsat 5 and Landsat 7 satellite imagery is incorporated in the LWQA Monitoring Program as a tool to provide annual regional and statewide lake trophic status assessments (Fuller and Minnerick, 2007). Using an image processing protocol developed by Olmanson (1997) at the University of Minnesota Remote Sensing Laboratory and Water Resources Center (RESAC). Landsat imagery research has shown that Secchi disk transparency is strongly related to satellite spectral-radiometric observations of lakes. After a period of years, regional lake clarity trends can be mapped and lake eutrophication evaluated using the Landsat imagery technology.

Data collected under the LWQA Monitoring Program and the Cooperative Lakes Monitoring Program (CLMP), Michigan's citizen volunteer lakes monitoring program, are used to calibrate and maintain the statewide transparency and TSI model for Michigan's inland lakes using Landsat satellite imagery (Fuller *et al.*, 2004).

1.4.1 Overview of Lake Selection

A minimum of 730 public access lakes in Michigan will be monitored and assessed as part of the LWQA Monitoring Program. Additional public access lakes greater than 25 acres in size will be added to the program as they are identified. The LWQA Monitoring Program is coordinated with other surface water monitoring programs identified in the Strategic Environmental Quality Monitoring Program for Michigan's Surface Waters report (MDEQ 1977). Targeted lakes are coordinated with current MDEQ water-quality monitoring activities. The LWQA Monitoring Program incorporates the watershed management units and five-year rotational cycle being used by MDEQ's Ambient Surface Water Chemistry Monitoring Program (MDEQ 1999).

The five-year basin monitoring cycle identifies 45 watershed-management units based on statewide drainage to the Great Lakes. Each year, 7 to 10 of the major watersheds are monitored and assessed. This is done to assure that specific watersheds are monitored in the five-year cycle so as to assist in (1) statewide water quality assessments, (2) the National Pollutant Discharge Elimination System (NPDS) permitting process, and (3) resource management decisions.

Approximately 60-80 lakes are monitored annually. Lake selection each year is established using a random selection process, without replacement. This allows for all 730-plus lakes to be monitored and assessed over the 14-year project period. The LWQA Monitoring Program Plan identifies the specific lakes and monitoring schedule under the watershed management units five-year monitoring cycles (MDEQ/USGS 2001).

1.4.2 Overview of Field Operations

Lakes are sampled during spring turnover and then again in late summer during maximum thermal stratification. Lake water during spring turnover is generally well mixed, and samples collected during this period will characterize baseline water quality conditions. Three discrete samples are collected with a Van Dorn style sampler. Samples are collected 3 ft below lake surface, 3 ft above lake bottom and at mid-depth. Samples for general water chemistry and major nutrients are collected from mid-depth, and only nutrients from the upper and lower depths. Summer sampling occurs during late summer, during maximum thermal stratification. The epilimnion, thermocline, and hypolimnion are identified. Three discrete samples are collected from each stratum. Samples are collected 3 ft below the lake surface, 3 ft above the lake bottom and from the metalimnion (mid-thermocline). Samples for major nutrients are collected from each stratum. Total phosphorus, chlorophyll *a*, and Secchi-disk transparency measurements from the summer sampling event are used to calculate Carlson TSIs.

The primary sampling locations are in the deepest portion of the lakes. Additional basins are monitored as appropriate in the lakes with distinct multiple deep

basins. Prior to sampling a vertical profile is made to determine the extent of thermal stratification and document water-quality characteristics throughout the water column. Specific conductance, water temperature, dissolved oxygen and pH are measured versus depth. Secchi disk measurements are made to determine transparency and define the euphotic zone. Water color is observed. A depth-integrated composite sampler is lowered through the euphotic zone (2x Secchi depth) to obtain a composite sample to be analyzed for chlorophyll *a*. A surface grab sample is collected during the summer sampling event to be analyzed for true color.

Macrophyte observations are made during the late summer sampling event. On larger lakes a minimum of two shores are visited. On smaller lakes four shorelines (North, South, East and West) are surveyed. A visual plant density estimate is made at each shoreline segment. The macrophyte observations and density estimates are used as an adjustment factor for the trophic state classification on macrophyte dominated lakes.

1.4.3 Overview of Laboratory Operations

The MDEQ Environmental Laboratory and its overflow laboratories perform all specified analyses on lake water quality samples collected for the project. Some analytical measurements begin during sampling (e.g. *in situ* profiles). Field and Analytical methods are summarized in the specific Field and Laboratory SOPs which are included as appendices in this QAPP.

1.4.4 Data Analysis and Reporting

The LWQA monitoring program team which is coordinated by the project chief is responsible for development of the data analysis plan that includes a verification and validation strategy as described in Section 4.0 Information Management. Validated data are transferred to the central data base managed by the project data management specialist. All validated data in the central data base are transferred to the USGS National Water Information System (NWIS) and eventually to the U.S. EPA Data Storage and Retrieval System (STORET).

Data collected in the LWQA monitoring program are used to assess water quality/trophic status conditions, nutrient enrichment, and water quality changes and trends in lakes enrolled in the program. Table 2 provides a summary of the parameters currently being monitored in the LWQA monitoring program. These data are utilized to assess the water quality status and update the trophic status classification of Michigan's inland lakes. Regional variation of water quality in lakes is examined by grouping lakes on the basis of five Omernik level III ecoregions present within Michigan. The current LWQA monitoring program data and the satellite remote sensing project results are compared to historical data to ascertain changes and trends in Michigan's inland lakes.

Table 2. Parameters Measured as Part of the LWQA Monitoring Program		
Parameter	Sample matrix	Measures
Secchi disk transparency	physical	water clarity, trophic state
temperature	physical	thermal stratification
dissolved oxygen	water chemistry	hypolimnetic oxygen depletion
pH	water chemistry	acid-base status
specific conductance	water chemistry	general water chemistry
total phosphorus	water chemistry	water chemistry, nutrient enrichment, trophic state
nitrogen as N02+N03	water chemistry	water chemistry, nutrient enrichment, trophic state
nitrogen as ammonia	water chemistry	water chemistry, nutrient enrichment, trophic state, aquatic life toxicity
Kjeldahl nitrogen	water chemistry	water chemistry, nutrient enrichment, trophic state
total calcium	water chemistry	water chemistry, watershed characteristics
total magnesium	water chemistry	water chemistry, watershed characteristics
total sodium	water chemistry	water chemistry, watershed characteristics
total potassium	water chemistry	water chemistry, watershed characteristics
total chloride	water chemistry	water chemistry, watershed characteristics, anthropogenic disturbance
total sulfate	water chemistry	water chemistry, watershed characteristics, metal mobility
true color	water chemistry	water chemistry, nutrient enrichment
chlorophyll a	biological	algal productivity, trophic state
aquatic macrophytes	biological	species present, relative abundance, exotic species, trophic state

The Carlson TSI approach is used for updating trophic status classification of Michigan's inland lakes (Carlson 1977). The TSI equations for calculating the individual trophic state indicators are listed in Table 3.

Table 3. Carlson TSI Equations	
$TSI_{SD} = 60 - 33.2 \log_{10}SD$	where, SD = Secchi depth transparency (m)
$TSI_{TP} = 4.2 + 33.2 \log_{10}TP$	TP = total phosphorus concentration (ug/l)
$TSI_{CHL} = 30.6 + 22.6 \log_{10}CHL$	CHL = chlorophyll a concentration (ug/l)

Individual TSI values are calculated for each trophic state indicator. An overall TSI is determined from the mean of the individual TSI values and the trophic status classification is determined based on the criteria listed in Table 4.

Trophic State	Carlson TSI	TP (ug/l)	SD-Trans. (ft)	SD-Trans. (m)	Chl-a (ug/l)
Oligotrophic	<38	<10	>15	>4.6	<2.2
Mesotrophic	38-48	10-20	7.5-15	2.3-4.6	2.2-6
Eutrophic	48-61	20-50	3-7.5	0.9-2.3	6-22
Hypereutrophic	>61	>50	<3	<0.9	>22

The trophic status classification updates are included biennially in the Water Quality and Pollution Control in Michigan Sections 303(d), 305(b), and 314 Integrated Reports (MDEQ 2006). Periodic data summary and interpretation reports will be published by the project team.

2.0 DATA QUALITY OBJECTIVES

The LWQA Monitoring Program monitors Michigan's major public access inland lakes to assess the current baseline water quality and trophic status of each lake. The list of parameters, and sampling schedule, were chosen to provide this information and provide current comparative data with historical data.

The remote sensing using Landsat satellite imagery will provide statewide lake trophic assessment and monitor changes in trophic status of public access lakes.

2.1 Laboratory Reporting Level (Sensitivity)

All water samples collected are analyzed by the MDEQ Environmental Laboratory or its overflow laboratories. Some analytical measurements begin during sampling (e.g. *in situ* profiles).

Table 5 provides performance requirements for water chemistry and chlorophyll a methods. The specific field and analytical methods are summarized in the specific Field and Laboratory SOPs which are included as appendices in this QAPP.

Parameter	Units	Potential Range of Samples	Water Reporting Limit	Method Reference
temperature	°C	4 - 28	0.5	NFM 6.1.3
dissolved oxygen	mg/L	0 - 16	0.1	NFM 6.2.1
pH	pH units	3.7 - 10	0.1	NFM 6.4.3
specific conductance	uS/cm at 25°C	11 - 1300	1.0	NFM 6.3.3
total phosphorus	mg P/L	0.005 - 0.240	0.005	EPA 365.4
nitrogen as N02+N03	mg N/L	<0.01 - 1.7	0.01	EPA 353.2

nitrogen as ammonia	mg N/L	<0.01 – 1.7	0.01	EPA 350.1
Nitrogen, Kjeldahl	mg N/L	<0.10 – 2.2	0.1	EPA 351.2
total calcium	mg Ca/L	<1.0 – 84.0	1.0	EPA 215.1/7140
total magnesium	mg Mg/L	<1.0 – 27.0	1.0	EPA 200.7/6010B
total sodium	mg Na/L	<1.0 – 170	1.0	EPA 273.1/7770
total potassium	mg K/L	<0.1 – 47.0	0.1	EPA 258.1/7610
total chloride	mg Cl/L	<1.0 – 350	1.0	EPA 325.2
total sulfate	mg SO ₄ /L	<2.0 - 60.0	2.0	EPA 375.2
alkalinity	mg CaCO ₃ /L	<20-225	20	EPA 2320B (SM)
true color(absorbance)	absorbance units	<1.0 – 193	0.007	EPA 204B (SM)
chlorophyll a	ug/L	<1.0 – 74.0	1.0	310.3-MDEQ

3.0 SAMPLING DESIGN AND SITE SELECTION

3.1 Network Design

The LWQA program was described in Section 1.4 - LWQA Monitoring Program Description. About 730 public access lakes greater than 25 acres in size will be monitored in the next 14 years (Attachment 1). Many of these lakes have historical water quality data collected under the historical MDEQ lake water quality program. Constituents measured will provide baseline water quality data, trophic status, and water quality variability for Michigan's inland lakes. Sampling techniques and analytical methods were kept consistent between the historical lake sampling program and the re-established LWQA monitoring program to provide comparable data.

The use of Remote Sensing technology will provide annual regional and statewide lake trophic status. This technology will be calibrated and ground truth with data collected under the LWQA and CLMP programs.

3.2 Sampling Methods

Sample collection and handling procedures, as well as laboratory submittal forms are addressed in the "Lake Water Quality Assessment Monitoring Program for Michigan Lakes Baseline Water Quality and Trophic Status Monitoring Protocol"(LWQA protocol) (Attachment 2).

3.3 Sample Handling and Custody

Sample handling, custody, and shipping procedures are described in LWQA protocol (Attachment 2).

3.4 Analytical Methods

Detailed analytical methods for nutrients, chlorophyll a, and selected ions listed in Table 5 are provided in Attachment 3.

3.5 Quality Control

Field quality control activities are described in Attachment 2. A number of replicates, field blanks, and trip blanks are collected (approximately 15%) of the total number of samples are collected are for QA/QC to ensure data quality.

The MDEQ laboratory and the contract laboratory, TriMatrix, provide analytical support for the LWQA monitoring project. Both laboratories participate in the USGS Standard Reference Sample project. The laboratories are evaluated by using performance evaluation samples, called Standard Reference Samples (SRS). The SRS are submitted to the laboratories semi-annually for performance comparison purposes. Although the SRS project is not a certification program, participation is required for all laboratories that provide water-quality data for the USGS.

3.6 Instrument and Equipment Testing

All field instrumentation used in the LWQA program will be incorporated into the USGS National Field Quality Assurance (NFQA) program. The program monitors the proficiency of alkalinity, pH, and specific conductance measurements determined by USGS field analysts. Prior to field use all field instrumentation will be calibrated in accordance to the manufactures recommendations. A summary of the calibration procedures is contained within the LWQA protocol (Attachment 2). Calibration notes will be recorded in the field and retained within the record.

3.7 Training

All water samples will be collected according to LWQA protocol (Attachment 2). In-house training will be provided as needed by USGS and MDEQ to assure that sampling crews adhere to all established protocol.

4.0 INFORMATION MANAGEMENT

Information management (IM) is integral to all aspects of the LWQA monitoring program from the initial selection of sampling sites through dissemination and reporting of final, validated data. The QA/QC measures implemented for the IM system are aimed at preventing corruption of data at the time of their initial incorporation into the system and maintaining the integrity of data and information after incorporation into the system.

4.1 Monitoring Site Information Files

Prior to sample collection, USGS site files will be created for each location that discreet water samples or field measurements will be made. This will allow the storage and archiving of data in the USGS National Water information System (NWIS). Each discreet sample or measurement will have a unique 15 digit, station number assigned. The last two digits of the station number represent the vertical location in the water column that the sample is collected from. Site files will contain descriptive information on the sample location such as latitude, longitude, state, county, and hydrologic unit where the sample is to be collected.

The assignment of the station number is based on the historical sampling location with consultation of USGS topographic maps, and Michigan Department of Natural resources (MDNR) bathymetry maps. Physical verification of the sample location is then made during the first site visit. Verification is made utilizing a hand-held global positioning system (GPS) in addition to a comparison of observed maximum lake depth using electronic sonar with historical recorded depths from past samplings. The site file is then updated if gross errors in the sample location are found during field verification. Additional information on the station number, location, and verification can be found in attachment 2, LWQA protocol

4.2 Sample Collection and Field Data Recording

All field observation and measurements will be recorded on the appropriate field form as noted in the LWQA protocol.

4.3 Laboratory Analyses and Data Recording

Upon receipt of the sample shipment, DEQ environmental laboratory sample receiving personnel check the condition and identification of each sample against the analysis request sheet. Each sample is identified by information written on the sample label. Any discrepancies, damaged samples, or missing samples are reported to the Project Chief by telephone.

The laboratory analyses for all of the LWQA monitoring program parameters are based on standard methods. Standard methods generally include requirements for QC checks and procedures. General QA/QC procedures for the monitoring program parameters are included in the Standard Operating Procedures (SOP) found in Attachment 3.

The DEQ environmental laboratory uses an electronic laboratory information management system (LIMS) for tracking samples in the analytical process and reporting results. Laboratory data records for each parameter are reviewed in batches by the DEQ unit supervisors. Errors are corrected if possible, and data

considered as suspect by laboratory analysts are qualified with a reporting code. All coded data are explained on the analytical results report. Private contract laboratories generally have similar laboratory quality assurance plan and established procedures for recording, reviewing, and validating analysis data.

Once analytical data have passed all of the laboratory's internal review procedures, a report with the analytical results is prepared and electronically submitted to the Project Chief and the Project Manager.

4.4 Data Review, Verification, and Validation Activities

Upon receipt of analytical data, the Project Chief will review values to assure reported values are reasonable. The Project Chief will notify the Project Manager of any values that may be outside of the expected range. These values will then be compared to any available historical data for that lake. If the reported values still appear to be questionable, the Project Manager will then contact the laboratory and request verification and review their QA records and notes to determine whether any unusual circumstances occurred with the sample or their equipment near the time of analysis. Field QA samples (trip blanks, replicates, etc) that may have been collected with the suspect sample are also reviewed. If no apparent reason is found to reject the results, the data are accepted and included in the database.

4.5 Data Analysis

Data collected will provide baseline water quality information on Michigan's inland lakes. Total phosphorus concentrations determined from samples collected from the epilimnion in late summer, total chlorophyll a concentration determined from samples collected from the photic zone late summer, and water column transparency will be used to classify each lakes trophic status using the Carlson Trophic State index. Those lakes that are macrophyte dominate will be reclassified at the next higher trophic status.

Regression model will be developed for statewide lake trophic assessment using Landstat satellite imagery. Correlation coefficient will be determined for the model to access its accuracy.

4.6 Data Transfer and Data Management

The DEQ environmental laboratory will submit electronic copies of the analysis reports to the USGS Project Chief and the MDEQ Project Manager for immediate review. The DEQ environmental laboratory will also provide electronic batch data files in spreadsheet format for all reported data for each spring and summer season to the USGS Project Chief.

Once USGS receives the batch data files this information will be entered into the USGS National Water Information System NWIS database. The data will also be entered into the U.S. Environmental Protection Agency (EPA) national database, the Storage and Retrieval (STORET) system, allowing other agencies and the public to access the information.

5.0 ASSESSMENT AND OVERSIGHT

5.1 Assessment and Response Actions

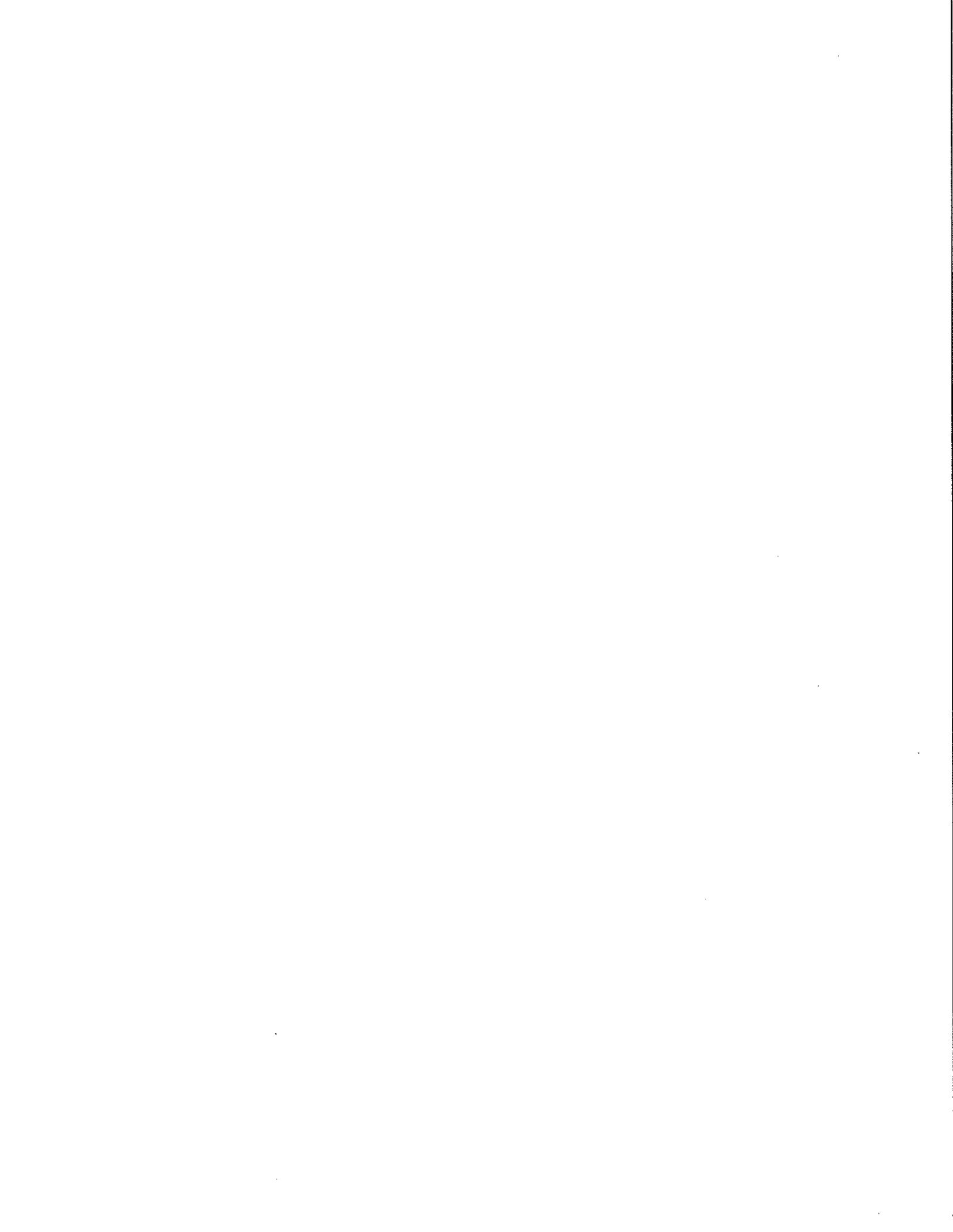
The implementation of the QAPP will be the responsibility of the Project Chief and the Project Manager. Periodic meetings will be held to review past sampling activities, laboratory results, data management, and future work.

The Project Chief will oversee all data collection activities and implement corrective action when needed to assure that guidelines established by the LWQA protocol and the QAPP are followed. The Project Manager will coordinate with the laboratory to assure that detection levels are met and data is provided in a timely manor.

6.0 REFERENCES

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ATTACHMENT 1
Lake Water Quality Assessment Monitoring Program
Lake Sampling Schedule (2001-2015)



LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI070044	Parent Lake	Baraga	M	4	2001	182	1	46.57278	-88.43612
MI110410	Paw Paw Lake	Berrien	E	90	2001	857	3	42.20667	-86.27584
MI140039	Diamond Lake	Cass	M	64	2001	1020	2	41.90306	-85.80334
MI140060	Belas Lake	Cass	E	17	2001	58	1	41.93945	-85.88889
MI140068	Stone Lake	Cass	E	56	2001	148	1	41.90334	-86.01695
MI140087	Kirk Lake	Cass	M	23	2001	42	1	41.92906	-85.87742
MI140105	Baldwins Lake	Cass	M	55	2001	266	1	41.77834	-85.82834
MI140106	South Twin Lake	Cass	M	41	2001	44	1	42.02917	-86.04723
MI180067	Big Long Lake	Clare	M	76	2001	210	1	44.09112	-84.76389
MI180108	Shingle Lake	Clare	M	35	2001	35	1	43.96306	-84.95028
MI310195	Rice Lake	Houghton	M	9	2001	675	1	47.15667	-88.28889
MI350076	Long Lake	Iosco	M	62	2001	493	3	44.41334	-83.85778
MI350078	Loon Lake	Iosco	M	128	2001	417	1	44.41195	-83.81917
MI350106	Londo Lake	Iosco	E	14	2001	176	1	44.34639	-83.86945
MI350107	West Londo Lake	Iosco	M	15	2001	190	1	44.35667	-83.87667
MI350111	Sand Lake	Iosco	M	25	2001	248	1	44.32723	-83.67639
MI350139	Indian Lake	Iosco	M	15	2001	218	1	44.3475	-83.64945
MI380244	Pleasant Lake	Jackson	M	50	2001	269	1	42.39473	-84.34695
MI380245	Portage Lake	Jackson	M	40	2001	360	2	42.32945	-84.24167
MI380287	Center Lake	Jackson	E	28	2001	850	1	42.20667	-84.31723
MI380290	Grass Lake	Jackson	E	13	2001	348	1	42.26834	-84.21806
MI380292	Round Lake	Jackson	M	40	2001	155	1	42.08389	-84.47195
MI420028	Fanny Hoe Lake	Keweenaw	M	40	2001	227	1	47.46389	-87.85639
MI420029	Medora Lake	Keweenaw	M	30	2001	696	1	47.43806	-87.96806
MI420030	Grafiot Lake	Keweenaw	O	70	2001	1438	1	47.36556	-88.12
MI520205	Dead River Storage Basin	Marquette	O	59	2001	2704	1	46.552222	-87.57167
MI520217	McClure Storage Reservoir	Marquette	O	48	2001	132	1	46.552222	-87.52
MI540057	Mecosta Lake	Mecosta	M	37	2001	297	2	43.61667	-85.29639
MI540072	Jehnsen Lake	Mecosta	M	18	2001	270	1	43.70139	-85.27028
MI540074	Bergess Lake	Mecosta	M	45	2001	60	1	43.72834	-85.37362
MI540081	Townline Lake	Mecosta	M	52	2001	73	1	43.71889	-85.44028

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI540092	Blue Lake	Mecosta	O	50	2001	235	1	43.62139	-85.28306
MI570015	Sapphire Lake	Missaukee	E	8	2001	264	1	44.31667	-85.26889
MI570017	Goose Lake	Missaukee	M	14	2001	100	1	44.35361	-85.24806
MI590130	Winfield Lake	Montcalm	M	50	2001	121	1	43.46723	-85.37
MI590131	Whitefish Lake	Montcalm	M	54	2001	501	2	43.32473	-85.53667
MI590146	Little Whitefish Lake	Montcalm	E	40	2001	181	1	43.35695	-85.53528
MI610253	Duck Lake	Muskegon	M	65	2001	313	2	43.3375	-86.39167
MI610358	Bear Lake	Muskegon	H	12	2001	415	1	43.24778	-86.29306
MI610407	East Twin Lake	Muskegon	E	19	2001	111	1	43.36889	-86.17528
MI620040	Sand Lake	Newaygo	M	15	2001	58	1	43.33	-85.91139
MI620058	Blanch Lake	Newaygo	E	18	2001	63	1	43.34112	-85.80334
MI620064	Croton Dam Pond	Newaygo	E	40	2001	1235	1	43.4458333	-85.6688889
MI620065	Hardy Dam Pond	Newaygo	M	110	2001	3750	1	43.4902778	-85.6275
MI670056	Big Lake	Osceola	M	85	2001	204	2	43.86695	-85.19917
MI670062	Hicks Lake	Osceola	E	33	2001	155	1	44.02306	-85.28417
MI670067	Sunrise Lake	Osceola	O	66	2001	80	1	44.02945	-85.32723
MI720026	Higgins Lake	Roscommon	O	135	2001	9600	4	44.49528	-84.76417
MI800241	Cedar Lake	Van Buren	O	84	2001	269	1	42.08889	-85.82834
MI800253	Rush Lake	Van Buren	E	58	2001	118	1	42.24361	-86.20612
MI800256	Shafer Lake	Van Buren	M	72	2001	81	1	42.195	-86.10362
MI800269	Ackley Lake	Van Buren	M	16	2001	65	1	42.23084	-85.87695
MI800271	Gravel Lake	Van Buren	O	31	2001	296	1	42.07834	-85.86639
MI800461	Fish Lake	Van Buren	E	27	2001	34	1	42.32445	-85.80723
MI810335	Mud Lake	Washtenaw	E	7	2001	92	1	42.34723	-84.12806
MI830074	Long Lake	Wexford	E	8	2001	190	1	44.325	-85.36945
MI1010040	Alcona Dam Pond	Alcona	M	43	2002	953	1	44.56306	-83.80473
MI1010041	Jewell Lake	Alcona	M	34	2002	193	1	44.67917	-83.61056
MI1010051	Brownlee Lake	Alcona	E	25	2002	87	1	44.68889	-83.40861
MI1070038	Lake Keewaydin	Baraga	M	25	2002	151	1	46.59973	-88.12
MI1070039	Ruth Lake	Baraga	M	36	2002	192	1	46.56056	-88.21445
MI180107	Arnold Lake	Clare	O	80	2002	118	1	44.07306	-84.75528

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI190093	Lake Ovid	Clinton	H	16	2002	412	2	42.94306	-84.415
MI200044	KP Lake	Crawford	M	25	2002	110	1	44.795	-84.54723
MI200058	Section One Lake	Crawford	O	27	2002	56	1	44.85723	-84.61889
MI200111	Shupac Lake	Crawford	O	97	2002	107	1	44.82028	-84.47575
MI220038	Rock Lake	Dickinson	M	30	2002	84	1	45.91056	-87.92973
MI220040	Bass Lake	Dickinson	M	58	2002	61	1	45.8525	-88.06778
MI220060	Hamilton Lake	Dickinson	M	31	2002	75	1	45.75584	-87.78278
MI220063	Silver Lake	Dickinson	E	20	2002	118	1	46.20361	-88.01723
MI260025	Wiggins Lake	Gladwin	E	25	2002	345	1	44.00278	-84.53167
MI260032	Pratt Lake	Gladwin	O	28	2002	180	1	44.02445	-84.54917
MI260034	Wixom Impoundment	Gladwin	E	40	2002	1980	1	43.81834	-84.37501
MI350074	Van Eitren Lake	Iosco	H	33	2002	1320	1	44.46417	-83.35389
MI350108	Footte Dam Pond	Iosco	O	40	2002	1824	1	44.435	-83.44306
MI360033	Ottawa Lake	Iron	M	90	2002	551	1	46.08334	-88.76362
MI360051	Emily Lake	Iron	H	32	2002	320	1	46.11278	-88.50084
MI360053	Indian Lake	Iron	M	36	2002	196	1	46.04237	-88.49639
MI360072	Buck Lake	Iron	M	39	2002	153	1	46.03278	-88.41306
MI360081	Gibson Lake	Iron	M	23	2002	78	1	46.19862	-88.4425
MI360082	Golden Lake	Iron	O	100	2002	285	1	46.17223	-88.88751
MI360088	Little Smoky Lake	Iron	M	20	2002	78	1	46.10723	-88.93473
MI360091	Winslow Lake	Iron	M	25	2002	255	1	46.34445	-88.76112
MI360102	Michigamme Reservoir	Iron	M	30	2002	5220	2	46.16445	-88.23
MI370063	Coldwater Lake	Isabella	M	65	2002	294	1	43.65695	-84.95028
MI370068	Halls Lake	Isabella	E	26	2002	68	1	43.58139	-85.07556
MI470134	East Crooked Lake	Livingston	M	35	2002	252	1	42.54778	-83.84473
MI470204	Appleton Lake	Livingston	M	36	2002	56	1	42.51028	-83.83528
MI470390	Hi-Land Lake	Livingston	E	12	2002	123	1	42.42889	-83.99139
MI520095	Michigamme Lake	Marquette	O	70	2002	4260	3	46.50889	-88.04889
MI520156	Witch Lake	Marquette	M	90	2002	211	1	46.27917	-88.00334
MI520204	Arfelin Lake	Marquette	O	35	2002	66	1	46.62917	-88.05778
MI520208	Horseshoe Lake	Marquette	M	10	2002	123	1	46.27917	-88.04723

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI540050	Chippewa Lake	Mecosta	E	40	2002	791	1	43.76112	-85.295
MI540076	Martiny Lake	Mecosta	E	47	2002	1420	2	43.7275	-85.2325
MI540079	Pretty Lake	Mecosta	M	22	2002	121	1	43.69611	-85.23334
MI590106	Crystal Lake	Montcalm	M	70	2002	724	2	43.25584	-84.93362
MI600013	East Twin Lake	Montmorency	M	20	2002	974	1	44.86861	-84.305
MI600014	West Twin Lake	Montmorency	M	30	2002	1327	1	44.87639	-84.33612
MI610321	Fox Lake	Muskegon	E	3	2002	80	1	43.37973	-86.2425
MI620061	Robinson Lake	Newaygo	M	30	2002	137	1	43.53195	-85.85612
MI620106	Crystal Lake	Newaygo	M	61	2002	125	1	43.50723	-85.86389
MI630421	Union Lake	Oakland	M	110	2002	465	3	42.60723	-83.43389
MI630534	Kent Lake	Oakland	E	35	2002	1000	1	42.52584	-83.66695
MI630706	Lower Pettibone Lake	Oakland	M	41	2002	89	2	42.62501	-83.60945
MI630745	Big Lake	Oakland	E	14	2002	215	2	42.7202778	-83.5222222
MI650053	Lake George	Ogemaw	O	70	2002	89	1	44.20806	-84.24695
MI650062	Tee Lake	Ogemaw	M	62	2002	33	1	44.20659	-84.35073
MI690049	Dixon Lake	Otsego	O	35	2002	80	1	44.99862	-84.635
MI690051	Emerald Lake	Otsego	M	35	2002	63	1	44.93945	-84.67
MI690065	Heart Lake	Otsego	M	123	2002	63	1	44.89111	-84.69223
MI690129	Opal Lake	Otsego	O	39	2002	122	1	44.92536	-84.61056
MI800150	Saddle Lake	Van Buren	M	32	2002	298	1	42.37806	-86.04778
MI800255	South Scott Lake	Van Buren	M	55	2002	124	1	42.32417	-86.00473
MI800273	Upper Jephtha Lake	Van Buren	M	42	2002	57	1	42.34945	-86.01056
MI810276	North Lake	Washtenaw	M	58	2002	227	1	42.39334	-84.00806
MI810330	Cedar Lake	Washtenaw	M	27	2002	73	1	42.31528	-84.08056
MI810337	Mill Lake	Washtenaw	M	25	2002	142	1	42.32528	-84.09056
MI810339	Green Lake	Washtenaw	E	11	2002	90	1	42.36695	-84.0725
MI821409	Belleville Lake	Wayne	H	16	2002	1270	3	42.21473	-83.44389
MI050054	Torch Lake	Antrim	O	285	2003	18770	2	44.98056	-85.30112
MI050056	Ellsworth Lake	Antrim	M	42	2003	120	1	45.16195	-85.24334
MI050090	Birch Lake	Antrim	M	53	2003	326	1	44.93334	-85.38167
MI050093	Ber-way Lake	Antrim	M	42	2003	131	1	45.1	-85.25834

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

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MI050103	Lake of the Woods	Antrim	M	14	2003	141	1	44.905	-85.18917
MI080064	Thornapple Lake	Barry	H	30	2003	409	1	42.62584	-85.18806
MI080089	Leach Lake	Barry	E	52	2003	109	2	42.69112	-85.28195
MI080091	Long Lake	Barry	M	3	2003	81	1	42.475	-85.24362
MI080094	Clear Lake	Barry	E	16	2003	184	1	42.50834	-85.27306
MI080096	Duncan Lake	Barry	E	55	2003	130	1	42.74945	-85.53445
MI100066	Crystal Lake	Benzie	O	160	2003	9711	1	44.66862	-86.18612
MI100082	Lake Ann	Benzie	O	70	2003	527	3	44.71195	-85.84334
MI100122	Little Platte Lake	Benzie	E	8	2003	805	1	44.70889	-86.06584
MI100139	Herendeene Lake	Benzie	M	37	2003	36	1	44.74064	-85.85959
MI100140	Turtle Lake	Benzie	E	22	2003	38	1	44.61534	-85.90448
MI10NES261001	Betsie Lake	Benzie	H	22	2003	250	1	44.63	-86.235
MI150062	Lake Charlevoix	Charlevoix	O	122	2003	17260	2	45.26362	-85.10612
MI150082	Deer Lake	Charlevoix	M	20	2003	443	1	45.16362	-84.9775
MI150115	Sixmile Lake	Charlevoix	E	31	2003	407	1	45.12028	-85.20223
MI240043	Paradise Lake	Emmet	E	15	2003	1900	1	45.69084	-84.75556
MI250417	Thread Lake	Genesee	H	5	2003	80	1	43.00028	-83.66945
MI250444	Holloway Reservoir	Genesee	H	15	2003	954	1	43.1125	-83.46278
MI270046	Thousand Island Lake	Gogebic	M	47	2003	1020	2	46.22528	-89.39917
MI270047	Little Oxbow Lake	Gogebic	M	85	2003	95	1	46.25945	-89.66334
MI270065	Langford Lake	Gogebic	M	10	2003	481	1	46.2775	-89.48223
MI270066	Pomeroy Lake	Gogebic	E	15	2003	314	1	46.27862	-89.57501
MI270105	Beatons Lake	Gogebic	O	90	2003	302	1	46.32834	-89.36389
MI270110	Imp Lake	Gogebic	O	86	2003	84	1	46.2175	-89.07778
MI270111	McDonald Lake	Gogebic	E	10	2003	485	1	46.38278	-90.01389
MI270112	Mooshead Lake	Gogebic	M	39	2003	54	1	46.24056	-89.60889
MI270113	Moraine Lake	Gogebic	M	20	2003	67	1	46.27667	-89.78445
MI270114	Ormes Lake	Gogebic	M	65	2003	50	1	46.27084	-89.64973
MI270122	Taylor Lake	Gogebic	M	35	2003	109	1	46.24695	-89.04056
MI270123	Allen Lake	Gogebic	M	40	2003	79	1	46.22389	-89.17223
MI270124	Bass Lake	Gogebic	M	18	2003	191	1	46.30362	-89.175

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

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MI270125	Clark Lake	Gogebic	O	75	2003	820	1	46.21612	-89.30556
MI270126	Dinner Lake	Gogebic	M	19	2003	110	1	46.20167	-89.13417
MI270127	Duck Lake	Gogebic	O	25	2003	610	1	46.21473	-89.21445
MI860017	Lac Vieux Desert	Gogebic	M	38	2003	4260	1	46.12084	-89.11723
MI280084	Long Lake	Grand Traverse	O	80	2003	2860	1	44.72473	-85.75611
MI280116	Silver Lake	Grand Traverse	O	98	2003	600	2	44.70528	-85.68667
MI280119	Skegemog Lake	Grand Traverse	M	26	2003	2560	1	44.81945	-85.34056
MI280131	Bass Lake	Grand Traverse	M	19	2003	349	1	44.69362	-85.71445
MI280133	Bass Lake	Grand Traverse	M	29	2003	89	2	44.60639	-85.80695
MI280137	Spider Lake	Grand Traverse	M	32	2003	459	2	44.67639	-85.49306
MI280142	Boardman Lake	Grand Traverse	E	73	2003	339	1	44.75278	-85.6125
MI280143	Brown Bridge Pond	Grand Traverse	M	29	2003	180	1	44.64445	-85.50834
MI280145	Dubonnet Lake	Grand Traverse	M	6	2003	182	1	44.6847222	-85.79444444
MI310120	Bob Lake	Houghton	M	15	2003	133	1	46.66278	-88.91139
MI360087	Norway Lake	Iron	O	20	2003	53	1	46.41389	-88.68612
MI360090	Tepce Lake	Iron	M	35	2003	124	1	46.38445	-88.87778
MI360092	Tamarack Lake	Iron	E	18	2003	335	1	46.24334	-88.98889
MI380173	Clark Lake	Jackson	O	55	2003	580	1	42.11945	-84.31306
MI380263	Vineyard Lake	Jackson	M	42	2003	505	2	42.075	-84.20417
MI410267	Lincoln Lake	Kent	E	67	2003	411	1	43.24223	-85.35973
MI410274	Campau Lake	Kent	M	50	2003	125	2	42.83278	-85.45001
MI410436	Camp Lake	Kent	M	50	2003	154	1	43.17667	-85.66612
MI410437	Big Pine Island Lake	Kent	E	45	2003	223	1	43.10334	-85.36723
MI410439	Campbell Lake	Kent	M	52	2003	60	1	42.81084	-85.42556
MI440094	Nepessing Lake	Lapeer	E	25	2003	414	1	43.01223	-83.37445
MI440103	Otter Lake	Lapeer	E	117	2003	68	1	43.21667	-83.45889
MI440105	Big Fish Lake	Lapeer	M	70	2003	105	1	42.88945	-83.39167
MI450047	North Lake Leelanau	Leelanau	O	121	2003	2950	1	45.04056	-85.73
MI450048	South Lake Leelanau	Leelanau	O	62	2003	5370	1	44.87362	-85.71056
MI450066	Lime Lake	Leelanau	O	67	2003	670	1	44.89723	-85.84278
MI450069	School Lake	Leelanau	M	6	2003	175	1	44.91306	-85.88195

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

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MI450070	Little Traverse Lake	Leelanau	O	54	2003	640	1	44.92306	-85.84861
MI460247	Hudson Lake	Lenawee	H	30	2003	2500	2	41.83389	-84.2575
MI460264	Sand Lake	Lenawee	E	53	2003	440	1	42.04806	-84.05556
MI590107	Townline Lake	Montcalm	E	49	2003	247	1	43.45417	-85.20167
MI590142	Clifford Lake	Montcalm	E	45	2003	200	2	43.31223	-85.19584
MI590171	Baldwin Lake	Montcalm	E	35	2003	72	1	43.16445	-85.26723
MI590172	Rainbow Lake	Montcalm	E	22	2003	155	1	43.32778	-85.30389
MI590179	Montcalm Lake	Montcalm	E	67	2003	68	1	43.3830556	-85.19166667
MI620062	Bills Lake	Newaygo	O	90	2003	204	1	43.39389	-85.65973
MI630842	Heron Lake	Oakland	E	40	2003	132	1	42.80834	-83.52167
MI660076	Bond Falls Flowage	Ontonagon	M	28	2003	2118	1	46.39945	-89.11389
MI660077	County Line Lake	Ontonagon	M	51	2003	65	1	46.33389	-89.2725
MI690131	Lake Twenty-seven	Otsego	M	22	2003	112	1	45.04767	-84.78539
MI030224	Selkirk Lake	Allegan	E	39	2004	94	2	42.61445	-85.62362
MI030256	Base Line Lake	Allegan	E	44	2004	187	1	42.425	-85.85639
MI030257	Big Lake	Allegan	M	30	2004	137	1	42.56	-85.68889
MI030259	Eagle Lake	Allegan	M	69	2004	225	1	42.42556	-85.93056
MI030260	Miner Lake	Allegan	M	83	2004	325	1	42.56945	-85.79528
MI030261	Swan Lake	Allegan	H	28	2004	200	1	42.46445	-85.96167
MI030262	Swan Creek Pond	Allegan	E	6	2004	140	1	42.55084	-85.98167
MI030472	Lake Allegan	Allegan	H	20	2004	1587	1	42.56306	-85.95278
MI080071	Crooked Lake	Barry	E	48	2004	735	1	42.49028	-85.43139
MI080090	Fish Lake	Barry	O	56	2004	165	1	42.55556	-85.49917
MI080100	Pine Lake	Barry	M	34	2004	660	2	42.49917	-85.52362
MI080101	Long Lake	Barry	O	49	2004	146	1	42.62306	-85.50334
MI100084	Upper Herring Lake	Benzie	E	25	2004	540	1	44.56112	-86.18056
MI100085	Lower Herring Lake	Benzie	M	60	2004	450	1	44.56223	-86.21056
MI130172	Duck Lake	Calhoun	M	50	2004	629	1	42.28473	-85.21167
MI130206	Upper Brace Lake	Calhoun	M	41	2004	70	1	42.22834	-84.945
MI130210	Wabascon Lake	Calhoun	E	45	2004	70	1	42.41112	-85.22389
MI130275	Winnipeg Lake	Calhoun	E	22	2004	38	1	42.30467	-84.80984

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

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MI130296	Lane Lake	Calhoun	E	24	2004	24	1	42.36389	-84.98667
MI170078	Carp Lake	Chippewa	M	30	2004	560	1	46.17775	-85.04362
MI170079	Frenchman Lake	Chippewa	E	20	2004	174	2	46.18195	-85.01556
MI170137	Shelldrake Impoundment	Chippewa	M	5	2004	266	1	46.71139	-85.06667
MI200036	Lake Margrethe	Crawford	M	65	2004	1920	3	44.62778	-84.7875
MI210113	Skeels Lake	Delta	M	50	2004	91	1	46.15806	-86.6225
MI210114	Camp 7 Lake	Delta	M	35	2004	60	1	46.05778	-86.55112
MI230173	Narrow Lake	Eaton	H	48	2004	121	1	42.43751	-84.77834
MI280080	Fife Lake	Grand Traverse	O	60	2004	617	1	44.56639	-85.3375
MI340090	Morrison Lake	Ionina	H	36	2004	330	3	42.86389	-85.20195
MI340179	Sessions Lake	Ionina	E	55	2004	135	1	42.94375	-85.12709
MI380293	Swains Lake	Jackson	M	64	2004	69	1	42.15111	-84.65
MI390211	Gull Lake	Kalamazoo	M	110	2004	2030	3	42.41695	-85.4275
MI390265	Morrow Pond	Kalamazoo	H	8	2004	1001	2	42.295	-85.48945
MI390382	Sherman Lake	Kalamazoo	M	36	2004	153	1	42.35139	-85.38473
MI390411	Eagle Lake	Kalamazoo	M	10	2004	248	1	42.21612	-85.71612
MI390519	Ruppert Lake	Kalamazoo	M	29	2004	28	1	42.40684	-85.73362
MI390520	Whitford Lake	Kalamazoo	M	25	2004	24	1	42.31009	-85.35737
MI400015	Indian Lake	Kalkaska	O	20	2004	70	1	44.80778	-84.93
MI400026	Bear Lake	Kalkaska	O	60	2004	316	1	44.72584	-84.93973
MI400032	East Lake	Kalkaska	E	20	2004	91	1	44.63612	-85.15723
MI400034	Manistee Lake	Kalkaska	M	18	2004	860	1	44.77639	-85.01611
MI430029	Big Bass Lake	Lake	M	45	2004	290	1	44.09278	-85.9725
MI430030	Harper Lake	Lake	M	59	2004	76	1	44.13528	-85.97612
MI480010	North Manistique Lake	Luce	O	50	2004	1722	1	46.28084	-85.73806
MI480013	Culhane Lake	Luce	E	49	2004	97	1	46.69514	-85.35084
MI480018	Pike Lake	Luce	M	43	2004	292	1	46.64639	-85.40639
MI480019	Bass Lake	Luce	M	74	2004	145	1	46.46528	-85.71667
MI480020	Kaks Lake	Luce	E	22	2004	60	1	46.30167	-85.57334
MI490033	Manistique Lake	Mackinac	M	20	2004	10131	1	46.23334	-85.75417
MI490034	South Manistique Lake	Mackinac	E	29	2004	4001	1	46.0275	-85.74723

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI490035	Milakokia Lake	Mackinac	M	25	2004	1956	1	46.40334	-85.22028
MI490037	Millicoquins Lake	Mackinac	M	12	2004	1062	1	46.15528	-85.50667
MI510091	Manistee Lake	Manistee	E	50	2004	930	1	44.24389	-86.30334
MI510174	Arcadia Lake	Manistee	M	31	2004	275	1	44.4891667	-86.2402778
MI510189	Healy Lake	Manistee	E	50	2004	39	1	44.43512	-85.99923
MI510191	Canfield Lake	Manistee	M	29	2004	29	1	44.21028	-86.32139
MI530104	Gun Lake	Mason	M	20	2004	219	1	44.08223	-86.17473
MI530142	Hackert Lake	Mason	M	52	2004	125	1	43.98306	-86.32778
MI610225	Mona Lake	Muskegon	H	42	2004	695	2	43.17278	-86.28112
MI630414	Lotus Lake	Oakland	M	65	2004	419	1	42.70167	-83.42056
MI630415	Maceday Lake	Oakland	M	117	2004	234	1	42.68723	-83.43
MI630542	Cass Lake	Oakland	M	125	2004	1281	4	42.60306	-83.37112
MI630563	Crescent Lake	Oakland	E	40	2004	90	2	42.64528	-83.39056
MI630583	Orchard Lake	Oakland	M	111	2004	788	1	42.58334	-83.36584
MI630670	Lakeville Lake	Oakland	E	66	2004	460	2	42.82917	-83.15195
MI630681	Oakland Lake	Oakland	E	64	2004	255	1	42.7007	-83.36028
MI630708	Deer Lake	Oakland	M	63	2004	137	1	42.73056	-83.43084
MI650022	Rifle Lake	Ogemaw	M	70	2004	183	2	44.41611	-83.97889
MI650032	Hardwood Lake	Ogemaw	H	35	2004	172	1	44.24639	-83.99223
MI650033	Peach Lake	Ogemaw	M	74	2004	208	1	44.295	-84.16528
MI650044	DeVoe Lake	Ogemaw	O	53	2004	130	2	44.4025	-84.02417
MI650046	Grousehaven Lake	Ogemaw	O	54	2004	95	1	44.41084	-84.02056
MI650054	Bush Lake	Ogemaw	M	35	2004	51	1	44.3425	-84.03528
MI670058	Rose Lake	Osceola	E	30	2004	370	2	44.06556	-85.37834
MI670066	Diamond Lake	Osceola	E	60	2004	61	1	44.08695	-85.48528
MI700422	Crockery Lake	Ottawa	E	54	2004	108	1	43.16584	-85.85639
MI770033	Gulliver Lake	Schoolcraft	M	22	2004	836	1	45.98056	-86.02389
MI770037	Dodge Lake	Schoolcraft	O	51	2004	88	2	46.11139	-86.26528
MI770038	Ross Lake	Schoolcraft	M	19	2004	196	1	46.47778	-86.25917
MI770059	Boot Lake	Schoolcraft	M	30	2004	108	1	46.26778	-86.44528
MI770060	Island Lake	Schoolcraft	O	30	2004	106	1	46.11695	-86.27723

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI1770070	Petes Lake	Schoolcraft	M	37	2004	194	1	46.22334	-86.63751
MI1770071	Snyder Lake	Schoolcraft	M	17	2004	60	1	46.4858333	-85.94777778
MI1800460	Three Legged Lake	Van Buren	E	20	2004	40	1	42.39861	-85.91889
MI1010020	Hubbard Lake	Alcona	O	75	2005	8850	1	44.83334	-83.6
MI1010050	Crooked Lake	Alcona	M	28	2005	89	1	44.73725	-83.86831
MI1020038	Au Train Lake	Alger	E	25	2005	830	1	46.4	-86.84473
MI1020039	Grand Sable Lake	Alger	M	60	2005	630	1	46.64056	-86.38751
MI1020041	Nawakwa Lake	Alger	E	26	2005	399	2	46.50056	-86.97473
MI1020054	Kingston Lake	Alger	M	20	2005	250	1	46.57917	-86.21945
MI1040064	Fletcher Pond	Alpena	E	8	2005	8970	1	44.98334	-83.87473
MI120102	Marble Lake	Branch	M	60	2005	780	2	41.89834	-84.90667
MI120123	Matteson Lake	Branch	E	38	2005	307	1	41.93028	-85.20695
MI120126	Union Lake	Branch	H	16	2005	525	1	42.04445	-85.19862
MI120130	Cary Lake	Branch	M	38	2005	79	1	41.90195	-85.10806
MI120139	South Lake	Branch	H	18	2005	118	1	41.93778	-85.035
MI120147	Silver Lake	Branch	M	40	2005	213	1	41.7775	-84.99473
MI120195	Kenyon Lake	Branch	E	29	2005	73	1	42.04889	-85.25223
MI1850006	Lake George	Branch	M	82	2005	565	1	41.75445	-85.00667
MI130189	Nottawa Lake	Calhoun	E	21	2005	116	1	42.15528	-84.98501
MI130191	Lee Lake	Calhoun	M	47	2005	116	1	42.18084	-85.11806
MI130205	Warner Lake	Calhoun	M	30	2005	59	1	42.14861	-85.05056
MI130238	Homer Lake	Calhoun	M	30	2005	74	2	42.1375	-84.82362
MI140053	Hemlock Lake	Cass	M	75	2005	64	1	42.06251	-85.80834
MI140063	Harwood Lake	Cass	M	55	2005	122	1	41.92889	-85.77028
MI140066	Mill Lake	Cass	E	7	2005	174	1	41.9872222	-85.78611111
MI140104	Driskels Lake	Cass	E	28	2005	37	1	41.90695	-85.8
MI150058	Thumb Lake	Charlevoix	O	150	2005	484	3	45.19223	-84.75111
MI160048	Black Lake	Cheboygan	M	50	2005	10130	1	45.45792	-84.27612
MI160050	Mullett Lake	Cheboygan	O	120	2005	17360	1	45.48445	-84.56028
MI160089	Lancaster Lake	Cheboygan	M	57	2005	52	1	45.62084	-84.70834
MI160169	Long Lake	Cheboygan	O	61	2005	400	1	45.53314	-84.39598

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI210151	Pole Creek Lake	Delta	E	10	2005	87	1	46.14528	-86.775
MI210171	Dana Lake	Delta	E	25	2005	98	1	46.11111	-86.62528
MI220036	Sawyer Lake	Dickinson	M	20	2005	241	1	46.18389	-88.06139
MI220061	Norway Lake	Dickinson	M	26	2005	52	1	46.07028	-87.8375
MI240045	Crooked Lake	Emmet	M	50	2005	2300	1	45.41473	-84.83445
MI240078	Larks Lake	Emmet	M	9	2005	605	1	45.60417	-84.92584
MI300112	Long Lake	Hillsdale	M	40	2005	210	1	41.86	-84.79417
MI300152	Baw Beese Lake	Hillsdale	M	70	2005	414	1	41.89917	-84.60889
MI300155	Round Lake	Hillsdale	M	35	2005	72	1	41.89667	-84.76889
MI300173	Diane Lake	Hillsdale	H	51	2005	295	2	41.71028	-84.65362
MI850005	Long Lake	Hillsdale	E	35	2005	146	1	41.74639	-84.8075
MI390208	Austin Lake	Kalamazoo	M	11	2005	1090	1	42.16778	-85.55056
MI390478	Portage Lake	Kalamazoo	M	43	2005	180	2	42.25667	-85.34723
MI390540	Hogset Lake	Kalamazoo	M	32	2005	81	1	42.14861	-85.5875
MI430032	Idlewild Lake	Lake	M	22	2005	105	1	43.88862	-85.78361
MI430050	Reed Lake	Lake	O	45	2005	45	1	43.85756	-85.97859
MI460179	Devils Lake	Lenawee	M	63	2005	1330	2	41.98778	-84.28834
MI460249	Round Lake	Lenawee	E	67	2005	67	1	42.07084	-84.13334
MI470094	Chemung Lake	Livingston	E	70	2005	310	1	42.58112	-83.85
MI470096	Thompson Lake	Livingston	M	55	2005	262	1	42.61417	-83.91612
MI480011	Muskallonge Lake	Luce	E	20	2005	786	1	46.665	-85.63223
MI520147	Bass Lake	Marquette	M	23	2005	271	1	46.26112	-87.37167
MI520200	Pike Lake	Marquette	M	37	2005	88	1	46.26667	-87.57334
MI520207	Greenwood Reservoir	Marquette	M	38	2005	1400	1	46.44334	-87.81584
MI520212	Little Shag Lake	Marquette	O	35	2005	103	1	46.25806	-87.49334
MI520213	Sporley Lake	Marquette	M	42	2005	76	1	46.33195	-87.3375
MI520214	Wolf Lake	Marquette	M	13	2005	124	1	46.59	-87.89667
MI520216	Bass Lake	Marquette	O	78	2005	77	1	46.2625	-87.59056
MI530144	Piness Lake	Mason	E	38	2005	81	1	43.86056	-86.24584
MI600019	Ess Lake	Montmorency	O	51	2005	113	1	45.11417	-83.98112
MI600023	Avery Lake	Montmorency	O	78	2005	180	2	44.93556	-84.18334

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

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MI600025	Long Lake	Montmorency	O	80	2005	294	2	45.13056	-83.975
MI600029	Rush Lake	Montmorency	M	18	2005	224	1	45.11973	-84.09667
MI600030	Sage Lakes	Montmorency	M	36	2005	51	1	44.89167	-84.1525
MI600031	McCormick Lake	Montmorency	O	78	2005	100	1	44.95973	-84.24945
MI620060	Nichols Lake	Newaygo	O	55	2005	160	1	43.72889	-85.90834
MI620188	Benton Lake	Newaygo	M	14	2005	33	1	43.67056	-85.88973
MI620189	Pettibone Lake	Newaygo	M	40	2005	44	1	43.7725	-85.81056
MI620191	Woodland Lake	Newaygo	M	51	2005	203	3	43.705	-85.86473
MI640034	Silver Lake	Oceana	E	22	2005	690	1	43.67278	-86.50278
MI640065	School Section Lake	Oceana	M	26	2005	182	1	43.78112	-86.09584
MI690132	Pickereel Lake	Oshtemo	O	33	2005	43	1	45.17637	-84.52264
MI710034	Long Lake	Presque Isle	M	25	2005	5652	1	45.2175	-83.48389
MI710057	Lake Nettle	Presque Isle	M	46	2005	278	2	45.29111	-83.98695
MI710058	Lost Lake	Presque Isle	M	17	2005	104	1	45.2925	-83.96612
MI710060	Sunken Lake	Presque Isle	E	21	2005	50	1	45.21028	-83.72306
MI710075	Shoepac Lake	Presque Isle	O	94	2005	45	1	45.24234	-84.17459
MI710076	Big Tomahawk Lake	Presque Isle	O	32	2005	40	1	45.22948	-84.16328
MI750164	Three Rivers Impoundment	St Joseph	E	9	2005	300	1	41.94945	-85.58584
MI750136	Klinger Lake	St. Joseph	M	72	2005	830	1	41.80278	-85.54389
MI750161	Sand Lake	St. Joseph	E	22	2005	120	1	41.915	-85.45445
MI750162	Sturgeon Lake	St. Joseph	E	24	2005	250	1	41.96945	-85.32861
MI750166	Clear Lake	St. Joseph	M	31	2005	240	1	41.95139	-85.73556
MI750245	Portage Lake	St. Joseph	E	60	2005	510	1	42.04473	-85.51584
MI800272	Huzzy Lake	Van Buren	E	34	2005	80	1	42.13334	-85.82223
MI821228	Newburgh Lake	Wayne	H	9	2005	100	1	42.365	-83.41305556
MI070033	King Lake	Baraga	E	22	2006	508	1	46.52056	-88.40639
MI070034	Vermilac Lake	Baraga	E	4	2006	602	1	46.54056	-88.49445
MI070036	Big Lake	Baraga	M	34	2006	127	2	46.61389	-88.58
MI070045	Prickett Dam	Baraga	E	56	2006	810	1	46.72223	-88.66806
MI140047	Fish Lake	Cass	E	45	2006	340	1	42.04973	-85.85862
MI140055	Christiana Lake	Cass	E	40	2006	179	1	41.80528	-85.99723

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

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MI140056	Donnell Lake	Cass	M	63	2006	246	1	41.90861	-85.88945
MI140058	Juno Lake	Cass	E	30	2006	282	1	41.81112	-85.98834
MI140061	Birch Lake	Cass	M	95	2006	295	1	41.88139	-85.85834
MI140065	Magician Lake	Cass	M	57	2006	498	1	42.0658333	-86.17916667
MI140067	Paradise Lake	Cass	M	56	2006	185	1	41.89028	-85.90945
MI140069	North Twin Lake	Cass	M	54	2006	69	1	42.03473	-86.04945
MI140071	Shavehead Lake	Cass	M	70	2006	289	2	41.84473	-85.8625
MI140103	Dewey Lake	Cass	E	58	2006	174	1	42.05278	-86.18417
MI180056	Lake George	Clare	M	25	2006	134	2	43.95584	-84.93834
MI180064	Cranberry Lake	Clare	M	20	2006	106	1	44.06056	-84.74417
MI180069	Windover Lake	Clare	M	66	2006	51	1	43.95473	-84.99862
MI180109	Silver Lake	Clare	O	52	2006	55	1	43.91973	-84.96667
MI310083	Otter Lake	Houghton	E	25	2006	890	1	46.91417	-88.57223
MI310084	Pike Lake	Houghton	M	50	2006	83	1	46.83278	-88.84611
MI310085	Roland Lake	Houghton	M	40	2006	292	1	46.88417	-88.85195
MI310105	Torch Lake	Houghton	M	100	2006	2659	1	47.16778	-88.41528
MI310114	Emily Lake	Houghton	O	90	2006	54	2	46.85862	-88.85528
MI310118	Boston Lake	Houghton	E	6	2006	72	1	47.17195	-88.52917
MI310119	Sandy Lake	Houghton	E	7	2006	101	1	46.85112	-88.86806
MI310194	Portage Lake	Houghton	M	19	2006	10970	1	47.07806	-88.49417
MI330137	Lake Lansing	Ingham	M	35	2006	452	3	42.76306	-84.40445
MI350110	Round Lake	Iosco	M	19	2006	91	1	44.34028	-83.65695
MI350112	Tawas Lake	Iosco	E	4	2006	1670	1	44.30556	-83.49834
MI350138	Floyd Lake	Iosco	M	35	2006	41	1	44.33056	-83.6675
MI360046	Perch Lake	Iron	M	14	2006	994	1	46.36139	-88.65834
MI360083	Hannah Webb Lake	Iron	M	35	2006	64	1	46.35389	-88.72139
MI360086	Kidney Lake	Iron	M	15	2006	151	1	46.39056	-88.72223
MI380288	Crispell Lake	Jackson	M	25	2006	82	1	42.11306	-84.45917
MI380289	Gilletts Lake	Jackson	E	30	2006	350	1	42.25639	-84.31028
MI380291	South Lime Lake	Jackson	O	27	2006	96	1	42.18417	-84.55084
MI380294	Vandercook Lake	Jackson	E	42	2006	144	1	42.19084	-84.40223

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

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MI390407	Paw Paw Lake	Kalamazoo	M	56	2006	126	1	42.15917	-85.745
MI420045	Lac LaBelle	Keweenaw	M	37	2006	1146	1	47.37556	-88.00667
MI420046	Bailey Lake	Keweenaw	E	6	2006	204	1	47.4575	-88.09778
MI420047	Thayer Lake	Keweenaw	E	10	2006	116	1	47.28834	-88.26389
MI520149	Independence Lake	Marquette	E	30	2006	1860	1	46.80834	-87.71139
MI540064	Hillsview Lake	Mecosta	E	40	2006	123	1	43.71389	-85.37306
MI540073	Round Lake	Mecosta	M	45	2006	155	1	43.62417	-85.30834
MI540075	Clear Lake	Mecosta	E	30	2006	129	1	43.68056	-85.39723
MI540080	School Section Lake	Mecosta	O	33	2006	126	1	43.6	-85.27695
MI540093	Horsehead Lake	Mecosta	M	54	2006	451	3	43.68667	-85.26028
MI540104	Rogers Dam Pond	Mecosta	M	80	2006	512	1	43.61528	-85.48112
MI570010	Missaukee Lake	Missaukee	M	27	2006	1880	1	44.32084	-85.21612
MI570014	Crooked Lake	Missaukee	M	12	2006	500	1	44.33584	-85.27917
MI570018	Long Lake	Missaukee	M	15	2006	60	1	44.35223	-85.26056
MI590077	Tamarack Lake	Montcalm	H	10	2006	323	3	43.44042	-85.26112
MI610229	Muskegon Lake	Muskegon	E	70	2006	4150	1	43.22292	-86.30236
MI610408	Wolf Lake	Muskegon	E	38	2006	207	1	43.2594444	-86.105
MI610440	North Lake	Muskegon	E	19	2006	59	1	43.37611	-86.18334
MI620029	Fremont Lake	Newaygo	E	88	2006	790	2	43.45473	-85.96917
MI620032	Hess Lake	Newaygo	H	28	2006	755	1	43.38862	-85.76806
MI620057	Baptist Lake	Newaygo	M	65	2006	85	1	43.33306	-85.58195
MI620059	Englewright Lake	Newaygo	M	66	2006	54	1	43.32223	-85.58056
MI620063	Brooks Lake	Newaygo	E	23	2006	293	1	43.38862	-85.76667
MI620107	Kimball Lake	Newaygo	E	52	2006	153	1	43.45639	-85.82861
MI650026	Sage Lake	Ogemaw	E	81	2006	785	3	44.35389	-83.94223
MI670068	Todd Lake	Osceola	M	50	2006	75	1	43.95	-85.45306
MI670121	Wells Lake	Osceola	E	82	2006	48	1	43.99728	-85.41303
MI720030	Houghton Lake	Roscommon	E	20	2006	20044	3	44.3075	-84.71334
MI790117	Murphy Lake	Tuscola	E	41	2006	209	1	43.29973	-83.46112
MI790168	Caro Reservoir	Tuscola	H	9	2006	200	1	43.47306	-83.40147
MI800160	Van Auken Lake	Van Buren	E	46	2006	244	1	42.25639	-86.18195

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

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M1800187	Lake of the Woods	Van Buren	M	30	2006	289	1	42.10945	-86.00028
M1800240	Brandywine Lake	Van Buren	H	25	2006	69	1	42.34473	-85.85445
M1800252	Round Lake	Van Buren	H	27	2006	194	1	42.07917	-86.20695
M1800259	Upper Reynolds Lake	Van Buren	M	33	2006	87.3	1	42.20167	-86.00084
M1800260	Lake Cora	Van Buren	O	61	2006	197	1	42.20334	-85.98611
M1800261	Eagle Lake	Van Buren	M	60	2006	198	1	42.16945	-85.97084
M1800275	Maple Lake	Van Buren	M	15	2006	172	1	42.23334	-85.88751
M1800276	School Section Lake	Van Buren	M	50	2006	78	1	42.2925	-85.94305556
M1800277	Threemile Lake	Van Buren	E	35	2006	176	1	42.19556	-85.94973
M1800459	Hall Lake	Van Buren	E	37	2006	22.5	1	42.21361	-86.09917
M1810338	Sugarloaf Lake	Washtenaw	M	20	2006	180	1	42.34306	-84.115
M1810344	Winnewanna Impoundment	Washtenaw	E	8	2006	275	1	42.3519444	-84.10611111
M1830039	Lake Cadillac	Wexford	E	28	2006	1150	1	44.24528	-85.40973
M1830040	Lake Mitchell	Wexford	E	25	2006	2580	3	44.23445	-85.47
M1830073	Berry Lake	Wexford	M	28	2006	68	1	44.22806	-85.34861
M1010017	Cedar Lake	Alcona	E	10	2007	1075	1	44.5275	-83.33195
M1010019	North Lake	Alcona	M	95	2007	90	2	44.57445	-83.70112
M1010049	Vaughn Lake	Alcona	M	65	2007	90	1	44.5407	-83.72637
M1030203	Hutchins Lake	Allegan	M	34	2007	376	1	42.585	-86.13584
M1030263	Osterhout Lake	Allegan	M	30	2007	168	1	42.43945	-86.03889
M1030269	Lower Scott Lake	Allegan	E	7	2007	130	1	42.48806	-86.07639
M1180039	Budd Lake	Clare	E	30	2007	175	2	44.02084	-84.79417
M1180051	Mud Lake	Clare	E	4	2007	217	1	43.89973	-85.0775
M1180061	Crooked Lake	Clare	M	73	2007	264	2	43.84834	-85.01945
M1180065	Five Lakes	Clare	M	67	2007	120	1	43.87501	-84.80584
M1180066	Lily Lake	Clare	E	9	2007	161	1	43.99417	-84.80584
M1180068	Perch Lake	Clare	M	17	2007	50	1	43.84806	-85.00528
M1180079	Little Long Lake	Clare	M	61	2007	43	1	44.0255	-84.78348
M1200112	Jones Lake	Crawford	M	37	2007	43	1	44.78236	-84.59212
M1220028	Antoine Lake	Dickinson	M	20	2007	748	1	45.83806	-88.03195
M1220037	Carney Lake	Dickinson	M	38	2007	117	1	45.89667	-87.93334

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI220039	Mary Lake	Dickinson	M	76	2007	86	1	45.75056	-87.82028
MI220049	Edey Lake	Dickinson	M	30	2007	79	1	46.20084	-88.06334
MI220062	Sixmile Lake	Dickinson	E	23	2007	100	1	46.02306	-87.93667
MI260033	Second Impoundment	Gladwin	M	40	2007	815	1	44.05362	-84.33945
MI260065	Lake Four	Gladwin	M	40	2007	35	1	44.15487	-84.44731
MI350109	Loud Dam Pond	Iosco	O	34	2007	937	1	44.46417	-83.72361
MI360031	Chicago Lake	Iron	M	115	2007	1100	1	46.06306	-88.49728
MI360032	Sunset Lake	Iron	M	55	2007	545	1	46.1325	-88.59667
MI360035	Swan Lake	Iron	M	20	2007	165	1	46.16723	-88.39362
MI360042	Hagerman Lake	Iron	O	50	2007	584	1	46.05834	-88.77612
MI360045	Smoky Lake	Iron	M	60	2007	590	1	46.10667	-88.93556
MI360052	Fire Lake	Iron	M	40	2007	128	1	46.19139	-88.46723
MI360054	Long Lake	Iron	M	105	2007	60	1	46.12084	-88.45084
MI360071	Mary Lake	Iron	M	48	2007	255	1	46.05834	-88.22834
MI360073	Runkle Lake	Iron	E	25	2007	76	1	46.10195	-88.29889
MI360075	Bass Lake	Iron	E	21	2007	96	1	46.04445	-88.77139
MI360076	Brule Lake	Iron	E	20	2007	250	1	46.05611	-88.83612
MI360077	Cable Lake	Iron	M	29	2007	333	1	46.35223	-88.58889
MI360078	Camp Lake	Iron	M	56	2007	101	1	46.04195	-88.71473
MI360079	Deer Lake	Iron	M	44	2007	78	1	46.32917	-88.32528
MI360080	First Fortune Lake	Iron	O	70	2007	199	1	46.08834	-88.42417
MI360084	Iron Lake	Iron	M	45	2007	396	1	46.13973	-88.65834
MI360085	James Lake	Iron	O	10	2007	212	1	46.19973	-88.88751
MI360089	Stanley Lake	Iron	M	39	2007	310	1	46.05834	-88.74917
MI370064	Littlefield Lake	Isabella	O	66	2007	183	2	43.77056	-84.94167
MI370069	Stevenson Lake	Isabella	M	47	2007	138	1	43.76195	-84.83278
MI470101	Woodland Lake	Livingston	E	35	2007	290	1	42.55223	-83.77612
MI470104	Whitmore Lake	Livingston	M	69	2007	677	1	42.43584	-83.74695
MI470149	Base Line Lake	Livingston	M	64	2007	254	1	42.42695	-83.89306
MI470241	Bishop Lake	Livingston	M	54	2007	119	1	42.50028	-83.83917
MI470363	West Crooked Lake	Livingston	M	19	2007	176	1	42.53445	-83.85667

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI550098	Long Lake	Menominee	E	41	2007	284	1	45.42112	-87.82306
MI560169	Sanford Lake	Midland	E	10	2007	1250	1	43.67723	-84.37848
MI590144	Derby Lake	Montcalm	O	87	2007	118	1	43.27389	-85.12945
MI590153	Loon Lake	Montcalm	M	53	2007	63	1	43.27723	-84.95778
MI590155	Nevins Lake	Montcalm	M	60	2007	53	1	43.28056	-85.13834
MI590178	Mud Lake	Montcalm	E	3	2007	127	1	43.2725	-84.91639
MI590230	Rock Lake	Montcalm	M	21	2007	50	1	43.40834	-84.94167
MI590257	Bass Lake	Montcalm	E	6	2007	104	1	43.40223	-84.92764
MI590260	Half Moon Lake	Montcalm	M	48	2007	49	1	43.25153	-85.06281
MI610230	White Lake	Muskegon	E	70	2007	2571	3	43.37278	-86.40223
MI610404	Big Blue Lake	Muskegon	M	49	2007	330	1	43.452222	-86.20833333
MI620035	Diamond Lake	Newaygo	M	25	2007	171	2	43.60167	-85.81556
MI630684	White Lake	Oakland	M	32	2007	540	2	42.66056	-83.56556
MI630729	Cedar Island Lake	Oakland	M	71	2007	144	1	42.63056	-83.47389
MI630730	Long Lake	Oakland	M	12	2007	156	1	42.61	-83.45584
MI630732	Middle Straits Lake	Oakland	M	55	2007	171	1	42.57889	-83.42612
MI630733	Upper Proud Lake	Oakland	M	39	2007	55	1	42.56778	-83.52139
MI630741	Wolverine Lake	Oakland	M	57	2007	241	1	42.55362	-83.49278
MI630744	Pontiac Lake	Oakland	E	31	2007	585	1	42.666111	-83.45333333
MI650042	Clear Lake	Ogemaw	M	49	2007	171	1	44.40417	-84.28223
MI650052	Au Sable Lake	Ogemaw	E	52	2007	271	1	44.4291667	-83.91527778
MI650063	Horseshoe Lake	Ogemaw	O	48	2007	37	1	44.415	-84.28056
MI680015	Tea Lake	Oscoda	O	69	2007	216	1	44.845	-84.29056
MI680047	Mio Dam Pond	Oscoda	M	30	2007	944	1	44.66011	-84.13387
MI690018	Otsego Lake	Otsego	M	23	2007	1972	1	44.95223	-84.68945
MI690036	Big Bradford Lake	Otsego	M	30	2007	228	2	44.86195	-84.71139
MI690041	Big Bear Lake	Otsego	M	102	2007	350	1	44.93778	-84.87973
MI690048	Big Bass Lake	Otsego	O	35	2007	70	1	44.95	-84.51334
MI690130	Manuka Lake	Otsego	M	27	2007	163	1	44.95956	-84.73934
MI720056	Lake St. Helen	Roscommon	M	25	2007	2400	1	44.35973	-84.47806
MI800147	Lake Fourteen	Van Buren	E	25	2007	69	1	42.3825	-86.01889

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI800270	Lake Eleven	Van Buren	M	32	2007	51	1	42.39528	-86.01112
MI810209	Ford Lake	Washtenaw	E	22	2007	975	3	42.21625	-83.58473
MI810248	Big Portage Lake	Washtenaw	M	84	2007	644	1	42.42056	-83.92139
MI810329	Bruin Lake	Washtenaw	M	48	2007	136	1	42.42	-84.03973
MI810331	Crooked Lake	Washtenaw	M	20	2007	113	1	42.32695	-84.11139
MI810334	Joslin Lake	Washtenaw	M	20	2007	187	1	42.41667	-84.0725
MI810336	South Lake	Washtenaw	O	83	2007	197	1	42.39778	-84.07056
MI030225	Green Lake	Allegan	M	69	2008	309	2	42.75445	-85.59473
MI050052	Lake Bellaire	Antrim	O	95	2008	1775	1	44.95334	-85.21889
MI050089	Elk Lake	Antrim	O	160	2008	7730	2	44.89639	-85.37389
MI050095	Wilson Lake	Antrim	M	47	2008	106	1	45.1325	-85.24306
MI050101	Clam Lake	Antrim	M	29	2008	420	1	44.93612	-85.27334
MI050102	Intermediate Lake	Antrim	M	20	2008	1520	1	45.0241667	-85.2272222
MI050104	St. Clair Lake	Antrim	M	32	2008	91	1	45.16862	-85.23917
MI070035	Beaufort Lake	Baraga	O	32	2008	462	2	46.53556	-88.18695
MI080066	Jordan Lake	Barry	E	60	2008	430	1	42.76862	-85.14223
MI080092	Bristol Lake	Barry	M	50	2008	142	1	42.48445	-85.24889
MI080093	Carter Lake	Barry	E	25	2008	70	1	42.67056	-85.31167
MI080097	Fire Lake	Barry	M	48	2008	320	1	42.44278	-85.2875
MI080098	Long Lake	Barry	M	48	2008	289	1	42.55	-85.38362
MI080099	Middle Lake	Barry	M	40	2008	131	1	42.69862	-85.27084
MI080177	Deep Lake	Barry	M	35	2008	32	1	42.6212	-85.45759
MI080208	Cloverdale Lake	Barry	M	50	2008	58	1	42.53945	-85.39389
MI100086	Platte Lake	Benzie	M	90	2008	2516	2	44.69973	-86.11334
MI100138	Stevens Lake	Benzie	E	54	2008	46	1	44.75981	-85.87067
MI100159	Pearl Lake	Benzie	M	32	2008	285	2	44.76056	-85.90473
MI150075	Walloon Lake	Charlevoix	O	94	2008	4320	2	45.26139	-84.93389
MI150112	Susan Lake	Charlevoix	E	9	2008	130	1	45.31917	-85.18473
MI190099	Park Lake	Clinton	E	27	2008	185	1	42.78973	-84.43112
MI250416	C.S. Mott Impoundment	Genesee	H	13	2008	1200	1	43.09834	-83.63362
MI250421	Kearsley Reservoir	Genesee	E	20	2008	250	1	43.0555556	-83.65527778

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI270048	Gogebic Lake	Gogebic	M	25	2008	12800	1	46.47584	-89.55834
MI270053	Cisco Lake	Gogebic	E	20	2008	506	1	46.24306	-89.44584
MI270106	Bobcat Lake	Gogebic	E	15	2008	76	1	46.35639	-89.66612
MI270107	Chaney Lake	Gogebic	E	20	2008	520	1	46.305	-89.92528
MI270108	Clearwater Lake	Gogebic	M	10	2008	172	1	46.25695	-89.41167
MI270109	Henry Lake	Gogebic	M	30	2008	50	1	46.32778	-89.78778
MI270119	Marion Lake	Gogebic	M	40	2008	318	1	46.26639	-89.08917
MI270120	Moon Lake	Gogebic	O	40	2008	93	1	46.17195	-89.21223
MI270121	Sunday Lake	Gogebic	E	5	2008	222	1	46.48223	-89.94278
MI270128	Eel Lake	Gogebic	M	20	2008	52	1	46.2775	-89.76028
MI280082	Green Lake	Grand Traverse	O	105	2008	2000	2	44.59695	-85.78709
MI280109	Arbutus Lake	Grand Traverse	O	44	2008	305	2	44.65917	-85.51973
MI280110	Duck Lake	Grand Traverse	O	90	2008	1930	3	44.62306	-85.74973
MI280134	Cedar Hedge Lake	Grand Traverse	O	69	2008	195	2	44.66917	-85.78889
MI280144	Cedar Lake	Grand Traverse	M	61	2008	50	1	44.74667	-85.79945
MI340100	Long Lake	Ionia	M	57	2008	356	2	43.11223	-85.12528
MI340120	Woodard Lake	Ionia	E	22	2008	73	1	43.08	-85.06056
MI360050	Ellen Lake	Iron	O	73	2008	144	1	46.1725	-88.15195
MI360074	Stager Lake	Iron	M	55	2008	112	1	45.98501	-88.33223
MI380249	Wamplers Lake	Jackson	M	37	2008	781	1	42.07445	-84.14639
MI400016	Big Blue Lake	Kalkaska	O	90	2008	114	2	44.80556	-84.89389
MI400033	Big Guernsey Lake	Kalkaska	O	45	2008	50	1	44.71167	-85.32639
MI410268	Murray Lake	Kent	M	72	2008	320	2	43.03056	-85.37278
MI410423	Big Myers Lake	Kent	E	41	2008	85	1	43.13806	-85.48389
MI410435	Bass Lake	Kent	E	20	2008	184	1	43.26639	-85.32501
MI410438	Big Wabasis Lake	Kent	M	57	2008	418	1	43.14	-85.37139
MI410517	Pratt Lake	Kent	H	14	2008	160	1	42.88167	-85.32278
MI410539	Lime Lake	Kent	E	79	2008	36	1	43.20684	-85.63748
MI440090	Lake Minnewanna	Lapeer	M	25	2008	60	1	42.94417	-83.35084
MI440092	Long Lake	Lapeer	E	26	2008	205	2	43.10195	-83.22917
MI440104	Davison Lake	Lapeer	M	67	2008	56	1	42.88556	-83.37473

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

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MI450049	Glen Lake	Leelanau	O	130	2008	4865	1	44.87889	-85.96278
MI450050	Little Glen Lake	Leelanau	O	13	2008	1400	1	44.865	-86.00875
MI450062	Cedar Lake	Leelanau	O	45	2008	253	1	44.79723	-85.6425
MI450098	Davis Lake	Leelanau	M	40	2008	30	1	44.77695	-85.86206
MI460225	Allen Lake	Lenawee	M	50	2008	63	1	42.05917	-84.18334
MI460263	Deep Lake	Lenawee	E	50	2008	65	1	42.03445	-84.24167
MI520158	Squaw Lake	Marquette	O	80	2008	221	2	46.30028	-88.06695
MI540078	Merrill Lake	Mecosta	E	27	2008	86	1	43.80889	-85.15695
MI590143	Cowden Lake	Montcalm	E	50	2008	128	1	43.35445	-85.35917
MI590145	Dickerson Lake	Montcalm	E	48	2008	225	1	43.29389	-85.17056
MI590152	Horseshoe Lake	Montcalm	E	44	2008	97	1	43.40889	-85.18667
MI590154	Muskellunge Lake	Montcalm	E	37	2008	134	1	43.31584	-85.34778
MI630739	Valley Lake	Oakland	M	45	2008	84	1	42.80334	-83.52223
MI630740	Wildwood Lake	Oakland	M	17	2008	84	1	42.80611	-83.51389
MI630843	Seven Lakes	Oakland	E	53	2008	170	1	42.80945	-83.675
MI630905	Dickinson-Lake	Oakland	O	65	2008	44	1	42.80773	-83.66709
MI640064	McLaren Lake	Oceana	M	70	2008	271	1	43.62278	-86.05445
MI790118	North Lake	Tuscola	M	46	2008	53	1	43.23417	-83.42945
MI800254	North Scott Lake	Van Buren	M	50	2008	79	1	42.32945	-85.99889
MI810332	Fournile Lake	Washtenaw	M	16	2008	256	1	42.33834	-83.97223
MI810333	Halfmoon Lake	Washtenaw	E	82	2008	236	1	42.41778	-84.01334
MI020042	Fish Lake	Alger	M	41	2009	150	1	46.24139	-86.63639
MI030258	Duck Lake	Allegan	E	39	2009	122	1	42.43056	-85.90667
MI030473	Kalamazoo Lake	Allegan	H	10	2009	160	1	42.64889	-86.2025
MI080069	Gun Lake	Barry	M	70	2009	2680	4	42.58264	-85.50848
MI080095	Lower Crooked Lake	Barry	E	12	2009	417	1	42.46612	-85.46862
MI080102	Baker Lake	Barry	E	30	2009	59	1	42.64945	-85.50778
MI080103	Payne Lake	Barry	M	43	2009	118	1	42.63834	-85.52111
MI080106	Chief Noonday Lake	Barry	E	7	2009	50	1	42.64223	-85.50778
MI130152	Goguac Lake	Calhoun	M	66	2009	352	3	42.28473	-85.21167
MI130207	Prairie Lake	Calhoun	E	24	2009	80	1	42.34667	-84.795

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
M1170077	Caribou Lake	Chippewa	E	20	2009	825	1	46.00056	-84.00056
M1170107	Monocle Lake	Chippewa	M	55	2009	146	1	46.47278	-84.64223
M1210112	Corner Lake	Delta	O	40	2009	156	1	46.15834	-86.61362
M1390304	Eagle Lake	Kalamazoo	M	31	2009	73	2	42.32612	-85.32056
M1400012	Big Twin Lake	Kalkaska	O	85	2009	215	2	44.82223	-84.96139
M1400030	Starvation Lake	Kalkaska	O	60	2009	125	1	44.84889	-84.94639
M1400031	Cub Lake	Kalkaska	O	23	2009	53	1	44.71889	-84.95278
M1400035	Pickereil Lake	Kalkaska	O	72	2009	100	1	44.80056	-84.97667
M1410270	Reeds Lake	Kent	E	51	2009	265	1	42.95195	-85.60139
M1480012	Bodi Lake	Luce	E	49	2009	306	1	46.70417	-85.33112
M1480021	Twin Lakes	Luce	M	62	2009	103	1	46.30806	-85.5325
M1490036	Brevoort Lake	Mackinac	E	30	2009	4230	1	46.00417	-84.95806
M1490048	Little Brevoort Lake	Mackinac	E	11	2009	144	1	46.01862	-85.00778
M1500418	Stony Creek Impoundment	Macomb	E	23	2009	700	1	42.73084	-83.08834
M1510090	Portage Lake	Manistee	M	60	2009	2110	2	44.36278	-86.22431
M1510122	Bear Lake	Manistee	E	20	2009	1744	1	44.43084	-86.16084
M1510175	Pine Lake	Manistee	M	50	2009	156	1	44.19723	-86.00473
M1530073	Hamlin Lake	Mason	E	80	2009	4990	3	44.05528	-86.46834
M1530076	Round Lake	Mason	E	10	2009	571	1	44.00834	-86.11209
M1530105	Ford Lake	Mason	M	75	2009	208	1	44.05139	-86.12584
M1530143	Lincoln Lake	Mason	E	13	2009	156	1	43.97778	-86.45778
M1610406	Half Moon Lake	Muskegon	M	82	2009	58	1	43.25889	-85.81112
M1630554	Orion Lake	Oakland	M	80	2009	470	2	42.78112	-83.24973
M1630731	Loon Lake	Oakland	M	73	2009	243	1	42.68278	-83.36195
M1630738	Squaw Lake	Oakland	M	51	2009	133	1	42.81306	-83.28473
M1650045	George Lake	Ogemaw	E	90	2009	186	1	44.39917	-83.96917
M1700239	Spring Lake	Ottawa	E	47	2009	1047	1	43.08056	-86.19223
M1770034	Indian Lake	Schoolcraft	E	15	2009	8659	1	45.98889	-86.31167
M1770035	McDonald Lake	Schoolcraft	M	10	2009	1600	1	45.97806	-85.96806
M1770066	Colwell Lake	Schoolcraft	O	25	2009	148	1	46.22111	-86.43917
M1770068	Gemini Lakes	Schoolcraft	M	18	2009	120	1	46.4880556	-86.30277778

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI1770069	Kennedy Lake	Schoolcraft	E	5	2009	131	1	46.2147222	-85.88416667
MI800148	Clear Lake	Van Buren	M	55	2009	62	1	42.41112	-85.81917
MI830041	Hodempyl Dam Pond	Wexford	M	70	2009	1680	1	44.36237	-85.8175
MI020055	Au Train Basin	Alger	E	15	2010	1022	1	46.33028	-86.84973
MI040097	Beaver Lake	Alpena	O	77	2010	665	1	44.93612	-83.8
MI120077	Coldwater Lake	Branch	M	92	2010	1610	2	41.82945	-84.97528
MI120078	Randall Lake	Branch	H	35	2010	513	1	41.9757	-85.04195
MI120111	Rose Lake	Branch	O	80	2010	355	3	41.855	-85.04139
MI120129	Archer Lake	Branch	E	36	2010	64	1	41.88389	-84.92167
MI120137	Craig Lake	Branch	E	25	2010	122	1	42.00417	-85.02778
MI120138	North Lake	Branch	H	35	2010	513	1	41.96056	-85.03
MI120140	Morrison Lake	Branch	E	46	2010	288	1	41.98806	-85.02834
MI120165	East Long Lake	Branch	E	45	2010	123	1	41.85334	-84.96389
MI120194	Oliverda Lake	Branch	M	35	2010	143	1	42.04195	-85.24806
MI150103	Hoffman Lake	Charlevoix	O	22	2010	120	1	45.13167	-84.77834
MI160074	Burt Lake	Cheboygan	O	72	2010	17120	2	45.48362	-84.65834
MI160090	Silver Lake	Cheboygan	O	90	2010	74	1	45.26945	-84.63278
MI210110	Round Lake	Delta	O	55	2010	455	2	46.14778	-86.74917
MI210166	Boney Falls Reservoir	Delta	M	31	2010	171	1	45.9816667	-87.26944444
MI220059	Pickeral Lake	Dickinson	M	66	2010	71	1	46.08112	-87.81112
MI240077	Pickeral Lake	Emmet	M	74	2010	1080	1	45.39612	-84.76945
MI240079	Round Lake	Emmet	M	14	2010	333	1	45.405	-84.89028
MI250243	Ponemah Lake	Genesee	M	76	2010	380	1	42.81945	-83.75001
MI300141	Bear Lake	Hillsdale	M	50	2010	117	1	41.86973	-84.68278
MI300153	Bird Lake	Hillsdale	M	64	2010	113	1	41.82778	-84.52445
MI390305	Indian Lake	Kalamazoo	M	75	2010	758	1	42.15	-85.49223
MI390306	Long Lake	Kalamazoo	M	57	2010	575	1	42.1925	-85.52584
MI390496	West Lake	Kalamazoo	E	12	2010	342	1	42.18695	-85.56945
MI430022	Big Star Lake	Lake	M	25	2010	912	1	43.83278	-85.95001
MI430026	Wolf Lake	Lake	M	12	2010	418	1	44.00723	-85.84417
MI430049	Paradise Lake	Lake	O	33	2010	39	1	43.8945	-85.79659

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
 Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI460304	Round Lake	Lenawee	M	50	2010	515	1	41.96417	-84.27417
MI480017	Perch Lake	Luce	M	50	2010	126	1	46.62973	-85.595
MI520199	Johnson Lake	Marquette	O	45	2010	76	1	46.2675	-87.42112
MI520203	Anderson Lake	Marquette	M	30	2010	50	1	46.22306	-87.49084
MI520206	Engman Lake	Marquette	M	36	2010	53	1	46.33611	-87.32861
MI520210	Little Lake	Marquette	O	50	2010	448	1	46.27361	-87.35778
MI520211	Big Shag Lake	Marquette	M	30	2010	194	1	46.27195	-87.50028
MI530075	Bass Lake	Mason	E	12	2010	524	1	43.83084	-86.415
MI530170	Pere Marquette	Mason	E	38	2010	554	1	43.94584	-86.45028
MI600021	Lake Fifteen	Montmorency	O	55	2010	89	1	44.98778	-84.17695
MI600022	Avalon Lake	Montmorency	O	74	2010	372	1	45.10278	-83.95556
MI600043	Grass Lake	Montmorency	M	6	2010	230	1	45.12467	-84.02187
MI620066	Pickrel Lake	Newaygo	M	73	2010	318	1	43.45723	-85.8075
MI630419	Tipsico Lake	Oakland	E	20	2010	301	1	42.71834	-83.67112
MI640062	Crystal Lake	Oceana	E	37	2010	76	1	43.65334	-86.38056
MI640089	Pentwater Lake	Oceana	E	40	2010	436	1	43.7725	-86.43028
MI680033	McCollum Lake	Oscoda	O	60	2010	224	1	44.77417	-83.89223
MI690039	Big Lake	Otsego	M	30	2010	120	2	45.00473	-84.58389
MI700415	Pigeon Lake	Ottawa	E	25	2010	225	1	42.90223	-86.20473
MI710035	Grand Lake	Presque Isle	O	25	2010	5660	2	45.29861	-83.51695
MI750124	Palmer Lake	St. Joseph	M	42	2010	448	1	41.94389	-85.31584
MI750139	Fishers Lake	St. Joseph	M	42	2010	327	1	41.995	-85.5725
MI750142	Corey Lake	St. Joseph	M	80	2010	530	2	41.92917	-85.73334
MI750144	Pleasant Lake	St. Joseph	M	53	2010	252	2	41.95834	-85.70223
MI750147	Big Fish Lake	St. Joseph	M	75	2010	153	1	41.87639	-85.47917
MI750148	Long Lake	St. Joseph	H	41	2010	211	2	41.95834	-85.75001
MI750160	Crotch Lake	St. Joseph	M	58	2010	123	1	41.84084	-85.42473
MI750261	Prairie River Lake	St. Joseph	E	57	2010	136	1	41.86056	-85.39806
MI120120	Gilead Lake	Branch	M	49	2015	130	2	41.79362	-85.16445
MI120122	Lake Lavine	Branch	M	66	2015	87	1	41.76834	-85.0375
MI250241	Fenton Lake	Genesee	O	33	2015	845	3	42.84681	-83.71653

LAKE WATER QUALITY ASSESSMENT MONITORING PROGRAM
Lake Sampling Schedule (2001-2015)

Waterbody ID	Lake Name	County	Trophic Status (historical)	Depth (feet)	Sampling Year	Surf. Area (acres)	Number of Basins	Latitude	Longitude
MI250242	Lobbell Lake	Genesee	E	78	2015	545	1	42.79167	-83.83278
MI300114	Hemlock Lake	Hillsdale	M	65	2015	140	1	41.89639	-84.7925
MI300154	Cub Lake	Hillsdale	M	43	2015	69	1	41.81723	-84.63528
MI390215	Barton Lake	Kalamazoo	E	52	2015	347	2	42.0975	-85.53445
MI390408	Sugarloaf Lake	Kalamazoo	M	30	2015	148	1	42.15612	-85.62834
MI390541	Gourdneck Lake	Kalamazoo	M	52	2015	222	1	42.15973	-85.57389
MI600020	Clear Lake	Montmorency	M	90	2015	133	1	45.12584	-84.17695
MI600027	Atlanta Lake	Montmorency	O	9	2015	94	1	45.00223	-84.14528
MI600028	Gaylanta Lake	Montmorency	M	30	2015	115	1	44.97889	-84.30223
MI640049	Stony Lake	Oceana	E	41	2015	276	3	43.565	-86.48667
MI700237	Lake Macatawa	Ottawa	H	40	2015	1780	2	42.77695	-86.18084
MI710061	Lake Emma	Presque Isle	M	10	2015	196	1	45.25861	-83.99639
MI710073	Lake Esau	Presque Isle	O	29	2015	275	1	45.31834	-83.46931
MI710074	Lake May	Presque Isle	M	20	2015	161	1	45.25528	-83.94934
MI750112	Long Lake	St. Joseph	E	32	2015	222	1	41.91862	-85.33862
MI750163	Thompson Lake	St. Joseph	M	30	2015	150	1	41.82667	-85.49223
MI800159	Bankson Lake	Van Buren	M	42	2015	202	1	42.11806	-85.79973

Lakes= 730

Basins= 873

	Lakes	Basins
Sampled 2001	56	69
Sampled 2002	64	76
Sampled 2003	79	91
Sampled 2004	83	103
Sampled 2005	84	97
Sampled 2006	83	100
Sampled 2007	85	96
Sampled 2008	76	92
Total=	610	724

ATTACHMENT 2

Lake Water Quality Assessment Monitoring Program for Michigan Inland Lakes Baseline Water Quality and Trophic Status Monitoring Protocol

INTRODUCTION

This document outlines the protocol and provides guidance for site verification, sample collection, processing, and shipment of water samples for laboratory analysis. These procedures were prepared in cooperation between the U.S. Geological Survey (USGS) and the Michigan Department of Environmental Quality (MDEQ).

STRATEGY

Lakes are classified by their physical, chemical, and biological characteristics into one of several trophic categories (oligotrophic, mesotrophic, eutrophic, and hypereutrophic). The trophic state is a measure of a lake's primary productivity and includes such factors as nutrient levels, organic matter content, dissolved oxygen levels and water transparency. The Carlson Trophic State Index (TSI) is commonly used to classify lakes as to their trophic status (Carlson, 1977). The Carlson TSI is based on water column transparency, which is correlated to total phosphorus and chlorophyll *a* concentration in the epilimnion and the photic zone, respectively. Carlson's TSI was developed for use with lakes that have few rooted aquatic plants and little non-algal turbidity. Knowledge of the relative abundance of macrophytes in a lake is therefore necessary to adjust the TSI classification for "macrophyte dominated" lakes to take into consideration nutrient uptake by the plant community. The Carlson's TSI is computed from concentration of total phosphorus (collected from the epilimnion), chlorophyll *a* concentrations (collected from the photic zone), and Secchi-disk depth in the open water of the lake.

Lakes will be sampled during spring turnover and then again in late summer during maximum thermal stratification. Lake water during spring turnover is generally well mixed, and samples collected during this period will characterize baseline water quality conditions. Samples for general water chemistry, nutrients, and chlorophyll *a* will be collected at this time and Secchi-disk depth measurements will be made.

Summer sampling is performed during maximum water column stratification.

Thermal strata

(epilimnion, thermocline, and hypolimnion) in the water column will be identified and discrete samples from each stratum will be collected. Water samples for nutrients, and chlorophyll *a* will be collected during this period and Secchi-disk depth measurement will be made. Additional tools used in the assessments include use of satellite imagery, inspection of USGS topographic maps, Michigan Department of Natural Resources (MDNR) bathymetry maps, and macrophyte reconnaissance of the littoral zone.

Sampling locations will be a single vertical in the deepest portion of the lake. Sampling sites will be provided by the MDEQ and identified with a U.S. Environmental Protection Agency (EPA) STORET number. A USGS site number will also be assigned to each sampling location (a unique 15 digit number). The first 13 digits of this site number represent the latitude and longitude location of the sampling location. The last 2 digits (sequence number) represent the vertical location in the water column where the sample was collected. The same 2 digit sequence number will also be used to identify sample depth with the STORET numbering system. These numbering systems will provide

consistency with historical lake data and will allow data to be stored and retrieved as discrete samples in the USGS National Water Information System (NWIS) database as well as the U.S. Environmental Protection Agency's STORET system. Sequence number assignments will be as follows:

Location in water column	Sequence number
Hypolimnion or 3 ft above lake bottom	02
Photic zone	03
Epilimnion or 3 ft below lake surface	05
Thermocline or mid-depth	06

A sampling crew will consist of two people. Sampling procedures are identified by specific tasks and are done simultaneously whenever possible for efficiency. These tasks with associated methodology and protocol are as follows:

Site verification will occur during the spring visit. The maximum depth of the lake and location of the previous sampling site will be located on lake maps and provided to field crews. The location of the historical sampling site will be verified by comparing the maximum depth provided with the recorded depth from an electronic depth finder. Once the maximum depth of the lake is located, the accuracy of the historical latitude and longitude will be verified with a hand-held global positioning system (GPS). If the lat-long provided for the sampling location, is determined to be outside of the deep basin or not at the deepest portion of the basin, the lat-long will be updated with the correct location determined by the GPS. The lat-long will also be updated in lakes with large basins with areas of consistent depth, once the maximum depth is located and if there is greater than 3 seconds difference between the lat-long provided and that of which is recorded by GPS. In all cases the difference between the provided location and the correct location by GPS should be recorded on the field data sheet.

Once the deepest point in the lake is located the boat will be anchored. An extra long anchor rope should be used which will allow the boat to drift back from any bottom disturbance.

Vertical profiles during the spring and summer visits are to determine the extent of stratification that has occurred and document water-quality characteristics throughout the water column. The profiles will be made with a Hydrolab™ or similar instrument. Specific conductance, water temperature, dissolved oxygen and pH will be measured versus depth. Total depth will be determined and profile measurements will be made at about 10 percent frequency of total depth with the first measurement taken 3 feet below lake surface and continued to 3 feet above lake bottom. Vertical profiling measurements should be made at a frequency not greater than every 3 feet through the thermocline at those lakes that are classified as a cold water fisheries by MDNR (attachment 4). All field data will be recorded on the field data sheet with associated time of each measurement (attachment 1).

Prior to data collection, the Hydrolab™ will be calibrated in accordance to the manufacturers guidelines (Hydrolab Corporation, 2000). The following pertinent calibration data will be recorded in the calibration section on the field data sheet (attachment 1).

Barometric pressure in (mm Hg)
Calibration air temperature
100 percent dissolved oxygen concentration by chart (Weiss, 1970)
100 percent dissolved oxygen concentration value by meter
pH of buffers used in calibration (temperature corrected)
Meter pH value after calibration
Specific conductance standards used in calibration
Meter specific conductance value after calibration, corrected to 25 deg. C

Calibration procedures for Hydrolab Quanta™

Depth

- Inspect depth sensor port for calcium deposits, clean with vinegar if necessary.
- Enter zero into display unit for the standard at the water's surface.

Dissolved oxygen (Saturated Air Method)

- Fill the calibration cup with de-ionized or tap water, until the water is just below the o-ring. Cap should be covered and sufficient time allowed for sensors to stabilize to water temperature.
- Carefully remove any water droplets from the membrane with a tissue.
- Enter the local barometric pressure into the display unit as the calibration standard.
- Dissolved oxygen by the meter should check 100 percent saturation by chart within 0.1 Milligrams per Liter (mg/L).

Repeat calibration process if needed.

pH

- Inspect Teflon Reference Junction, clean if needed according to manufactures recommendations.
- Rinse pH probe and calibration cup with pH 7.0 standard and fill with standard.
- Enter corrected pH value for temperature into display unit.
- Repeat above process with another pH standard that would bracket the expected range.
- The pH from the meter should check a third pH standard within 0.1 units.

Repeat calibration process if needed.

Specific Conductance

- Rinse with standard and fill the calibration cup with a specific conductance standard that would be slightly less than the expected water to be measured, and enter value into display unit.
- Rinse cup with another standard that would bracket expected measurement range.
- Specific conductance by the meter should check the second standard by 5 microsiemens per centimeter ($\mu\text{S}/\text{cm}$).

Repeat process if needed.

Secchi disk will be used to determine transparency and define the photic zone. The photic zone is considered twice the Secchi transparency depth. Ideally Secchi disk readings should be taken between 10:00 a.m. and 4:00 p.m. whenever possible. Sunglasses should not be worn when making Secchi-disk observations. Disk measurements should be made by lowering the disk into the water suspended on a graduated line (one foot increments) on the shaded side of the boat. The observer should lean over the side of the boat, directly over the disk as it is lowered. The depth at which the disk disappears is noted. The disk is then raised slowly until it again becomes visible, and the depth is noted. The average of these two readings is the Secchi disk measurement and will be recorded on the field data sheet (attachment 1). Secchi-disk measurements should be recorded to the nearest 0.5 foot. This task can be performed in conjunction with vertical profiling and prior to sample collection.

Chlorophyll *a* will be sampled during the spring and summer visits. A depth-integrated composite sampler will be lowered through the photic zone to obtain a composite sample. The transit rate should be uniform and slow enough to obtain the maximum amount of water without completely filling the sampler. If the sampler overfills the bottle should be swirled and the sample discarded. The process should be repeated at a slightly faster transit rate. In shallow lakes with depths less than twice the Secchi disk transparency the sampler should only be lowered to within several feet of the lake bottom to avoid bottom disturbance. The maximum depth of the composite sample should be recorded on the field data

sheet. Once a sample is collected the bottle is mixed before a sub-sample is collected.

Processing and Filtration

- A homogenous sub-sample is poured into a 250 ml brown plastic bottle.
- 5 drops of $MgCO_3$ are added to the sample. Sample is then placed on ice and in the dark until filtered.
- Place a 47-mm, 0.45μ filter (HAWP 047 00) on the filtration apparatus.
- Measure 50 ml of well mixed sample into a graduated cylinder.
- The sample is then filtered with no more than 250 mm Hg vacuum pressure.
- Rinse the sides of the graduated cylinder and the filtration unit with a few milliliters of chilled distilled water.
- Using tweezers, fold the filter twice with the plankton on the inside and place into a vial. The vial should be labeled with lake's name, date, time, STORET number, sequence number, bottle code **Ca**. Record all information on field data sheet and laboratory analysis sheet (attachment 1 and 2).
- Add 10 ml of 90% acetone to the vial. Mark acetone level on the vial with a marker then wrap the glass vial with tin foil to prevent exposure to light, place on ice.

Spring sampling will occur during turnover (generally 7-10 days after ice-out). Three discrete samples will be collected with a vertical Van Dorn style sampler. Samples will be collected 3 ft below lake surface, 3 ft above lake bottom and at mid-depth. Care must be taken not to disturb the lake bottom when collecting the bottom sample. The top, mid-depth, and bottom samples will be analyzed for major nutrients (total phosphorus, nitrogen as $NO_2 + NO_3$, nitrogen as ammonia, and Kjeldahl nitrogen) bottle code **GA**. The sample collected at mid-depth will also be analyzed for major ions (Ca, Mg, Na, K, Cl, SO_4 , alkalinity and hardness) bottle code **MN** and **MA**. If the lake has not turned over or stratification has started to occur then samples for major ions will be collected from all three vertical locations.

Prior to any field work the sampler should be cleaned with a phosphate free laboratory grade detergent and rinsed with de-ionized water. The sample rope should be inspected and washed if needed to eliminate any source of sample contamination. The sampler should then be transported and stored at all times in a clean plastic bag. Prior to sample collection on the lake the sampler will be rinsed with lake water. After all three sample sets are collected the sampler should be rinsed with de-ionized water (before any residue can dry) then returned to a clean plastic bag. While handling and processing samples, powderless vinyl gloves should be worn. Safety glasses must be worn when handling preservatives.

All samples will be collected as whole water samples. Sample bottles provided by the laboratory should be rinsed with a small amount of sample water prior to filling. A small amount of space should be left in the bottle for the addition of preservatives. Each set of samples will be identified with the lake's name, and STORET number, 2 digit sequence number, date, time, depth and bottle code. This same information should be recorded on the field data sheet (attachment 1) and laboratory request form (attachment 2).

Processing

- Visually inspect sample for excessive turbidity and signs that the sampler may not have properly tripped by the messenger, resample if necessary. If the bottom was disturbed and causing excessive turbidity, the sample location should be moved and re-sampled.
- Release air valve on top of sampler to allow sample to be drawn.
- Rinse and fill each bottle allowing room for the addition of preservatives.
- One 250 ml plastic bottle. Bottle code **GA** add 5 drops of H₂SO₄ to pH < 2.
- One 250 ml plastic bottle. Bottle code **MA** add 2 ml of HNO₃ to pH < 2.
- The sample pH can then be checked with litmus paper. If checked, the paper should never be inserted into the bottle but a small amount of sample is poured onto the paper strip.
- One 250 ml plastic bottle. Bottle code **MN** has no preservatives.
- All samples should be put on ice.

Summer sampling will occur during late summer, during maximum thermal stratification. The epilimnion, thermocline, and hypolimnion will first be identified taking vertical profiles (water temperature, specific conductance, pH, and dissolved oxygen) at the sampling site. The epilimnion (uppermost stratum) should be fairly uniform in temperature; the middle stratum (thermocline) will have a significant drop in temperature per unit of depth; the lowermost stratum (hypolimnion) is the coldest but is fairly uniform in temperature (Welch, 1952).

Three discrete samples will be collected during this period. The sampling methodology will be the same as used in the spring except the mid-depth sample will be collected from the approximate middle of the thermocline. Only major nutrients (total phosphorus, nitrogen as NO₂ + NO₃, nitrogen as ammonia, and Kjeldahl nitrogen) bottle code **GA**, will be analyzed from each sample stratum.

A qualitative macrophyte survey will be made during the late summer sampling. These sites will be evaluated when possible to support satellite imagery technology in developing quantitative survey methods. On larger lakes a minimum of two shores will be visited. On smaller lakes four shorelines, (North, South, East and West) will be evaluated. A visual plant density estimate will be made at each site. An Aquatic Vegetation Assessment Site (AVAS) will be

established which is approximately 300 to 600 feet along the shoreline then out past the littoral zone (evaluation will be made within this area).

During the survey drive the boat through the AVAS parallel to the shoreline in a zigzag fashion. Grappling hooks or a plant rake will be used to collect a macrophyte sample for identification. "*A Citizens Guide for the Identification, Mapping and Management of the common rooted aquatic plants of Michigan lakes*", will be the field guide for plant identification. Lake bottom type should also be noted during the macrophyte survey, all information will be recorded on field form (attachment 3). A sample should be collected of any dense population of macrophytes, which cannot be positively identified. The plant should be laid flat between wet paper towels and placed into a zip-lock bag. The sample is then shipped to MDEQ attention of Ralph Bednarz at 116 West Allegan, Lansing, Michigan 48933.

The following guidelines can be used in estimating density and completing field notes (attachment 3) on each AVAS:

FOUND- one or two plants of a species located in the AVAS. This corresponds to being present in less than 2 percent of the AVAS.

SPARSE- plants of a species found scattered in the AVAS. This corresponds to being present in 2 to 20 percent of the AVAS.

MODERATE- plants commonly present and easily found, usually the major species in a plant rake throw. This corresponds to being present in 21 to 60 percent of the AVAS.

DENSE- plants of this species present in considerable quantity or found on most rake throws. This corresponds to being present in 61 to 100 percent of the AVAS.

QUALITY CONTROL PROCEDURES

Approximately 10 percent of all sample types collected will be QC samples. Regardless of the number of lakes assigned to a sampling crew, each sampling crew will collect a minimum of one QC sample of each type of analysis or 10 percent of total lakes assigned (whichever is greater). All applicable information concerning acid lot numbers and QC samples will be recorded on the field data sheets and the analysis request forms (attachment 1 and 2). Bottle labels should be filled out completely, QC designation as well as the bottle code that indicates analysis should be shown. The QC sample time should be one minute different from the primary sample.

TRIP BLANK- designated as **TB**: Preservatives will be added to empty sample bottle at the beginning of a trip; samples are chilled then shipped to the lab at the end of a trip.

EQUIPMENT BLANK-designated as **EB**: De-ionized water, supplied by the MDEQ laboratory will be used to completely fill the sampler. Sub-samples will be drawn and preservatives added following standard procedures. Samples are chilled and shipped to the lab.

SAMPLE REPLICATES- designated as **SR**: A second sample is drawn from the Van Dorn style sampler or the chlorophyll a sampler immediately after the primary sample is collected. Standard procedures are followed for processing and preservation

SAMPLE SHIPMENT

The Monday prior to sample collection, the MDEQ Environmental Laboratory should be notified of the number of analyses which have a limited holding time (phosphorus, chlorophyll a and the nitrogen series) that the lab may expect to receive that week (example: 12 total phosphorus, 8 chlorophyll etc.). Dawn Hartig is the primary contact for this and any shipping problems. She may be reached at 517-335-9800, (e-mail: hartigd@state.mi.us).

With proper filtration and preservation techniques, water samples and chlorophyll a samples can be shipped on a weekly basis. All samples must be kept chilled on ice until ready to be shipped. Shipping coolers should be doubled lined with plastic bags to prevent leaking of ice water. Laboratory analysis request forms and safety information sheets must be filled out completely. Copies of all laboratory request forms should be kept and originals placed in zip-lock bags taped to the top of the inside of the coolers. Doug Wood is the primary contact for ordering bottles and preservatives. He may be contacted at 517-335-9686 or 517-327-2646. The laboratory will not accept weekend deliveries and any hand deliveries should be made prior to 12 noon on Friday. All other samples should be shipped overnight express to:

SAMPLE RECEIVING
**MDEQ
DWRPD
ENVIRONMENTAL LAB
3350 N. Martin Luther King Jr. Blvd.
Bldg. #44, Third Floor
Lansing, Michigan 48906-2933**

REFERENCES

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Wandell, H.D., Wolfson, L., 2000, A Citizen's Guide for the Identification, Mapping and Management of the Common Rooted Aquatic Plants of Michigan Lakes, Department of Fisheries and Wildlife, Michigan State University, [variously paged].

Weiss, R.F., *Deep Sea Research*, v.17, p.721

Welch, P.S., 1952, *Limnology* (2nd ed.): New York, McGraw-Hill Book Company, p 50-53.



ATTACHMENT 3
MDEQ Laboratory Services Standard Operating Procedure Documents

- SOP 304.2 Determination of Total Phosphorus in Water
- SOP 318.1 Nitrate Plus Nitrite as Nitrogen in Water
- SOP 316.1 Ammonia As Nitrogen in Water
- SOP 303.2 Determination of Total Kjeldahl Nitrogen in Water
- SOP 340.2 Calcium, Magnesium, Potassium, and Sodium Atomic Absorption, Direct Aspiration
- SOP 302.1 Sulfate (Colorimetric, Automated Methylthymol Blue, TRAACS 800) Total in Water
- SOP 300.1 Chloride (Colorimetric, Automated Methylthymol Blue, TRAACS 800) Total in Water
- SOP 310.3 Chlorophyll A
- SOP 361.0 Absorbance (Color) Measurement by Spectrophotometry





EFFECTIVE DATE: 03/2006

SOP# 304

REVISION # 2

DETERMINATION OF TOTAL PHOSPHORUS IN WATER

Table of Contents

1.0	Applicable Analytical Methods	1
2.0	Matrix or Matrices.....	2
3.0	Method Detection Limits.....	2
4.0	Scope and Application	2
5.0	Method Summary	2
6.0	Definitions	3
7.0	Interferences	4
8.0	Safety	4
9.0	Equipment and Supplies	5
10.0	Reagents and Standards	6
11.0	Sample Collection, Preservation, Shipment, and Storage	8
12.0	Quality Control (QC).....	8
13.0	Calibration and Standardization	9
14.0	Procedure.....	9
15.0	Calculations.....	12
16.0	Method Performance.....	13
17.0	Pollution Prevention	13
18.0	Data Assessment	13
19.0	Corrective Actions	14
20.0	Waste Management	15
21.0	References	15
22.0	Attachments	16
	Signature Page	17

1.0 Applicable Analytical Methods

- 1.1 Phosphorus, Total (Colorimetric, Automated, Block Digestor AAll), Method 365.4, U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes (MCAWW) – EPA/600/4-79-020 – Revised March, 1983.
- 1.2 Total Nitrogen and Total Phosphorus BD-40 Digestion Procedure for Water, Brann & Lubbe, August 1974.
- 1.3 AutoAnalyzer Applications, Nitrogen and Phosphorus in Acid Digests, Brann & Lubbe, Method US-329-74A.
- 1.4 AutoAnalyzer Applications, Phosphorus, Total, Brann & Lubbe, Method 696A-82W.

2.0 Matrix or Matrices

2.1 Drinking water.

2.2 Ground water.

2.3 Surface water.

2.4 Domestic and industrial wastewater.

3.0 Method Detection Limits

3.1 All method detection limits (MDL) shall be performed according to the Code of Federal Regulations 40 CFR, Part 136, Appendix B. See internal procedure SOP 103.

3.2 MDL's must be established by using a low level standard (Detection Verification Standard - DVS) at a concentration of two to three times the estimated instrument detection limit to determine the MDL values. At least seven replicate aliquots of the standard must be processed through the entire analytical method. Perform all calculations defined in the method. Report the concentration values in the appropriate unit. Calculate the MDL as follows:

$$\text{MDL} = (t) \times (\text{SD})$$

Where: t = student's "t" value for a 99% confidence limit and a standard deviation (SD) estimate with $N - 1$ degrees of freedom.
SD = standard deviation of the replicate analyses.

3.3 In the DEQ Environmental Laboratory, 28 replicate analyses of a DVS with a mean concentration of 0.0175 mg P/l resulted in a SD of 0.0011 mg P/l and MDL (99%) of 0.0027 mg P/l.

3.4 MDL's should be determined annually, when a new operator begins work, or whenever there is a significant change in the background or instrument response.

4.0 Scope and Application

4.1 This method covers the determination of total phosphorus in drinking or surface waters and in domestic or industrial wastewater.

4.2 The applicable range of this method is 0.005 to 1.0 mg P/l. The range may be extended by sample dilution.

5.0 Method Summary

5.1 The sample is heated (digested) in the presence of sulfuric acid, potassium sulfate, and mercuric oxide. Polyphosphates and organic phosphorus compounds are converted to orthophosphate by the digestion. Only orthophosphate forms a blue color in this test. The residue is cooled, diluted to 10.0 mL, and analyzed for phosphorus by

an automated ascorbic acid reduction method. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue colored complex by ascorbic acid. The color is proportional to the phosphorus concentration. This digested sample may also be used for total Kjeldahl nitrogen.

6.0 Definitions

- 6.1 Calibration Blank/0% standard (CB) – A volume of reagent water fortified with the same matrix as the calibration standards but without the analytes, internal standards, or surrogate analytes.
- 6.2 Calibration Standard (CAL) – A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument's response with respect to analyte concentration.
- 6.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS/MSDs are analyzed exactly like a sample, and their purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSDs corrected for background concentrations. Percent recovery of the added analyte (standard) must be within the acceptable range established for the assay. Percent relative difference the MS and the MSD must be within acceptable range established for the assay. MS/MSDs should be run at a rate of 1 pair for every 13 or fewer samples.
- 6.4 Reporting Limit (RL) – The RL is 0.005 mg P/L in the Michigan DEQ Environmental Laboratory.
- 6.5 Laboratory Bottle Blank (LBB) – An aliquot of reagent water is add to a sample container and treated exactly like a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LBB is used to determine whether method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 6.6 Field Blank (FB) – Reagent water placed in a sample container in the field and treated exactly like a sample including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FB is to determine if method analytes or other interferences are present in the field environment.
- 6.7 Field Duplicates (FD1 and FD2) – Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, transportation, storage, and laboratory procedures.
- 6.8 Stock Standard Solution (STOCK I) – A concentrated solution containing a single certified standard that is a method analyte or a concentrated solution of a single

analyte prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source. STOCK I's are used to prepare primary dilution standards.

- 6.9** Primary (intermediate) Dilution Standard Solution (STOCK II) – A solution of several analytes prepared in the laboratory from STOCK I's and diluted as needed to prepare calibration solutions and other needed analyte solutions.
- 6.10** Quality Control Sample (QCS) – A sample matrix containing method analytes or a solution of method analytes in water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is generated from a source of reagents different than those used to prepare the primary dilution standards and the CAL and is used to check laboratory performance. The QCS should be run at a rate of 1 for every 13 or fewer samples.

7.0 Interferences

- 7.1** If the sample remains turbid after digestion, the digested sample may be centrifuged before analysis.
- 7.2** If dark, stringy, solid material appears after digestion, not all of the organic material has been digested. The sample should be redigested using a smaller aliquot.
- 7.3** Sample turbidity must be removed prior to analysis for phosphorus. Samples for total phosphorus should be centrifuged if necessary only after digestion. Sample color that absorbs in the photometric range used for analysis will also interfere.
- 7.4** Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that will bias analyte response.
- 7.5** Phosphorus in the laboratory may easily become an interference in this test method from contamination of reagents, caps, pipettes, or from the laboratory atmosphere. Care should be taken to ensure that phosphorus compounds, either as reagents or in cleaning solutions, are not used in the same work area.

8.0 Safety

- 8.1** Safety glasses and shoes that cover the feet are required in all designated laboratory areas.
- 8.2** It is recommended that the analyst wear gloves and a lab coat when performing this procedure.
- 8.3** The analyst must be familiar with the Laboratory Chemical Hygiene Plan.
- 8.4** The analyst must be familiar with the Laboratory Safety Policy (SOP 100).
- 8.5** The analyst must be familiar with any material safety data sheets applicable to this method.

- 8.6** The analyst must be familiar with the location of safety equipment including showers, eye wash stations, and spill kits.
- 8.7** The analyst should always thoroughly wash hands in warm soapy water when leaving the work area and before handling food or drink.
- 8.8** The analyst should assume that all samples have the potential to be hazardous and should always exercise caution when transporting, handling, and/or opening any samples.
- 8.9** General good laboratory practices are required. The analyst should take all necessary precautions in order to minimize the potential of exposure to samples and reagents used in this method.
- 8.10** The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Cautions are included for known extremely hazardous materials or procedures. The laboratory and each analyst 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 MSDS should also be made available to all personnel involved in chemical analysis. Review of the Department's safety plan is also advisable.
- 8.11** The following list of raw materials marks those known to have the potential to be highly toxic or hazardous. Consult the MSDS for further information.

<u>Chemical</u>	<u>Safety Classification</u>
Adenosine 5'-Monophosphate (AMP)	N/A
Aerosol 22 solution	N/A
Ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	Harmful
Antimony potassium tartrate, $(\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2 \text{H}_2\text{O})$	Toxic
Ascorbic acid, $(\text{C}_6\text{H}_8\text{O}_6)$	N/A
Acetone (nanograde)	Toxic
Mercuric oxide (HgO)	Toxic
Hydrochloric acid, 36.5-38% HCl	Corrosive
Potassium phosphate, mono-basic (KH_2PO_4)	N/A
Potassium sulfate (K_2SO_4)	N/A
Sodium chloride	N/A
Sulfuric acid, 95-98% H_2SO_4	Corrosive

9.0 Equipment and Supplies

- 9.1** Brann & Lubbe AA3 dual channel autoanalyzer system (or equivalent) consisting of:
- 9.1.1** Compact sampler.
- 9.1.2** Dual speed proportioning pump.
- 9.1.3** Multi chemistry manifolds (for both TKN and TP).
- 9.1.4** Dual channel digital colorimeters.
- 9.1.5** Computer.

- 9.1.6 AACCE software.
- 9.1.7 Block digester – 40 or 50 place digester with tube rack and side shields.
- 9.1.8 Digestion tubes – 75 mL Pyrex tubes.

- 9.2 Vortex mixer.

- 9.3 Magnetic stirrer plate.

- 9.4 Sample cups – Disposable, 5 mL, plastic.

- 9.5 Boiling stones – Teflon (TFE).

- 9.6 Disposable pipettes – 10 mL, plastic.

- 9.7 Repeat pipettors (adjustable) and disposable tips – 5 and 10 mL, Finnpiquette (or equivalent).

- 9.8 Oxford pipettor adjustable dispenser – 1 L capacity, 0-10 mL range (or equivalent).

- 9.9 Beakers – Pyrex, 500 and 1000 mL, several of each.

- 9.10 Graduated cylinders – Pyrex, 50 and 100 mL, several of each.

- 9.11 Nalgene carboys – 1 and 5 gallon capacity.

- 9.12 Bottles – Plastic, screw-cap for holding reagents and standard solutions, 250-1000 mL, as needed.

- 10.0 **Reagents and Standards**

- 10.1 All reagents, solvents, and standards must be traceable to the stock inventory tracking log.

- 10.2 All reagents, solvents, and standards must be labeled with: date received, date opened, expiration date, tracking number, and receiver's initials.

- 10.3 All prepared reagents and standards must be labeled with: date prepared, expiration date, preparer's initials, tracking number, diluent, and description.

- 10.4 All standard logbooks must be completely filled out.

- 10.5 All certificates of analysis must include the stock inventory tracking number that was assigned to the standard.

- 10.6 Acid/saline solution – Dissolve 47.0 g of sodium chloride in 800 mL of deionized (DI) water. Add 6.8 mL of concentrated sulfuric acid. Dilute to 1 L. Store at room temperature. This solution is stable for three months.

- 10.7 Digestion mixture – Cautiously add 200 mL of H₂SO₄ to 600 mL of DI water (always add acid to the water). Add 2.0 g of HgO. Mix until dissolved. Add 133 g of potassium

sulfate. Allow solution to cool for two to three minutes. Dilute to 1.0 L with DI water. Store at 30°C to 40°C to avoid precipitation of the mixture. This solution is stable for six months.

- 10.8** Sulfuric acid wash solution (4%) – Add 40 mL of H₂SO₄ to 800 mL of DI water. Let cool. Dilute to 1.0 L. Store at room temperature. This solution is stable for six months.
- 10.9** Molybdate/antimony reagent – Dissolve 2.15 g of ammonium molybdate and 0.055 g of antimony potassium tartrate in 400 mL of DI water. Add 0.5 mL aerosol 22. Dilute to 500 mL. Stir for at least two hours to ensure that reagents are completely dissolved. Refrigerate. This solution is stable for one week.
- 10.10** Ascorbic acid reagent – Dissolve 42.8 g of ascorbic acid in 400 mL of DI water. Add 1 mL of nanograde acetone and 1.0 mL of aerosol. Dilute to 500 mL. Refrigerate. This solution is stable for one week.
- 10.11** Phosphorus standard stock solution, 50 ppm (0.050 mg P/l) – Purchased from Ricca Chemical Company (catalog #5830-16), 500 mL bottle. Refrigerate. This solution is stable for one year after opening.
- 10.12** Acidic 100% full scale (undigested) phosphorus standard (1.000 mg P/l) – Add 40 mL of H₂SO₄ to 600 mL of DI water in a 1 L volumetric flask. Add 0.40 g of HgO. Mix until dissolved. Add 20.0 mL of phosphorus standard stock solution. Dilute to the 1 L mark. Divide into four 250 mL bottles. Refrigerate. This solution is stable for six months. NOTE: Combine with Kjeldahl nitrogen standard to make a dual standard.
- 10.13** Intermediate phosphorus stock solution (1.000 mg P/l) – Dilute 10.0 mL of phosphorus standard stock and 0.50 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Refrigerate. This solution is stable for six months. NOTE: Combine with Kjeldahl nitrogen standard to make a dual standard.
- 10.14** Detection verification standard (DVS) (0.021 mg P/l) – Dilute 10.0 mL of intermediate stock standard and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Divide into two 250 mL bottles. Refrigerate. This solution is stable for one month. NOTE: Combine with Kjeldahl nitrogen standard to make a dual standard.
- 10.15** Quality Control Standard (QCS) – AMP standard (0.478 mg P/L) – Dilute 25.0 mL of stock AMP and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Refrigerate. This solution is stable for one month.
- 10.16** Hydrochloric acid cleaning/soaking solution (10%) – Place 5400 mL of DI water in a 6 L nalgene container. Carefully add 600 mL of concentrated HCl. Cover tightly. Mix by swirling gently. Draw off as needed. This solution may be reused. This solution is good for one month of average workload use.
- 10.17** Stock AMP (0.010 mg P/ml) – Dissolve 0.1121 g of dried adenosine 5'-monophosphate in DI water. Bring to volume in a 1 L volumetric flask. Refrigerate. This solution is stable for three months.

- 10.18 90% (CAL) full scale phosphorus CAL (0.900 mg P/l) – Dilute 9.0 mL of phosphorus stock and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Refrigerate. This solution is stable for one month. NOTE: Combine with Kjeldahl nitrogen standard to make a dual standard.
- 10.19 50% (CAL) full scale phosphorus CAL (0.500 mg P/l) – Dilute 5.0 mL of phosphorus stock and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Refrigerate. This solution is stable for one month. NOTE: Combine with Kjeldahl nitrogen standard to make a dual standard.
- 10.20 10% (CAL) full scale phosphorus CAL (0.100 mg P/l) – Dilute 1.0 mL of phosphorus stock and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Refrigerate. This solution is stable for one month. NOTE: Combine with Kjeldahl nitrogen standard to make a dual standard.
- 10.21 0.1 N NaOH solution for cleaning TP channel – Dilute 10 mL of 5N/20% NaOH stock solution to 500 mL with DI water. Store at room temperature in a plastic screw cap bottle. This solution is stable for six months.
- 10.22 0.1 N HCl solution for cleaning TKN channel – Dilute 4.17 mL of concentrated HCl to 500 mL with DI water. Store at room temperature in a plastic screw cap bottle. This solution is stable for six months.
- 10.23 MS/MSD spiking standard (0.300 mg/L P) – dilute 120 mL of phosphorus stock standard and 0.5 mL H₂SO₄ in DI water and bring to volume in a 500 mL volumetric flask. Refrigerate. Stable for one month. (Note: combine with Kjeldahl nitrogen standard to make a dual standard). Analyze the combined standard a minimum of ten times; calculate the mean and standard deviation. Use the mean value as the standard's assayed value in the calculation for percent recovery of MS/MSD.
- 11.0 **Sample Collection, Preservation, Shipment, and Storage**
- 11.1 A 500 mL plastic bottle is the recommended sample container to be used. The proper bottle code is GA for sulfuric acid preserved samples or GAD if the sample is field filtered.
- 11.2 Samples should be preserved by adding a minimum of 0.5 mL of concentrated sulfuric acid per 500 mL of sample (to a pH equal to or less than 2) and refrigerated at 4°C.
- 11.3 The recommended maximum holding time for refrigerated acid preserved samples is 28 days.
- 12.0 **Quality Control (QC)**
- 12.1 Check system audits with each analytical batch, and investigate when performance changes significantly. System audits are in control if:
- 12.1.1 The heating bath temperature is between 35.0°C and 39.0°C.

- 12.1.2 The reagent baseline is at (or can be set to) 5% without a large change in the previous baseline calibration setting.
- 12.1.3 The full scale undigested standard/primer is at (or can be set with) the gain control to 90% of chart scale without a large change in the previous gain calibration setting.
- 12.2 Check calibration audits with each analytical batch. Audits are in control if (as of 03/02/05):
- 12.2.1 The 90% of full scale standard is between 0.885 and 0.916 mg P/l.
- 12.2.2 The 10% of full scale standard is between 0.095 and 0.111 mg P/l.
- 12.2.3 The detection verification standard is between 0.017 and 0.025 mg P/l.
- 12.2.4 The 50% of full scale standard is between 0.484 and 0.515 mg P/l.
- 12.2.5 QCS (AMP) results are between 0.455 and 0.503 mg P/l.
- 12.3 Analyze a MS/MSD sample pair for approximately every 13 unknown samples. MS/MSD samples are in control if their relative percent difference (RPD) is not greater than $\pm 20\%$ and percent spike recover is $100\% \pm 20\%$.

13.0 Calibration and Standardization

- 13.1 Calibration is performed automatically by the computer using five standards at five concentrations, 0% (blank), 10%, 50% and 90%. The DVS and AMP are run as check standards during the run but are not used to calibrate the instrument. Each calibrant is measured twice, and the results are averaged to produce the calibration "curve." This is done to try to eliminate any effects of carryover from a previous sample or differences in digestions of the calibration samples. Three blanks, two 10%, two 50% and one 90% standards are each measured twice, averaged, and plotted to make the curve. The chemistry is linear over the range used and should produce a straight line.
- 13.2 The computer, using linear regression to produce a "best fit" calibration line, plots calibration values measured by the system. Sample values are compared to this graph to compute actual sample values.
- 13.3 All measurements are made at 660 nm. The sampler is set at 50 samples per hour with a sample/wash ratio of 4 to 1.

14.0 Procedure

- 14.1 Digestion.
- 14.1.1 Add 10 mL of DI water to digestion tubes 1, 2, and 3.
- 14.1.2 Add 10 mL of 10% CAL to digestion tubes 4 and 5; 10 mL of 50% CAL to digestion tubes 6 and 7; and 10 mL of 90% CAL to digestion tube 8.
- 14.1.3 To digestion tube 9 add 10 mL DVS check standard and to digestion tube 10 add 10 mL of AMP CAL.
- 14.1.4 To digestion tubes 11 through 40 (for the 40-place rack) or 11 through 50 (for the 50-place rack); add 10 mL (or a suitable aliquot) of well shaken samples, *with the following exceptions*: To digestion tubes 24 (MS) and 25 (MSD), add 10 mL of sample and 0.25 mL of MS/MSD spiking standard, using a sample in the first group of 13 unknowns analyzed. To tubes 39 (MS) and 40 (MSD), add 10 mL of a sample that

- appears in the end group of 13 unknown samples analyzed and 0.25 mL of MS/MSD spiking standard. Three MS/MSD pairs are analyzed on the 50 tube run, beginning, middle and end. Only two pairs are analyzed on a 40 tube run or approximately every 13 samples. Record the sample ID numbers used for the MS/MSD pairs on the run sheet. Refer to the actual 40 or 50 tube run sheets for the current tube number designations for samples and QC/QA positions.
- 14.1.5** Add 3-4 Teflon boiling stones (previously cleaned with HCl) to each tube. Too many stones may cause the sample to boil over.
- 14.1.6** Add 2.0 mL of digestion mixture to each tube. Vortex each tube. Verify that all tubes contain boiling stones and are at the same volume.
- 14.1.7** 40-place block digester: With side shields in place, place rack of tubes on block digester. Set low temperature at 160°C. When digester attains low temperature, let the tubes heat for 30 minutes. Set block digester temperature at 380°C. When digester attains high temperature, let tubes heat for 30 minutes. Check the progress of the digester periodically to see that the controller cycles properly. Record that the high temperature has been reached.
- 14.1.8** 50-place block digester: Place the rack in the block. Turn on the control unit. Press "run." Select 1 to answer the "what program" question on the display. Press "E" to enter your choice. The run should begin. No further input is needed until the digestion run is completed (approximately two and one half to three hours). An alarm will sound when the run is complete.
- 14.1.9** Remove the rack from the digester. Let the tubes cool for 10 to 15 minutes. Add 9.6 mL of DI water to each tube. Mix thoroughly on a vortex mixer. If the tubes cool too much, the acid and salts will solidify and cause difficulty in returning solid into solution.
- 14.2** Colorimetric analysis.
- 14.2.1** Check the level of all reagent containers to ensure an adequate supply. Start the computer. When the main Windows screen appears, start the AACCE program by double clicking on the icon. Turn on the power (at the power strip) to the sampler, colorimeter, and pump.
- 14.2.2** Select "charting" from the open window in the AACCE program. This will begin the data link between the instrument and the computer. Place the pump platen on the pump. Lock it down.
- 14.2.3** The proportioning pump will start by itself when the download is through. Pump DI water, with channel appropriate wetting agent, through the system for at least 30 minutes.
- 14.2.4** Flush the sampler wash receptacle with approximately 25 mL of 4% H₂SO₄ if ammonia has accumulated in the reservoir. Normally, the pumping of 4% acid through the wash cup during the 30-minute startup is sufficient to clear out any buildup.
- 14.2.5** Excluding the salicylate line, attach all reagents to their respective containers. When the reagents have been pumping for at least five minutes, attach the salicylate line to its container. Allow the system to equilibrate. If a precipitate forms after the addition of salicylate, the pH is too low. Immediately stop the proportioning pump. Flush the coils with water. Check the concentration of the sulfuric acid solutions and/or the working buffer before restarting the program.
- 14.2.6** To prevent precipitation of salicylate in the waste, keep salicylate-containing waste separate from acidic wastes.
- 14.2.7** Continue to pump reagents through the instrument for at least 45 minutes. Right click the mouse on each channel's chart. Select "set base" from the menu. This will set the

baseline to 5% automatically. After a stable baseline has been obtained, the analyses may be started.

- 14.2.8** Remove the sampler tray. Place it next to the digested and rehydrated samples.
- 14.2.9** From the rough run sheet, enter the sample ID numbers into the computer run. Do this by clicking on "set-up" in the menu at the top of the page. Select "analysis" from the drop-down menu. Click once on "40 place template" (or "50 place template" for the larger run). Go to the menu on the right side of the page. Click on "copy run." This will generate a new run with an ID of "today's date" and a letter A-Z (for 1st to 26th run of the day [i.e., 991215A]).
- 14.2.10** Click on the "tray protocol" tab. Enter the sample ID numbers by clicking on the appropriate slot. Type in the information. Do not change any of the information or settings of the cups 1 to 11. These do not change from run to run and are programmed into the tray set up. Do not change any of the information on any of the other three tabs. This is not necessary in any case and could result in a ruined run. Do not change the entries for the AMP or MS/MSD cups other than to enter the ID numbers of the samples used in the sample name blank. Be sure the designation of MS or MSD appears in the blank as well.
- 14.2.11** Once all the sample ID numbers are entered into the list, click on the "print" icon on the bottom of the page to get a hard copy printout of the run to use while loading the cups. Once the printing is done, click "OK" to save the run protocol.
- 14.2.12** Place the correct number of clean rinsed sample cups in the sampler tray. Using the tray protocol printout as a guide, pipette the samples into the appropriate cup.
- 14.2.13** Place the sampler tray back on the compact sampler. Place a cup of full scale undigested standard (with acid and mercury) in slot #88. If the computer is not "charting" (monitoring the colorimeter), click on the "chart" button. From the main menu, click on the sampler icon to bring up the sampler control window. Click on the "wash" button to zero the sampler. Enter the cup number (88) in the sample window. Click on the "sample" button. The probe will go to the designated cup. Allow the sampler to aspirate the undigested standard for at least three minutes. Click on the "wash" button to return the probe to the wash cup. Click "cancel" to remove the sampler window.
- 14.2.14** Approximately seven to eight minutes later, the peaks will begin to appear on the computer screen (first the TP and then the TKN channel). One minute after the peak first appears in a channel, right click on that channel's chart and select "set gain" from the menu. Repeat for the other channel. This will set the full scale peak to be approximately 90% of the computer chart screen. Allow the channels to return to baseline before proceeding.
- 14.2.15** Click "stop" from the program (white) menu to end the charting process.
- 14.2.16** Click "run" from the same menu. Select the run that was previously set up. Click "OK." On the window that appears, fill in your name and any comment(s) that should be attached to the printout of this run. Be sure that the "autobase" box is checked. Click "OK" when finished. The run will start. No further operator input is required until the run is over.
- 14.2.17** When the run is finished, a message window will appear indicating this. Click "OK."
- 14.2.18** Click "retrieve." Click "view chart" in the menu at the top of the page. This will display the run chart showing the peaks one channel at a time starting with TKN. Using the arrow keys at the bottom, move through the chart. Check the location at which the computer chose to mark (measure) each peak. It may be necessary to move some of the marks to better locations. This can be done by clicking on the button at the top of the window showing a peak with a mark on it. Click on this button to enable the "move

- peak mode." Click and hold on the mark that you wish to move. Release the mouse button when the mark has been placed in the desired place. Continue to review the peaks. Move the marks of any peaks that require it. After all the peaks for that channel have been reviewed, click on the calculator icon button to save the marks in their new locations. Recalculate the chart. Click on the drop-down box with the number "1" in it. Select "2" to bring up the chart for channel 2 (TP). Repeat the above process to review and correct (if necessary) the peak marks for the TP channel. When finished, click "OK" to exit this window.
- 14.2.19** Click "retrieve." Click "print chart." Click "OK" to print out the hard copy of the run chart. Click "retrieve." Click "report" to print out the final report for the run. Click "retrieve." Click "calibration curve" to print out the calibration curves for each channel. Select the channels as done in the view chart window, one at a time. When all printing has been completed, proceed to clean up.
- 14.3** Clean up.
- 14.3.1** Unhook TP lines and place them in a solution of 1.0 mL of Brij-35 diluted to 1 L with DI water. The sampler rinse line should be placed in a container of plain DI water. The system should be allowed to rinse out for at least 30 minutes at the normal pump speed or 15 minutes at the fast pump speed. This can be selected from the pump control window brought up by the pump icon on the main window.
- 14.3.2** When it is certain that the remaining samples left in the digestion tubes are not needed, pour the tubes out into a plastic jug properly labeled to collect this hazardous waste. Save the Teflon boiling stones.
- 14.3.3** Block digester tubes should be rinsed with tap water, rinsed with DI water, and soaked in 10% HCl for at least 12 hours. After soaking, the tubes should be rinsed twice with tap water, twice with DI water, and inverted to dry. If the tubes have not been used within the last day, they should be rinsed with tap and DI water before use.
- 14.3.4** Soak boiling stones in 10% HCl for at least 24 hours. Soak in 10% H₂SO₄ for at least 24 hours. Rinse the stones with DI water several times. Allow them to dry before the next use.
- 14.3.5** Wastes with mercury should be disposed of in the manner prescribed by the Laboratory's waste handling procedure (SOP 111).
- 15.0** **Calculations**
- 15.1** Results are printed in appropriate concentration units (mg/L).
- 15.2** Diluted samples should be manually calculated.
- 15.3** Analyze a MS/MSD sample pair for approximately every 13 unknown samples. MS/MSD sample are in control if their RPD is not greater than ± 20% and the percent spike recovery is between 80 and 120 percent. RPD and percent MS/MSD spike recovery are calculated as follows:
- $$\text{RPD} = \left[\frac{\text{absolute value}(\text{MS}-\text{MSD})}{\frac{(\text{MS}+\text{MSD})}{2}} \right] \times 100$$
- $$\% \text{ Spike Recovery} = \left[\frac{(\text{M} - \text{S})}{\text{T}} \right] \times 100$$

Where: M = measured concentration MS or MSD
S = measured concentration of sample
T = MS/MSD spike concentration

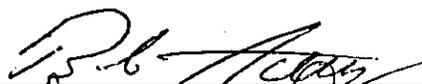
- 15.4 All samples are corrected automatically by the computer for baseline shift, carryover, and drift in sensitivity.
- 16.0 **Method Performance**
- 16.1 MDL – In the DEQ Environmental Laboratory, 28 replicate analyses of a low level standard with a mean concentration of 0.0175 mg P/l resulted in a SD of 0.0011 mg P/l and an MDL (99%) of 0.0027 mg P/l.
- 16.2 Precision – In the DEQ Environmental Laboratory, using composite water samples with mean concentrations of 0.0120, 0.2553, and 0.6208 mg P/l, the SD's were 0.0010, 0.0022, and 0.0049 mg P/l, and the relative SD's were 8.3, 0.9, and 0.8%, respectively.
- 16.3 Accuracy – In the DEQ Environmental Laboratory, using composite water samples with mean concentrations of 0.0070 and 0.2457 mg P/l and theoretical spikes of 0.10 and 0.20 mg P/l (using AMP), the mean spike recoveries were 97.0 and 94.0%, respectively.
- 17.0 **Pollution Prevention**
- 17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.
- 17.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.
- 17.3 For information concerning pollution prevention which may be applicable to laboratory operations, consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, DC 20036.
- 18.0 **Data Assessment**
- 18.1 Data reported must be within the linear range of the assay, >0.005 and <1.000 mg P/L.
- 18.2 Dilutions must be greater than 10% of full scale to be reported (i.e., the diluted sample results must be >0.100 mg P/L).

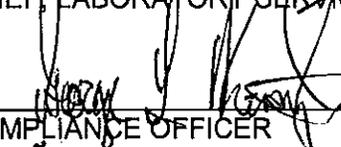
- 18.3 "High" reporting samples are reported out to two significant figures.
- 18.4 "Low" reporting samples are reported out as read unless greater than 0.200 mg P/L which are then reported to two significant figures.
- 18.5 Dilution multiplies the detection limit for a sample (i.e., detection limit of 0.005 mg P/L x 10 (dilution factor) = 0.05 (detection limit for sample diluted 1/10 when analyzed). Results of the analysis of a diluted sample must be above 0.05 mg p/L to be reported.
- 18.6 Appropriate laboratory reporting codes for dilutions, low values, interference, holding times, etc., will be appended to the test result according to laboratory policy. Reference Laboratory Result Remark Codes (SOP 106).
- 18.7 MS/MSD data for a run must be acceptable for the run data to be reported. Standards and controls must be in range for the run data to be reported.
- 18.8 Out of range values must be diluted, redigested, and rerun to be reported. High carryover samples (low value following a high value) are automatically repeated at the end of the batch to verify the result.
- 18.9 The lead worker or supervisor must review all data before the final reporting out of results.
- 19.0 **Corrective Actions**
- 19.1 Excessive rise in the TKN baseline or excessive carryover in the TP channel may indicate buildup of precipitate or protein in the respective channel. Clean the channel (TKN with 2N HCl and TP with 2N NaOH) according to the manufacturer's instructions. The samples can then be run again.
- 19.2 A rise in the standard's or sample's value from previous runs (or expected results) may indicate: (1) contamination of the 15 x 80 sample tube (repipette into a new, clean tube); (2) contamination from a dirty pipette (repipette into a new, clean tube and/or redigest if this does not change the value back to normal); (3) carryover from an unusually high sample preceding the one in question (repeat sample in another location in the run away from the high valued sample and repipette if necessary); or (4) contamination of the standard stock container (use the backup standard bottle, if available, or remake the standard and repeat the run).
- 19.3 If precision or accuracy samples or repeated samples within the run are not as expected, begin troubleshooting the equipment as outlined in the manufacturer's manuals to locate the problem. Correct the problem. Repeat the digestion if necessary. Repeat the batch run.
- 19.4 If a high sample runs off scale, repeat the sample at a dilution on the next run. The two samples immediately after it will automatically be repeated at the end of the run to remove the effect that carryover from the out-of-range sample has on them.

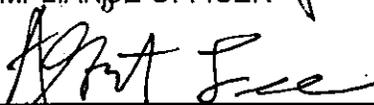
- 19.5 Consult with manufacturer's manuals, lead worker, co-workers, company help lines, and any other resources available to troubleshoot and correct problems with analyzer operation. Alert the supervisor of any long-term downtime for the analysis.
- 19.6 Refer to the AA3 Operator's Manual located at the instrument's workstation for additional information on the following: (1) setting up a new analysis; (2) maintenance, repair, and troubleshooting of hardware and software problems; (3) parts; (4) service; (5) company contact numbers; (6) proof and explanation of calculations and corrections; (7) identification and correction of common operating problems; (8) printer operation and troubleshooting; (9) operation/maintenance/troubleshooting of block digester; and (10) explanation of additional system capabilities and hardware.
- 20.0 **Waste Management**
- 20.1 Three types of liquid wastes are generated by the assays. These are: (1) sulfuric acid (4%) with mercury and color reagents (antimony and molybdate); (2) sodium hydroxide (2N) with mercury and color reagents (cyanide, salicylate, and bleach); and (3) sulfuric acid (4%) spent wash solution. The waste containers must be labeled with the type of waste contained, the notation "hazardous waste," and the operator's initials. The containers are held until the monthly waste collection occurs and a licensed hazardous waste disposal company can properly dispose of them. The spent acid wash solution may be disposed of down the drain with accompanying soda ash (to neutralize the acid) and a large amount of water to flush it down.
- 20.2 Broken/waste glass (sample tubes) is collected at the bench in a plastic pail until transferred to a collection barrel for recycling.
- 20.3 Liquid wastes generated by excess samples, and dilutions can be disposed of down the drain with copious amounts of water if they do not contain other hazardous material (i.e., samples from an industrial site, etc.) that requires them to be handled as a hazardous waste.
- 21.0 **References**
- 21.1 United States Code of Federal Regulations, Title 40, U.S. Government Printing Office, Washington, D.C., Appendix A & B.
- 21.2 Test Methods for Evaluating Solid Waste, U.S. Environmental Protection Agency, Document SW-846, Third Edition, 1986, Final Update III, December 1996.
- 21.3 Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA-600/4-79-020, March 1983.
- 21.4 Phosphorus, Total (Colorimetric, Automated, Block Digester AAll), Methods for Chemical Analysis of Water and Wastes, Method 365.4, U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes (MCAWW) – EPA/600/4-79-020 – Revised March, 1983.

- 21.5 Simultaneous and Automated Determination of Total Phosphorus and Total Kjeldahl Nitrogen, Gales, M.E. and Booth, R.L., Methods Development and Quality Assurance Research Laboratory, May 1974.
- 21.6 Technicon AutoAnalyzer Applications, Method US-329-74-A, Nitrogen and Phosphorus in Acid Digests, December 1997.
- 21.7 Total Kjeldahl Nitrogen and Total Phosphorus BD-40 Digestion Procedure for Water, Technicon, August 1974.
- 21.8 Evaluation of the Technicon Block Digestor System for the Measurement of Total Kjeldahl Nitrogen and Total Phosphorus, Gales, M.E. and Booth, R.L., EPA-600/4-78-015, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 1978.
- 21.9 Standard Test Methods for Total Kjeldahl Nitrogen in Water, ASTM Annual Book of Standards, Volume 11.01, Method D 3590-89 (Reapproved 1994).
- 21.10 Ultra-micro Semi-Automated Method for the Simultaneous Determination of Total Phosphorus and Total Kjeldahl Nitrogen in Wastewaters, Jirka, A.M., Carter, M.J., May D., and Fuller, F.D., U.S. Environmental Protection Agency, Central Regional Laboratory, Chicago, Illinois.
- 21.11 AIM500 Block Digestion System User Manual, A.I. Scientific Pty. Ltd., CAN 009 938 498, 91 Landsborough Avenue, Scarborough, Queensland 4020, Australia, September 1997.
- 21.12 Operation and Maintenance Manual, Brann & Lubbe Autoanalyzer 3, 1999.
- 22.0 **Attachments**
- 22.1 Manifold diagram – Total Phosphorus, AA2/AA3 Multitest Manifold, February 2, 1998.
- 22.2 Sample run sheet for BD-40 (40 tube) batch run.
- 22.3 Sample run sheet for AIM-50 (50 tube) batch run.

Signature Page

APPROVED BY  DATE 3/14/06
CHIEF, LABORATORY SERVICES SECTION

APPROVED BY  DATE 3/8/2006
COMPLIANCE OFFICER

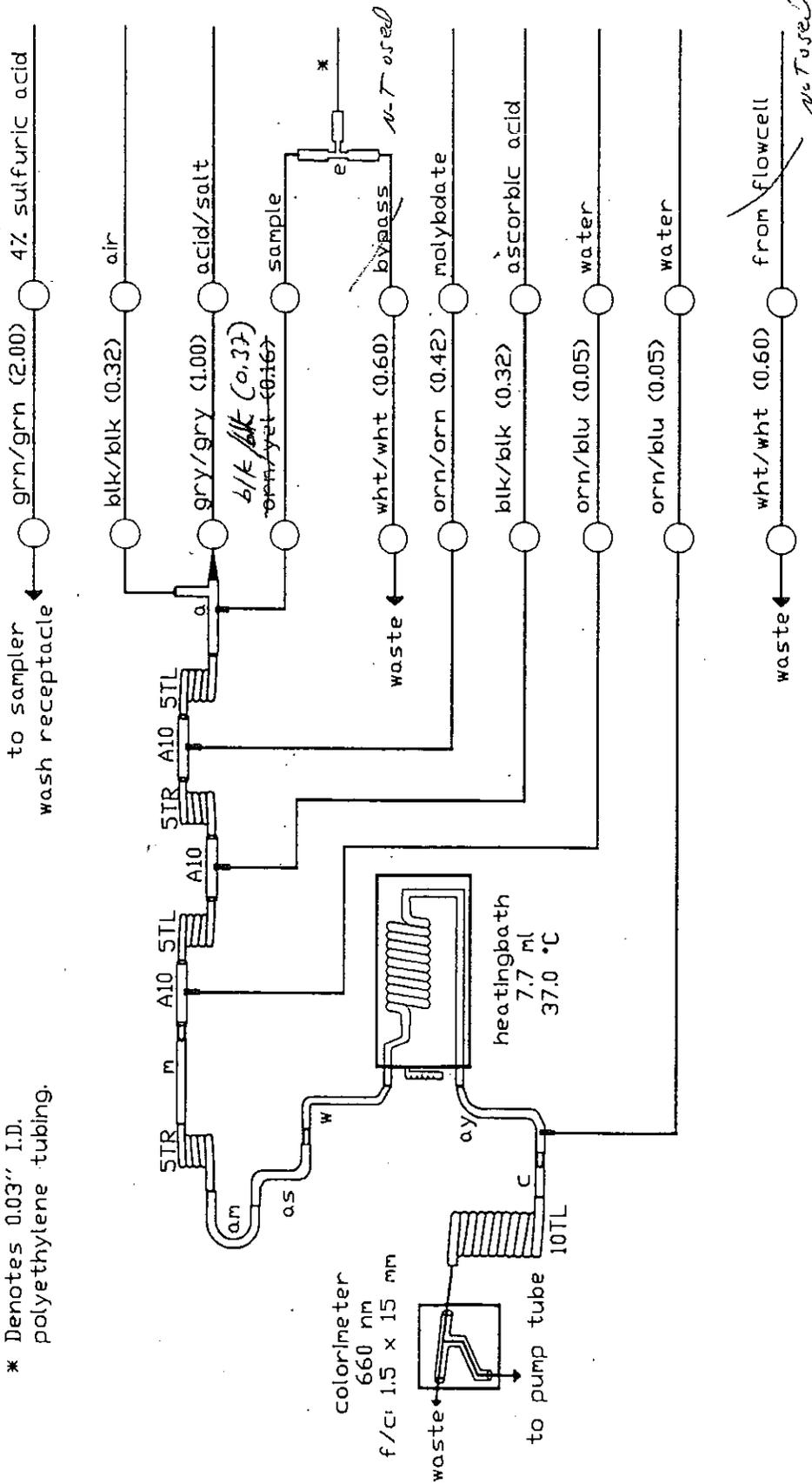
APPROVED BY  DATE 3/6/2006
QA OFFICER

APPROVED BY  DATE 2-28-2006
UNIT MANAGER

APPROVED BY  DATE 3-1-06
ANALYST

Attachment 22.1

NOTES: Figures in parantheses are flowrates in ml/min.
 * Denotes 0.03" I.D. polyethylene tubing.



DRAWN		M. Peters	DATE	25.02.98	FLOWCHART	AA II	PARAMETER	Phosphorus	BRAN+LUEBBE <small>ANALYSER DIVISION * 22844 NÜRNBERGER STR. * GERMANY</small> <small>PROPRIETARY NOTE</small> <small>This drawing contains information proprietary to Bran+Luebbe GmbH and must be kept confidential. Reprint and disclosure are not permitted without written consent of Bran+Luebbe GmbH</small>	
CHANGED		<i>PS</i>	DATE	6.30.2001	METHOD NO:	US-696A82A 54502529.5000	MATRIX:	Water & Waste Water		
APPROVED		<i>S.D.</i>	DATE	25.2.98		Multitest MT12	RANGE:	0 to 5 mg/l as P		
RELEASED		<i>E. Hill</i>	DATE	21.2.98						

Sampler Cup No.	Digestion Tube No.	Kjeldahl Nitrogen		Total Phosphorus		Date:	Rack No:	Block	(High)
		Work Order #	Sample ID	Dilution	Hi/Lo Rpt.	KN	TP	Comments	Temp:
1	n/a		Primer						QA Batch Number - Dlg:
2	1		Blank cal 1						TKN:
3	2		Blank cal 2						TP:
4	3		Blank cal 3						
5	4		10% cal 1					KN#	exp.
6	5		10% cal 2						
7	6		50% cal 1					KN#	exp.
8	7		50% cal 2						
9	8		90% cal					KN#	exp.
2	1		Blank check 1						
10	9		DVS 1					KN#	exp.
11	10		AMP 1					KN#	exp.
12	11								
13	12								
14	13								
15	14								
16	15								
17	16								
18	17								
19	18								
20	19								
21	20								
22	21								
23	22								
24	23								
25	24		MS1						
26	25		MSD1						
3	2		Blank check 2						
10	9		DVS 2						
11	10		AMP 2						
27	26								
28	27								
29	28								
30	29								
31	30								
32	31								
33	32								
34	33								
35	34								
36	35								

Kjeldahl Nitrogen		Total Phosphorus		Date:	Rack No.:	Block	380	(High)	
				Run No:	Analyst:	DNS	Temp:	160	(Low)
Kjeldahl Nitrogen:					Blank 1			-03/05	
Baseline			-19832/-17731		Blank 2 (SB ₁)			-03/05	
Gain			14/23		Blank 3 (SB ₂)			-03/05	
Sensitivity			.3727/.5811		DVS 1			.15/25	
Temperature			35-37°C		DVS 2			.15/25	0.20
Blank cal stds			-.03/.04		DVS 3			.15/25	
10% cal stds			.45/.54		AMP 1 (L ₁)			.96/1.11 (80-120%)	
50% cal stds			2.40/2.58		AMP 2 (C ₁)			.96/1.11 (80-120%)	1.04
90% cal std			4.42/4.60		AMP 3 (C ₂)			.96/1.12 (80-120%)	
End Cal Blanks			-.03/.05						
End 10 % Cal stds			.45/.55		TKN Reagent lot numbers and expiration date				
End 50% Cal stds			2.42/2.60		Digestion Mixture:	KN#		exp.	
End 90% Cal std			4.41/4.61		0.2% Bleach Solution	KN#		exp.	
					Salicylate/Cyanide Sol.	KN#		exp.	
					Working TKN Buffer	KN#		exp.	
	MS-1	MSD-1	MS-2	MSD-2	MS-3	MSD-3			
Sample ID									
Original sample value									
Run value									
Difference (ms-msd)								MS/MSD Spike Standard	
Relative % Difference								KN#	Exp.
% Spike Recovery									Spike value TKN
	(M ₁₋₁)	(M ₁₋₂)	(M ₂₋₁)	(M ₂₋₂)	(M ₃₋₁)	(M ₃₋₂)			1.50
Total Phosphorus:									
Baseline			-15311/-12493		Blank 1			-.004/.004	
Gain			106/156		Blank 2 (SB ₁)			-.004/.004	
Sensitivity			.0546/.0805		Blank 3 (SB ₂)			-.004/.004	
Temperature			35-37°C		DVS 1			.017/.025	
Blank cal stds			-.004/.005		DVS 2			.017/.025	0.021
10% cal stds			.095/.105		DVS 3			.017/.025	
50% cal stds			.484/.515		AMP 1 (L ₁)			.455/.501 (80-120%)	
90% cal std			.885/.916		AMP 2 (C ₁)			.456/.502 (80-120%)	0.478
End Cal Blanks			-.004/.005		AMP 3 (C ₂)			.456/.503 (80-120%)	
End 10 % Cal stds			.093/.106						
End 50% Cal stds			.485/.518		TP Reagent lot numbers and expiration date				
End 90% Cal std			.881/.916		4% H ₂ SO ₄ :	KN#		exp.	
					Acid/Salt Diluent	KN#		exp.	
					Molybdate/Antimony	KN#		exp.	
					Ascorbic Acid Sol.	KN#		exp.	
	MS-1	MSD-1	MS-2	MSD-2	MS-3	MSD-3			
Sample ID									Spike value TP
Original sample value									0.300
Run value									
Difference (ms-msd)									
Relative % Difference									
% Spike Recovery									
	(M ₁₋₁)	(M ₁₋₂)	(M ₂₋₁)	(M ₂₋₂)	(M ₃₋₁)	(M ₃₋₂)			

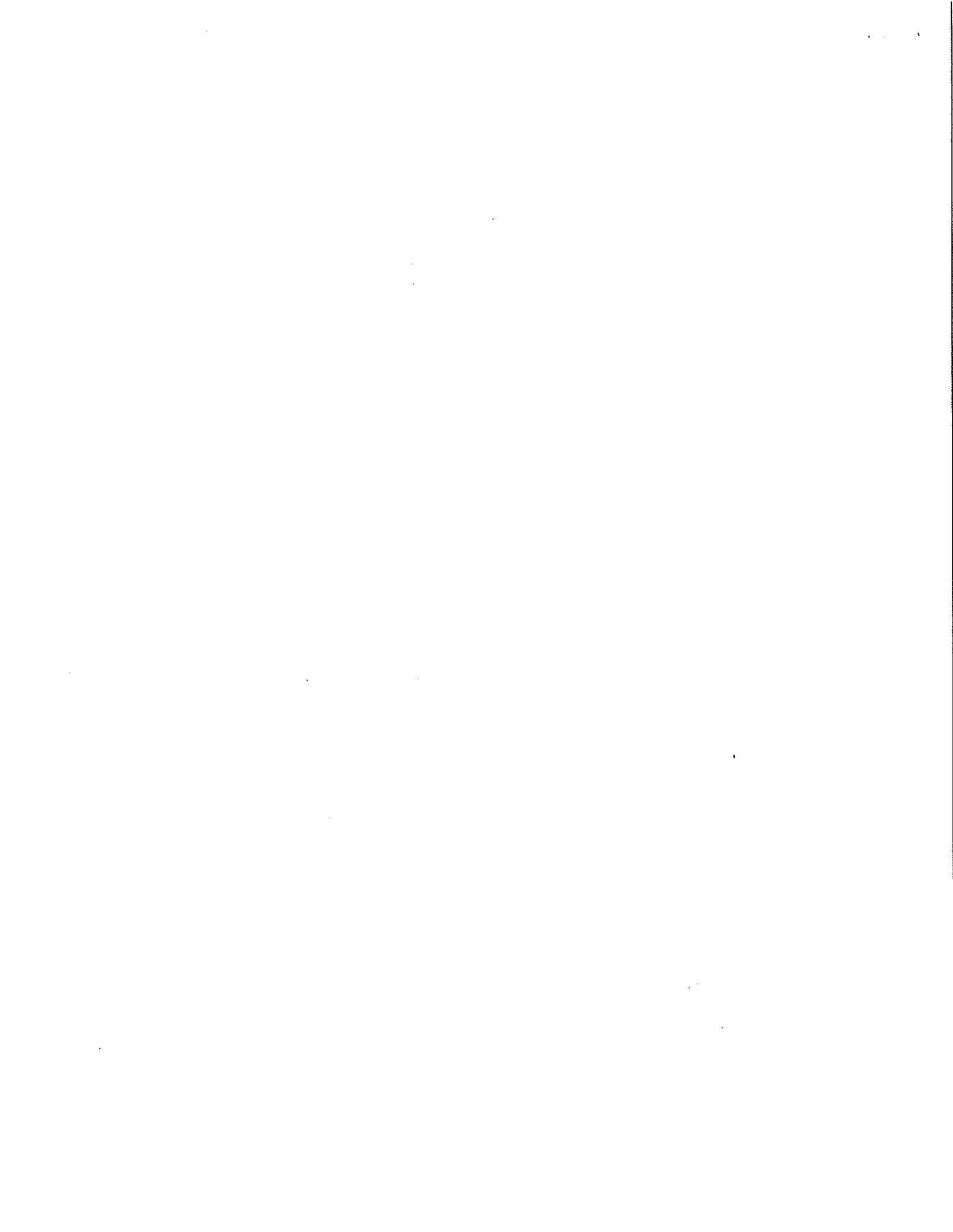
		Kjeldahl Nitrogen		Total Phosphorus		Date:	Rack No:	Block	380	(High)	
						Run No.:	Analyst:	DNS	Temp:	160	(Low)
Sampler Cup No.	Digestion Tube No.	Work Order #	Sample ID	Dilution	Hi/Lo Rpt.	KN	TP	Comments			
1	n/a		Primer					QA Batch Number - Dig.:			
2	1		Blank cal 1					TKN:			
3	2		Blank cal 2					TP:			
4	3		Blank cal 3								
5	4		10% cal 1					KN#	exp.		
6	5		10% cal 2								
7	6		50% cal 1					KN#	exp.		
8	7		50% cal 2								
9	8		90% cal					KN#	exp.		
2	1		Blank check 1								
10	9		DVS 1					KN#	exp.		
11	10		AMP 1					KN#	exp.		
12	11										
13	12										
14	13										
15	14										
16	15										
17	16										
18	17										
19	18										
20	19										
21	20										
22	21										
23	22	MS1									
24	23	MSD1									
25	24										
26	25										
27	26										
3	2		Blank check 2								
10	9		DVS 2								
11	10		AMP 2								
28	27										
29	28										
30	29										
31	30										
32	31										
33	32										
34	33										
35	34										
36	35										

Sampler cup No.	Digestion Tube No.	Kjeldahl Nitrogen		Total Phosphorus			Date:	Rack No.:	Block	380 (High)
		Work Order #	Sample ID	Dilution	HI/Lo Rpt.	KN	TP	Run No.:	Analyst:	DNS
37	36	MS2								
38	37	MSD2								
39	38									
40	39									
41	40									
42	41									
43	42									
44	43									
45	44									
46	45									
4	3		Blank check 3							
10	11		DVS 3							
11	10		AMP 3							
47	46									
48	47									
49	48									
50	49	MS3								
51	50	MSD3								
2	1		Blank 1							
3	2		Blank 2							
4	3		Blank 3							
5	4		10% cal 1							
6	5		10% cal 2							
7	6		50% cal 1							
8	7		50% cal 2							
9	8		90% cal							

22.3 (cont.)

Kjeldahl Nitrogen		Total Phosphorus				Date:	Rack No.:	Block	380	(High)	
						Run No:	Analyst:	DNS	Temp:	160	(Low)
Kjeldahl Nitrogen:											
Baseline					-19832/-17731	Blank 1				-03/05	
Gain					14/23	Blank 2 (SB ₁)				-03/05	
Sensitivity					.3727/.5811	Blank 3 (SB ₂)				-03/05	
Temperature					35-37°C	DVS 1				.15/.25	
Blank cal stds					-.03/.04	DVS 2				.15/.25	0.20
10% cal stds					.45/.54	DVS 3				.15/.25	
50% cal stds					2.40/2.58	AMP 1 (L ₁)				.96/1.11 (80-120%)	
90% cal std					4.42/4.60	AMP 2 (C ₁)				.96/1.11 (80-120%)	1.04
End Cal Blanks					-.03/.05	AMP 3 (C ₂)				.96/1.12 (80-120%)	
End 10 % Cal stds					.45/.55	TKN Reagent lot numbers and expiration date					
End 50% Cal stds					2.42/2.60	Digestion Mixture:	KN#	exp.			
End 90% Cal std					4.41/4.61	0.2% Bleach Solution	KN#	exp.			
						Salicylate/Cyanide Sol.	KN#	exp.			
						Working TKN Buffer	KN#	exp.			
	MS-1	MSD-1	MS-2	MSD-2	MS-3	MSD-3					
Sample ID											
Original sample value											
Run value											
Difference (ms-msd)										MS/MSD Spike Standard	
Relative % Difference										KN#	Exp.
% Spike Recovery											Spike value TKN
	(M _{1,1})	(M _{1,2})	(M _{2,1})	(M _{2,2})	(M _{3,1})	(M _{3,2})					1.50
Total Phosphorus:											
Baseline					-15311/-12493	Blank 1				-004/.004	
Gain					106/156	Blank 2 (SB ₁)				-004/.004	
Sensitivity					.0546/.0805	Blank 3 (SB ₂)				-004/.004	
Temperature					35-37°C	DVS 1				.017/.025	
Blank cal stds					-.004/.005	DVS 2				.017/.025	0.021
10% cal stds					.095/.105	DVS 3				.017/.025	
50% cal stds					.484/.515	AMP 1 (L ₁)				.455/.501 (80-120%)	
90% cal std					.885/.916	AMP 2 (C ₁)				.456/.502 (80-120%)	0.478
End Cal Blanks					-.004/.005	AMP 3 (C ₂)				.456/.503 (80-120%)	
End 10 % Cal stds					.093/.106	TP Reagent lot numbers and expiration date					
End 50% Cal stds					.485/.518	4% H ₂ SO ₄ :	KN#	exp.			
End 90% Cal std					.881/.916	Acid/Salt Diluent	KN#	exp.			
						Molybdate/Antimony	KN#	exp.			
						Ascorbic Acid Sol.	KN#	exp.			
	MS-1	MSD-1	MS-2	MSD-2	MS-3	MSD-3					
Sample ID											Spike value TP
Original sample value											0.300
Run value											
Difference (ms-msd)											
Relative % Difference											
% Spike Recovery											
	(M _{1,1})	(M _{1,2})	(M _{2,1})	(M _{2,2})	(M _{3,1})	(M _{3,2})					

22.3/amt.)





EFFECTIVE DATE: 04/2006

SOP# 318

REVISION # 1

NITRATE PLUS NITRITE AS NITROGEN IN WATER
Colorimetric, Automated Cadmium Reduction, TrAAcs

Table of Contents

1.0	Applicable Analytical Methods	1
2.0	Matrix or Matrices.....	2
3.0	Method Detection Limits (MDLs).....	2
4.0	Scope and Application	2
5.0	Method Summary	2
6.0	Definitions	2
7.0	Interferences	4
8.0	Safety	4
9.0	Equipment and Supplies	5
10.0	Reagents and Standards	6
11.0	Sample Collection, Preservation, Shipment, and Storage	8
12.0	QC.....	8
13.0	Calibration and Standardization.....	10
14.0	Procedure.....	10
15.0	Calculations.....	13
16.0	Method Performance.....	13
17.0	Pollution Prevention	13
18.0	Data Assessment.....	14
19.0	Corrective Actions	14
20.0	Waste Management.....	15
21.0	References.....	15
22.0	Attachments	15
	Signature Page.....	16

1.0 Applicable Analytical Methods

- 1.1** Nitrogen, Nitrate-Nitrite (Colorimetric, Automated, Cadmium Reduction), Methods for Chemical Analysis of Water and Wastes, USEPA, Cincinnati, Ohio, March 1983, EPA-600/4-79-020, Method 353.2 (revised 1978). Storet #00630.
- 1.2** Nitrate/Nitrite in Water and Wastewater, Technicon TrAAcs 800™ Industrial Method No. 824-87T (revised July 1987).
- 1.3** Nitrogen (Nitrate), Automated Cadmium Reduction Method, Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 20th Edition, 1998, Method 4500-NO₃⁻ F., pp. 4-118-4-119.

2.0 Matrix or Matrices

2.1 Ground water.

2.2 Surface water.

2.3 Saline water.

2.4 Domestic waste.

2.5 Industrial waste.

3.0 Method Detection Limits (MDLs)

3.1 All MDLs shall be performed according to the Code of Federal Regulations 40 CFR, Part 136, Appendix B. See internal procedure SOP 103.

3.2 An annual MDL is determined by analyzing seven replicate aliquots of a water sample spiked to yield a theoretical concentration of about 0.005 mg/L. The replicates are analyzed in a manner identical to routine samples.

3.3 The MDL is calculated using a formula that applies the student t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Section 16.1.

3.4 The MDL for this method is determined annually or whenever there is a significant change in the procedure including a change in the analyst.

3.5 Reporting limit (RL) – The RL for this method has been set at 0.01 mg/L.

4.0 Scope and Application

4.1 This method applies to ground water, surface water, saline water, domestic waste, and industrial waste.

4.2 The working range of this method is 0.01 to 2.0 mg/L. Higher samples may be analyzed by diluting samples with 0.1% H₂SO₄.

5.0 Method Summary

5.1 The sample is passed through a hollow cadmium wire, treated with copper, to reduce nitrate to nitrite. The nitrite originally present plus the reduced nitrate is diazotized with sulfanilamide and coupled with N-(1-Naphthyl) ethylenediamine dihydrochloride to form a red dye suitable for photometric measurement at 520 nm.

6.0 Definitions

6.1 Analyte – Nitrate plus nitrite as nitrogen.

- 6.2** Calibration Blank (CB) – Prepared by adding reagents to blank water in the same concentration as the samples and standards. The CB is used to zero the instrument, for all initial and continuing CB determinations, and to flush the system between samples and standards. The CB is the 0.1% H₂SO₄ baseline and sample wash.
- 6.3** Initial Calibration Blank (ICB) – A CB analyzed at the beginning of the analysis run to demonstrate that the instrument is capable of acceptable performance. The ICB is the baseline reading just prior to the first standard.
- 6.4** Continuing Calibration Blank (CCB) – A CB analyzed in the course of the analysis run to demonstrate that the instrument is capable of continuous acceptable performance. Cups of 0.1% H₂SO₄ are run after each 15 samples. The final baseline is used to calculate baseline drift.
- 6.5** Calibration Standard (CAL) – A solution prepared from the primary standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 6.6** Calibration Curve – A plot of concentrations of known analyte standards versus the instrument response to the analyte. Standards are prepared by successively diluting a standard solution to produce working standards that cover the working range of the instrument. Standards should be prepared at the frequency specified in this SOP. The standards should be prepared using the same type of reagents and at the same concentration as will result in the samples following sample preparation. These standards are used to verify the accuracy of the calibration and the linearity of the test.
- 6.7** Initial Calibration Verification (ICV) – Second source standards to check the accuracy of the CALs. ICV is located in cup #7 and is also called H in the tray protocol for carryover calculation.
- 6.8** Continuing Calibration Verification (CCV) – A control standard analyzed in the course of the analysis run to demonstrate that the initial calibration determined remains valid throughout the course of the analytical run. Cups of CCV are run after each 15 samples.
- 6.9** Linear Calibration Range (LCR) – The concentration range over which the instrument response is linear.
- 6.10** Gain Calibration Standard (Gain) – A cup of the high CAL located near the end of the run and used for calculating the Gain correction.
- 6.11** Detection Verification Standard (DVS) – A low level standard with a concentration at or near the reporting limit used to verify the capability to analyze low concentration samples.

- 6.12** MDL – The minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. See internal procedure SOP 103.
- 6.13** Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – Aliquots of a sample to which known quantities of the method's analytes are added in the laboratory. The MS and MSD are analyzed and prepared exactly like samples. The purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.
- 6.14** Relative Percent Difference (RPD)-The absolute value difference between the MS and MSD measurements divided by the average of the MS and MSD expressed as per cent. RPD is a measurement of laboratory precision which combines the precision of the instrumental analysis and the precision of the spiking technique.
- 7.0 Interferences**
- 7.1** Turbidity can usually be significantly reduced by centrifuging the sample. A small syringe filter assembly may be helpful for some samples.
- 7.2** Sample color may be minimized through dilution. The result may need to be coded: I – Dilution required due to matrix interference; reporting limit (RL) raised.
- 7.3** Chlorine and sulfide (common oxidizing and reducing agents) can affect this analysis. Dilution may diminish their effects. Sample agitation in the presence of adequate fresh air oxidizes sulfide for samples that need to be run undiluted.
- 8.0 Safety**
- 8.1** Safety glasses and shoes that cover the feet are required in all designated laboratory areas.
- 8.2** It is recommended that the analyst wear gloves and a lab coat when performing this procedure.
- 8.3** The analyst must be familiar with the Laboratory Chemical Hygiene Plan.
- 8.4** The analyst must be familiar with the Laboratory Safety Policy (internal procedure SOP 100).
- 8.5** The analyst must be familiar with any material safety data sheets (MSDSs) applicable to this method.
- 8.6** Sulfuric acid and hydrochloric acid have the potential to be hazardous. Consult the MSDSs before proceeding with the analysis.

- 8.7 The analyst must be familiar with the location of safety equipment including showers, eye wash stations, and spill kits.
- 8.8 The analyst should always thoroughly wash hands in warm soapy water when leaving the work area and before handling food or drink.
- 8.9 The analyst should assume that all samples have the potential to be hazardous and should exercise caution when transporting, handling, and/or opening any samples.
- 8.10 General good laboratory practices are required. The analyst should take all necessary precautions in order to minimize the potential of exposure to samples and reagents used in this method.
- 9.0 **Equipment and Supplies**
- 9.1 Technicon TrAAcs 800.
- 9.1.1 Manifold #165-D008-01.
- 9.1.2 10 mm flow cell.
- 9.1.3 520 nm optical filter.
- 9.2 Bottles – 500 mL, plastic, with screw caps.
- 9.3 Diluter – Hamilton, digital or equivalent.
- 9.4 Disposable 5 mL cups #171-0354P01.
- 9.5 Mechanical pipettes – 1 to 5 mL and 40-200 uL with pipette tips to fit.
- 9.6 Disposable 16x75 mm Neutrex soda lime glass tubes Cat No. M-190.
- 9.7 Reagent filters: straw & filter assembly, 178-B651-01.
- 9.8 pH strips.
- 9.9 pHydrion vivid 1-11 pH indicator solution.
- 9.10 Volumetric flasks – Various volumes.
- 9.11 Graduated cylinders – Various volumes.
- 9.12 Volumetric pipettes – Various volumes.
- 9.13 Reagent bottles – Brown plastic.
- 9.14 Compressed nitrogen regulated to 17 PSI.
- 9.15 Compressed air regulated to 40 PSI.

10.0 Reagents and Standards

- 10.1** All reagents, solvents, and standards must be traceable to the stock inventory tracking log.
- 10.2** All reagents, solvents, and standards must be labeled with: date received, date opened, expiration date, tracking number, and receiver's initials.
- 10.3** All prepared reagents and standards must be labeled with: date prepared, expiration date, preparer's initials, tracking number, diluent, and description.
- 10.4** All standard logbooks must be completely filled out.
- 10.5** All certificates of analysis must include the stock inventory tracking number that was assigned to the standard. Original certificates are maintained by the Laboratory's Quality Assurance/Quality Control Officer.
- 10.6** All reagents (except Triton X-100) are prepared with DI water. DI water is normal tap water that has first passed through a set of US Filter deionization tanks and then through a Millipore, Super Q™ water purification system and has an industry standard resistivity of 18MΩ.
- 10.7** **50% Triton X-100 solution:** To 25 mL of isopropanol in a dropper bottle, add 25 mL of Triton X-100. Mix thoroughly.
- 10.8** **Stock copper sulfate, 0.01 M:** Dissolve 2.5 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in deionized (DI) water and dilute to one liter.
- 10.9** **Dilute copper sulfate, 0.001 M:** Dilute 10 mL of stock copper sulfate, 0.01 M to 100 mL with DI water.
- 10.10** **Copper activating solution, 0.005 M:** Dilute 50 mL of stock copper sulfate, 0.01 M and 0.1 mL of 50% Triton X-100 to 100 mL with DI water.
- 10.11** **Stock Imidazole buffer, 0.1 M:** Dissolve 6.81 g of "highest purity" imidazole in about 900 mL of DI water. Adjust the pH to 7.50 ± 0.05 with 1:1 hydrochloric acid (HCl) or 10 normal NaOH. Dilute to 1 liter with DI water. Mix thoroughly and recheck pH. Refrigerate.
- 10.12** **Working imidazole, 0.05 M:** Place the following into a beaker: 150 mL of stock imidazole buffer, 0.1 M; 148 mL of DI water; 0.6 mL of 50% Triton X-100; and 1.5 mL of dilute copper sulfate. Mix thoroughly and warm to room temperature. Prepare fresh daily.
- 10.13** **Working SAN solution:** Add 50 mL of conc. HCl to about 600 mL of DI water. Add 5 g of sulfanilamide and mix thoroughly. Dilute to 1 liter. Add 0.5 mL of 50% Triton X-100 and mix. Store in refrigerator.

- 10.14 **Working NED solution:** Dissolve 0.5 g of N-(1-naphthyl)ethylene-diamine dihydrochloride in DI water. Dilute to 1 liter, add 0.5 mL of 50% Triton X-100 and mix. Store in refrigerator.
- 10.15 **2 N nitric acid:** Cautiously, with mixing, slowly add 12.5 mL of nitric acid to 60 mL of DI water. Cool to room temperature, dilute to 100 mL with DI water and mix.
- 10.16 **Hydrochloric acid (HCl) – Concentrated,** Mallinckrodt #5587 or equivalent.
- 10.17 **2 N hydrochloric acid activating solution:** Cautiously, with mixing, slowly add 33 mL of HCl to 120 mL of DI water. Cool to room temperature, dilute to 200 with DI water, add 0.1 mL of 50% Triton X-100 and mix.
- 10.18 **System wash solution:** Add 0.2 mL of 50% Triton X-100 and 6 drops H₂SO₄ to 200 mL of DI water and mix thoroughly.
- 10.19 **Stock standard (1000 mg/L as N):** Purchase certified stock standard, or add 7.218 g of potassium nitrate and 28 drops H₂SO₄ to 500 mL DI water in a 1000 mL volumetric flask. Mix until thoroughly dissolved, dilute to 1000 mL with DI water and mix thoroughly. Stable for two years if refrigerated. An additional Second Source Stock Standard should be purchased or prepared.
- 10.20 **ISS - Intermediate stock standard (100 mg/L as N):** Add 14 drops conc. H₂SO₄ and 50 mL stock standard to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for one year if refrigerated. An additional Second Source ISS should be prepared from a second source stock standard. This Second Source ISS may be prepared in combination with NH₃.
- 10.21 **2 mg/L standard:** Add 28 drops H₂SO₄ and 20 mL of 100 mg/L ISS to a 1000 mL volumetric flask containing 500 mL DI water. Mix, dilute to 1000 mL with DI water, and mix thoroughly. Stable for 1 month if refrigerated. Note: Nitrate standards may be prepared in combination with ammonia standards. You may need to prepare a special intermediate 1 mg/L standard with the appropriate concentration of ammonia for use in preparing the DVS.
- 10.22 **1.5 mg/L standard:** Add 14 drops conc. H₂SO₄ and 7.5 mL of 100 mg/L ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.
- 10.23 **1 mg/L standard:** Add 14 drops conc. H₂SO₄ and 5.0 mL of 100 mg/L ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.
- 10.24 **0.5 mg/L standard:** Add 14 drops conc. H₂SO₄ and 2.5 mL of 100 mg/L ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.

- 10.25 0.2 mg/L standard:** Add 14 drops conc. H_2SO_4 and 1.0 mL of 100 mg/L ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.
- 10.26 0.015 mg/L Detection Verification Standard (DVS):** Add 14 drops conc. H_2SO_4 and 7.5 mL of 1 mg/L standard to a 500 mL volumetric flask containing 250 mL of DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for one month if refrigerated.
- 10.27 ICV 2 mg/L standard:** Add 14 drops conc. H_2SO_4 and 10 mL of 100 mg/L Second Source ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.
- 10.28 Spiking standard (20 mg/L):** Add 28 drops conc. H_2SO_4 and 20.0 mL of 1000 mg/L stock standard to a 1000 mL volumetric flask containing 500 mL DI water. Mix, dilute to 1000 mL with DI water, and mix thoroughly. Stable for 6 months if refrigerated. When 100 μ L of this standard is spiked into 4.0 mL of sample, the resulting spike concentration is about 0.50 mg/L.
- 10.29 Wash reservoir solution, ICB, CCB, sample dilution diluent:** To one liter of DI water known to be pure, add 28 drops of conc. H_2SO_4 and mix thoroughly.
- 11.0 Sample Collection, Preservation, Shipment, and Storage**
- 11.1** Water samples are collected in 500 mL high-density polyethylene screw cap bottles. The proper bottle codes are GA and, if field filtered, GAD:
- 11.2** Sample should be preserved with 10 drops of concentrated sulfuric acid per 500 mL of sample. Avoid adding excess quantities of H_2SO_4 unnecessarily. The sample should then be checked to determine that the pH of the sample has been lowered to a pH of 2. Samples with excess particulates or higher than normal pH may require some extra H_2SO_4 , which should be noted on the sample label and/or the analysis request sheet. Avoid adding H_2SO_4 to highly caustic samples—a violent, explosive reaction may occur. After proper preservation, store the sample at 4°C.
- 11.3** The maximum holding time is 28 days, although analyses should be performed as soon as possible after receipt.
- 11.4** Samples being shipped should be packed with sufficient ice that the samples remain cold until checked in at the laboratory.
- 12.0 QC**
- 12.1** The minimum QC for this method includes an initial demonstration of capability (IDOC), MDL determination, LCR, routine analysis of reagent blanks, fortified blanks, and other laboratory solutions as continuing checks on performance.

12.2 IDOC

12.2.1 Prior to analyzing samples by this method, 4 CCB samples spiked with nitrate standard must be analyzed as described in Section 14 of this method. The results are statistically tabulated to obtain the average percent recovery (X), the standard deviation (s) of the percent recoveries and the % relative standard deviation (% RSD). The obtained value for X is compared to the criteria in Section 12.4.2. The % RSD calculated from s and X must be less than 20%. If both % RSD and X are acceptable, the IDOC is acceptable. If the % RSD or X fails, corrective action must be taken, and the IDOC must be repeated. Repeat the above steps until acceptable values for % RSD and X are obtained.

12.3 System audits are checked at least once per analytical batch and are in control if the following criteria are met:

12.3.1 The relative absorbance of 2.0 mg/L standard is from 0.23 to 0.46.

12.3.2 The 75% of full scale standard is from 1.471 to 1.522 mg/L.

12.3.3 The 50% of full scale standard is from 0.983 to 1.014 mg/L.

12.3.4 The 25% of full scale standard is from 0.488 to 0.510 mg/L.

12.3.5 The 10% of full scale standard is from 0.195 to 0.208 mg/L.

12.3.6 The ICV standard (cup 7) is between 90% and 110%.

12.3.7 The DVS (cup 11) is 0.012 to 0.020 mg/L.

12.3.8 The CCB (cups 28 & 48) is between -0.005 and +0.005 mg/L.

12.3.9 The CCV (cups 29 & 51) is from 90% to 110%.

12.3.10 The "Last base" minus the "Init base" in A to D counts is from -12 to +13.

12.4 Samples audits should be analyzed with the frequency of 1 per each 15 sample segment and consist of a MS & MSD pair of a sample analyzed within that segment of the run.

12.4.1 The RPD of the MS & MSD pair is in control if it is less than 20%.

12.4.2 MS and MSD audits are 4.0 mL of sample spiked with 100 uL of 20. mg/L standard resulting in a final volume of 4.1 mL. Recoveries are in control if they are between 80% and 120%.

12.5 The CCBs (Cups 28 & 48) must be less than one half of the RL. If the blank is outside of the limit, verify that there is no contamination. Prepare fresh if necessary. Small corrections to samples may be needed if CCBs indicate that the mid-run baseline is not adequately calculated by the end of run drift correction.

12.6 The ICV (Cup #7) and CCV (Cups 29 & 51) standard recoveries must be within $\pm 10\%$ (90 – 110%) of the true values. If the CCV is outside of the limits, check for problem samples or failing Cd Coil. Rerun. If the CCV continues to fail, the analysis must be stopped. Bracketed samples must be reanalyzed.

12.7 Proficiency audit samples are obtained from an independent source at least biannually. Two samples at different concentrations are received for each evaluation. The samples are prepared and analyzed according to the instructions

provided. The results are submitted to the supplier for evaluation. Participation in these studies is used as a means to independently monitor this method's performance and to compare its performance against that of other participants.

13.0 Calibration and Standardization

13.1 Calibration and operation of the instrument are performed according to the TrAAcs user manual and the procedure section of this SOP. Each day, an approximate calibration is done before the first run using the adjusting base and gain settings section. Each run is individually calibrated using standards denoted in the procedure section.

14.0 Procedure

14.1 Specific instructions about the programming, operation and maintenance of the Technicon TrAAcs system may be found in the manual furnished with the instrument.

14.2 The typical input file will include the following information: # of anal.=2; channel=1 2 3 4; samples/hr=060; sample/wash=4.0; pecking=n; sample time=48; wash time=12; base corr=y; raw output=n. For analysis #1(nitrate plus nitrite): fit=l; inv chem=n; base concent=.00; carryover=.00(unless programming in a manual carryover factor with no "H,2L" in the tray protocol); dilution carryover=.00; chem name=NO3NO2; units=mg/L; base in calib=y. For analysis #2(ammonia): fit=l; inv chem=n; base concent=.00; carryover=.00(unless programming in a manual carryover factor with no "H,2L" in the tray protocol); dilution carryover=.00; chem name=NH3; units=mg/L; base in calib=y. The calibrant values for analysis #1 are: 1=2.00; 2=1.50; 3=1.00; 4=.50; 5=.20; 6=6.0; 7=7.0; 8=8.0 The calibrant values for analysis #2 are: 1=1.00; 2=.75; 3=.50; 4=.25; 5=.10; 6=6.0; 7=7.0; 8=8.0 The # to resample=2; duel probe system=n; tray protocol (for a typical run)= p,c,4s,h,2l,42s,g,8s,e; gain peak #=002.

14.3 Use and care of the cadmium coil: The cadmium coil must be cleaned and activated before it is used for the first time. If the absorbance of the full scale standard falls below the acceptable limit, the pH of the working imidazole may need to be adjusted or the coil may need reactivation or possibly even cleaning and reactivation or replacement. The coil will be stored between uses full of working imidazole, and introduction of air into the coil will be minimized by using nitrogen instead of air bubbles.

14.4 Cleaning the cadmium coil: Remove the tygon connectors from the coil. Using vacuum or a 10. mL pipettor, run 1. mL of 2N nitric acid through the coil, which will cause the coil to become quite warm. Then run 5 mL of conc. HCl, 5 mL of DI water, 5 mL of conc. HCl, 5 mL of DI water, 5 mL of conc. HCl, 5 mL of DI water, 5 mL of conc. HCl, and 5 mL of DI water through the coil. Finally run an additional 20 mL of DI water through the coil, and carefully replace the tygon connectors ensuring a good tight butt joint.

- 14.5** Activating the cadmium coil: Complete instrument startup (14.6). After connecting the coil, sequentially pump through the working imidazole line: 2N HCl activating solution for 1 minute, the copper activating solution for 2 minutes, and then the 2N HCl activating solution for 5 more minutes. Attach the working imidazole line to the reagent container and allow an additional 10 minutes or so for equilibration.
- 14.6** Instrument startup: Warm reagents and standards to room temperature. Prepare the working imidazole. Turn on the compressed air (40 PSI) which drives the sampler. Turn on the power switches. Turn on the nitrogen gas (17 PSI) which is used instead of compressed air for the segmentation bubbles. If the pressure is too high, bleed off the excess. Readjust the regulator, if necessary. Check the date and time (correct if necessary) by typing DATE (enter), (correct if necessary) and TIME (enter), (correct if necessary). Switch to the bottom screen partition (push and hold ALT key and push ESC key) and in the menu, select CR. Using the F4 command, input: B1 (enter), TrAAcs response should be 0; CK (enter), TrAAcs response should be 0; DM0 (enter-the "0" in DM0 and DL0 is a number, not a letter), TrAAcs response should be OK; DL0 (enter), TrAAcs response should be OK. If any of the above four responses are other than 0 or OK, quit chart & run (F2, Y, enter). Then download: EDOWNL (enter); EPSLON3.COM (enter); 24 (enter); push in the red reset button on the circuit board which is on the door of the master module and press enter to start download. After download is complete, return to the "select CR" point in the instructions and continue. It may be necessary to download more than once. If ready to continue, input OP1 (enter, to start the pump-the cadmium coil should still be disconnected-the reagent lines should be in DI rinse water). Latch the pump platen. Place the sampler probe into the bottle of system wash solution to cleanse the probe and the polyethylene sample line and to provide wetting agent for easier pumping throughout the manifold. After several minutes, turn on the chart F9, select channels 12 (if also running NH3) and select 15 inches/hour. Check for a suitable baseline and set it at about 5% of scale using the VB1 and CB1 _ commands (see section 14.7). Attach the pump tubes to the proper reagent containers (with adequate volumes of reagents-do not run out of working imidazole) and let pump for a few minutes until after the working imidazole has reached the point where the coil will be attached. Stop the pump F4 QP1, carefully connect the cadmium coil to the proper connectors with a good tight fit, place sampler probe back into wash reservoir and restart the pump. After several minutes, inspect the system for good bubble pattern (the bubble size may be changed by varying the length of the loop of silicone tubing between the air bar pincers), no leaks, and smooth baseline on the chart. The reagent baseline should not be a lot higher than the rinse baseline. A higher than normal baseline may indicate that the reagents need to be changed.
- 14.7** Adjusting base and gain settings: The base setting controls the intercept of the chart trace and the gain setting controls the slope (peak heights). Using the VB1, and VG1 commands, ascertain the current base and gain settings and record those settings on the chart paper. Set the baseline at 4% to 8% of scale using the CB1 _ command. Activate the sampler using the SS command and sample the full scale primer cup for 3 or 4 minutes. Return the probe to the wash reservoir using the SW1 command. When the chart trace for the standard reaches steady state, set the trace at 85% to 92% of scale using the CG1 _ command.

- 14.8** Sample handling and tray positions: The sample bottles should be shaken when picked up in sample receiving (before they are placed in the storage trays in the refrigerator) to assure that the preservative and sample are completely mixed. Since supernatant is analyzed, letting the bottles sit overnight in the refrigerator permits most of the interfering particulates to settle out. Sample aliquots should be taken from the bottles with a 4 mL pipettor with disposable tip. The pipetting sequence is: draw up a full 4 mL of DI water and discard, draw up about 3 1/2 mL of sample and discard, then draw up 3 mL of sample and discharge into the sample cup. The cups should be rinsed with DI water before use. Place cups in appropriate positions and place a 16x75 mm glass tube in position 1 (larger volume of primer standard for setting gain). Pipette blanks (0.1% H₂SO₄) first, and then standards from low to high. Blank positions are: 8, 9, 27, 28, 47, 48, 53-60. If keeping the polyethylene sample line clean throughout the run is difficult, putting system wash solution in cups 27 and 47 may be helpful. Cup #10 is for 0.1% H₂SO₄ diluent from the dilutor. Standard positions are: 1=8 mL of 2.0, 2=2.0, 3=1.5, 4=1.0, 5=.50, 6=.20, 7=2.0 (ICV), 11=DVS, 29=2.0, 51=2.0, 52=2.0, 30, 31, 49, & 50 each get 100 uL of 20 mg/L spiking standard (these are the MS & MSD cups). Samples are placed in cups: 12-26, and 32-46. A sample likely to be less than 1.5 mg/L and located in the first half of the run is chosen as the first MS & MSD. A 4.0 mL aliquot is placed in each of cups 30 and 31. Another sample likely to be less than 1.5 mg/L and located after cup 31, is the second MS & MSD. A 4.0 mL aliquot is placed in each of cups 49 & 50. Using parafilm, mix thoroughly cups 30, 31, 49 and 50. Also mix any dilutions. Blanks in cups 55-60 may be replaced by dilutions or repeats (bad peaks) from the run.
- 14.9** Starting the run: Check for smooth baseline and good bubble pattern. Switch to the upper screen partition, call up the editor (E) and create an input file. One way to accomplish this is to set up a template input file with the variables that stay the same from run to run all set (sec. 14.2). If you have a template, read the template file from the disk, rename the file, change the tray protocol if needed, and write the new input file to the disk. Always go back to the template when creating a new file-don't try renaming a working input file. Set the chart speed at 60 inches/hour. Start the run (F7) and follow the menu. Use the same file name for chart file as for the input file. Ctrl B accepts the baseline. The baseline reading just prior to the primer peak is used as the ICB and should be devoid of excessive noise. While the run is in progress, watch for off scale peaks (dilute), bad peaks (investigate and rerun), over diluted samples (run at the proper dilution), and monitor QC audits. Also you can be setting up another run. At the end of the run, replace dilutions with straight samples and check the pH of the samples with a pH indicator solution which is capable of measuring down to a pH of 2.
- 14.10** Shut down: When the results of the run have printed out and while the reagents are still connected, stop the pump. Disconnect the cadmium coil's output end first to avoid siphoning. Then disconnect the input end. Isolate and close the coil by connecting the ends of the polyethylene tubing (which are still connected to the ends of the coil), trapping the working imidazole inside the full coil. Connect the ends of the two pieces of polyethylene tubing (which are connected to the manifold tubing)

together. Restart the pump, place the reagent lines into DI rinse water, and let rinse for 0.5 hour. Stop the pump (QP1), release the pump platen, shut off the nitrogen, exit from chart & run and from editor, shut off the power, and turn off the compressed air. Cover the sampler probe and wash reservoir to keep dust out.

15.0 Calculations

15.1 The TrAAcs makes most calculations automatically, including baseline drift, gain correction, and much of the carryover.

15.2 Diluted samples are calculated after the baseline has been corrected.

15.3 Calculation of the RPD and % Recovery of the MS & MSD audits where:

MS=Measured concentration of spiked sample in MS cup.

MSD= Measured concentration of spiked sample in MSD cup.

SA=Concentration of sample used for MS & MSD.

SP=Spiking standard concentration=20. mg/L.

$X=SA*4.0/4.1 =SA*0.9756$ =Theoretical conc. of sample in MS or MSD cup.

$Y=SP*0.1/4.1 =0.4878$ =Theoretical conc. of spike in MS or MSD cup.

$Z= (MS+MSD)/2$ =Average conc. of MS & MSD pair.

MS % Recovery= $100*(MS-X)/Y$.

MSD % Recovery= $100*(MSD-X)/Y$.

RPD= $100*[absolute\ value\ of\ (MS-MSD)/Z]$.

16.0 Method Performance

16.1 MDL – MDL studies are determined annually for this method using the Code of Federal Regulations 40 CFR, Part 136, Appendix B, and internal procedure SOP 103. Seven replicate analyses of a low level standard with a mean concentration of 0.0041 mg/L resulted in a standard deviation of 0.0009 mg/L and a MDL of 0.0030 mg/L.

16.2 Precision – The Relative Percent Difference between MS & MSD should be less than 20%.

16.3 Accuracy – The percent recovery of the MS & MSD should fall within the range of 80% to 120%.

16.4 RL – After examining several factors such as normal precision of samples near the RL, normal blank levels, and the MDL, the RL has been set at 0.01 mg/L.

17.0 Pollution Prevention

17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Whenever feasible, staff should use pollution prevention techniques to address their waste generation. When

wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

17.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

17.3 For information concerning pollution prevention which may be applicable to laboratory operations, consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, DC 20036.

18.0 Data Assessment

18.1 Analytical data reported must be within the linear range of the assay (<2.5 mg/L).

18.2 Data is reported to a maximum of three significant figures as follows: if <0.01, then low is reported as 0.00X with T or W code, .000 is reported as ND with W code, and high is reported as ND; if < 0.2, then low is reported .XXX and high is reported 0.XX; if < 1.0, then reported 0.XX; if between 1.0 & 2.0, then reported X.XX; if >2.0, then reported X.X, XX., or XX0.

18.3 Dilutions increase the RL (i.e., RL of .01 mg/L multiplied by the dilution factor).

18.4 Appropriate laboratory reporting codes for dilutions, interferences, holding times, improper preservation, etc., will be appended to the test result according to laboratory policy. See internal procedure SOP 106.

18.5 Precision and accuracy data for an analytical batch must be within the acceptance criteria in Section 12 before the data can be reported. Standards and controls must also be within the acceptance criteria in Section 12 before the data can be reported.

18.6 Out of range values must be diluted, rerun, and acceptable before they can be reported.

18.7 Samples suspected of having excessive carryover must be rerun for verification before they can be reported.

18.8 Sample peaks are reviewed.

18.9 The analyst and the Unit Manager review all data before the final reporting out of results.

19.0 Corrective Actions

19.1 Preventative maintenance is performed on a routine basis. A maintenance logbook is kept with the instrument.

- 19.2 Samples with misshapen peaks are investigated for pH or matrix problems or some other flow dynamics problem such as inadvertent extra bubbles. Repeat samples or code results, as appropriate.
- 19.3 Low relative absorbance may indicate poorly performing Cd Column (see use and care of the cadmium coil), malfunctioning pump tube, or ineffective reagent. You may need to adjust the pH of the working imidazole (to about 7.3 when using 0.1% H₂SO₄ as level of preservation for baseline, standards and samples) using dilute NaOH or HCl as appropriate.
- 20.0 **Waste Management**
- 20.1 Liquid wastes generated by the analyses and excess out-dated reagents should be collected in a waste jug and be given to a waste hauler for disposal.
- 20.2 Liquid wastes generated by excess samples, and dilutions can be disposed of down the drain with copious amounts of water if they do not carry some other hazardous material (i.e., samples from an industrial site, etc.) that requires them to be handled as a hazardous waste.
- 20.3 Broken/waste glass is collected at the bench in a plastic pail until transferred to a collection barrel for disposal.
- 21.0 **References**
- 21.1 Nitrogen, Nitrate-Nitrite (Colorimetric, Automated, Cadmium Reduction), Methods for Chemical Analysis of Water and Wastes, USEPA, Cincinnati, Ohio, March 1983, EPA-600/4-79-020, Method 353.2 (revised 1978). Storet #00630.
- 21.2 Nitrate/Nitrite in Water and Wastewater, Technicon TrAAcs 800™ Industrial Method No. 824-87T (revised July 1987).
- 21.3 Nitrogen (Nitrate), Automated Cadmium Reduction Method, Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 20th Edition, 1998, Method 4500-NO₃⁻ F., pp. 4-118-4-119.
- 22.0 **Attachments**
- 22.1 Pump tube flow diagram.

Signature Page

APPROVED BY *[Signature]* DATE 4/20/06
CHIEF, LABORATORY SERVICES SECTION

APPROVED BY *[Signature]* DATE 4/12/06
COMPLIANCE OFFICER

APPROVED BY *[Signature]* DATE 4/7/2006
QA OFFICER

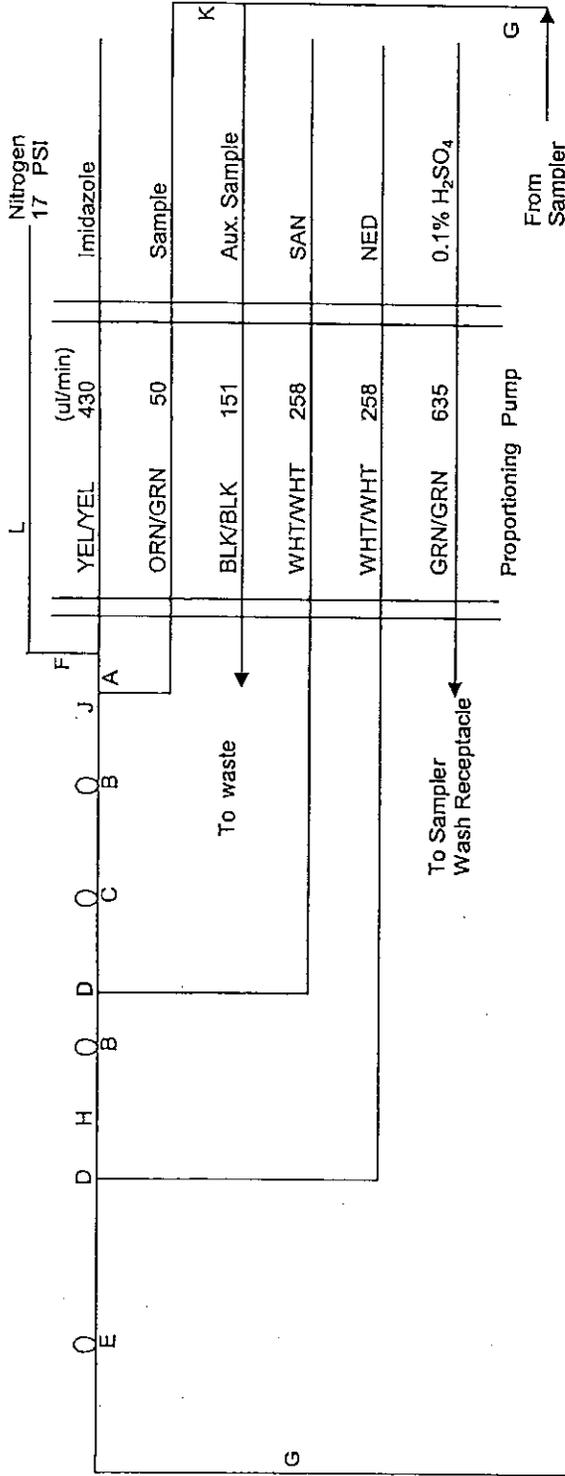
APPROVED BY *Sandra Gregg* DATE 4-3-06
UNIT MANAGER

APPROVED BY *Roger A. Anderson* DATE 3/22/2006
ANALYST

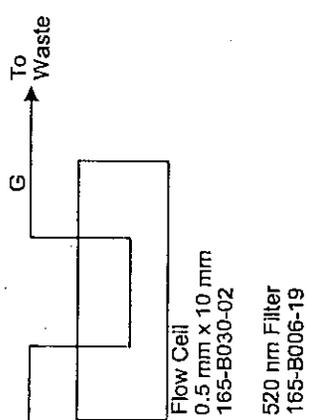
Method No. SOP 318

Manifold No. 165-D008-01

Nitrate plus Nitrite as Nitrogen

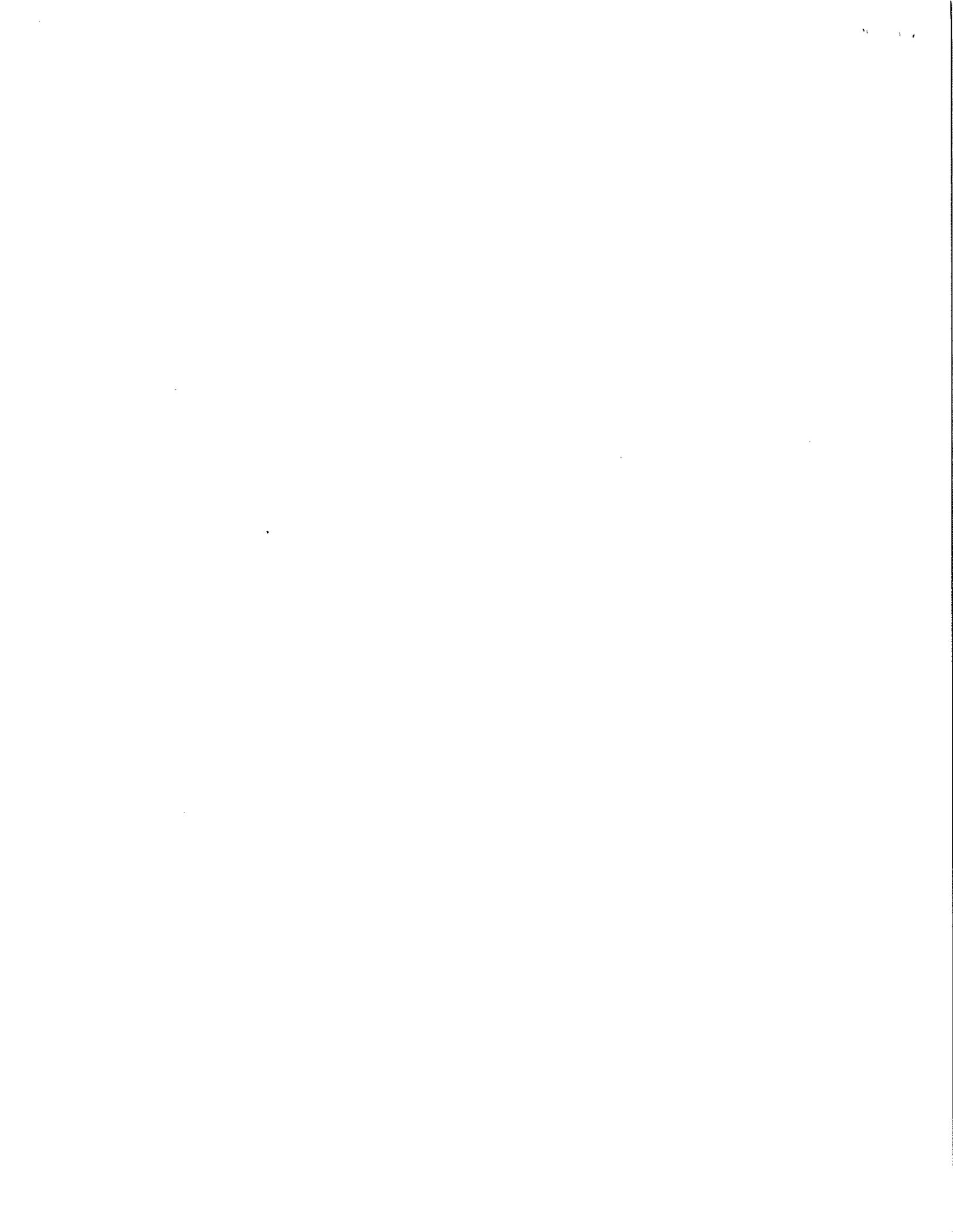


- A Inlet 3-pt 178-B482-01
- B 5 Turn Coil 165-G005-01
- C Cad. Coil 165-G006-01
- D T Fitting 178-G215-01
- E 20 Turn Coil 165-G005-03
- F Silicone Tubing 116-0558-02
- G Polyethylene Tube, 0.030 in. ID
- H U Connector 178-G224-02
- J L Connector 178-G233-01
- K Splitter, Glass/Sapphire
- L Air Valve 165-B028-01



Note: An auxiliary sample pump tube, which pumps to waste, may be needed if no additional channel, such as ammonia, is used.

County	ID	Type	Depth	Lat (frac)	Long (frac)	Lat (dms)	Long (dms)	Description	EPABasin	USGSBasin
Baraga	070088	River/Stream		0 46.759342	-88.455004	46 45 33	-89 32 41	LINDEN CREEK - GLEC MERCURY PROJECT		04020105
Baraga	070083	River/Stream		0 46.75857	-88.45110	46 45 30	-89 32 56	LINDEN CREEK AT DIVISION ROAD, LANSE TOWNSHIP, SECTION 5		04020105
Baraga	070068	River/Stream		0 46.756388	-88.4525	46 45 22	-89 32 50	LINDEN CREEK AT DOWNSTREAM OF L'ANSE WWTP; T50N R33W S05		04020105
Baraga	070067	River/Stream		0 46.756389	-88.4525	46 45 23	-89 32 50	LINDEN CREEK AT UPSTREAM OF L'ANSE WWTP; T50N R33W S04		04020105
Baraga	070084	River/Stream		0 46.76039	-88.44550	46 45 37	-89 33 16	LINDEN CREEK AT WWTP, LANSE TOWNSHIP, SECTION 4		04020105





EFFECTIVE DATE: 04/2006

SOP# 316

REVISION # 1

AMMONIA AS NITROGEN IN WATER
Colorimetric, Automated Phenate, TrAAcs

Table of Contents

1.0	Applicable Analytical Methods	1
2.0	Matrix or Matrices.....	2
3.0	Method Detection Limits (MDLs).....	2
4.0	Scope and Application	2
5.0	Method Summary.....	2
6.0	Definitions	2
7.0	Interferences	4
8.0	Safety	4
9.0	Equipment and Supplies	5
10.0	Reagents and Standards	6
11.0	Sample Collection, Preservation, Shipment, and Storage	8
12.0	QC.....	9
13.0	Calibration and Standardization	10
14.0	Procedure.....	10
15.0	Calculations.....	12
16.0	Method Performance.....	13
17.0	Pollution Prevention	13
18.0	Data Assessment.....	13
19.0	Corrective Actions.....	14
20.0	Waste Management	14
21.0	References	15
22.0	Attachments	15
	Signature Page.....	16

1.0 Applicable Analytical Methods

- 1.1 Nitrogen, Ammonia (Colorimetric, Automated, Phenate), Methods for Chemical Analysis of Water and Wastes, USEPA, Cincinnati, Ohio, March 1983, EPA 600/4 79-020, Method 350.1 (revised 1978). Storet #00610.
- 1.2 Ammonia in Water and Wastewater, Technicon TrAAcs 800™ Industrial Method No. 780-86T (revised June 1987).
- 1.3 Nitrogen (Ammonia), Automated Phenate Method, Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 20th Edition, 1998, Method 4500-NH₃ G, pp. 4-109-4-110.

2.0 Matrix or Matrices

2.1 Ground water.

2.2 Surface water.

2.3 Saline water.

2.4 Domestic waste.

2.5 Industrial waste.

3.0 Method Detection Limits (MDLs)

3.1 All MDLs shall be performed according to the Code of Federal Regulations 40 CFR, Part 136, Appendix B. See internal procedure SOP 103.

3.2 An annual MDL is determined by analyzing seven replicate aliquots of a water sample spiked to yield a theoretical concentration of about .005 mg/L. The replicates are analyzed in a manner identical to routine samples.

3.3 The MDL is calculated using a formula that applies the student t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Section 16.1.

3.4 The MDL for this method is determined annually or whenever there is a significant change in the procedure including a change in the analyst.

3.5 Reporting limit (RL) – The RL for this method has been set at 0.01 mg/L.

4.0 Scope and Application

4.1 This method applies to ground water, surface water, saline water, domestic waste, and industrial waste.

4.2 The working range of this method is 0.01 to 1.0 mg/L. Higher samples may be analyzed by diluting samples with 0.1% H₂SO₄.

5.0 Method Summary

5.1 Alkaline phenol and hypochlorite react with ammonia to form an indophenol like blue complex which is proportional to the ammonia concentration. The blue color is intensified with sodium nitroferricyanide solution.

6.0 Definitions

6.1 Analyte – Ammonia as nitrogen.

- 6.2** Calibration Blank (CB) – Prepared by adding reagents to blank water in the same concentration as the samples and standards. The CB is used to zero the instrument, for all initial and continuing CB determinations, and to flush the system between samples and standards. The CB is the 0.1% H₂SO₄ baseline and sample wash.
- 6.3** Initial Calibration Blank (ICB) – A CB analyzed at the beginning of the analysis run to demonstrate that the instrument is capable of acceptable performance. The ICB is the baseline reading just prior to the first standard.
- 6.4** Continuing Calibration Blank (CCB) – A CB analyzed in the course of the analysis run to demonstrate that the instrument is capable of continuous acceptable performance. Cups of 0.1% H₂SO₄ are run after each 15 samples. The final baseline is used to calculate baseline drift.
- 6.5** Calibration Standard (CAL) – A solution prepared from the primary standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 6.6** Calibration Curve – A plot of concentrations of known analyte standards versus the instrument response to the analyte. Standards are prepared by successively diluting a standard solution to produce working standards that cover the working range of the instrument. Standards should be prepared at the frequency specified in this SOP. The standards should be prepared using the same type of reagents and at the same concentration as will result in the samples following sample preparation. These standards are used to verify the accuracy of the calibration and the linearity of the test.
- 6.7** Initial Calibration Verification (ICV) – Second source standards to check the accuracy of the CALs. ICV is located in cup #7 and is also called H in the tray protocol for carryover calculation.
- 6.8** Continuing Calibration Verification (CCV) – A control standard analyzed in the course of the analysis run to demonstrate that the initial calibration determined remains valid throughout the course of the analytical run. Cups of CCV are run after each 15 samples.
- 6.9** Linear Calibration Range (LCR) – The concentration range over which the instrument response is linear.
- 6.10** Gain Calibration Standard (Gain) – A cup of the high CAL located near the end of the run and used for calculating the Gain correction.
- 6.11** Detection Verification Standard (DVS) – A low level standard with a concentration at or near the reporting limit used to verify the capability to analyze low concentration samples.

- 6.12 MDL – The minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. See internal procedure SOP 103.
- 6.13 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – Aliquots of a sample to which known quantities of the method's analytes are added in the laboratory. The MS and MSD are analyzed and prepared exactly like samples. The purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.
- 6.14 Relative Percent Difference (RPD)-The absolute value difference between the MS and MSD measurements divided by the average of the MS and MSD expressed as per cent. RPD is a measurement of laboratory precision which combines the precision of the instrumental analysis and the precision of the spiking technique.
- 7.0 **Interferences**
- 7.1 Turbidity can usually be significantly reduced by centrifuging the sample. A small syringe filter assembly may be helpful for some samples.
- 7.2 Sample color may be minimized through dilution. The result may need to be coded: I-Dilution required due to matrix interference; reporting limit (RL) raised.
- 7.3 Chlorine and sulfide (common oxidizing and reducing agents) can affect this analysis. Dilution may diminish their effects. Sample agitation in the presence of adequate fresh air oxidizes sulfide for samples that need to be run undiluted.
- 7.4 Calcium and magnesium ions may be present in concentrations sufficient to cause precipitation problems. This interference is eliminated by the addition of EDTA solution to the sample stream.
- 8.0 **Safety**
- 8.1 Safety glasses and shoes that cover the feet are required in all designated laboratory areas.
- 8.2 It is recommended that the analyst wear gloves and a lab coat when performing this procedure.
- 8.3 The analyst must be familiar with the Laboratory Chemical Hygiene Plan.
- 8.4 The analyst must be familiar with the Laboratory Safety Policy (internal procedure SOP 100).
- 8.5 The analyst must be familiar with any material safety data sheets (MSDSs) applicable to this method.

- 8.6 Sulfuric acid, phenol, and sodium hydroxide have the potential to be hazardous. Consult the MSDSs before proceeding with the analysis.
- 8.7 The analyst must be familiar with the location of safety equipment including showers, eye wash stations, and spill kits.
- 8.8 The analyst should always thoroughly wash hands in warm soapy water when leaving the work area and before handling food or drink.
- 8.9 The analyst should assume that all samples have the potential to be hazardous and should exercise caution when transporting, handling, and/or opening any samples.
- 8.10 General good laboratory practices are required. The analyst should take all necessary precautions in order to minimize the potential of exposure to samples and reagents used in this method.
- 9.0 **Equipment and Supplies**
- 9.1 Technicon TrAAcs 800.
- 9.1.1 Manifold #165-D000-01.
- 9.1.2 10 mm flow cell.
- 9.1.3 660 nm optical filter.
- 9.1.4 37°C heating bath.
- 9.2 Bottles – 500 mL, plastic, with screw caps.
- 9.3 Diluter – Hamilton, digital or equivalent.
- 9.4 Disposable 5 mL cups #171-0354P01.
- 9.5 Mechanical pipettes – 1 to 5 mL and 40 to 200 uL with pipette tips to fit.
- 9.6 Disposable 16x75 mm Neutrex soda lime glass tubes Cat No. M-190.
- 9.7 Reagent filters: straw & filter assembly, 178-B651-01.
- 9.8 pH strips.
- 9.9 pHydriion vivid 1-11 pH indicator solution.
- 9.10 Volumetric flasks – Various volumes.
- 9.11 Graduated cylinders – Various volumes.
- 9.12 Volumetric pipettes – Various volumes.

- 9.13 Reagent bottles – Brown plastic.
- 9.14 Compressed nitrogen regulated to 17 PSI.
- 9.15 Compressed air regulated to 40 PSI.
- 10.0 **Reagents and Standards**
- 10.1 All reagents, solvents, and standards must be traceable to the stock inventory tracking log.
- 10.2 All reagents, solvents, and standards must be labeled with: date received, date opened, expiration date, tracking number, and receiver's initials.
- 10.3 All prepared reagents and standards must be labeled with: date prepared, expiration date, preparer's initials, tracking number, diluent, and description.
- 10.4 All standard logbooks must be completely filled out.
- 10.5 All certificates of analysis must include the stock inventory tracking number that was assigned to the standard. Original certificates are maintained by the Laboratory's Quality Assurance/Quality Control Officer.
- 10.6 All reagents (except Triton X-100) are prepared with DI water. DI water is normal tap water that has first passed through a set of US Filter deionization tanks and then through a Millipore, Super Q™ water purification system and has an industry standard resistivity of 18MΩ.
- 10.7 **Brij-35 solution**, part no. T21-0110.
- 10.8 **Sodium hydroxide (NaOH) 10. N:** CAREFULLY, using a hood and a cool water bath, dissolve 200 g NaOH in about 250 mL of DI water. Cool and dilute to 500 mL with DI water.
- 10.9 **Alkaline phenol:** Use a hood for weighing and preparing this reagent. Add 38 g of phenol crystals to about 300 mL of deionized (DI) water. Mix and let cool. While mixing, add 60 mL of 10 N NaOH and let cool. Dilute to 500 mL with DI water and mix thoroughly. Refrigerate when not in use.
- 10.10 **Sodium hypochlorite 4.3%:** Use commercial unscented regular Ultra (6.0%) or germicidal (6.15%) Clorox bleach. Refrigerated undiluted Clorox seems to be stable. Other formulations may have different concentrations of sodium hypochlorite and need to be adjusted to obtain a 4.3% final concentration; they may have a relatively short shelf life also. If using Ultra (6.0%), dilute 36 mL of Clorox Ultra to 50 mL with DI water. If using germicidal (6.15%), dilute 35 mL of Clorox germicidal to 50 mL with DI water. Prepare weekly. Refrigerate when not in use.

- 10.11 Sodium nitroprusside:** Shield from light while mixing. Dissolve 0.275 g of sodium nitroprusside (sodium nitroferricyanide) in DI water and dilute to 250 mL. Store in a light resistant container. Refrigerate when not in use.
- 10.12 Disodium EDTA:** To about 800 mL of DI water, add 3.05 mL (for 0.1% H₂SO₄ preserved samples) of 10 N NaOH and 41 g of disodium EDTA. Mix, dilute to 1.00 L with DI water, and add 3 mL of Brij-35. Mix and store at room temperature.
- 10.13 50% Triton X-100 solution:** To 25 mL of isopropanol in a dropper bottle, add 25 mL of Triton X-100. Mix thoroughly.
- 10.14 System wash solution:** Add 0.2 mL of 50% Triton X-100 and 6 drops H₂SO₄ to 200 mL of DI water and mix thoroughly.
- 10.15 Stock standard (1000 mg/L as N):** Purchase certified stock standard, or add 3.819 g of ammonium chloride (dried at 105°C) and 28 drops H₂SO₄ to 500 mL DI water in a 1000 mL volumetric flask. Mix until thoroughly dissolved, dilute to 1000 mL with DI water and mix thoroughly. Stable for two years if refrigerated. An additional Second Source Stock Standard should be purchased or prepared.
- 10.16 ISS - Intermediate stock standard (100 mg/L as N):** Add 14 drops conc. H₂SO₄ and 50 mL stock standard to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for one year if refrigerated.
- 10.17 Combined ISS - (50 mg/L as N):** Add 14 drops conc. H₂SO₄ and 25 mL stock standard to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for one year if refrigerated. An additional Second Source Combined ISS should be prepared from a second source stock standard. This Combined ISS may be prepared in combination with NO₃.
- 10.18 CAL 1.00 mg/L standard:** Add 28 drops conc. H₂SO₄ and 10.0 mL of 100 mg/L ISS to a 1000 mL volumetric flask containing 500 mL DI water. Mix, dilute to 1000 mL with DI water, and mix thoroughly. Stable for 1 month if refrigerated. Note: Nitrate standards may be prepared in combination with ammonia standards. You may need to prepare a special intermediate 1.0 mg/L standard with the appropriate concentration of nitrate for use in preparing the DVS.
- 10.19 0.75 mg/L standard:** Add 14 drops conc. H₂SO₄ and 7.5 mL of 50 mg/L Combined ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.
- 10.20 0.50 mg/L standard:** Add 14 drops conc. H₂SO₄ and 5.0 mL of 50 mg/L Combined ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.

- 10.21** **0.25 mg/L standard:** Add 14 drops conc. H₂SO₄ and 2.5 mL of 50 mg/L Combined ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.
- 10.22** **0.10 mg/L standard:** Add 14 drops conc. H₂SO₄ and 1.0 mL of 50 mg/L Combined ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.
- 10.23** **0.015 mg/L Detection Verification Standard (DVS):** Add 14 drops conc. H₂SO₄ and 7.5 mL of 1.00 mg/L standard to a 500 mL volumetric flask containing 250 mL of DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for one month if refrigerated.
- 10.24** **ICV 1.00 mg/L standard:** Add 14 drops conc. H₂SO₄ and 10.0 mL of 50 mg/L Second Source Combined ISS to a 500 mL volumetric flask containing 250 mL DI water. Mix, dilute to 500 mL with DI water, and mix thoroughly. Stable for 3 months if refrigerated.
- 10.25** **Spiking standard (10 mg/L):** Add 28 drops conc. H₂SO₄ and 10.0 mL of 1000 mg/L stock standard to a 1000 mL volumetric flask containing 500 mL DI water. Mix, dilute to 1000 mL with DI water, and mix thoroughly. Stable for 6 months if refrigerated. When 100 uL of this standard is spiked into 4.0 mL of sample, the resulting spike concentration is about 0.25 mg/L.
- 10.26** **Wash reservoir solution, ICB, CCB, sample dilution diluent:** To one liter of DI water known to be pure, add 28 drops of conc. H₂SO₄ and mix thoroughly.
- 11.0** **Sample Collection, Preservation, Shipment, and Storage**
- 11.1** Water samples are collected in 500 mL high-density polyethylene screw cap bottles. The proper bottle codes are GA and, if field filtered, GAD.
- 11.2** Samples should be preserved with 10 drops of concentrated sulfuric acid per 500 mL of sample. Avoid adding excess quantities of H₂SO₄ unnecessarily. Samples should then be checked to determine that the pH has been lowered to 2. Samples with excess particulates or higher than normal pH may require some extra H₂SO₄, which should be noted on the sample label and/or the analysis request sheet. Avoid adding H₂SO₄ to highly caustic samples-a violent, explosive reaction may occur. After proper preservation, store samples at 4°C.
- 11.3** The maximum holding time is 28 days, although analyses should be performed as soon as possible after receipt.
- 11.4** Samples being shipped should be packed with sufficient ice that the samples remain cold until checked in at the laboratory.

- 12.0** QC
- 12.1** The minimum QC for this method includes an initial demonstration of capability (IDOC), MDL determination, LCR, routine analysis of reagent blanks, fortified blanks, and other laboratory solutions as continuing checks on performance.
- 12.2** IDOC
- 12.2.1** Prior to analyzing samples by this method, 4 CCB samples spiked with ammonia standard must be analyzed as described in Section 14 of this method. The results are statistically tabulated to obtain the average percent recovery (X), the standard deviation (s) of the percent recoveries and the % relative standard deviation (% RSD). The obtained value for X is compared to the criteria in Section 12.4.2. The % RSD calculated from s and X must be less than 20%. If both % RSD and X are acceptable, the IDOC is acceptable. If the % RSD or X fails, corrective action must be taken, and the IDOC must be repeated. Repeat the above steps until acceptable values for % RSD and X are obtained.
- 12.3** System audits are checked at least once per analytical batch and are in control if the following criteria are met:
- 12.3.1** The relative absorbance of 1.0 mg/L standard is from 0.16 to 0.27.
- 12.3.2** The 75% of full scale standard is from 0.730 to 0.773 mg/L.
- 12.3.3** The 50% of full scale standard is from 0.488 to 0.515 mg/L.
- 12.3.4** The 25% of full scale standard is from 0.241 to 0.262 mg/L.
- 12.3.5** The 10% of full scale standard is from 0.096 to 0.112 mg/L.
- 12.3.6** The ICV standard (cup 7) is between 90% and 110%.
- 12.3.7** The DVS (cup 11) is 0.011 to 0.021 mg/L.
- 12.3.8** The CCB (cups 28 & 48) is between -0.005 and +0.005 mg/L.
- 12.3.9** The CCV (cups 29 & 51) is from 90% to 110%.
- 12.3.10** The "Last base" minus the "Init base" in A to D counts is from -23 to +44.
- 12.3.11** The manifold temperature is about 38°C.
- 12.4** Samples audits should be analyzed with the frequency of 1 per each 15 sample segment and consist of a MS & MSD pair of a sample analyzed within that segment of the run.
- 12.4.1** The RPD of the MS & MSD pair is in control if it is less than 20%.
- 12.4.2** MS and MSD audits are 4.0 mL of sample spiked with 100 uL of 10 mg/L standard resulting in a final volume of 4.1 mL. Recoveries are in control if they are between 80% and 120%.
- 12.5** The CCBs (Cups 28 & 48) must be less than one half of the RL. If the blank is outside of the limit, verify that there is no contamination. Prepare fresh if necessary. Small corrections to samples may be needed if CCBs indicate that the mid-run baseline is not adequately calculated by the end of run drift correction.

- 12.6 The ICV (Cup #7) and CCV (Cups 29 & 51) standard recoveries must be within $\pm 10\%$ (90 – 110%) of the true values. If the CCV is outside of the limits, check for problem samples or failing pump tube. Rerun. If the CCV continues to fail, the analysis must be stopped. Bracketed samples must be reanalyzed.
- 12.7 Proficiency audit samples are obtained from an independent source at least biannually. Two samples at different concentrations are received for each evaluation. The samples are prepared and analyzed according to the instructions provided. The results are submitted to the supplier for evaluation. Participation in these studies is used as a means to independently monitor this method's performance and to compare its performance against that of other participants.
- 13.0 **Calibration and Standardization**
- 13.1 Calibration and operation of the instrument are performed according to the TrAAcs user manual and the procedure section of this SOP. Each day, an approximate calibration is done before the first run using the adjusting base and gain settings section. Each run is individually calibrated using standards denoted in the procedure section.
- 14.0 **Procedure**
- 14.1 Specific instructions about the programming, operation and maintenance of the Technicon TrAAcs system may be found in the manual furnished with the instrument.
- 14.2 The typical input file will include the following information: # of anal.=2; channel=1 2 3 4; samples/hr=060; sample/wash=4.0; pecking=n; sample time=48; wash time=12; base corr=y; raw output=n. For analysis #1(nitrate plus nitrite): fit=l; inv chem=n; base concent=.00; carryover=.00(unless programming in a manual carryover factor with no "H,2L" in the tray protocol); dilution carryover=.00; chem name=NO3NO2; units=mg/L; base in calib=y. For analysis #2(ammonia): fit=l; inv chem=n; base concent=.00; carryover=.00(unless programming in a manual carryover factor with no "H,2L" in the tray protocol); dilution carryover=.00; chem name=NH3; units=mg/L; base in calib=y. The calibrant values for analysis #1 are: 1=2.00; 2=1.50; 3=1.00; 4=.50; 5=.20; 6=6.0; 7=7.0; 8=8.0 The calibrant values for analysis #2 are: 1=1.00; 2=.75; 3=.50; 4=.25; 5=.10; 6=6.0; 7=7.0; 8=8.0 The # to resample=2; duel probe system=n; tray protocol (for a typical run)= p,c,4s,h,2l,42s,g,8s,e; gain peak #=002.
- 14.3 Instrument startup: Warm reagents and standards to room temperature. Turn on the compressed air (40 PSI) which drives the sampler. Turn on the power switches. Turn on the nitrogen gas (17 PSI) which is used instead of compressed air for the segmentation bubbles. If the pressure is too high, bleed off the excess. Readjust the regulator, if necessary. Check the date and time (correct if necessary) by typing DATE (enter), (correct if necessary) and TIME (enter), (correct if necessary). Switch to the bottom screen partition (push and hold ALT key and push ESC key) and in the menu, select CR. Using the F4 command, input: B1 (enter), TrAAcs response should be 0; CK (enter), TrAAcs response should be 0; DM0 (enter-the "0" in DM0

and DL0 is a number, not a letter), TrAAcs response should be OK; DL0 (enter), TrAAcs response should be OK. If any of the above four responses are other than 0 or OK, quit chart & run (F2, Y, enter). Then download: EDOWNL (enter); EPSLON3.COM (enter); 24 (enter); push in the red reset button on the circuit board which is on the door of the master module and press enter to start download. After download is complete, return to the "select CR" point in the instructions and continue. It may be necessary to download more than once. If ready to continue, input OP1 (enter, to start the pump, the reagent lines should be in DI rinse water). Latch the pump platen. Place the sampler probe into the bottle of system wash solution to cleanse the probe and the polyethylene sample line and to provide wetting agent for easier pumping throughout the manifold. After several minutes, turn on the chart F9, select channels 12 (if also running NO3) and select 15 inches/hour. Check for a suitable baseline and set it at about 5% of scale using the VB2 and CB2 _ commands (see section 14.4). Attach the pump tubes to the proper reagent containers (with adequate volumes of reagents) and place sampler probe back into wash reservoir. After several minutes, inspect the system for good bubble pattern (the bubble size may be changed by varying the length of the loop of silicone tubing between the air bar pincers), no leaks, and smooth baseline on the chart. The reagent baseline should not be a lot higher than the rinse baseline. A higher than normal baseline may indicate that the reagents need to be changed.

14.4 Adjusting base and gain settings: The base setting controls the intercept of the chart trace and the gain setting controls the slope (peak heights). Using the VB2, and VG2 commands, ascertain the current base and gain settings and record those settings on the chart paper. Set the baseline at 4% to 8% of scale using the CB2 _ command. Activate the sampler using the SS command and sample the full scale primer cup for 3 or 4 minutes. Return the probe to the wash reservoir using the SW1 command. When the chart trace for the standard reaches steady state, set the trace at 85% to 92% of scale using the CG2 _ command.

14.5 Sample handling and tray positions: The sample bottles should be shaken when picked up in sample receiving (before they are placed in the storage trays in the refrigerator) to assure that the preservative and sample are completely mixed. Since supernatant is analyzed, letting the bottles sit overnight in the refrigerator permits most of the interfering particulates to settle out. Sample aliquots should be taken from the bottles with a 4 mL pipettor with disposable tip. The pipetting sequence is: draw up a full 4 mL of DI water and discard, draw up about 3 1/2 mL of sample and discard, then draw up 3 mL of sample and discharge into the sample cup. The cups should be rinsed with DI water before use. Place cups in appropriate positions and place a 16x75 mm glass tube in position 1 (larger volume of primer standard for setting gain). Pipette blanks (0.1% H₂SO₄) first, and then standards from low to high. Blank positions are: 8, 9, 27, 28, 47, 48, 53-60. If keeping the polyethylene sample line clean throughout the run is difficult, putting system wash solution in cups 27 and 47 may be helpful. Cup #10 is for 0.1% H₂SO₄ diluent from the dilutor. Standard positions are: 1=8 mL of 1.0, 2=1.0, 3=.75, 4=.50, 5=.25, 6=.10, 7=1.0 (ICV), 11=DVS, 29=1.0, 51=1.0, 52=1.0, 30, 31, 49, & 50 each get 100 uL of 10. mg/L spiking standard (these are the MS & MSD cups). Samples are placed in cups: 12-26, and 32-46. A sample likely to be less than .75 mg/L and located in the first half

of the run is chosen as the first MS&MSD. A 4.0 mL aliquot is placed in each of cups 30 and 31. Another sample likely to be less than .75 mg/L and located after cup 31, is the second MS&MSD. A 4.0 mL aliquot is placed in each of cups 49 & 50. Using parafilm, mix thoroughly cups 30, 31, 49 and 50. Also mix any dilutions. Blanks in cups 55-60 may be replaced by dilutions or repeats (bad peaks) from the run.

- 14.6** Starting the run: Check for smooth baseline and good bubble pattern. Switch to the upper screen partition, call up the editor (E) and create an input file. One way to accomplish this is to set up a template input file with the variables that stay the same from run to run all set (sec. 14.2). If you have a template, read the template file from the disk, rename the file, change the tray protocol if needed, and write the new input file to the disk. Always go back to the template when creating a new file-don't try renaming a working input file. Set the chart speed at 60 inches/hour. Start the run (F7) and follow the menu. Use the same file name for chart file as for the input file. Ctrl B accepts the baseline. The baseline reading just prior to the primer peak is used as the ICB and should be devoid of excessive noise. While the run is in progress, watch for off scale peaks (dilute), bad peaks (investigate and rerun), over diluted samples (run at the proper dilution), and monitor QC audits. Also you can be setting up another run. At the end of the run, replace dilutions with straight samples and check the pH of the samples with a pH indicator solution which is capable of measuring down to a pH of 2.
- 14.7** Shut down: When the results of the run have printed out, place the reagent lines into DI rinse water, and let rinse for 0.5 hour. Stop the pump (QP1), release the pump platen, shut off the nitrogen, exit from chart & run and from editor, shut off the power, and turn off the compressed air. Cover the sampler probe and wash reservoir to keep dust out.
- 15.0** **Calculations**
- 15.1** The TrAAcs makes most calculations automatically, including baseline drift, gain correction, and much of the carryover.
- 15.2** Diluted samples are calculated after the baseline has been corrected.
- 15.3** Calculation of the RPD and % Recovery of the MS & MSD audits where:
- MS=Measured concentration of spiked sample in MS cup.
MSD= Measured concentration of spiked sample in MSD cup.
SA=Concentration of sample used for MS & MSD.
SP=Spiking standard concentration=10. mg/L.
 $X=SA*4.0/4.1 =SA*0.9756$ =Theoretical conc. of sample in MS or MSD cup.
 $Y=SP*0.1/4.1 =0.2439$ =Theoretical conc. of spike in MS or MSD cup.
 $Z=(MS+MSD)/2$ =Average conc. of MS & MSD pair.
MS % Recovery= $100*(MS-X)/Y$.
MSD % Recovery= $100*(MSD-X)/Y$.
RPD= $100*[absolute\ value\ of\ (MS-MSD)/Z]$.

16.0 Method Performance

- 16.1** MDL – MDL studies are determined annually for this method using the Code of Federal Regulations 40 CFR, Part 136, Appendix B, and internal procedure SOP 103. Seven replicate analyses of a low level standard with a mean concentration of 0.0052 mg/L resulted in a standard deviation of 0.0004 mg/L and a MDL of 0.0012 mg/L.
- 16.2** Precision – The Relative Percent Difference between MS & MSD should be less than 20%.
- 16.3** Accuracy – The percent recovery of the MS & MSD should fall within the range of 80% to 120%.
- 16.4** RL – After examining several factors such as normal precision of samples near the RL, normal blank levels, and the MDL, the RL has been set at 0.01 mg/L.

17.0 Pollution Prevention

- 17.1** Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Whenever feasible, staff should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.
- 17.2** The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.
- 17.3** For information concerning pollution prevention which may be applicable to laboratory operations, consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, DC 20036.

18.0 Data Assessment

- 18.1** Analytical data reported must be within the linear range of the assay (<1.3 mg/L).
- 18.2** Data is reported to a maximum of three significant figures as follows: if <0.01, then low is reported as 0.00X with T or W code, .000 is reported as ND with W code, and high is reported as ND; if < 0.2, then low is reported .XXX and high is reported 0.XX; if < 1.0, then 0.XX; if >1.0, then X.X, XX., or XX0.
- 18.3** Dilutions increase the RL (i.e., RL of .01 mg/L multiplied by the dilution factor).

- 18.4 Appropriate laboratory reporting codes for dilutions, interferences, holding times, improper preservation, etc., will be appended to the test result according to laboratory policy. See internal procedure SOP 106.
- 18.5 Precision and accuracy data for an analytical batch must be within the acceptance criteria in Section 12 before the data can be reported. Standards and controls must also be within the acceptance criteria in Section 12 before the data can be reported.
- 18.6 Out of range values must be diluted, rerun, and acceptable before they can be reported.
- 18.7 Samples suspected of having excessive carryover must be rerun for verification before they can be reported.
- 18.8 Sample peaks are reviewed.
- 18.9 The analyst and the Unit Manager review all data before the final reporting out of results.
- 19.0 **Corrective Actions**
- 19.1 Preventative maintenance is performed on a routine basis. A maintenance logbook is kept with the instrument.
- 19.2 Samples with misshapen peaks are investigated for pH or matrix problems or some other flow dynamics problem such as inadvertent extra bubbles. Repeat samples or code results, as appropriate.
- 19.3 Low relative absorbance may indicate malfunctioning pump tube, or ineffective reagent.
- 20.0 **Waste Management**
- 20.1 Liquid wastes generated by the analyses and excess out-dated reagents should be collected in a waste jug and be given to a waste hauler for disposal.
- 20.2 Liquid wastes generated by excess samples, and dilutions can be disposed of down the drain with copious amounts of water if they do not carry some other hazardous material (i.e., samples from an industrial site, etc.) that requires them to be handled as a hazardous waste.
- 20.3 Broken/waste glass is collected at the bench in a plastic pail until transferred to a collection barrel for disposal.

21.0 References

- 21.1 Nitrogen, Ammonia (Colorimetric, Automated, Phenate), Methods for Chemical Analysis of Water and Wastes, USEPA, Cincinnati, Ohio, March 1983, EPA-600/4-79-020, Method 350.1 (revised 1978). Storet #00610.
- 21.2 Ammonia in Water and Wastewater, Technicon TrAAcs 800™ Industrial Method No. 780-86T (revised June 1987).
- 21.3 Nitrogen (Ammonia), Automated Phenate Method, Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 20th Edition, 1998, Method 4500-NH₃ G, pp. 4-109-4-110.

22.0 Attachments

- 22.1 Pump tube flow diagram.

Signature Page

APPROVED BY *Bob H. Lewis* DATE 4/23/06
CHIEF LABORATORY SERVICES SECTION

APPROVED BY *[Signature]* DATE 4/19/06
COMPLIANCE OFFICER

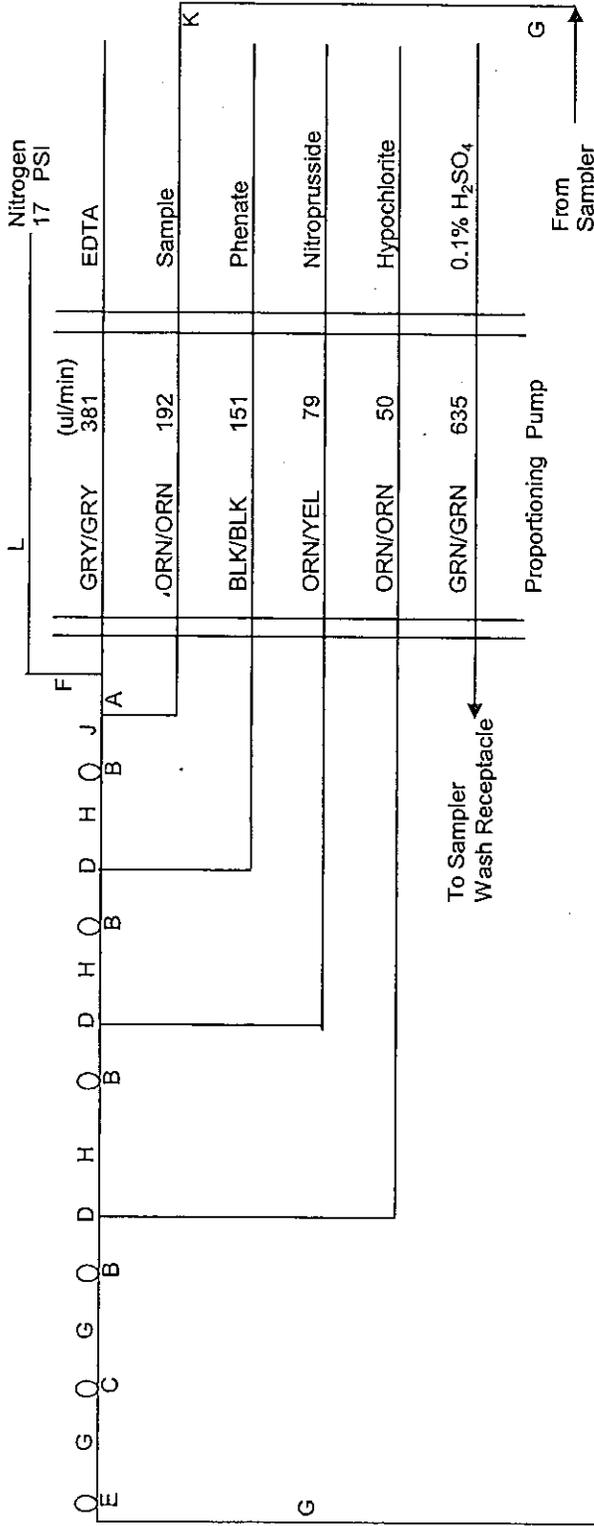
APPROVED BY *Albert Lee* DATE 4/11/2006
QA OFFICER

APPROVED BY *Sandra K. Gregg* DATE 4-4-2006
UNIT MANAGER

APPROVED BY *Roger A. Anderson* DATE 3/22/2006
ANALYST

Method No. SOP 316
 Manifold No. 165-D000-01

Ammonia as Nitrogen



- A Inlet 3-pt 178-B482-01
- B 5 Turn Coil 165-G005-01
- C Heating Bath, 37 Deg 178-B822-01
- D T Fitting 178-G202-01
- E 20 Turn Coil 165-G005-03
- F Silicone Tubing 116-0558-02
- G Polyethylene Tube, 0.030 in. ID
- H U Connector 178-G224-02
- J L Connector 178-G233-01
- K Splitter, Glass/Sapphire (if needed for splitting sample line)
- L Air Valve 165-B028-01

Note: An auxiliary sample pump tube, which pumps to waste, may need to be added if no additional channel, such as nitrate plus nitrite, is used.



EFFECTIVE DATE: 03/2006

SOP# 303

REVISION # 2

DETERMINATION OF TOTAL KJELDAHL NITROGEN IN WATER

Table of Contents

1.0	Applicable Analytical Methods	1
2.0	Matrix or Matrices.....	1
3.0	Method Detection Limits.....	2
4.0	Scope and Application	2
5.0	Method Summary	2
6.0	Definitions	3
7.0	Interferences	4
8.0	Safety	4
9.0	Equipment and Supplies	5
10.0	Reagents and Standards	6
11.0	Sample Collection, Preservation, Shipment, and Storage	8
12.0	Quality Control (QC).....	9
13.0	Calibration and Standardization	9
14.0	Procedure.....	9
15.0	Calculations.....	12
16.0	Method Performance.....	13
17.0	Pollution Prevention	13
18.0	Data Assessment	14
19.0	Corrective Actions	14
20.0	Waste Management	15
21.0	References	15
22.0	Attachments	16
	Signature Page	17

1.0 Applicable Analytical Methods

1.1 Nitrogen, Kjeldahl, Total (Colorimetric, Semi-Automated Digester, AAll, Method 351.2, U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes (MCAWW) – EPA/600/4-93-020 – Revised August 1993.

1.2 Total Nitrogen and Total Phosphorus BD-40 Digestion Procedure for Water, Brann & Lubbe, US 329-74A, December 1997.

1.3 Nitrogen, Total Kjeldahl, Brann & Lubbe, AA3, US 696C-82W, August 14, 1999.

2.0 Matrix or Matrices

2.1 Drinking water.

2.2 Ground water.

2.3 Surface water.

2.4 Domestic and industrial wastewater.

3.0 Method Detection Limits

3.1 All method detection limits (MDL) shall be performed according to the Code of Federal Regulations 40 CFR, Part 136, Appendix B. See internal procedure SOP 103.

3.2 MDL's must be established by using a low level standard (Detection Verification Standard-DVS) at a concentration of two to three times the estimated instrument detection limit to determine the MDL values. At least seven replicate aliquots of the standard must be processed through the entire analytical method. Perform all calculations defined in the method. Report the concentration values in the appropriate unit. Calculate the MDL as follows:

$$\text{MDL} = (t) \times (\text{SD})$$

Where: t = student's "t" value for a 99% confidence limit and a standard deviation (SD) estimate with $N - 1$ degrees of freedom.

SD = standard deviation of the replicate analyses.

3.3 In the DEQ Environmental Laboratory, 28 replicate analyses of a low level DVS standard with a mean concentration of 0.0871 mg N/L resulted in a SD of 0.0256 mg N/L and MDL of 0.0633 mg N/L.

3.4 MDL's should be determined annually, when a new operator begins work, or whenever there is a significant change in the background or instrument response.

4.0 Scope and Application

4.1 This method covers the determination of total Kjeldahl nitrogen in drinking or surface waters and in domestic or industrial wastewater. The procedure converts nitrogen compounds of biological origin such as amino acids, proteins, and peptides to ammonia but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oxides, semi-carbazones, and some refractory tertiary amines.

4.2 The applicable range of this method is 0.10 to 5.0 mg N/L. The range may be extended by sample dilution.

5.0 Method Summary

5.1 The sample is heated in the presence of sulfuric acid, potassium sulfate, and mercuric oxide. The residue is cooled, diluted to 10.0 mL, and analyzed for ammonia by an automated salicylate method. This digested sample may also be used for total phosphorus determination.

6.0 Definitions

- 6.1** Calibration Blank/0% Standard (CB) – A volume of reagent water fortified with the same matrix as the calibration standards but without the analytes, internal standards, or surrogate analytes.
- 6.2** Calibration Standard (CAL) – A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument's response with respect to analyte concentration.
- 6.3** Matrix Spike/Matrix Spike Duplicate (MS/MSD) – An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS/MSDs are analyzed exactly like a sample, and their purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSDs corrected for background concentrations. Percent recovery of the added analyte (standard) must be within the acceptable range established for the assay. Percent relative difference the MS and the MSD must be within acceptable range established for the assay. MS/MSDs should be run at a rate of 1 pair for every 10 samples.
- 6.4** Reporting Limit (RL) – The RL is 0.10 mg N/L in the Michigan DEQ Environmental Laboratory.
- 6.5** Laboratory Bottle Blank (LBB) – An aliquot of reagent water placed in a sample container in the laboratory that is treated exactly like a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LBB is used to determine whether method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 6.6** Field Blank (FB) – Reagent water placed in a sample container in the field and treated exactly like a sample including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FB is to determine if method analytes or other interferences are present in the field environment.
- 6.7** Field Duplicates (FD1 and FD2) – Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, transportation, storage, and laboratory procedures.
- 6.8** Stock Standard Solution (STOCK I) – A concentrated solution containing a single certified standard that is a method analyte or a concentrated solution of a single analyte prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source. STOCK I's are used to prepare primary dilution standards (N and OP stock solutions).

- 6.9 Primary (intermediate) Dilution Standard Solution (STOCK II) – A solution of several analytes prepared in the laboratory from STOCK I's and diluted as needed to prepare calibration solutions and other needed analyte solutions.
- 6.10 Quality Control Sample (QCS) – A sample matrix containing method analytes or a solution of method analytes in water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is generated from a source of reagents different than those used to prepare the primary dilution standards and the CAL and is used to check laboratory performance. The QCS should be run at a rate of 1 for every 13 samples.
- 7.0 Interferences**
- 7.1 If the sample remains turbid after digestion, the digested sample may be centrifuged before analysis.
- 7.2 If dark, stringy, solid material appears after digestion, not all of the organic material has been digested. The sample should be redigested using a smaller aliquot.
- 7.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that will bias analyte response.
- 7.4 Ammonia in the laboratory may easily become an interference in this test method from contamination of reagents, caps, pipettes, or from the laboratory atmosphere. Care should be taken to ensure that ammonium hydroxide, either as a reagent or as a cleaning solution, is not used in the same work area.
- 8.0 Safety**
- 8.1 Safety glasses and shoes that cover the feet are required in all designated laboratory areas.
- 8.2 It is recommended that the analyst wear gloves and a lab coat when performing this procedure.
- 8.3 The analyst must be familiar with the Laboratory Chemical Hygiene Plan.
- 8.4 The analyst must be familiar with the Laboratory Safety Policy (SOP 100).
- 8.5 The analyst must be familiar with any material safety data sheets applicable to this method.
- 8.6 The analyst must be familiar with the location of safety equipment including showers, eye wash stations, and spill kits.
- 8.7 The analyst should always thoroughly wash hands in warm soapy water when leaving the work area and before handling food or drink.

- 8.8 The analyst should assume that all samples have the potential to be hazardous and should always exercise caution when transporting, handling, and/or opening any samples.
- 8.9 General good laboratory practices are required. The analyst should take all necessary precautions in order to minimize the potential of exposure to samples and reagents used in this method.
- 8.10 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Cautions are included for known extremely hazardous materials or procedures. The laboratory and each analyst 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 MSDS should also be made available to all personnel involved in chemical analysis. Review of the Department's safety plan is also advisable.
- 8.11 The following list of raw materials marks those known to have the potential to be highly toxic or hazardous. Consult the MSDS for further information.

<u>Chemical</u>	<u>Safety Classification</u>
Adenosine 5'-Monophosphate (AMP)	N/A
Ammonium chloride, NH_4Cl	Irritant
Brij-35, 30% solution	N/A
Mercuric oxide, HgO	Toxic
Hydrochloric acid, 36.5-38%, HCl	Corrosive
Potassium phosphate, mono-basic, KH_2PO_4	N/A
Potassium sulfate, K_2SO_4	N/A
Sodium hydroxide, NaOH	Corrosive
Sodium hypochlorite, 5.25%, (e.g., Clorox)	Corrosive
Sodium nitroprusside, $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$	Toxic
Sodium phosphate, dibasic, $\text{Na}_2\text{HPO}_4\cdot 7\text{H}_2\text{O}$	N/A
Sodium potassium tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6\cdot 4\text{H}_2\text{O}$	N/A
Sodium salicylate, $\text{NaC}_7\text{H}_5\text{O}_3$	Harmful
Sulfuric acid, 95-98% H_2SO_4	Corrosive

9.0 Equipment and Supplies

- 9.1 Brann & Lubbe AA3 dual channel autoanalyzer system (or equivalent) consisting of:
- 9.1.1 Compact sampler (auto-sampler).
 - 9.1.2 Dual speed proportioning pump.
 - 9.1.3 Multi chemistry manifolds (for both TKN and TP).
 - 9.1.4 Dual channel digital colorimeters.
 - 9.1.5 Computer.
 - 9.1.6 AACCE software.
 - 9.1.7 Block digester - 40 or 50 place block digester with tube rack and side shields.
 - 9.1.8 Digestion tubes - 75 mL Pyrex tubes.

- 9.2 Vortex mixer.
- 9.3 Magnetic stirrer plate.
- 9.4 Sample cups – Disposable, 5 mL, plastic.
- 9.5 Boiling stones – Teflon (TFE).
- 9.6 Disposable pipettes – 10 mL, plastic.
- 9.7 Repeat pipettors (adjustable) and disposable tips – 5 and 10 mL, Finnpiette (or equivalent).
- 9.8 Oxford pipettor adjustable dispenser - 1 L capacity, 0-10 mL range (or equivalent).
- 9.9 Beakers – Pyrex, 500 and 1000 mL, several of each.
- 9.10 Graduated cylinders – Pyrex, 50 and 100 mL, several of each.
- 9.11 Nalgene carboys – 1 and 5 gallon capacity.
- 9.12 Bottles – Plastic, screw-cap for holding reagents and standard solutions, 250-1000 mL, as needed.
- 10.0 Reagents and Standards**
- 10.1 All reagents, solvents, and standards must be traceable to the stock inventory tracking log.
- 10.2 All reagents, solvents, and standards must be labeled with: date received, date opened, expiration date, tracking number, and receiver's initials.
- 10.3 All prepared reagents and standards must be labeled with: date prepared, expiration date, preparer's initials, tracking number, diluent, and description.
- 10.4 All standard logbooks must be completely filled out.
- 10.5 All certificates of analysis must include the stock inventory tracking number that was assigned to the standard.
- 10.6 Digestion mixture – Cautiously add 200 mL of H_2SO_4 to 600 mL of deionized (DI) water (always add acid to water). Add 2.0 g of HgO. Mix until dissolved. Add 133 g potassium sulfate. Allow solution to cool for 20 to 30 minutes. Dilute to 1 L with DI water. Store at 30°C to 40°C to avoid precipitation of the mixture. The mixture is stable for six months.
- 10.7 Sulfuric acid wash solution (4%) – Add 40 mL of H_2SO_4 to 800 mL of DI water. Let cool. Dilute to 1.0 L. Store at room temperature. This solution is stable for six months.

- 10.8** Stock sodium hydroxide (5N/20% W/W) – Dissolve 200 g of sodium hydroxide in 700 mL of DI water. Let cool. Dilute to 1 L. Store at room temperature. This solution is stable for six months.
- 10.9** Stock buffer solution – Dissolve 134 g of sodium phosphate, dibasic in 800 mL of DI water. Add 20 g of sodium hydroxide. Stir until dissolved. Dilute to 1 L. Store at room temperature. This solution is stable for up to four months.
- 10.10** Stock sodium potassium tartrate solution (50%) – Sodium potassium tartrate 50% solution is purchased from VWR. Store at room temperature. Check expiration date for stability.
- 10.11** Sodium salicylate/sodium nitroferricyanide solution – Dissolve 0.30 g of sodium nitroferricyanide and 143 g of sodium salicylate in 600 mL of DI water. Add 1 mL of Brij-35. Dilute to 1 L. Filter if necessary. Refrigerate. This solution is stable for one month.
- 10.12** Sodium hypochlorite – Add 17.1 mL of sodium hypochlorite to 200 mL of DI water. Add 0.5 mL Brij-35. Dilute to 500 mL. Refrigerate. This solution is stable for two weeks.
- 10.13** Working buffer solution – Reagents should be combined in the following order: Add 200 mL of stock buffer solution, 100 mL of stock sodium potassium tartrate solution (50%), 120 mL stock sodium hydroxide solution (20%), and 1.0 mL Brij-35 to 300 mL of DI water. Bring QS volume to 1 L with DI water. Mix well. This solution is stable for one month. Store at room temperature.
- 10.14** Nitrogen standard stock solution 1000 ppm (1.00 mg N/mL) – Purchased from Solutions Plus Inc. (catalog # N065200) in a 500 mL bottle. Refrigerate. This solution is stable for one year after opening.
- 10.15** Acidic (undigested) 100% full scale nitrogen standard/primer (5.00 mg N/l) – In a 1 L volumetric flask, add 40 mL of H₂SO₄, 0.40 g of HgO, and 5.0 mL of nitrogen standard stock solution to 600 mL of DI water. Dilute to 1 L. Divide into four 250 mL bottles. Refrigerate. This solution is stable for six months. NOTE: Combine with phosphorus standard to make a dual standard.
- 10.16** 90% (CAL) full scale nitrogen standard (4.50 mg N/l) – Dilute 2.25 mL of nitrogen standard stock and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Refrigerate. This solution is stable for one month. NOTE: Combine with phosphorus standard to make a dual standard.
- 10.17** 50% (CAL) full scale nitrogen standard (2.50 mg N/l) – Dilute 1.25 mL of nitrogen standard stock and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Refrigerate. This solution is stable for one month. NOTE: Combine with phosphorus standard to make a dual standard.
- 10.18** 10% (CAL) full scale nitrogen standard (0.50 mg N/l) – Dilute 0.25 mL of nitrogen standard stock and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL

- volumetric flask. Refrigerate. This solution is stable for one month. NOTE: Combine with phosphorus standard to make a dual standard.
- 10.19 Intermediate nitrogen standard stock solution (10.00 mg N/l) – Dilute 5.0 mL of nitrogen standard stock and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Refrigerate. This solution is stable for three months. NOTE: Combine with phosphorus standard to make a dual standard.
- 10.20 Detection verification standard (DVS) (0.20 mg N/l) – Dilute 10.0 mL of intermediate stock standard and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Divide into two 250 mL bottles. Refrigerate. This solution is stable for one month. NOTE: Combine with phosphorus standard to make a dual standard.
- 10.21 QCS (AMP) standard (1.04 mg N/l) – Dilute 25.0 mL of stock AMP and 0.5 mL of H₂SO₄ in DI water. Bring to volume in a 500 mL volumetric flask. Refrigerate. This solution is stable for one month.
- 10.22 0.1 N NaOH solution for cleaning TP channel – Dilute 10 mL of 5N/20% NaOH stock solution to 500 mL with DI water. Store at room temperature in a plastic screw cap bottle. This solution is stable for six months.
- 10.23 0.1 N HCl solution for cleaning TKN channel – Dilute 4.17 mL of concentrated HCl to 500 mL with DI water. Store at room temperature in a plastic screw cap bottle. This solution is stable for six months.
- 10.24 Hydrochloric acid cleaning/soaking solution (10%) – Place 5400 mL of DI water in a 6 L Nalgene container. Carefully add 600 mL of concentrated HCl. Cover tightly. Mix by swirling gently. Draw off as needed. This solution may be reused. This solution is good for one month of average workload use.
- 10.25 Stock AMP (0.0226 mg N/ml) – Dissolve 0.1121 g of dried adenosine 5'-monophosphate in DI water. Bring to volume in a 1 L volumetric flask. Refrigerate. This solution is stable for three months.
- 10.26 MS/MSD spiking standard (1.50 mg/L N) – dilute 120 mL of phosphorus stock standard and 0.5 mL H₂SO₄ in DI water and bring to volume in a 500 mL volumetric flask. Refrigerate. Stable for one month. (Note: combine with Total Phosphorus standard to make a dual standard). Analyze the combined standard a minimum of ten times; calculate the mean and standard deviation. Use the mean value as the standard's assayed value in the calculation for percent recovery of MS/MSD.
- 11.0 **Sample Collection, Preservation, Shipment, and Storage**
- 11.1 A 500 mL plastic bottle is the recommended sample container to be used. The proper bottle code is GA for sulfuric acid preserved samples or GAD if the sample is field filtered.
- 11.2 Samples should be preserved by adding a minimum of 0.5 mL of concentrated sulfuric acid per 500 mL of sample (to a pH equal to or less than 2) and refrigerated at 4°C.

- 11.3 The recommended maximum holding time for refrigerated acid preserved samples is 28 days.
- 12.0 **Quality Control (QC)**
- 12.1 Check system audits with each analytical batch, and investigate when performance changes significantly. System audits are in control if:
- 12.1.1 The heating bath temperature is between 35.0°C and 39.0°C.
- 12.1.2 The reagent baseline is at (or can be set to) 5% without a large change in the previous baseline calibration setting.
- 12.1.3 The full scale undigested standard/primer is at (or can be set with) the gain control to 90% of chart scale without a large change in the previous gain calibration setting.
- 12.2 Check calibration audits with each analytical batch. Audits are in control if (as of 03/02/2005):
- 12.2.1 The 90% of full scale standard is between 4.42 and 4.60 mg N/l.
- 12.2.2 The 10% of full scale standard is between 0.45 and 0.54 mg N/l.
- 12.2.3 The detection verification standard is between 0.15 and 0.25 mg N/l.
- 12.2.4 The 50% of full scale standard is between 2.40 and 2.58 mg N/l.
- 12.2.5 QCS (AMP) results are between 0.96 and 1.12 mg N/l.
- 12.3 Analyze a MS/MSD sample pair for approximately every 13 unknown samples. MS/MSD samples are in control if their relative percent difference (RPD) is not greater than $\pm 20\%$ and percent spike recover is $100\% \pm 20\%$.
- 13.0 **Calibration and Standardization**
- 13.1 Calibration is performed automatically by the computer using five standards at five concentrations, 0% (blank), 10%, 50% and 90%. The DVS and AMP are run as check standards during the run but are not used to calibrate the instrument. Each calibrant is measured twice, and the results are averaged to produce the calibration "curve." This is done to try to eliminate any effects of carryover from a previous sample or differences in digestions of the calibration samples. Three blanks, two 10%, two 50% and one 90% standards are each measured twice, averaged, and plotted to make the curve. The chemistry is linear over the range used and should produce a straight line.
- 13.2 The computer, using linear regression to produce a "best fit" calibration line, plots calibration values measured by the system. Sample values are compared to this graph to compute actual sample values.
- 13.3 All measurements are made at 660 nm. The sampler is set at 45 samples per hour with a sample/wash ratio of 3.5 to 1.
- 14.0 **Procedure**
- 14.1 Digestion.
- 14.1.1 Add 10 mL of DI water to digestion tubes 1, 2, and 3.

- 14.1.2 Add 10 mL of 10% CAL to digestion tubes 4 and 5; 10 mL of 50% CAL to digestion tubes 6 and 7; and 10 mL of 90% CAL to digestion tube 8.
- 14.1.3 To digestion tube 9 add 10 mL DVS check standard and to digestion tube 10 add 10 mL of AMP CAL.
- 14.1.4 To digestion tubes 11 through 40 (for the 40-place rack) or 11 through 50 (for the 50-place rack); add 10 mL (or a suitable aliquot) of well shaken samples, *with the following exceptions*: To digestion tubes 24 (MS) and 25 (MSD), add 10 mL of sample and 0.25 mL of MS/MSD spiking standard, using a sample in the first group of 13 unknowns analyzed. To tubes 39 (MS) and 40 (MSD), add 10 mL of a sample that appears in the end group of 13 unknown samples analyzed and 0.25 mL of MS/MSD spiking standard. Three MS/MSD pairs are analyzed on the 50 tube run, beginning, middle and end. Only two pairs are analyzed on a 40 tube run or approximately every 13 samples. Record the sample ID numbers used for the MS/MSD pairs on the run sheet. Refer to the actual 40 or 50 tube run sheets for the current tube number designations for samples and QC/QA positions.
- 14.1.5 Add 3-4 Teflon boiling stones (previously cleaned with HCl) to each tube. Too many stones may cause the sample to boil over.
- 14.1.6 Add 2.0 mL of digestion mixture to each tube. Vortex each tube. Verify that all tubes contain boiling stones and are at the same volume.
- 14.1.7 40-place block digester: With side shields in place, place rack of tubes on block digester. Set low temperature at 160°C. When digester attains low temperature, let the tubes heat for 30 minutes. Set block digester temperature at 380°C. When digester attains high temperature, let tubes heat for 30 minutes. Check the progress of the digester periodically to see that the controller cycles properly. Record that the high temperature has been reached.
- 14.1.8 50-place block digester: Place the rack in the block. Turn on the control unit. Press "run." Select 1 to answer the "what program" question on the display. Press "E" to enter your choice. The run should begin. No further input is needed until the digestion run is completed (approximately two and one half to three hours). An alarm will sound when the run is complete.
- 14.1.9 Remove the rack from the digester. Let the tubes cool for 10 to 15 minutes. Add 9.6 mL of DI water to each tube, Mix thoroughly on a vortex mixer. If the tubes cool too much, the acid and salts will solidify and cause difficulty in returning solid into solution.
- 14.2 Colorimetric analysis.
- 14.2.1 Check the level of all reagent containers to ensure an adequate supply. Start the computer. When the main Windows screen appears, start the AACCE program by double clicking on the icon. Turn on the power (at the power strip) to the sampler, colorimeter, and pump.
- 14.2.2 Select "charting" from the open window in the AACCE program. This will begin the data link between the instrument and the computer. Place the pump platen on the pump. Lock it down.
- 14.2.3 The proportioning pump will start by itself when the download is through. Pump DI water, with channel appropriate wetting agent, through the system for at least 30 minutes.
- 14.2.4 Flush the sampler wash receptacle with approximately 25 mL of 4% H₂SO₄ if ammonia has accumulated in the reservoir. Normally, the pumping of 4% acid through the wash cup during the 30-minute startup is sufficient to clear out any buildup.

- 14.2.5** Excluding the salicylate line, attach all reagents to their respective containers. When the reagents have been pumping for at least five minutes, attach the salicylate line to its container. Allow the system to equilibrate. If a precipitate forms after the addition of salicylate, the pH is too low. Immediately stop the proportioning pump. Flush the coils with water. Check the concentration of the sulfuric acid solutions and/or the working buffer before restarting the program.
- 14.2.6** To prevent precipitation of salicylate in the waste, keep salicylate-containing waste separate from acidic wastes.
- 14.2.7** Continue to pump reagents through the instrument for at least 45 minutes. Right click the mouse on each channel's chart. Select "set base" from the menu. This will set the baseline to 5% automatically. After a stable baseline has been obtained, the analyses may be started.
- 14.2.8** Remove the sampler tray. Place it next to the digested and rehydrated samples.
- 14.2.9** From the rough run sheet, enter the sample ID numbers into the computer run. Do this by clicking on "set-up" in the menu at the top of the page. Select "analysis" from the drop-down menu. Click once on "40 place template" (or "50 place template" for the larger run). Go to the menu on the right side of the page. Click on "copy run." This will generate a new run with an ID of "today's date" and a letter A-Z (for 1st to 26th run of the day [i.e., 991215A]).
- 14.2.10** Click on the "tray protocol" tab. Enter the sample ID numbers by clicking on the appropriate slot. Type in the information. Do not change any of the information or settings of the cups 1 to 11. These do not change from run to run and are programmed into the tray set up. Do not change any of the information on any of the other three tabs. This is not necessary in any case and could result in a ruined run. Do not change the entries for the AMP or MS/MSD cups other than to enter the ID numbers of the samples used in the sample name blank. Be sure the designation of MS or MSD appears in the blank as well.
- 14.2.11** Once all the sample ID numbers are entered into the list, click on the "print" icon on the bottom of the page to get a hard copy printout of the run to use while loading the cups. Once the printing is done, click "OK" to save the run protocol.
- 14.2.12** Place the correct number of clean rinsed sample cups in the sampler tray. Using the tray protocol printout as a guide, pipette the samples into the appropriate cup.
- 14.2.13** Place the sampler tray back on the compact sampler. Place a cup of full scale (100%) undigested standard (with acid and mercury) in slot #88. If the computer is not "charting" (monitoring the colorimeter), click on the "chart" button. From the main menu, click on the sampler icon to bring up the sampler control window. Click on the "wash" button to zero the sampler. Enter the cup number (88) in the sample window. Click on the "sample" button. The probe will go to the designated cup. Allow the sampler to aspirate the undigested standard for at least three minutes. Click on the "wash" button to return the probe to the wash cup. Click "cancel" to remove the sampler window.
- 14.2.14** Approximately seven to eight minutes later, the peaks will begin to appear on the computer screen (first the TP and then the TKN channel). One minute after the peak first appears in a channel, right click on that channel's chart and select "set gain" from the menu. Repeat for the other channel. This will set the full scale peak to be approximately 90% of the computer chart screen. Allow the channels to return to baseline before proceeding.
- 14.2.15** Click "stop" from the program (white) menu to end the charting process.
- 14.2.16** Click "run" from the same menu. Select the run that was previously set up. Click "OK." On the window that appears, fill in your name and any comment(s) that should

- be attached to the printout of this run. Be sure that the "autobox" is checked. Click "OK" when finished. The run will start. No further operator input is required until the run is over.
- 14.2.17** When the run is finished, a message window will appear indicating this. Click "OK."
- 14.2.18** Click "retrieve." Click "view chart" in the menu at the top of the page. This will display the run chart showing the peaks one channel at a time starting with TKN. Using the arrow keys at the bottom, move through the chart. Check the location at which the computer chose to mark (measure) each peak. It may be necessary to move some of the marks to better locations. This can be done by clicking on the button at the top of the window showing a peak with a mark on it. Click on this button to enable the "move peak mode." Click and hold on the mark that you wish to move. Release the mouse button when the mark has been placed in the desired place. Continue to review the peaks. Move the marks of any peaks that require it. After all the peaks for that channel have been reviewed, click on the calculator icon button to save the marks in their new locations. Recalculate the chart. Click on the drop-down box with the number "1" in it. Select "2" to bring up the chart for channel 2 (TP). Repeat the above process to review and correct (if necessary) the peak marks for the TP channel. When finished, click "OK" to exit this window.
- 14.2.19** Click "retrieve." Click "print chart." Click "OK" to print out the hard copy of the run chart. Click "retrieve." Click "report" to print out the final report for the run. Click "retrieve." Click "calibration curve" to print out the calibration curves for each channel. Select the channels as done in the view chart window, one at a time. When all printing has been completed, proceed to clean up.
- 14.3** Clean up.
- 14.3.1** Unhook salicylate reagent line five minutes before unhooking other reagent lines to avoid precipitation.
- 14.3.2** Unhooked TKN reagent lines should be placed in a solution of 1.0 mL of Brij-35 diluted in 1 L of DI water for rinsing out the system. The sampler rinse line should be placed in a container of plain DI water. The system should be allowed to rinse out for at least 30 minutes at the normal pump speed or 15 minutes at the fast pump speed. This can be selected from the pump control window brought up by the pump icon on the main window.
- 14.3.3** When it is certain that the remaining samples left in the digestion tubes are not needed, pour the tubes out into a plastic jug properly labeled to collect this hazardous waste. Save the Teflon boiling stones.
- 14.3.4** Block digester tubes should be rinsed with tap water, rinsed with DI water, and soaked in 10% HCl for at least 12 hours. After soaking, the tubes should be rinsed twice with tap water, twice with DI water, and inverted to dry. If the tubes have not been used within two days, they should be rinsed with DI water before use.
- 14.3.5** Soak boiling stones in 10% HCl for at least 24 hours. Soak in 10% H₂SO₄ for at least 24 hours. Rinse the stones with DI water several times. Allow them to dry before the next use.
- 14.3.6** Wastes with mercury should be disposed of in the manner prescribed by the Laboratory's waste handling procedure (SOP 111).
- 15.0** Calculations
- 15.1** Results are printed in appropriate concentration units (mg/L).

- 15.2 Diluted samples should be manually calculated.
- 15.3 Analyze a MS/MSD sample pair for approximately every 13 unknown samples. MS/MSD sample are in control if their RPD is not greater than $\pm 20\%$ and the percent spike recovery is between 80 and 120 percent. RPD and percent MS/MSD spike recovery are calculated as follows:

$$\text{RPD} = \frac{[\text{absolute value}(\text{MS}-\text{MSD})/(\text{MS}+\text{MSD})]}{2} \times 100$$

$$\% \text{ Spike Recovery} = [(M - S)/T] \times 100$$

Where: M = measured concentration MS or MSD
S = measured concentration of sample
T = MS/MSD spike concentration

- 15.4 All samples are corrected automatically by the computer for baseline shift, carryover, and drift in sensitivity.

16.0 Method Performance

- 16.1 MDL – In the DEQ Environmental Laboratory, 28 replicate analyses of a low level standard with a mean concentration of 0.0871 mg N/l resulted in a SD of 0.0256 mg N/l and an MDL (99%) of 0.0633 mg N/l.

- 16.2 Precision – In the DEQ Environmental Laboratory, using composite water samples with mean concentrations of 0.217, 0.990, and 4.160 mg N/l, the SD's were 0.021, 0.034, and 0.035 mg N/l, and the relative SD's were 9.7, 3.4, and 0.8%, respectively.

- 16.3 Accuracy – In the DEQ Environmental Laboratory, using composite water samples with mean concentrations of 0.193 and 1.280 mg N/l and theoretical spikes of 0.50 and 1.00 mg N/l (using nicotinic acid), the mean spike recoveries were 93.0 and 97.8%, respectively.

17.0 Pollution Prevention

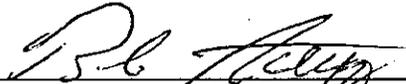
- 17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.
- 17.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

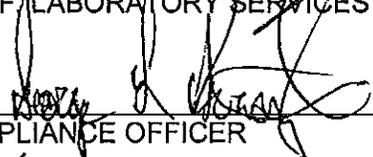
- 17.3 For information concerning pollution prevention which may be applicable to laboratory operations, consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, DC 20036.
- 18.0 **Data Assessment**
- 18.1 Data reported must be within the linear range of the assay, >0.10 and <5.0 mg N/L.
- 18.2 Dilutions must be greater than 10% of full scale to be reported (i.e., the diluted sample results must be >0.5 mg N/L).
- 18.3 "High" reporting samples are reported out to two significant figures.
- 18.4 "Low" reporting samples are reported out as read unless greater than 2.0 mg N/L which are then reported to two significant figures.
- 18.5 Dilution multiplies the detection limit for a sample (i.e., detection limit of 0.10 mg N/L x 10 (dilution factor) = 1.0 (detection limit for sample diluted 1/10 when analyzed). Results of the analysis of a diluted sample must be above 1.0 mg N/L to be reported.
- 18.6 Appropriate laboratory reporting codes for dilutions, low values, interference, holding times, etc., will be appended to the test result according to laboratory policy. Reference Laboratory Result Remark Codes (SOP 106).
- 18.7 MS/MSD data for a run must be acceptable for the run data to be reported. Standards and controls must be in range for the run data to be reported.
- 18.8 Out of range values must be diluted, redigested, and rerun to be reported. High carryover samples (low value following a high value) are automatically repeated at the end of the batch to verify the result.
- 18.9 The lead worker or supervisor must review all data before the final reporting out of results.
- 19.0 **Corrective Actions**
- 19.1 Excessive rise in the TKN baseline or excessive carryover in the TP channel may indicate buildup of precipitate or protein in the respective channel. Clean the channel (TKN with 2N HCl and TP with 2N NaOH) according to the manufacturer's instructions. The samples can then be run again.
- 19.2 A rise in the standard's or sample's value from previous runs (or expected results) may indicate: (1) contamination of the sample cup (repipette into a new, clean cup); (2) contamination from a dirty pipette (repipette into a new, clean tube and/or redigest if this does not change the value back to normal); (3) carryover from an unusually high sample preceding the one in question (repeat sample in another location in the run away from the high valued sample and repipette if necessary); or (4) contamination of the standard stock container (use the backup standard bottle, if available, or remake the standard and repeat the run).

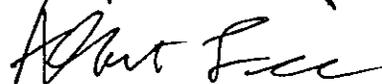
- 19.3 If MS/MSD samples or repeated samples within the run are not as expected, begin troubleshooting the equipment as outlined in the manufacturer's manuals to locate the problem. Correct the problem. Repeat the digestion (if necessary) and the batch run.
- 19.4 If a high sample runs off scale, repeat the sample at a dilution on the next run. The two samples immediately after it will automatically be repeated at the end of the run to remove the effect that carryover from the out-of-range sample has on them.
- 19.5 Consult with manufacturer's manuals, lead worker, co-workers, company help lines, and any other resources available to troubleshoot and correct problems with analyzer operation. Alert the supervisor of any long-term downtime for the analysis.
- 19.6 Refer to the AA3 Operator's Manual located at the instrument's workstation for additional information on the following: (1) setting up a new analysis; (2) maintenance, repair, and troubleshooting of hardware and software problems; (3) parts; (4) service; (5) company contact numbers; (6) proof and explanation of calculations and corrections; (7) identification and correction of common operating problems; (8) printer operation and troubleshooting; (9) operation/maintenance/troubleshooting of block digester; and (10) explanation of additional system capabilities and hardware.
- 20.0 Waste Management**
- 20.1 Three types of liquid wastes are generated by the assays. These are: (1) sulfuric acid (4%) with mercury and color reagents (antimony and molybdate; (2) sodium hydroxide (2N) with mercury and color reagents (cyanide, salicylate, and bleach); and (3) sulfuric acid (4%) spent wash solution. The waste containers must be labeled with the type of waste contained, the notation "hazardous waste," and the operator's initials. The containers are held until the monthly waste collection occurs and a licensed hazardous waste disposal company can properly dispose of them. The spent acid wash solution may be disposed of down the drain with accompanying soda ash (to neutralize the acid) and a large amount of water to flush it down.
- 20.2 Broken/waste glass is collected at the bench in a plastic pail until transferred to a collection barrel for recycling.
- 20.3 Liquid wastes generated by excess samples, and dilutions can be disposed of down the drain with copious amounts of water if they do not contain other hazardous material (i.e., samples from an industrial site, etc.) that requires them to be handled as a hazardous waste.
- 21.0 References**
- 21.1 United States Code of Federal Regulations, Title 40, U.S. Government Printing Office, Washington, D.C., Appendix A & B.
- 21.2 Test Methods for Evaluating Solid Waste, U.S. Environmental Protection Agency, Document SW-846, Third Edition, 1986, Final Update III, December 1996.

- 21.3 Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA-600/4-79-020, March 1983.
- 21.4 Nitrogen, Kjeldahl, Total (Colorimetric, Semi-Automated Block Digestor, AAll), Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, Method 351.2 (issued August 1993), EPA-600/4-93-020, Cincinnati, Ohio, August 1993.
- 21.5 Simultaneous and Automated Determination of Total Phosphorus and Total Kjeldahl Nitrogen, Gales, M.E. and Booth, R.L., Methods Development and Quality Assurance Research Laboratory, May 1974.
- 21.6 Technicon AutoAnalyzer Applications, Method US-329-74-A, Nitrogen and Phosphorus in Acid Digests, December 1997.
- 21.7 Total Kjeldahl Nitrogen and Total Phosphorus BD-40 Digestion Procedure for Water, Technicon, August 1974.
- 21.8 Evaluation of the Technicon Block Digestor System for the Measurement of Total Kjeldahl Nitrogen and Total Phosphorus, Gales, M.E. and Booth, R.L., EPA-600/4-78-015, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 1978.
- 21.9 Standard Test Methods for Total Kjeldahl Nitrogen in Water, ASTM Annual Book of Standards, Volume 11.01, Method D 3590-89 (Reapproved 1994).
- 21.10 Ultra-micro Semi-Automated Method for the Simultaneous Determination of Total Phosphorus and Total Kjeldahl Nitrogen in Wastewaters, Jirka, A.M., Carter, M.J., May D., and Fuller, F.D., U.S. Environmental Protection Agency, Central Regional Laboratory, Chicago, Illinois.
- 22.0 **Attachments**
- 22.1 Manifold diagram -- Total Kjeldahl Nitrogen, AA2/AA3 Multitest Manifold, August 4, 1999.
- 22.2 Sample run sheet for BD-40 (40 tube) batch run.
- 22.3 Sample run sheet for AIM-50 (50 tube) batch run.

Signature Page

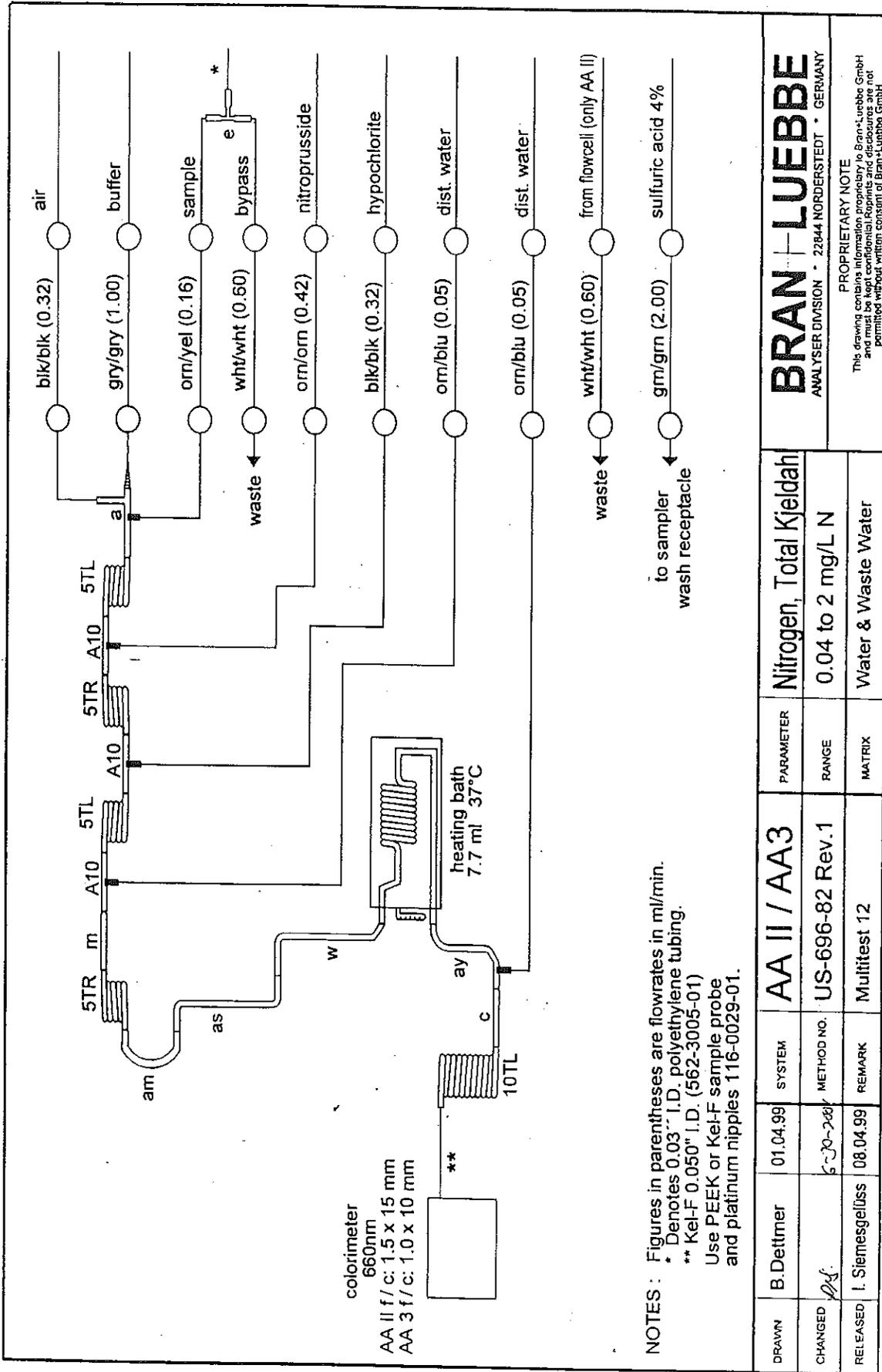
APPROVED BY  DATE 3/14/06
CHIEF LABORATORY SERVICES SECTION

APPROVED BY  DATE 3/8/2006
COMPLIANCE OFFICER

APPROVED BY  DATE 3/3/2006
QA OFFICER

APPROVED BY  DATE 2-28-2006
UNIT MANAGER

APPROVED BY  DATE 3-1-06
ANALYST



NOTES: Figures in parentheses are flowrates in ml/min.
 * Denotes 0.03" I.D. polyethylene tubing.
 ** Kel-F 0.050" I.D. (562-3005-01)
 Use PEEK or Kel-F sample probe and platinum nipples 116-0029-01.

DRAWN	B. Dettmer	01.04.99	SYSTEM	AA II / AA3	PARAMETER	Nitrogen, Total Kjeldahl
CHANGED	<i>Df</i>	5-30-288	METHOD NO.	US-696-82 Rev.1	RANGE	0.04 to 2 mg/L N
RELEASED	I. Siemesgeüss	08.04.99	REMARK	Multitest 12	MATRIX	Water & Waste Water

		Kjeldahl Nitrogen		Total Phosphorus		Date:	Rack No:	Block	(High)
						Run No.:	Analyst:	Temp:	(Low)
Sampler Cup No.	Digestion Tube No.	Work Order #	Sample ID	Dilution	Hi/Lo Rpt.	KN	TP	Comments	
1	n/a		Primer					QA Batch Number - Dig.:	
2	1		Blank cal 1					TKN:	
3	2		Blank cal 2					TP:	
4	3		Blank cal 3						
5	4		10% cal 1					KN# exp.	
6	5		10% cal 2						
7	6		50% cal 1					KN# exp.	
8	7		50% cal 2						
9	8		90% cal					KN# exp.	
2	1		Blank check 1						
10	9		DVS 1					KN# exp.	
11	10		AMP 1					KN# exp.	
12	11								
13	12								
14	13								
15	14								
16	15								
17	16								
18	17								
19	18								
20	19								
21	20								
22	21								
23	22								
24	23								
25	24	MS1							
26	25	MSD1							
3	2		Blank check 2						
10	9		DVS 2						
11	10		AMP 2						
27	26								
28	27								
29	28								
30	29								
31	30								
32	31								
33	32								
34	33								
35	34								
36	35								

		Kjeldahl Nitrogen		Total Phosphorus		Date:	Rack No:	Block	380	(High)		
Sampler Cup No.	Digestion Tube No.	Work Order #	Sample ID	Dilution	H/L o Rpt.	KN	TP	Analyst:	DNS	Temp:	160	(Low)
								Comments				
1	n/a		Primer					QA Batch Number - Dig.:				
2	1		Blank cal 1					TKN:				
3	2		Blank cal 2					TP:				
4	3		Blank cal 3									
5	4		10% cal 1					KN#		exp.		
6	5		10% cal 2									
7	6		50% cal 1					KN#		exp.		
8	7		50% cal 2									
9	8		90% cal					KN#		exp.		
2	1		Blank check 1									
10	9		DVS 1					KN#		exp.		
11	10		AMP 1					KN#		exp.		
12	11											
13	12											
14	13											
15	14											
16	15											
17	16											
18	17											
19	18											
20	19											
21	20											
22	21											
23	22	MS1										
24	23	MSD1										
25	24											
26	25											
27	26											
3	2		Blank check 2									
10	9		DVS 2									
11	10		AMP 2									
28	27											
29	28											
30	29											
31	30											
32	31											
33	32											
34	33											
35	34											
36	35											

Sampler cup No.	Digestion Tube No.	Kjeldahl Nitrogen		Total Phosphorus			Date:	Rack No.:	Block	380 (High)	
		Work Order #	Sample ID	Dilution	HI/Lo Rpt.	KN	TP	Run No.:	Analyst:	DNS	Temp:
							Comments				
37	36	MS2									
38	37	MSD2									
39	38										
40	39										
41	40										
42	41										
43	42										
44	43										
45	44										
46	45										
4	3		Blank check 3								
10	11		DVS 3								
11	10		AMP 3								
47	46										
48	47										
49	48										
50	49	MS3									
51	50	MSD3									
2	1		Blank 1								
3	2		Blank 2								
4	3		Blank 3								
5	4		10% cal 1								
6	5		10% cal 2								
7	6		50% cal 1								
8	7		50% cal 2								
9	8		90% cal								



EFFECTIVE DATE: 03/2006

SOP# 340

REVISION # 2

**CALCIUM, MAGNESIUM, POTASSIUM, AND SODIUM
ATOMIC ABSORPTION, DIRECT ASPIRATION**

Table of Contents

1.0	Applicable Analytical Methods	1
2.0	Matrix or Matrices.....	2
3.0	Method Detection Limits.....	2
4.0	Scope and Application	3
5.0	Method Summary	3
6.0	Definitions	3
7.0	Interferences	4
8.0	Safety	5
9.0	Equipment and Supplies	5
10.0	Reagents and Standards	6
11.0	Sample Collection, Preservation, Shipment, and Storage	8
12.0	Quality Control (QC).....	9
13.0	Calibration and Standardization	10
14.0	Procedure.....	10
15.0	Calculations.....	11
16.0	Method Performance.....	11
17.0	Pollution Prevention	12
18.0	Data Assessment	12
19.0	Corrective Actions	13
20.0	Waste Management	13
21.0	References.....	13
22.0	Attachments	14
	Signature Page.....	15

1.0 Applicable Analytical Methods

- 1.1 Calcium (AA, Direct Aspiration), U.S. Environmental Protection Agency, Method 215.1, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00915 and #00916.
- 1.2 Magnesium (AA, Direct Aspiration), U.S. Environmental Protection Agency, Method 242.1, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00925 and #00927.
- 1.3 Potassium (AA, Direct Aspiration), U.S. Environmental Protection Agency, Method 258.1, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00935 and #00937.

- 1.4 Sodium (AA, Direct Aspiration), U.S. Environmental Protection Agency, Method 273.1, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00929 and #00930.
- 1.5 Calcium (Atomic Absorption, Direct Aspiration), U.S. Environmental Protection Agency, Method 7140, Test Methods for Evaluating Solid Waste, SW-846, Update III, 1996.
- 1.6 Magnesium (Atomic Absorption, Direct Aspiration), U.S. Environmental Protection Agency, Method 7450, Test Methods for Evaluating Solid Waste, SW-846, Update III, 1996.
- 1.7 Potassium (Atomic Absorption, Direct Aspiration), U.S. Environmental Protection Agency, Method 7610, Test Methods for Evaluating Solid Waste, SW-846, Update III, 1996.
- 1.8 Sodium (Atomic Absorption, Direct Aspiration), U.S. Environmental Protection Agency, Method 7770, Test Methods for Evaluating Solid Waste, SW-846, Update III, 1996.

2.0 **Matrix or Matrices**

- 2.1 Drinking water.
- 2.2 Surface water.
- 2.3 Saline water.
- 2.4 Domestic waste.
- 2.5 Industrial waste.
- 2.6 Soils.
- 2.7 Sludges.
- 2.8 Sediments.

3.0 **Method Detection Limits**

- 3.1 All MDLs shall be performed according to the Code of Federal Regulations 40 CFR, Part 136, Appendix B. See internal procedure SOP 103.
- 3.2 An annual MDL is determined by analyzing seven replicate water samples spiked with calcium, magnesium, potassium, and sodium standards to yield a theoretical concentration of 1.0, 1.0, 0.1, and 1.0 mg/L, respectively. The replicates are analyzed in a manner identical to routine samples.
- 3.3 The MDL is calculated using a formula that applies the student t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

- 3.4 The MDL for this method is determined annually or whenever there is a significant change in the procedure including a change in the analyst.
- 3.5 Reporting limit (RL) – The RLs for this method have been set at 1.0 mg/L calcium, 1.0 mg/L magnesium, 0.1 mg/L potassium, and 1.0 mg/L sodium for water samples. The RLs for this method have been set at 50 mg/Kg calcium, 50 mg/Kg magnesium, 5.0 mg/Kg potassium, and 50 mg/Kg sodium for solid matrices.
- 4.0 **Scope and Application**
- 4.1 This method applies to drinking water, surface water, saline water domestic waste, industrial waste, soils, sludges, and sediments.
- 4.2 This method applies to dissolved calcium, magnesium, potassium, and sodium.
- 5.0 **Method Summary**
- 5.1 In direct aspiration atomic spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp (in which the cathode is made of the element to be determined) is directed through the flame into a monochromator and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample.
- 6.0 **Definitions**
- 6.1 Analyte – Calcium, magnesium, potassium, and sodium.
- 6.2 Calibration Blank (CB) – Prepared by adding reagents to blank water in the same concentration as the samples and standards. The CB is used to zero the instrument, for all initial and continuing CB determinations, and to flush the system between samples and standards.
- 6.3 Initial Calibration Blank (ICB) – A CB analyzed at the beginning of the analysis run to demonstrate that the instrument is capable of acceptable performance.
- 6.4 Continuing Calibration Blank (CCB) – A CB analyzed in the course of the analysis run to demonstrate that the instrument is capable of continuous acceptable performance.
- 6.5 Calibration Standard (CAL) – A solution prepared from the primary standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 6.6 Calibration Curve – A plot of concentrations of known analyte standards versus the instrument response to the analyte. CALs are prepared by successively diluting a standard solution to produce working standards that cover the working range of the instrument. Standards should be prepared at the frequency specified in this SOP.

The CALs should be prepared using the same type of reagents and at the same concentration as will result in the samples following sample preparation.

- 6.7** Initial Calibration Verification (ICV) – Second source standards to check the accuracy of the CALs.
- 6.8** Continuing Calibration Verification (CCV) – A control standard analyzed in the course of the analysis run to demonstrate that the initial calibration determined remains valid throughout the course of the analytical run.
- 6.9** Laboratory Control Sample (LCS) – An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed and prepared exactly like a sample. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 6.10** Linear Calibration Range (LCR) – The concentration range over which the instrument response is linear.
- 6.11** Laboratory Duplicates (LD1 and LD2) or Precision Control (PC) – Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.
- 6.12** MDL – The minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. See internal procedure SOP 103.
- 6.13** Matrix Spike (MS) or Accuracy Control (AC) – An aliquot of a sample to which known quantities of the method's analytes are added in the laboratory. The MS or AC is analyzed and prepared exactly like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or AC corrected for background concentrations.
- 6.14** Mixed Control (MC) or Second Source Standard (SSS) – A composite sample of clean water samples for water analyses. The MC is analyzed and prepared in the same manner as routine samples. It is also a second source standard and a check on the primary standards. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 7.0 Interferences**
- 7.1** Chemical interferences are caused by the lack of absorption of atoms bound in molecular combination in the flame. Silicon, aluminum, phosphate, and sulfate cause suppression for calcium. Silicon and aluminum cause a decrease in sensitivity for magnesium. These interferences are corrected by the addition of lanthanum chloride to standards and samples. Calcium and magnesium are released due to the preferential bonding of lanthanum with the interfering anions.

- 7.2 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positive charged ion. Potassium and sodium are partially ionized in an air/acetylene flame suppressing its signal. Cesium chloride is added to standards and samples to eliminate this interference.
- 7.3 Levels greater than 5% nitric acid eliminate the suppression of nitrate on calcium and magnesium.
- 8.0 **Safety**
- 8.1 Safety glasses and shoes that cover the feet are required in all designated laboratory areas.
- 8.2 It is recommended that the analyst wear gloves and a lab coat when performing this procedure.
- 8.3 The analyst must be familiar with the Laboratory Chemical Hygiene Plan.
- 8.4 The analyst must be familiar with the Laboratory Safety Policy (internal procedure SOP 100).
- 8.5 The analyst must be familiar with any material safety data sheets (MSDSs) applicable to this method.
- 8.6 Barium chloride and hydrochloric acid have the potential to be highly toxic or hazardous. Consult the MSDSs before proceeding with the analysis.
- 8.7 The analyst must be familiar with the location of safety equipment including showers, eye wash stations, and spill kits.
- 8.8 The analyst should always thoroughly wash hands in warm soapy water when leaving the work area and before handling food or drink.
- 8.9 The analyst should assume that all samples have the potential to be hazardous and should exercise caution when transporting, handling, and/or opening any samples.
- 8.10 General good laboratory practices are required. The analyst should take all necessary precautions in order to minimize the potential of exposure to samples and reagents used in this method.
- 9.0 **Equipment and Supplies**
- 9.1 Atomic absorption spectrophotometer – Perkin-Elmer, model #5100 or equivalent.
- 9.1.1 Air/acetylene burner head.
- 9.1.2 Hollow cathode lamps - For Ca, Mg, K, and Na.
- 9.1.3 Auto-sampler – Perkin-Elmer AS-51 or equivalent.
- 9.1.4 Software – Perkin-Elmer GEM.
- 9.1.5 Personal computer – IBM or equivalent.

- 9.1.6 Printer – Epson LQ 850 or equivalent.
- 9.2 Bottles – 500 mL, plastic, with screw caps.
- 9.3 Diluter – Hamilton, digital or equivalent.
- 9.4 Vortex mixer – Daigger or equivalent.
- 9.5 Mechanical pipettes – 20 to 200 μ L with pipette tips to fit, 1 to 5 mL with pipette tips to fit.
- 9.6 Re-pipetors – Oxford, 500 mL, capable of delivering 0.4 mL and 0.5 mL.
- 9.7 Sample tubes – 15 mL, capped centrifuge, VWR #21008-220 or equivalent.
- 9.8 pH strips.
- 9.9 Volumetric flasks – 500 mL and 1000 mL capacity.
- 9.10 Graduated cylinders – Various volumes.
- 9.11 Volumetric pipettes – 10 mL.
- 9.12 Reagent bottles – Glass, clear
- 10.0 Reagents and Standards**
- 10.1 All reagents, solvents, and standards must be traceable to the stock inventory tracking log.
- 10.2 All reagents, solvents, and standards must be labeled with: date received, date opened, expiration date, tracking number, and receiver's initials.
- 10.3 All prepared reagents and standards must be labeled with: date prepared, expiration date, preparer's initials, tracking number, diluent, and description.
- 10.4 All standard logbooks must be completely filled out.
- 10.5 All certificates of analysis must include the stock inventory tracking number that was assigned to the standard. Original certificates are maintained by the Laboratory's Quality Assurance/Quality Control Officer.
- 10.6 All reagents are prepared with DI water. DI water is normal tap water that has been passed through a Millipore, Super QTM water purification system and has an industry standard resistivity of 18M Ω .
- 10.7 Nitric acid (HNO₃) – Concentrated, trace metal grade is preferred, JT Baker #9598-34 or equivalent.
- 10.8 Hydrochloric acid (HCl) – Concentrated, Mallinckrodt #5587 or equivalent.

- 10.9 Lanthanum oxide (La_2O_3) – Fisher brand or equivalent.
- 10.10 Cesium chloride (CeCl) – Mallinckrodt brand or equivalent.
- 10.11 Lanthanum-cesium chloride solution
- 10.11.1 Very slowly and in small portions, add 23.2 g of La_2O_3 to 200 mL of concentrated HCl in a hood.

NOTE: Reaction is violent.

- 10.11.2 Stir continuously.
- 10.11.3 Dissolve 5.06 g of cesium chloride in 200 mL of DI water.
- 10.11.4 Carefully add this solution to the La_2O_3 solution in a hood while continuing to stir.
- 10.12 Blank solutions – Reagent blank, CB, and rinse blank.
 - 10.12.1 Reagent blank – Prepare by adding 0.4 mL of lanthanum-cesium chloride solution and 0.4 mL of HNO_3 to 5 mL of reagent water. This solution is used throughout the entire sample preparation and analytical process.
 - 10.12.2 CB – Prepare by adding 0.4 mL of lanthanum-cesium chloride solution and 0.4 mL of HNO_3 to 5 mL of reagent water. This solution is used for instrument calibration and for subsequent calibration verification analyses.
 - 10.12.3 Rinse blank – This is the same as reagent water.
- 10.13 Standard stock solutions
 - 10.13.1 Calcium, stock standard – 1000 mg/L, VWR #VW42407-1 or equivalent.
 - 10.13.2 Magnesium, stock standard – 1000 mg/L, VWR #VW4207-1 or equivalent.
 - 10.13.3 Potassium, stock standard – 1000 mg/L, VWR #VW4207-1 or equivalent.
 - 10.13.4 Sodium, stock standard – 1000 mg/L, VWR #VW4207-1 or equivalent.
- 10.14 CAL solutions
 - 10.14.1 Ca, Mg, Na, and K CAL #1 (S1) – 10 mg Ca, 5 mg/L Mg, 10 mg/L Na, and 0.5 mg/L K
 - 10.14.1.1 Pipette 10 mL of Ca and Na stock standard, 5 mL of Mg stock standard, and 0.5 mL of K standard into a 1 L volumetric flask. Bring to volume with DI water. Store in a glass reagent bottle.
 - 10.14.2 Ca, Mg, Na, and K CAL #2 (S2) – 20 mg/L Ca, 10 mg/L Mg, 20 mg/L Na, and 1.0 mg/L K
 - 10.14.2.1 Pipette 10 mL of Ca and Na stock standard, 5 mL of Mg stock standard, and 0.5 mL of K standard into a 500 mL volumetric flask. Bring to volume with DI water. Store in a glass reagent bottle.
 - 10.14.3 Ca, Mg, Na, and K CAL #3 (S3) - 50 mg/L Ca, 20 mg/L Mg, 50 mg/L Na, and 2.5 mg/L K

- 10.14.3.1** Pipette 25 mL of Ca and Na stock standard, 10 mL of Mg stock standard, and 1.25 mL of K standard into a 500 mL volumetric flask. Bring to volume with DI water. Store in a glass reagent bottle.
- 10.14.4** Ca, Mg, Na, and K CAL #4 (S4) - 100 mg/L Ca, 40 mg/L Mg, 100 mg/L Na, and 5.0 mg/L K
- 10.14.4.1** Pipette 50 mL of Ca and Na stock standard, 20 mL of Mg stock standard, and 2.5 mL of K standard into a 500 mL volumetric flask. Bring to volume with DI water. Store in a glass reagent bottle.
- 10.15** Mixed Ca, Mg, Na, and K standard spike – 1500 mg/L Ca, 500 mg/L Mg, 1500 mg/L Na, and 80 mg/L K.
- 10.15.1** In a 500 mL volumetric flask, dissolve 1.238 g of magnesium sulfate in 10 μ L of HNO₃. Add 1.9065 g of sodium chloride and 0.0763 g of potassium chloride. Suspend 1.8728 g of calcium carbonate in 75 mL of DI water. Add concentrated HCl (~15 mL) to dissolve. Add this solution to the volumetric flask. Bring to volume with DI water.
- 10.15.2** Pipette 100 μ L into 5 mL of sample (for the accuracy spike). Pipette 100 μ L into the reagent blank (for control) to yield 30 mg/L Ca and Na, 10 mg/L Mg, and 1.6 mg/L K.
- 10.16** ICV spike – 5000 mg/L Ca, Mg, Na, and K, Spex Certiprep standard.
- 10.16.1** Pipette 10 μ L into 5 mL of calibration blank to yield 10 mg/L of Ca, Mg, Na, and K.
- 10.17** MC – Composite several clean water samples that have been previously analyzed for Ca, Mg, Na, and K. Analyze the composite at least ten times. Calculate the mean and standard deviation. The MC is analyzed as a quality control (QC) check on each analytical batch of Ca, Mg, Na, and K once the mean and standard deviation are determined.
- 10.18** Argon – Commercial grade, with all necessary connections to connect to the Perkin-Elmer 5100 atomic absorption spectrophotometer.
- 10.19** Soda ash – To neutralize acid solutions.
- 11.0** **Sample Collection, Preservation, Shipment, and Storage**
- 11.1** Water samples are collected in 500 mL high-density polyethylene screw cap bottles. The bottles should be completely filled. The proper bottles codes are:
- 11.1.1** MA (total recoverable).
- 11.1.2** MAD (dissolved, field filtered).
- 11.1.3** MD (dissolved, laboratory filtered).
- 11.2** Water samples are preserved with 1:1 nitric acid to a pH<2 at the time of collection or as soon thereafter as practically possible (within 24 hours). Dissolved water samples are filtered through a 0.45 μ m pore diameter membrane filter at the time of collection or as soon thereafter as practically possible (within 24 hours) prior to preserving with

1:1 nitric acid to a pH<2. Following acidification to a pH<2, the samples are mixed, are held for a minimum of 16 hours, and the pH is verified to be <2. If the pH is not <2, more acid should be added. The sample is then held for 16 hours until the pH is verified to be <2.

11.3 Water samples are stored at room temperature.

11.4 The recommended maximum holding time for water samples is six months providing they have been properly preserved.

11.5 Solid samples are collected in 250 mL glass jars with aluminum or teflon lined screw caps. The proper bottle code is MS.

11.6 Solid samples are stored at 4°C. No chemical preservation is necessary.

11.7 The recommended maximum holding time for solid samples is six months.

12.0 Quality Control (QC)

12.1 The minimum QC for this method includes an initial demonstration of capability (IDOC), MDL determination, LCR, routine analysis of reagent blanks, fortified blanks, and other laboratory solutions as continuing checks on performance.

12.2 IDOC

12.2.1 Prior to analyzing samples by this method, 4 DI water samples spiked with Ca, Mg, Na, and K standards must be analyzed as described in Section 13 of this method. The results are statistically tabulated to obtain the average percent recovery (X) and the standard deviation (s) of the percent recoveries. Obtained values for s and X are compared to the criteria in Section 12.3. If both s and X are acceptable, this method may be used to generate data. If s or X fails, corrective action must be taken, and the IDOC must be repeated. Repeat the above steps until acceptable values for s and X are obtained.

12.3 System audits are checked at least once per analytical batch and are in control if the following criteria are met:

12.3.1 The sensitivity for the S1 (Ca, Mg, Na, and K CAL #1, 10 mg/L Ca and Na, 5 mg/L Mg, and 0.50 mg/L K) is:

- 12.3.1.1 Ca – absorbance of at least 0.021.
- 12.3.1.2 Na – absorbance of at least 0.020.
- 12.3.1.3 Mg – absorbance of at least 0.240.
- 12.3.1.4 K – absorbance of at least 0.110.

12.3.2 The S1, S2, and S3 as check standards are within $\pm 5\%$ of the true values.

12.3.3 The MC is within $\pm 10\%$ of the true values.

12.4 Samples audits should be analyzed with the frequency of 1 per every 1 to 15 samples, 2 per every 16 to 30 samples, etc.

- 12.4.1 PC samples (LD1 and LD2) should have a range (difference) no greater than 10%.
- 12.4.2 AC samples (MS) are 5 mL of sample spiked with 100 μ L of the mixed standard spike solution (Section 10.15). Recoveries should be $\pm 15\%$ of the spike value plus the average of the sample and sample duplicate.
- 12.4.3 The LCSs are 5 mL of DI water spiked with 100 μ L of the mixed standard spike solution (Section 10.15). Recoveries should be $\pm 10\%$ of the true value.
- 12.4.4 The ICB and CCBs must be less than one half of the RL for Ca (RL = 1.0 mg/L), Mg (RL = 1.0 mg/L), Na (RL = 1.0 mg/L), and K (RL = 0.1 mg/L). If the blank is outside of the limit, verify that there is no contamination. Prepare fresh if necessary. Rerun until the CCB is $< 1/2$ the RLs.
- 12.4.5 The ICV and CCV standard recoveries must be within $\pm 10\%$ (90 – 100%) of the true values. If the CCV is outside of the limits, prepare fresh if necessary. Rerun. If the CCV continues to fail, the analysis must be stopped. Bracketed samples must be reanalyzed.
- 12.4.6 Proficiency audit samples are obtained from an independent source at least biannually. Two samples at different concentrations are received for each evaluation. The samples are prepared and analyzed according to the instructions provided. The results are submitted to the supplier for evaluation. Participation in these studies is used as a means to independently monitor this method's performance and to compare its performance against that of other participants.
- 13.0 Calibration and Standardization**
- 13.1 Calibration of the instrument is performed according to Perkin-Elmer 5100 atomic absorption instrument protocol. See Section 4 and Section 5 of the Perkin-Elmer 5100 atomic absorption manual.
- 13.1.1 General procedure for operation
- 13.1.1.1 After choosing the proper hollow cathode lamp for the analysis, allow the lamp to warm up for 5 to 15 minutes.
- 13.1.1.2 Align the burner head (angled for Ca and Mg).
- 13.1.1.3 Light the flame.
- 13.1.1.4 Adjust the nebulizer flow (approximately 6 mL/min.) for maximum percent absorption and stability.
- 13.1.1.5 Balance the photometer.
- 13.1.2 Run a series of CALs (blank, S1, S3, and S4) of the element to be analyzed. A calibration curve is calculated by the instrument (concentration vs. absorbance). If the correlation coefficient of the curve is less than 0.9980, the curve is rejected and must be reanalyzed until acceptable.
- 13.1.3 The instrument software automatically calculates sample concentration. The sample concentrations and QC are then printed.
- 14.0 Procedure**
- 14.1 Solid samples must be digested prior to analysis.

- 14.2 Pipette 5 mL of DI water for blanks into eight 15mL culture tubes using the Oxford macro-set pipettor. Pipette 5 mL of each CAL into separate 15 mL culture tubes. Set up eight 15 mL cultures tubes for S1 and four 15 mL culture tubes for S2, S3, and S4.
- 14.3 Pipette 5 mL of each well-shaken water sample or digested solid sample to be analyzed into separate 15 mL culture tubes.
- 14.4 Spike each AC sample and LCS with 100 µL of the mixed standard (Section 10.15).
- 14.5 Pipette 0.5 mL of lanthanum-cesium solution (Section 10.11) and 0.4 mL of concentrated ultra nitric acid to each tube. Vortex the tubes to mix them. The samples are ready to be analyzed using flame atomic absorption.
- 14.6 Each analyses (for each element) starts with a CB, an S1 (Section 10.14.1), an S3 (Section 10.14.3), and an S4 (Section 10.14.4) to establish the calibration curve. The curve is followed with a CCB (Section 12.4.4), a CCV (Section 12.4.5), and an SSS (mixed control). A CCB and a CCV are analyzed after every ten samples to check the baseline and curve integrity.
- 14.7 Repeat Section 14.5 for each element that needs to be analyzed.
- 14.8 If a sample concentration is above the S4, it is diluted 1/10 and reanalyzed.
- 15.0 **Calculations**
- 15.1 The Perkin-Elmer 5100 atomic absorption spectrophotometer automatically calculates the concentration of the analyzed element.
- 15.1.1 Water samples are calculated in mg/L.
- 15.1.2 Sediment/solid samples are calculated in mg/Kg (dry weight). A 1/50 dilution factor is used in the calculation for sediment/solid samples because 1 g of sample is used per 50 mL of digestate.
- 15.2 Calculation of the % recovery for AC audits is as follows:
- $$\% \text{ Recovery AC} = (M/T)100$$
- where: M = measured spike sample concentration.
T = theoretical spike sample concentration.
(T = (X + C) where C = concentration of spiking standard and X = average concentration of the two duplicates used for precision).
- 16.0 **Method Performance**
- 16.1 MDL – MDL studies are determined annually for this method using the Code of Federal Regulations 40 CFR, Part 136, Appendix B, and internal procedure SOP 103.
- 16.2 Precision – See Attachment 22.2.
- 16.3 Accuracy – See Attachment 22.2.

- 16.4 RL – After examining several factors such as normal precision of samples near the RL, normal blank levels, and the MDL, the RL has been set at 1.0 mg/L for Ca, Mg, and Na. The RL has been set at 0.1 mg/L for
- 17.0 **Pollution Prevention**
- 17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Whenever feasible, staff should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.
- 17.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.
- 17.3 For information concerning pollution prevention which may be applicable to laboratory operations, consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, DC 20036.
- 18.0 **Data Assessment**
- 18.1 Analytical data reported must be within the linear range of the assay (>1.0 mg/L and <100 mg/L for Ca and Na, >1.0 mg/L and <40 mg/L for Mg, and >0.1 mg/L and <5.0 mg/L for K).
- 18.2 Data is reported to a maximum of three significant figures as follows: 0.XX, X.X, XX.X, XXX, or XX0.
- 18.3 Dilutions increase the RL (i.e., RL of 1.0 and 0.1 mg/L for water samples or 50. and 5. mg/Kg multiplied by the dilution factor).
- 18.4 Appropriate laboratory reporting codes for dilutions, interferences, holding times, improper preservation, etc., will be appended to the test result according to laboratory policy. See internal procedure SOP 106.
- 18.5 Precision and accuracy data for an analytical batch must be within the acceptance criteria in Section 12 before the data can be reported. Standards and controls must also be within the acceptance criteria in Section 12 before the data can be reported.
- 18.6 Out of range values must be diluted, rerun, and acceptable before they can be reported.
- 18.7 Suspected samples with carryover must be rerun for verification before they can be reported.
- 18.8 The analyst and the Unit Manager review all data before the final reporting out of results.

19.0 Corrective Actions

- 19.1 Preventative maintenance is performed on a routine basis. A maintenance logbook is kept with the instrument.
- 19.2 The nebulizer and burner head are cleaned as needed. The waste collection jug is neutralized and dumped as needed.
- 19.3 An ion balance is calculated for samples with results for alkalinity, chloride, sulfate, and dissolved calcium, magnesium, sodium, and potassium. If the ion balance is out by more than $\pm 10\%$, it should be investigated, and the samples should be reanalyzed if necessary. High iron concentrations may cause the ion balance to be $>\pm 10\%$.

20.0 Waste Management

- 20.1 Liquid wastes generated by the analyses, excess samples, and dilutions can be disposed of down the drain with copious amounts of water if they do not contain identified hazardous material (i.e., samples from an industrial site, etc.) that requires handling and proper disposal as hazardous waste.
- 20.2 Broken/waste glass is collected at the bench in a plastic pail until transferred to a collection barrel for disposal.

21.0 References

- 21.1 Calcium (AA, Direct Aspiration), U.S. Environmental Protection Agency, Method 215.1, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00915 and #00916.
- 21.2 Magnesium (AA, Direct Aspiration), U.S. Environmental Protection Agency, Method 242.1, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00925 and #00927.
- 21.3 Potassium (AA, Direct Aspiration), U.S. Environmental Protection Agency, Method 258.1, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00935 and #00937.
- 21.4 Sodium (AA, Direct Aspiration), U.S. Environmental Protection Agency, Method 273.1, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00929 and #00930.
- 21.5 Calcium (Atomic Absorption, Direct Aspiration), U.S. Environmental Protection Agency, Method 7140, Test Methods for Evaluating Solid Waste, SW-846, Update III, 1996.
- 21.6 Magnesium (Atomic Absorption, Direct Aspiration), U.S. Environmental Protection Agency, Method 7450, Test Methods for Evaluating Solid Waste, SW-846, Update III, 1996.

- 21.7 Potassium (Atomic Absorption, Direct Aspiration), U.S. Environmental Protection Agency, Method 7610, Test Methods for Evaluating Solid Waste, SW-846, Update III, 1996.
- 21.8 Sodium (Atomic Absorption, Direct Aspiration), U.S. Environmental Protection Agency, Method 7770, Test Methods for Evaluating Solid Waste, SW-846, Update III, 1996.
- 21.9 United States Code of Federal Regulations, Title 40, U.S. Government Printing Office, Washington, DC, Part 136, Appendix A and B.
- 22.0 **Attachments**
- 22.1 Sample batch sheet for cations.
- 22.2 Quality Control Summary 2005.

Signature Page

APPROVED BY *Bob H. Henry* DATE *3/14/06*
CHIEF, LABORATORY SERVICES SECTION

APPROVED BY *[Signature]* DATE *3/8/06*
COMPLIANCE OFFICER

APPROVED BY *[Signature]* DATE *2/21/06*
QA OFFICER

APPROVED BY *Sandra K. Gregg* DATE *2-15-06*
UNIT MANAGER

APPROVED BY *Lynn A. Vetzko* DATE *2-15-06*
ANALYST

Calcium, Magnesium, Potassium, and Sodium

ANALYST: _____

RUN #: _____

ANALYSIS DATE: _____

	SAMPLE NUMBER	DISS.	SED.	% TS	COMMENTS
8	BLANK 1				
9	CONTROL 1				
10	MC				
11	ICP STANDARD				
12					
13					
14					
15					
16					
17					
18	BLANK (CCB)				
19	S1(CCV)				
20					
21					
22					
23					
24					
25					
26					
27					
28					
29					
30	BLANK (CCB)				
31	S1(CCV)				
32					
33					
34					
35					
36					
37					
38					
39					
40					
41					
42	BLANK (CCB)				
43	S1(CCV)				
44					
45					
46					
47					
48					
49					
50					
51					
52					
53					

CHEMICAL TRACKING NUMBERS:

HNO₃: _____
 La-Ce: _____
 S1: _____

S2: _____
 S3: _____
 S4: _____

MDEQ Environmental Laboratory

ENV. INORGANIC UNIT 2005 AC AND PC SUMMARY

ELEMENT	EPA NO.	MATRIX	ACCURACY					PRECISION *		
			CONC (mg/l)	%RECOVERY			N	MC (mg/l)		N
				MEAN	S.D.	RSD		MEAN	S.D.	
Calcium	7140	water	30	99.9	4.84	4.8	206	27	0.83	109
Magnesium	7450	water	10	97.9	3.2	3.3	209	7.37	0.13	113
Potassium	7610	water	1.6	101.4	3.53	3.5	154	1.12	0.02	82
Sodium	7770	water	30	101.3	4.05	4.0	162	11	0.5	87

*Precision is based on samples of known concentration and indicates between run precision.





EFFECTIVE DATE: 01/2007

SOP# 302

REVISION # 1

**SULFATE (COLORIMETRIC, AUTOMATED METHYLTHYMOL BLUE, TRAACS 800)
TOTAL IN WATER**

Table of Contents

1.0	Applicable Analytical Methods.....	1
2.0	Matrix or Matrices.....	1
3.0	Method Detection Limits.....	2
4.0	Scope and Application.....	2
5.0	Method Summary.....	2
6.0	Definitions.....	2
7.0	Interferences.....	3
8.0	Safety.....	4
9.0	Equipment and Supplies.....	4
10.0	Reagents and Standards.....	5
11.0	Sample Collection, Preservation, Shipment, and Storage.....	8
12.0	Quality Control (QC).....	8
13.0	Calibration and Standardization.....	9
14.0	Procedure.....	9
15.0	Calculations.....	10
16.0	Method Performance.....	11
17.0	Pollution Prevention.....	11
18.0	Data Assessment.....	11
19.0	Corrective Actions.....	12
20.0	Waste Management.....	13
21.0	References.....	13
22.0	Attachments.....	13
	Signature Page.....	14

1.0 Applicable Analytical Methods

1.1 Sulfate (Colorimetric, Automated, Methylthymol Blue), Method 375.2, U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00095.

2.0 Matrix or Matrices

2.1 Drinking water, surface water, and saline water.

2.2 Domestic and industrial wastes.

3.0 Method Detection Limits

- 3.1 All MDLs are performed according to the Code of Federal Regulations 40 CFR, Part 136, Appendix B. See internal procedure SOP 103.
- 3.2 The MDL was determined by analyzing seven replicate samples. Seven deionized (DI) water samples were spiked with sulfate standard to yield a theoretical concentration of 1.0 mg/L. The replicates were analyzed identical to normal samples.
- 3.3 Analytical results for the seven replicates were tabulated statistically. The MDL was calculated using a formula that applies the student t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See section 16.1.
- 3.4 The MDL for this method is determined annually or whenever there is a significant change in the procedure including a change in the analyst.
- 3.5 Reporting limit (RL) – The RL for this method has been set at 2.0 mg/L.

4.0 Scope and Application

- 4.1 This method applies to drinking water, surface water, and saline water and domestic and industrial waste.
- 4.2 The applicable range is 2.0 to 100 mg/L as sulfate.
- 4.3 Approximately 30 samples per hour can be analyzed.

5.0 Method Summary

- 5.1 The sample is first passed through a cation exchange column to remove multivalent metal ions. The sample containing sulfate is then reacted with an alcohol solution of barium chloride and methylthymol blue (MTB) at a pH of 2.5 to 3.0 to form barium sulfate. The combined solution is then raised to a pH of 12.5 to 13.0 so that excess barium reacts with the MTB. The uncomplexed MTB is gray. The color is blue when it is entirely complexed with barium. Initially, the barium and MTB are equimolar. Therefore, the amount of uncomplexed MTB (measured at 460 nm) is directly proportional to the sulfate present.

6.0 Definitions

- 6.1 Analyte – Sulfate.
- 6.2 Calibration Blank (CB) - Prepared by adding reagents to blank water in the same concentration as the samples and standards. The CB is used to zero the instrument, for all initial and continuing CB determinations, and to flush the system between samples and standards.

- 6.3 Initial Calibration Blank (ICB) - A CB analyzed at the beginning of the analysis run to demonstrate that the instrument is capable of acceptable performance.
- 6.4 Continuing Calibration Blank (CCB) - A CB analyzed in the course of the analysis run to demonstrate that the instrument is capable of continuous acceptable performance.
- 6.5 Calibration Standard (CAL) - A solution prepared from the primary standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 6.6 Calibration Curve - A plot of concentrations of known analyte standards versus the instrument response to the analyte. CALs are prepared by successively diluting a standard solution to produce working standards that cover the working range of the instrument. Standards should be prepared at the frequency specified in this SOP. The CALs should be prepared using the same type of reagents and at the same concentration as will result in the samples following sample preparation.
- 6.7 Initial Calibration Verification (ICV) - Second source standards to check the accuracy of the CALs.
- 6.8 Continuing Calibration Verification (CCV) - A control standard analyzed in the course of the analysis run to demonstrate that the initial calibration determined remains valid throughout the course of the analytical run.
- 6.9 Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed and prepared exactly like a sample. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 6.10 Linear Calibration Range (LCR) - The concentration range over which the instrument response is linear.
- 6.11 Laboratory Duplicates (LD1 and LD2) - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.
- 6.12 MDL - The minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. See internal procedure SOP 103 for details.
- 7.0 **Interferences**
- 7.1 An ion exchange column is used to overcome interferences from calcium, magnesium, aluminum, and iron. Most natural water samples have no significant interferences. High levels of calcium and magnesium (>100 mg/L) and iron and

aluminum (>100 mg/L) cause a negative bias (>2%) while levels of phosphates (>10 mg/L), sulfite (>10 mg/L), and sulfide cause a positive bias (>4%).

7.2 Calcium can be released from the ion exchange column whenever an acidic or highly ionic sample passes through it. Samples with pH below two should be neutralized before analysis.

7.3 Turbid samples should be filtered, allowed to settle, or centrifuged before analysis.

7.4 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that bias analyte response.

8.0 Safety

8.1 Safety glasses and shoes that cover the feet are required in all designated laboratory areas.

8.2 It is recommended that the analyst wear gloves and a lab coat when performing this procedure.

8.3 The analyst must be familiar with the Laboratory Chemical Hygiene Plan.

8.4 The analyst must be familiar with the Laboratory Safety Policy (SOP 100).

8.5 The analyst must be familiar with any material safety data sheets (MSDSs) applicable to this method. Barium chloride and hydrochloric acid have the potential to be highly toxic or hazardous. Consult the MSDSs before proceeding with the analysis.

8.6 The analyst must be familiar with the location of safety equipment including showers, eye wash stations, and spill kits.

8.7 The analyst should always thoroughly wash hands in warm soapy water when leaving the work area and before handling food or drink.

8.8 The analyst should assume that all samples have the potential to be hazardous and should always exercise caution when transporting, handling, and/or opening any samples.

8.9 General good laboratory practices are required. The analyst should take all necessary precautions in order to minimize the potential of exposure to samples and reagents used in this method.

9.0 Equipment and Supplies

9.1 Bran-Luebbe Traacs 800 system

- 9.1.1 Linear random access sampler.
- 9.1.2 Analytical console – Including pump control and air distributor.
- 9.1.3 Multi chemistry manifolds - Alkalinity, chloride, and sulfate.
- 9.1.4 Colorimeters.
- 9.1.5 Software - Traacs.
- 9.1.6 Computer - IBM personal system 2.
- 9.1.7 Printer - Citizen MSD-20 dot matrix.
- 9.1.8 Voltage regulator - Sola MCR.
- 9.1.9 Vials - Bran-Luebbe, 5 mL.

- 9.2 Bottles - 500 mL, plastic, with screw cap.

- 9.3 Diluter - digital.

- 9.4 Volumetric flasks - 500 mL and 1000 mL capacity.

- 9.5 Analytical balance - Capable of weighing 0.1 mg.

- 9.6 Calibration weights - For calibrating balance and verification.

- 9.7 pH strips.

- 9.8 Graduated cylinders - Various volumes.

- 9.9 Volumetric pipettes - 10 mL.

- 9.10 Beakers - Pyrex, 500 and 1000 mL.

- 9.11 Glass storage containers - Clear and amber.

- 9.12 Glass wool.

- 9.13 Silicon Tubing, 0.065 inches inner diameter (ID), 4.5 inches per column.

- 9.14 Polyethylene Nipples, N6, two per column.

- 9.15 Tygon transmission tubing, 0.110 inches ID, at least 4 inches.

- 9.16 Disposable Syringe, 20 cc, Luer Tip.

- 10.0 **Reagents and Standards**

- 10.1 All reagents, solvents, and standards must be traceable to the stock inventory tracking log.

- 10.2 All reagents, solvents, and standards must be labeled with the date received, date opened, expiration date, tracking number, and receiver's initials.

- 10.3 All prepared reagents and standards must be labeled with the date prepared, expiration date, preparer's initials, tracking number, diluent, and description.
- 10.4 All standard logbooks must be completely filled out.
- 10.5 All certificates of analysis must include the stock inventory tracking number that was assigned to the standard. Original certificates are kept by the Laboratory's Quality Assurance/Quality Control Officer.
- 10.6 All reagents are prepared with DI water. DI water is normal tap water that has been passed through a Millipore, Super Q™ water purification system and has an industry standard resistivity of 18MΩ.
- 10.7 Barium chloride solution – Dissolve 0.80 g of barium chloride dihydrate in approximately 400 mL of DI water. Dilute to 500 mL with DI water. Mix thoroughly.
- 10.8 Hydrochloric acid, 0.25 N – Cautiously and while swirling add 2 mL of hydrochloric acid (specific gravity 1.19) to approximately 600 mL of DI water. Dilute to 1L with DI water. Mix thoroughly.
- 10.9 Barium/methylthymol blue (MTB) solution – Transfer 0.060 g of MTB into a 250 mL volumetric flask. Add 10.0 mL of barium chloride solution (Section 10.7), 10.0 mL of 0.25 N hydrochloric acid (Section 10.8), and 30.0 mL of DI water. Swirl to dissolve the MTB. Dilute to 250 mL with 2-propanol. Mix thoroughly. De-aerate before use. Prepare fresh daily. This reagent can be used for two days with a slight loss in sensitivity the second day. If kept more than one day, refrigerate when not in use.
- 10.10 Sodium hydroxide solution, 0.40 N – Transfer 16.0 g of sodium hydroxide into a 1 L volumetric flask containing 600 mL of DI water. Stir to dissolve. Cool to room temperature. Dilute to 1 L with DI water. Mix thoroughly. Store in a polyethylene container.
- 10.11 Sodium hydroxide buffer solution, 0.04 N – Transfer 50 mL of 0.40 N sodium hydroxide solution (Section 10.10) into a 500 mL volumetric flask containing 200 mL of 2-propanol. Add 150 mL of DI water. Mix. Cool to room temperature. Dilute to 500 mL with DI water. Mix thoroughly. De-aerate before use.
- 10.12 Triton X-100, 50% solution, volume/volume – Combine 50 mL of Triton X-100 with 50 mL of 2-propanol. Mix thoroughly.
- 10.13 Diluent solution – Add 0.2 g of sodium chloride to 2000 mL of DI water. Mix. Add 6 mL of Triton X-100 50% solution to the sodium chloride. Mix thoroughly.
- 10.14 System wash solution – Dissolve 50 g of tetrasodium EDTA in approximately 600 mL of DI water. Dilute to 1 L with DI water. Mix thoroughly.
- 10.15 Sampler baseline solution – Use DI water.

- 10.16 Sulfate, stock standard, 1000 mg/L – Purchased from VWR, EMD-19813 or equivalent.
- 10.17 Second source stock standard (SSS), sulfate, 1000 mg/L – Purchased from I-CAL, ICS041-5 or equivalent.
- 10.18 Sulfate, working standard, 2 mg/L – In a 500 mL volumetric flask, dilute 1.0 mL of stock sulfate standard (Section 10.16) to 500 mL with DI water. Store in a 500 mL plastic reagent bottle.
- 10.19 Sulfate, working standard, 20 mg/L – In a 500 mL volumetric flask, dilute 10.0 mL of stock sulfate standard (Section 10.16) to 500 mL with DI water. Store in a 500 mL plastic reagent bottle.
- 10.20 Sulfate, working standard, 50 mg/L – In a 500 mL volumetric flask, dilute 25.0 mL of stock sulfate standard (Section 10.16) to 500 mL with DI water. Store in a 500 mL plastic reagent bottle.
- 10.21 Sulfate, working standard, 100 mg/L – In a 500 mL volumetric flask, dilute 50.0 mL of stock sulfate standard (Section 10.16) to 500 mL with DI water. Store in a 500 mL plastic reagent bottle.
- 10.22 ICV – Add 25 mL of second source stock sulfate standard (section 10.17) to a 500 mL volumetric flask and dilute with DI water to the mark. Store in a 500 mL plastic bottle; it is stable for one year.
- 10.23 LCS – Pipette 100 μ L of the SSS (section 10.17) into 4.9 mL of DI water to yield a 20 mg sulfate/L in a test tube. Make fresh per analytical batch.
- 10.24 DVS – Pipette 2 mL of stock sulfate standard (section 10.16) into 1000 mL volumetric flask, dilute to mark with DI water and mix. Store in a 1000 mL plastic bottle; it is stable for one year.
- 10.25 Cation Ion Exchange Resin, 20-50 mesh, about 5 grams (sodium form).
- 10.26 Preparation of ion exchange resin and column.
- 10.26.1 Transfer enough resin to a 100 mL beaker so that there is about ½ inch of resin in the beaker. Cover the resin with DI water, mix gently and then decant the water. Repeat treatment with water until it appears clear and free of fines. Leave the resin covered with the DI water.
- 10.26.2 Cut a 4.5 inch length of 0.058 inch inner diameter (ID) silicone tubing, this is the column.
- 10.26.3 Attach the column to a disposable 20 cc syringe.
- 10.26.4 Pull some DI water through the column. Be careful to exclude air from the column. Place the free end of the column beneath the surface of the resin in the beaker and draw the suspension into the column using the syringe. The object is to completely fill the column.

- 10.26.5 Attach the filled column to the analytical manifold of the Traacs 800.
- 11.0 **Sample Collection, Preservation, Shipment, and Storage**
- 11.1 Samples are collected in 500 mL high-density polyethylene screw cap bottles. The bottles should be filled completely. The proper bottle code is MN.
- 11.2 Samples are stored at 4°C. Avoid freezing. No chemical preservation is necessary.
- 11.3 The recommended maximum holding time is 28 days. However, analysis should be completed as soon as possible.
- 12.0 **Quality Control (QC)**
- 12.1 The minimum QC for this method includes an initial demonstration of capability (IDOC), MDL determination, LCR, routine analysis of reagent blanks, fortified blanks, and other laboratory solutions as continuing checks on performance.
- 12.2 IDOC
- 12.2.1 Prior to analyzing samples by this method, the analyst must analyze 4 DI water samples spiked with the sulfate standard and analyze as described in Section 13 of this method. The results are statistically tabulated to obtain the average percent recovery (X) and the standard deviation (s) of the percent recoveries. Obtained values for s and X are compared to the criteria in Section 12.3. If both s and X are acceptable, this method may be used to generate data. If s or X fails, the analyst must take corrective action and repeat the IDOC. The analyst must repeat the above steps until acceptable values for s and X are obtained.
- 12.3 System audits are checked at least once per analytical batch and are in control if the following criteria are met:
- 12.3.1 The sensitivity at 100 mg/L is .33 to .40 au.
- 12.3.2 The correlation coefficient is .9995 to 1.000.
- 12.3.3 The CCV of 50 mg/L sulfate is 45. to 55. mg/L.
- 12.3.4 The LCS of 20 mg/L sulfate is 18. to 22. mg/L.
- 12.3.5 The ICV (second source standard) of 50 mg/L sulfate is 45. to 55. mg/L.
- 12.3.6 The DVS of 2 mg/L sulfate quantification is 1.6 mg/L to 2.4 mg/L.
- 12.4 Sample audits are to be analyzed with the frequency of 1 per every 1 to 15 samples, 2 per every 16 to 30 samples, etc.
- 12.4.1 Duplicate samples, should be within percent difference of $\pm 10\%$.
- 12.4.2 Matrix spike (MS) samples are spiked with 100 μ L of the second source stock sulfate standard (1000 mg/L sulfate) standard into 4.9 mL of sample. The spiked sample recovery should be 90% to 110%.

- 12.4.3 CCBs must be less than one half the RL (<0.5 mg/L). If the blank is outside the limit, verify that there is no contamination. Prepare fresh if necessary and rerun until it is < ½ RL.
- 12.4.4 CCV standards recovery must be within ±10% (90% to 110%). If the CCV is outside the limits, prepare fresh if necessary and rerun. If the CCV continues to fail, the analysis must be stopped and bracketed samples reanalyzed.
- 12.4.5 Proficiency audit samples are obtained from an independent source bi-annually. Two samples at different concentration levels are received for each evaluation. The samples are prepared and analyzed according to the provided instructions. The results are then submitted to the source for evaluation. Participation in these studies is used as a means to independently monitor this method's performance and to compare its performance against that of the other participants.

13.0 Calibration and Standardization

- 13.1 Calibration of the instrument is performed according to Bran-Luebbe instrument protocol.
 - 13.1.1 The baseline and gain are set manually. To set the baseline a 0% CB is run, and the baseline is set between 5% to 10% deflection of scale. To set the gain, the high CAL (100 mg/L) is run, and the gain is set between 90% to 95% deflection of scale.
 - 13.1.2 After the baseline and gain have been set, the primer (100 mg/L sulfate), gain, one 100 mg/L sulfate standard, one 50 mg/L sulfate standard, one 20 mg/L sulfate standard, and one 2 mg/L sulfate standard are run. The computer software calculates the standard curve and displays the correlation coefficient.
 - 13.1.3 The software then calculates carryover drift by analyzing one 100 mg/L sulfate standard and two 50 mg/L sulfate standards.
 - 13.1.4 If the criteria that are stated in Section 12 are met, the instrument is ready to run samples.
 - 13.1.5 At the end of the run, two or three blanks and a gain are analyzed to check for carryover drift. The software automatically adjusts for the carryover drift and calculates sample concentration. The sample concentrations are then printed.

14.0 Procedure

- 14.1 Operate the Bran-Luebbe Traacs 800 system according to basic operating procedures in the operating manual.
 - 14.1.1 Change all DI water reservoirs.
 - 14.1.2 Turn on the compressed air to the instrument.
 - 14.1.3 Turn on the sampler.
 - 14.1.4 Engage the pump-tube platen.
 - 14.1.5 Start the peristaltic pump.
 - 14.1.6 Pump DI water and diluent solution through the system for 15 minutes.
 - 14.1.7 Connect the barium/MTB solution and 0.04 N sodium hydroxide buffer reagent lines.
 - 14.1.8 Continue pumping with the reagent lines attached until a stable baseline with a good bubble pattern is achieved.
 - 14.1.9 Set the baseline to between 5% and 10% using the VB3 and CB3 commands.

- 14.1.10 If necessary, a manual gain correction can be made at this time using the VG3 and CG3 commands. The gain should be set between 90% and 95% of scale.
- 14.2 Manually set the base and gain after each new reagent is made for that particular analysis according to the Bran-Luebbe procedure.
- 14.3 Turbidity interference should be minimized through the analysis of supernatant or the centrifugation of the samples. Filtration may be used with proper precautions to prevent possible sample contamination due to extra handling.
- 14.4 Each run of samples should begin with two 100 mg/L standards (the first being the primer standard and the second being the gain standard) followed by one 50 mg/L standard, one 20 mg/L standard, and one 5 mg/L standard. The 50 mg/L standard is also used to calculate the carryover factor. After every ten samples, a standard of varying concentration and two blanks are analyzed to check the baseline and curve integrity. To minimize the affect of carryover, the instrument is run at 30 samples per hour.
- 14.5 Starting the run – Check for a smooth baseline and good bubble pattern. Input the run with sample IDs and initial dilutions, if any, into the appropriate edit file. Save to disk. Print out run information. Return to chart. Run (CR). Start the run by choosing "F7". Follow the on-screen menu. Typing "control B" accepts and forces the baseline. While the analytical run is in progress, monitor the analysis for off scale and irregular peaks and over-diluted samples. The QC audit samples should also be monitored.
- 14.6 Shut down – When the results of the run have printed out, disconnect the reagent lines. Place the 0.04 N sodium hydroxide line in the diluent solution. Place the barium/MTB solution line into the tetrasodium EDTA rinse solution for 15 minutes. After 15 minutes, pump diluent solution through both lines for 30 minutes. After approximately 30 minutes, lift the plattens from the pump tubes. Turn off the pumps. Turn off the sampler. Turn off the computer. Turn off the compressed air.
- 15.0 **Calculations**
- 15.1 The Traacs makes calculations minimal. Since it automatically calculates the baseline drift, change in sensitivity, and most of the carryover, the analyst looks at the peaks on the chart to verify that the peaks are well formed and compares blanks throughout the run. Data from bad peaks are rejected.
- 15.2 Diluted samples are calculated after baseline correction.
- 15.3 Calculation of the % recovery for matrix spike (MS) audits is as follows:

$$\% \text{ Recovery MS} = (M/T)100$$

where:

M = Measured spike sample concentration.

T = Theoretical spike sample concentration.

($T = (X + C)$ where C = Concentration of spiking standard and X = Average concentration of the two duplicates used for precision).

16.0 Method Performance

16.1 MDL – An initial MDL was determined using 7 replicate analyses of a low level sample with a mean concentration of 5.791 resulting in a standard deviation of 0.328 mg/L sulfate and an MDL of 1.274 mg/L at 95% confidence. MDL studies are determined annually for this method using the Code of Federal Regulations 40 CFR, Part 136, Appendix B and internal procedure SOP 103.

16.2 Precision – Using surface water samples with mean concentrations of 5.791 mg/L, 40.603 mg/L, and 78.1441 mg/L, the standard deviations were 0.378 mg/L, 1.139 mg/L and 0.953 sulfate mg/L, respectively.

16.3 Accuracy – Using a surface water sample with a mean concentration of 5.791 mg/L spiked using 10 mg/L of standard and 50 mg/L of standard, the mean spike sample recoveries were 93.3% and 91.9%, respectively.

16.4 RL – After examining several factors such as normal precision of samples near the RL, normal blank levels, and the MDL, the RL has been set a 2.0 mg/L sulfate.

17.0 Pollution Prevention

17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Whenever feasible, staff should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

17.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

17.3 For information concerning pollution prevention which may be applicable to laboratory operations, consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N. W., Washington, DC 20036.

18.0 Data Assessment

18.1 Analytical data reported must be within the linear range of the assay (>2.0 mg/L and <100 mg/L).

- 18.2 Data is reported to a maximum of three significant figures and no decimals as follows: X, XX, XXX, or XX0.
- 18.3 Dilutions must be greater than 10% of full scale to be reported (i.e., the diluted sample results must be >20 mg/L).
- 18.4 Dilutions increase the RL (i.e., RL of 2.0 mg/L multiplied by the dilution factor).
- 18.5 Appropriate laboratory reporting codes for dilutions, interferences, holding times, improper preservation, etc., will be appended to the test result according to laboratory policy. See SOP 106.
- 18.6 Precision and accuracy data for an analytical batch must be within the acceptance criteria stated in Section 12 of this method before the data can be reported. Standards and controls must be within the acceptance criteria stated in Section 12 of this method before the data can be reported.
- 18.7 Out of range values must be diluted, rerun, and acceptable before they can be reported.
- 18.8 Suspected samples with carryover must be rerun for verification before they are reported.
- 18.9 The Unit Manager reviews all data before the final reporting out of results.
- 19.0 **Corrective Actions**
- 19.1 Preventative maintenance is done on a routine basis. A maintenance logbook is kept with the instrument.
- 19.2 Pump tubes are changed at least every three months.
- 19.3 If the sensitivity starts to decline, new barium/methylthymol blue reagent is prepared.
- 19.4 If a sample produces a negative baseline on the chart, the pH of the sample is determined. If the sample itself is determined to have a low pH by comparing the pH of other neutral samples, the sample result is reported as interference. If, upon investigation, the sample has a low pH due to contamination with an acid preservative, a new sample is analyzed from a different neutral bottle of the sample if available. If a different neutral sample is not available, the sample result is reported as interference and qualified with a P code to indicate that the sample was not preserved correctly.
- 19.5 An ion balance is calculated for samples with results for alkalinity, chloride, sulfate and dissolved calcium, magnesium, sodium, and potassium. If the ion balance is out by more than $\pm 10\%$, it is investigated, and samples are reanalyzed if necessary. High iron concentrations may cause the ion balance to be $> \pm 10\%$.

20.0 Waste Management

- 20.1** Liquid wastes generated by the assays include mercuric nitric acid waste and color reagent and sample waste. The waste containers are labeled with the type of waste, the notation "hazardous waste" if hazardous, and the operator's initials. The hazardous waste containers are held until the monthly waste collection occurs and a licensed hazardous waste disposal company can properly dispose of them. The color reagent/sample waste can be disposed of down the drain with copious amounts of water.
- 20.2** Broken/waste glass is collected at the bench in a plastic pail until transferred to a collection barrel for disposal.
- 20.3** Excess samples and dilutions can be disposed of down the drain with copious amounts of water if they do not contain other hazardous material (i.e., samples from an industrial site, etc.) that requires them to be handled as a hazardous waste.

21.0 References

- 21.1** Sulfate (Colorimetric, Automated Methylthymol Blue), Method 375.2, Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA-600/4-79-020, March 1983.
- 21.2** United States Code of Federal Regulations, Title 40, U. S. Government Printing Office, Washington, DC, Part 136, Appendix A & B.
- 21.3** Sulfate in Water and Wastewater, Revision B, Technicon TRAACS 800™ Method, Industrial Method No. 847-87T, August 1987.
- 21.4** Standard Methods for the Examination of Water and Wastewater, 20th Edition, Sulfate Automated Methylthymol Blue Method, 4500-SO₄²⁻, 1998.

22.0 Attachments

- 22.1** Manifold diagram -- Sulfate in water and wastewater manifold #165-D006-03, Revision 3.
- 22.2** Sample batch sheet for anions.

Signature Page

APPROVED BY *Bob H. Acery* DATE *2/13/07*
CHIEF, LABORATORY SERVICES SECTION

APPROVED BY *[Signature]* DATE *2/13/07*
COMPLIANCE OFFICER

APPROVED BY *[Signature]* DATE *2/2/2007*
QA OFFICER

APPROVED BY *Sandra K. Gregg* DATE *1-3-2007*
UNIT MANAGER

APPROVED BY *Laura C. Ulmer* DATE *1-5-2007*
ANALYST

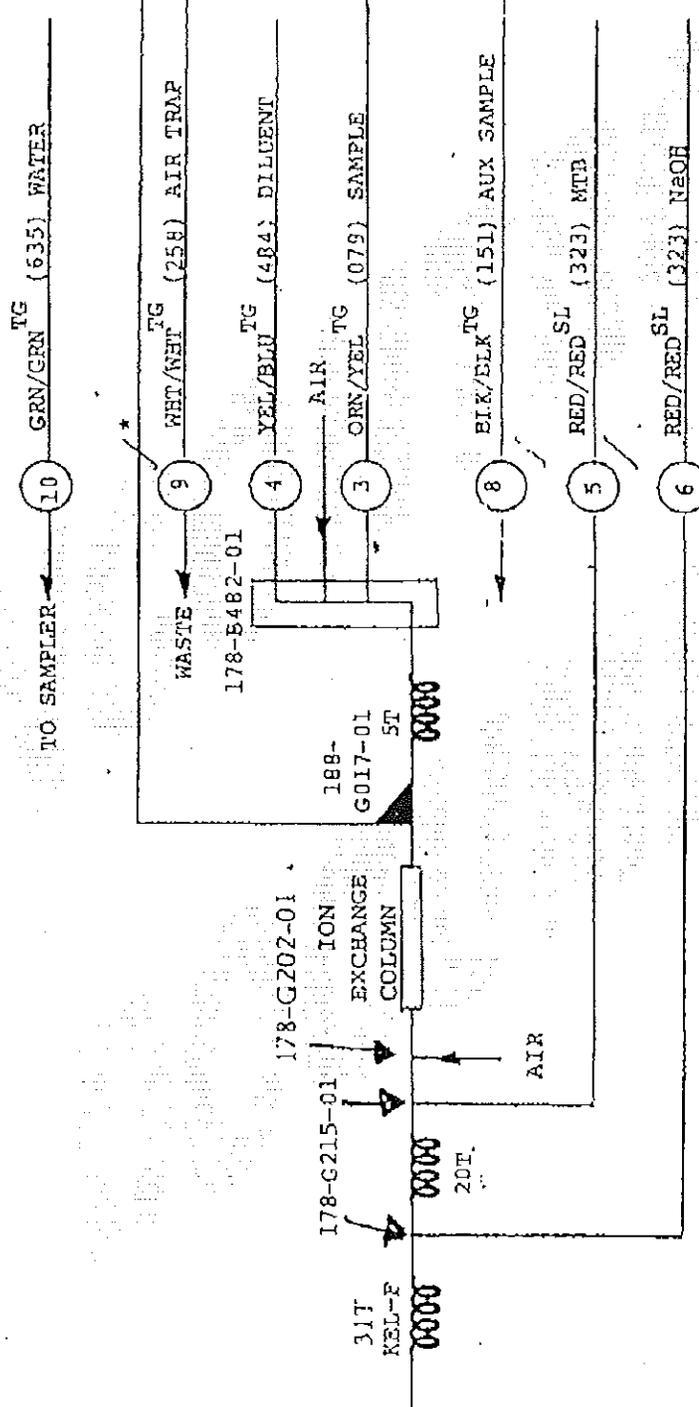
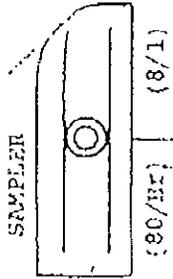
METHOD NO. 847-87K

MANIFOLD NO. 165-D006-03
Revision B

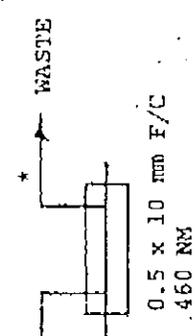
SULFATE IN WATER AND WASTEWATER

(RANGE: 2-100 mg/L SO_4^{2-})

Attachment # 1



NOTES: (XXX) = FLOWRATE IN ul/Min.
 CIRCLES = PUMP TUBE POSITION
 * = 0.030" ID. POLYETHYLENE TUBING
 5T = 165 G005-01
 20T = 165-B005-03
 3IT = 170-B213-01
 COLUMN = 4.5" x 0.065" ID SILICONE TUBING
 TG = TYGON
 SL = SILICONE



Attachment 22.2

DATE: _____
 ANALYST: _____

ANIONS

RUN # _____

#	ORDER #	SAMPLE #	ALK	CL	SO4	COMMENTS	QUALITY CONTROL		
							STD	DIFF	%DIFF
1	HIGH STD						ALKALINITY		
2	HIGH STD						STD		RANGE
3	MID STD						CCV		225-275 PPM
4	MID STD 2						ICV		225-275 PPM
5	LOW STD						LCS		225-275 PPM
6	ICB						REL. ABS.		.54-.66
7	CCV						COR COEF		.9995-1.0005
8									
9							PRECISION		DIFF %DIFF
10									
11									
12									
13							ACCURACY		%REC 90-110
14									
15									
16		PC							
17		MS							
18		CCB					STD		RANGE
19		CCV					CCV		45-55 PPM
20							ICV		45-55 PPM
21							LCS		18-22 PPM
22							REL. ABS.		.68-.84
23							COR COEF		.9995-1.0005
24									
25							PRECISION		DIFF %DIFF
26									
27									
28									
29							ACCURACY		%REC 90-110
30									
31									
32		PC							
33		MS							
34		CCB					STD		RANGE
35		CCV					CCV		45-55 PPM
36		LCS					ICV		45-55 PPM
37		ICV					LCS		18-22 PPM
38							REL. ABS.		.36-.44
39							COR COEF		.9995-1.0005
40									
41							PRECISION		DIFF %DIFF
42									
43									
44									
45							ACCURACY		% REC 90-110
46									
47									
48									
48							COMMENTS:		
50									
51									
52									
53									
54									
55									

Attachment 22.2

DATE: _____
 ANALYST: _____

ANIONS

RUN # _____

#	ORDER #	SAMPLE #	ALK	CL	SO4	COMMENTS	QUALITY CONTROL				
58							ALKALINITY				
57							PRECISION		DIFF	%DIFF	
58											
59											
60											
61											
62											
63							ACCURACY		%REC 90-110		
64											
65											
66											
67											
68											
69											
70											
71											
72							CHLORIDE				
73							PRECISION		DIFF	%DIFF	
74											
75											
76											
77											
78											
79							ACCURACY		%REC 90-110		
80											
81											
82											
83											
84											
85											
86											
87											
88							SULFATE				
89							PRECISION		DIFF	%DIFF	
90											
91											
92											
93											
94											
95							ACCURACY		%REC 90-110		
96											
97											
98											
99											
100											
101											
102											
103											
104							COMMENTS:				
105											
106											
107											
108											
109											
110											



EFFECTIVE DATE: 01/2007

SOP# 300

REVISION # 1

**CHLORIDE (COLORIMETRIC, AUTOMATED FERRICYANIDE, TRAACS 800)
TOTAL IN WATER**

Table of Contents

1.0	Applicable Analytical Methods.....	1
2.0	Matrix or Matrices.....	1
3.0	Method Detection Limits.....	2
4.0	Scope and Application.....	2
5.0	Method Summary.....	2
6.0	Definitions.....	2
7.0	Interferences.....	3
8.0	Safety.....	4
9.0	Equipment and Supplies.....	4
10.0	Reagents and Standards.....	5
11.0	Sample Collection, Preservation, Shipment, and Storage.....	6
12.0	Quality Control (QC).....	7
13.0	Calibration and Standardization.....	8
14.0	Procedure.....	8
15.0	Calculations.....	9
16.0	Method Performance.....	9
17.0	Pollution Prevention.....	10
18.0	Data Assessment.....	10
19.0	Corrective Actions.....	11
20.0	Waste Management.....	11
21.0	References.....	12
22.0	Attachments.....	12
	Signature Page.....	13

1.0 Applicable Analytical Methods

1.1 Chloride (Colorimetric, Automated, Ferricyanide), U.S. Environmental Protection Agency, Method 325.2, Methods for Chemical Analysis of Water and Wastes, 1983, Storet #00940.

1.2 Chloride (Colorimetric, Automated Ferricyanide), U.S. Environmental Protection Agency, Method 9251, Test Methods for Evaluating Solid Waste, SW-846, 1993.

2.0 Matrix or Matrices

2.1 Drinking water, surface water, ground water, and saline water.

2.2 Domestic and industrial wastes.

2.3 Leachates.

3.0 Method Detection Limits

3.1 All MDLs are performed according to the Code of Federal Regulations 40 CFR, Part 136, Appendix B. See internal procedure SOP 103.

3.2 The MDL was determined by analyzing seven replicate samples. Seven deionized (DI) water samples were spiked with chloride standard, to yield a theoretical concentration of .50 mg/L. The replicates were analyzed identical to normal samples.

3.3 Analytical results for the seven replicates were tabulated statistically. The MDL was calculated using a formula that applies the student t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See section 16.1.

3.4 The MDL for this method is determined annually or whenever there is a significant change in the procedure including a change in the analyst.

3.5 Reporting limit (RL) – The RL for this method has been set at 1.00 mg/L.

4.0 Scope and Application

4.1 This automated method applies to drinking, surface, ground and saline water, and domestic and industrial waste and leachates.

4.2 The applicable range is 1.00 to 100 mg/L chloride. The range can be expanded through dilution of the samples.

4.3 Approximately 30 to 50 samples per hour can be analyzed.

5.0 Method Summary

5.1 Thiocyanate ion is released from mercuric thiocyanate by the withdrawal of mercury by chloride to form soluble unionized mercuric chloride. The liberated thiocyanate combines with ferric ions to form highly colored ferric thiocyanate, which is then quantified at 480 nm.

6.0 Definitions

6.1 Analyte - Chloride.

6.2 Calibration Blank (CB) - Prepared by adding reagents to blank water in the same concentration as the samples and standards. The CB is used to zero the instrument, for all initial and continuing CB determinations, and to flush the system between samples and standards.

- 6.3** Initial Calibration Blank (ICB) - A CB analyzed at the beginning of the analysis run to demonstrate that the instrument is capable of acceptable performance.
- 6.4** Continuing Calibration Blank (CCB) - A CB analyzed in the course of the analysis run to demonstrate that the instrument is capable of continuous acceptable performance.
- 6.5** Calibration Curve - A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards (CALs) are prepared by successively diluting a standard solution to produce working standards that cover the working range of the instrument. Standards should be prepared at the frequency specified in this SOP. The CALs should be prepared using the same type of reagents and at the same concentration as will result in the samples following sample preparation.
- 6.6** Calibration Standard (CAL) - A solution prepared from the primary standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 6.7** Initial Calibration Verification (ICV) - Second source standards to check the accuracy of the CALs.
- 6.8** Continuing Calibration Verification (CCV) - A control standard analyzed in the course of the analysis run to demonstrate that the initial calibration determined remains valid throughout the course of the analytical run.
- 6.9** Laboratory Control Sample (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed and prepared exactly like a sample. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 6.10** Linear Calibration Range (LCR) - The concentration range over which the instrument response is linear.
- 6.11** Laboratory Duplicates (LD1 and LD2) - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.
- 6.12** MDL - The minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. See internal procedure SOP 103 for details.
- 7.0 Interferences**
- 7.1** There are no common significant interferences.

- 7.2 Sample turbidity and high color concentrations may interfere. Turbidity, which is usually noted by a noisy recorder peak, may be removed by centrifuging or filtering the samples. Color interference can be reduced by dilution.
- 7.3 Many uncommon anions such as bromide, iodide, cyanide, thiocyanate, and thiosulfate react stoichiometrically the same as chloride and would result in a positive interference if present in significant quantities. Alternatively, another method (such as ion chromatography) could be used.
- 8.0 **Safety**
- 8.1 Safety glasses and shoes that cover the feet are required in all designated laboratory areas.
- 8.2 It is recommended that the analyst wear gloves and a lab coat when performing this procedure.
- 8.3 The analyst must be familiar with the Laboratory Chemical Hygiene Plan.
- 8.4 The analyst must be familiar with the Laboratory Safety Policy (SOP 100).
- 8.5 The analyst must be familiar with any material safety data sheets applicable to this method.
- 8.6 The analyst must be familiar with the location of safety equipment including showers, eye wash stations, and spill kits.
- 8.7 The analyst should always thoroughly wash hands in warm soapy water when leaving the work area and before handling food or drink.
- 8.8 The analyst should assume that all samples have the potential to be hazardous and should always exercise caution when transporting, handling, and/or opening any samples.
- 8.9 General good laboratory practices are required. The analyst should take all necessary precautions in order to minimize the potential of exposure to samples and reagents used in this method.
- 9.0 **Equipment and Supplies**
- 9.1 Bran-Luebbe Traacs 800 system
- 9.1.1 Linear random access sampler.
- 9.1.2 Analytical console - Including pump control and air distributor.
- 9.1.3 Multi chemistry manifolds - Alkalinity, chloride, and sulfate.
- 9.1.4 Flowcell - .5 x 10 mm.
- 9.1.5 Filter assembly - 480 nm.
- 9.1.6 Colorimeters.

- 9.1.7 Software - Traacs.
- 9.1.8 Computer - IBM personal system 2.
- 9.1.9 Printer - Citizen MSD-20 dot matrix.
- 9.1.10 Voltage regulator - Sola MCR.
- 9.1.11 Vials - Bran-Luebbe, 5 mL, catalog #171-0354P01.

- 9.2 Bottles - 500 mL, plastic, with screw cap.
- 9.3 Diluter - Digital.
- 9.4 Volumetric flasks - 500 mL and 1000 mL capacity.
- 9.5 Analytical balance - Capable of weighing 0.1mg.
- 9.6 Calibration weights - For calibrating balance and verification.
- 9.7 pH strips.
- 9.8 Graduated cylinders - Various volumes.
- 9.9 Volumetric pipettes - 10 mL.
- 9.10 Beakers - Pyrex, 500 mL and 1000 mL.
- 9.11 Glass storage containers – Clear, amber.
- 9.12 Glass wool.

- 10.0 Reagents and Standards**
- 10.1 All reagents, solvents, and standards must be traceable to the stock inventory-tracking log.
- 10.2 All reagents, solvents, and standards must be labeled with: date received, date opened, expiration date, tracking number, and receiver's initials.
- 10.3 All prepared reagents and standards must be labeled with: date prepared, expiration date, preparer's initials, tracking number, diluent, and description.
- 10.4 All standard logbooks must be completely filled out.
- 10.5 All certificates of analysis must include the stock inventory tracking number that was assigned to the standard. Original certificates are kept by the Laboratory's Quality Assurance/Quality Control Officer.
- 10.6 All reagents are prepared with DI water. DI water is normal tap water that has been passed through a Millipore, Super Q™ water purification system and has an industry standard resistivity of 18MΩ.

- 10.7 Stock mercuric thiocyanate solution – Dissolve 4.17 g of mercuric thiocyanate in approximately 800 mL of methanol. Dilute to 1 L with methanol. Mix thoroughly. Filter.
- 10.8 Stock ferric nitrate solution – Dissolve 202 g of ferric nitrate in approximately 600 mL of DI water. Slowly add 31.5 mL of nitric acid while mixing. Dilute to 1 L with DI water. Mix thoroughly. Filter through filter paper. Store in a well sealed amber reagent bottle.
- 10.9 Chloride color reagent – Add 174 mL of stock mercuric thiocyanate and 174 mL of stock ferric nitrate solution to approximately 300 mL of DI water. Mix thoroughly. Dilute to 1 L with DI water. Mix thoroughly.
- 10.10 Diluent water – Use DI water.
- 10.11 Stock chloride standard, 1000 mg/L chloride – Purchased from VWR, EM-19897-1 or equivalent
- 10.12 Second source stock chloride standard (SSS), 1000 mg/L chloride – Purchased from I-CAL, ICCL1-5 or equivalent.
- 10.13 Working chloride standards

<u>mL Stock Chloride Standard</u>	<u>mg/L Chloride</u>
0.5	1.0
10.0	20.0
25.0	50.0 (CCV)
50.0	100.0

NOTE: Pipette required amount of stock chloride standard in a 500 mL volumetric flask. Bring to volume with DI water. Store in a 500 mL plastic bottle.

- 10.14 ICV – Add 25 mL of second source stock chloride standard (section 10.12) to a 500 mL volumetric flask and dilute with DI water to the mark. Store in a 500 mL plastic bottle; it is stable for one year.
- 10.15 LCS – Pipette 100 μ L of the SSS (section 10.12) into 4.9 mL of DI water to yield a 20 mg chloride/L in a test tube. Make fresh per analytical batch.
- 10.16 DVS – Pipette 1 mL of stock chloride standard (section 10.11) into 1000 mL volumetric flask, dilute to mark with DI water and mix. Store in a 1000 mL plastic bottle; it is stable for one year.

11.0 Sample Collection, Preservation, Shipment, and Storage

- 11.1 Samples are collected in 500 mL high-density polyethylene screw cap bottles. The bottles should be filled completely. The proper bottle code is MN.

- 11.2 Samples are stored at 4°C. Avoid freezing. No chemical preservation is necessary.
- 11.3 The recommended maximum holding time is 28 days. However, analysis should be completed as soon as possible.
- 12.0 **Quality Control (QC)**
- 12.0 The minimum QC for this method includes an initial demonstration of capability (IDOC), MDL determination, LCR, routine analysis of reagent blanks, fortified blanks, and other laboratory solutions as continuing checks on performance.
- 12.1 IDOC
- 12.1.1 Prior to analyzing samples by this method, the analyst must analyze 4 DI water samples spiked with the chloride standard and analyze as described in Section 13. The results are statistically tabulated to obtain the average percent recovery (X) and the standard deviation (s) of the percent recoveries. Obtained values for s and X are compared to the criteria in Section 12.3. If both s and X are acceptable, this method may be used to generate data. If s or X fails, the analyst must take corrective action and repeat the IDOC. The analyst must repeat the above steps until acceptable values for s and X are obtained.
- 12.2 System audits are checked at least once per analytical batch and are in control if the following criteria are met:
- 12.2.1 The sensitivity at 100 mg/L chloride is .69 to .84 au.
- 12.2.2 The correlation coefficient is .9995 to 1.000.
- 12.2.3 The CCV of 50 mg/L chloride is 45. to 55. mg/L.
- 12.2.4 The LCS of 20 mg/L chloride is 18. to 22. mg/L.
- 12.2.5 The ICV (second source standard) of 50 mg/L chloride is 45. to 55. mg/L.
- 12.2.6 The DVS of 1 mg/L chloride quantification is .8 mg/L to 1.2 mg/L.
- 12.3 Sample audits are to be analyzed with the frequency of 1 per every 1 to 15 samples, 2 per every 16 to 30 samples, etc.
- 12.3.1 Duplicate samples, should be within percent difference of $\pm 10\%$.
- 12.3.2 Matrix spike (MS) samples are spiked with 100 μL of the second source stock chloride standard (1000 mg/L chloride) standard into 4.9 mL of sample. The spiked sample recovery should be 90% to 110%.
- 12.3.3 CCBs must be less than one half the RL (< 0.5 mg/L). If the blank is outside the limit, verify that there is no contamination. Prepare fresh if necessary and rerun until it is $< \frac{1}{2}$ RL.
- 12.3.4 CCV standards recovery must be within $\pm 10\%$ (90% to 110%). If the CCV is outside the limits, prepare fresh if necessary and rerun. If the CCV continues to fail, the analysis must be stopped and bracketed samples reanalyzed.
- 12.3.5 Proficiency audit samples are obtained from an independent source bi-annually. Two samples at different concentration levels are received for each evaluation. The samples are prepared and analyzed according to the provided instructions. The

results are then submitted to the source for evaluation. Participation in these studies is used as a means to independently monitor this method's performance and to compare its performance against that of the other participants.

13.0 Calibration and Standardization

- 13.1** Calibration of the instrument is performed according to Bran-Luebbe instrument protocol.
- 13.1.1** The baseline and gain are set manually. To set the baseline, a 0% CB is run and the baseline is set between 5% and 10% deflection of scale. To set the gain, the high CAL (100 mg/L) is run, and the gain is set between 90% to 95% deflection of scale.
- 13.1.2** After the baseline and gain have been set, the primer (100 mg/L chloride), gain, one 100 mg/L chloride standard, one 50 mg/L chloride standard, one 20 mg/L chloride standard, and one 1.00 mg/L chloride standard are run. The computer software calculates the standard curve and displays the correlation coefficient.
- 13.1.3** The software then calculates carryover drift by analyzing one 100 mg/L chloride standard and two 20 mg/L chloride standards.
- 13.1.4** If the criteria in Section 12 are met, the instrument is ready to run samples.
- 13.1.5** At the end of the run, two or three blanks and a gain are analyzed to check for carryover drift. The software automatically adjusts for the carryover drift and calculates sample concentration. The sample concentrations are then printed.

14.0 Procedure

- 14.1** Operate the Bran-Luebbe Traacs 800 system according to basic operating procedures in the operating manual.
 - 14.1.1** Change all DI water reservoirs.
 - 14.1.2** Turn on the compressed air to the instrument.
 - 14.1.3** Turn on the sampler.
 - 14.1.4** Engage the pump-tube platen.
 - 14.1.5** Start the peristaltic pump.
 - 14.1.6** Pump DI water through the system for 15 minutes.
 - 14.1.7** Connect the chloride color reagent lines.
 - 14.1.8** Continue pumping with the reagent lines attached until a stable baseline is achieved.
- 14.2** Manually set the base and gain after each new reagent is made for that particular analysis according to the Bran-Luebbe procedure.
- 14.3** Turbidity interference should be minimized through the analysis of supernatant or the centrifugation of the samples. Filtration may be used with proper precautions to prevent possible sample contamination due to extra handling.
- 14.4** Each run of samples should begin with two 100 mg/L standards (the first being the primer standard, and the second being the gain standard) followed by one 20 mg/L standard, one 50 mg/L standard, and one 5.0 mg/L standard. The 20 mg/L standard is also used to calculate the carryover factor. After every ten samples, a standard of

varying concentration (CCV) and two blanks (CCB) are analyzed to check the baseline and curve integrity. To minimize the affect of carryover, the instrument is operated at 30 samples per hour.

- 14.5** Starting the run – Check for a smooth baseline and good bubble pattern. Input the run with sample IDs and initial dilutions, if any, into the appropriate edit file. Save to disk. Print out run information. Return to chart. Run (CR). Start the run by choosing "F7". Follow the on-screen menu. Typing "control B" accepts and forces the baseline. While the analytical run is in progress, monitor the analysis for off-scale and irregular peaks and over-diluted samples. The QC audit samples should also be monitored.
- 14.6** Shut down – When the results of the run have printed out, disconnect the reagent lines. Place the reagent line into a system cleaning solution of 0.1 N HCl for 15 minutes followed by a 30 minute rinse with DI water. After approximately 30 minutes, lift the plattens from the pump tubes. Shut the pumps off. Turn off the sampler. Turn off the computer. Turn off the compressed air.
- 15.0** **Calculations**
- 15.1** The Traacs makes calculations minimal. Since it automatically calculates the baseline drift, change in sensitivity, and most of the carryover, the analyst looks at the peaks on the chart to verify that the peaks are well formed and compares blanks throughout the run. Data from bad peaks are rejected.
- 15.2** Diluted samples are calculated after baseline correction.
- 15.3** Calculation of the % recovery for Matrix Spike (MS) audits is as follows:
- $$\% \text{ Recovery AC} = (M/T)100$$
- M = Measured spike sample concentration.
T = Theoretical spike sample concentration - $T = (X + C)$.
C = Concentration of spiking standard.
X = Average concentration of the two duplicates used for precision.
- 16.0** **Method Performance**
- 16.1** MDL – An initial MDL was determined using 25 replicate analyses of a low level sample with a mean concentration of 9.803 mg/L of chloride resulting in a standard deviation of 0.196 mg/L of chloride and an MDL of 0.671 mg/L of chloride at 95% confidence. MDL studies are determined annually for this method using the Code of Federal Regulations 40 CFR, Part 136, Appendix B and internal procedure SOP 103.
- 16.2** Precision – Using surface water samples with mean concentrations of 9.803 mg/L, 50.086 mg/L, and 89.361 mg/L, the standard deviations were 0.196 mg/L, 0.100 mg/L and 0.276 mg/L, respectively.

- 16.3 Accuracy – Using a surface water sample with a mean concentration of 9.803 mg/L and spiked using 10 mg/L of chloride and 50 mg/L of chloride, the mean spike sample recoveries were 96.7% and 99.7%, respectively.
- 16.4 RL – After examining several factors such as normal precision of samples near the RL, normal blank levels, and the MDL, the RL has been set a 1.00 mg/L chloride.
- 17.0 **Pollution Prevention**
- 17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Whenever feasible, staff should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.
- 17.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.
- 17.3 For information concerning pollution prevention which may be applicable to laboratory operations, consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N. W., Washington, DC 20036.
- 18.0 **Data Assessment**
- 18.1 Analytical data reported must be within the linear range of the assay, (>1.00 mg/L and <100 mg/L).
- 18.2 Data is reported to a maximum of three significant figures and no decimals as follows: X, XX, XXX, or XX0.
- 18.3 Dilutions must be greater than 10% of full scale to be reported (i.e., the diluted sample results must be >10 mg/L).
- 18.4 Dilutions increase the RL (i.e., RL of 1.00 mg/L multiplied by the dilution factor).
- 18.5 Appropriate laboratory reporting codes for dilutions, interferences, holding times, improper preservation, etc., will be appended to the test result according to laboratory policy. See internal procedure SOP 106.
- 18.6 Precision and accuracy data for an analytical batch must be within the acceptance criteria stated in Section 12 before the data can be reported. Standards and controls must be within the acceptance criteria stated in Section 12 before the data can be reported.

- 18.7 Out-of-range values must be diluted, rerun, and acceptable before they can be reported.
- 18.8 Suspected samples with carryover must be rerun for verification before they can be reported.
- 18.9 The Unit Manager reviews all data before the final reporting out of results.
- 19.0 **Corrective Actions**
- 19.1 Preventative maintenance is done on a routine basis. A maintenance logbook is kept with the instrument.
- 19.2 Pump tubes are changed at least every three months.
- 19.3 If the relative absorbance starts to decline, new chloride color reagent is prepared.
- 19.4 If a sample produces a negative baseline on the chart, the pH of the sample is determined. If the sample itself is determined to have a low pH by comparing the pH of other neutral samples, the sample result is reported as interference. If, upon investigation, the sample has a low pH due to contamination with an acid preservative, a new sample is analyzed from a different neutral bottle of the sample if available. If a different neutral sample is not available, the sample result is reported as interference and qualified with a P code to indicate sample was not preserved correctly.
- 19.5 An ion balance is calculated for samples with results for alkalinity, chloride, sulfate and dissolved calcium, magnesium, sodium, and potassium. If the ion balance is out by more than $\pm 10\%$, it is investigated, and samples are reanalyzed if necessary. High iron concentrations may cause the ion balance to be $> \pm 10\%$.
- 20.0 **Waste Management**
- 20.1 Liquid waste that is generated by the assays include mercuric nitric acid waste and color reagent and sample waste. The waste containers are labeled with the type of waste, the notation "hazardous waste" if hazardous, and the operator's initials. The hazardous waste containers are held until the monthly waste collection occurs and a licensed hazardous waste disposal company can properly dispose of them. The color reagent/sample waste can be disposed of down the drain with copious amounts of water.
- 20.2 Broken/waste glass is collected at the bench in a plastic pail until transferred to a collection barrel for disposal.
- 20.3 Excess samples and dilutions can be disposed of down the drain with copious amounts of water if they do not contain other hazardous material (i.e., samples from an industrial site, etc.) that requires them to be handled as a hazardous waste.

21.0 References

- 21.1 Chloride (Colorimetric, Automated, Ferricyanide), Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, Method 325.2 (issued 1978), EPA-600 4-79-020, Cincinnati, Ohio, March 1983, Storet #00940.
- 21.2 Chloride (Colorimetric, Automated Ferricyanide), Test Methods for Evaluating Solid Waste, SW-846, U.S. Environmental Protection Agency, Method 9251, 1993.
- 21.3 United States Code of Federal Regulations, Title 40, U. S. Government Printing Office, Washington, DC, Appendix A & B.
- 21.4 Methyl Orange Alkalinity, Technicon TRAACS 800™ Method, Industrial Method No. 788-86T, February 1987.
- 21.5 Chloride: Automated Ferricyanide Method, Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, 20th Edition 1998, Method 4500-Cl-E, p 4-70 to 4-71.

22.0 Attachments

- 22.1 Manifold diagram.
- 22.2 Sample batch sheet for anions.

Signature Page

APPROVED BY *P. B. H. Acary* DATE 2/13/07
CHIEF, LABORATORY SERVICES SECTION

APPROVED BY *Joseph J. Kuntz* DATE 2/13/07
COMPLIANCE OFFICER

APPROVED BY *Sharon Hendry* DATE 2/8/2007
QA OFFICER

APPROVED BY *Landra K. Gregg* DATE 1-8-2007
UNIT MANAGER

APPROVED BY *Louis C. Ultes, TB* DATE 1-5-2007
ANALYST

Attachment 23.1

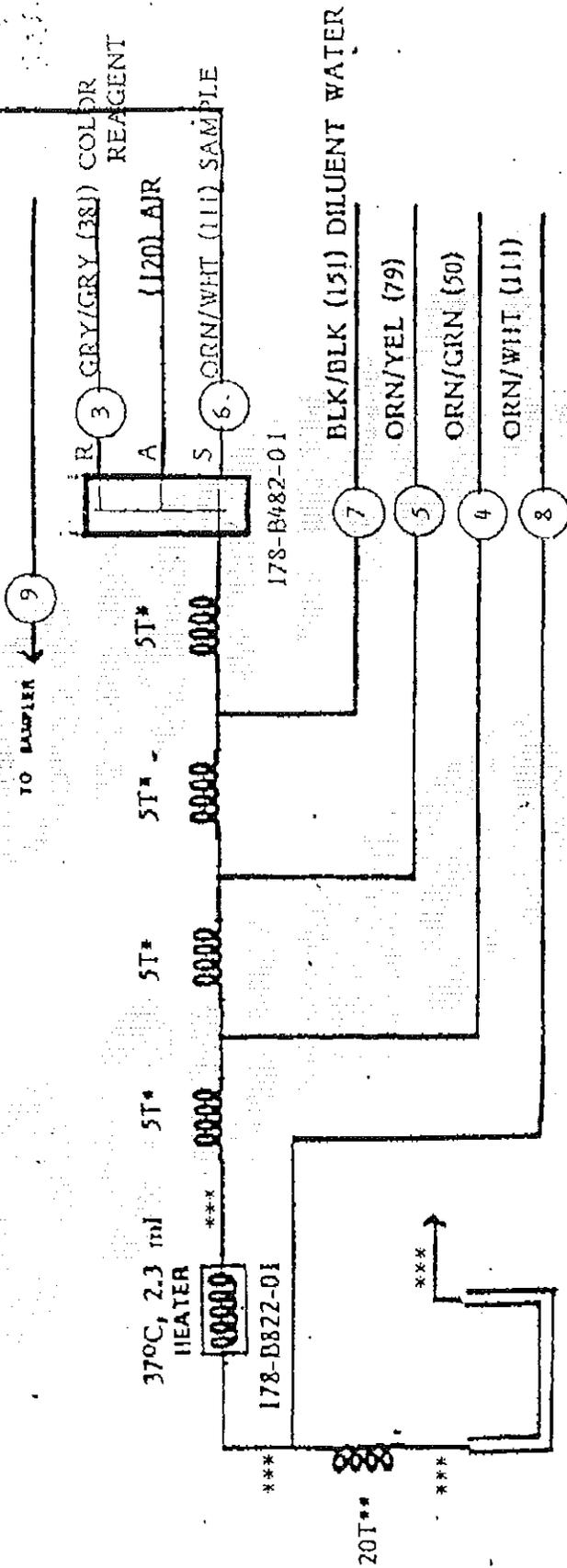
MANIFOLD NO.
165-D000-01

METHOD NO. 783 86T

ENVIRONMENTAL MULTI-TEST CARTRIDGE

CHLORIDE

RANGE: 2.0-100.0 mg/L



COLORIMETER
1/c - 10 x 0.5 mm I.D.
165-D030-02
= 480 mm

NOTES: NUMBERS IN PARENTHESES DENOTE FLOWRATES IN UL/MIN.

CIRCLED NUMBERS ARE PUMP TUBE POSITIONS

*165-G005-01

**165-G005-03

***DENOTES 0.030" x 0.062" I.D. POLYETHYLENE TUBING

Attachment 22.2

DATE: _____
ANALYST: _____

ANIONS

RUN # _____

#	ORDER #	SAMPLE #	ALK	CL	SO4	COMMENTS	QUALITY CONTROL		
1	HIGH STD						ALKALINITY		
2	HIGH STD						STD		RANGE
3	MID STD						CCV		225-275 PPM
4	MID STD 2						ICV		225-275 PPM
5	LOW STD						LCS		225-275 PPM
6	ICB						REL. ABS.		.54-.66
7	CCV						COR COEF.		.9995-.9995
8									
9							PRECISION		DIFF %DIFF
10									
11									
12									
13							ACCURACY		%REC 90-110
14									
15									
16		PC							
17		MS					CHLORIDE		
18		CCB					STD		RANGE
19		CCV					CCV		45-55 PPM
20							ICV		45-55 PPM
21							LCS		18-22 PPM
22							REL. ABS.		.68-.84
23							COR COEF.		.9995-.9995
24									
25							PRECISION		DIFF %DIFF
26									
27									
28									
29							ACCURACY		%REC 90-110
30									
31									
32		PC							
33		MS					SULFATE		
34		CCB					STD		RANGE
35		CCV					CCV		45-55 PPM
36		LCS					ICV		45-55 PPM
37		ICV					LCS		18-22 PPM
38							REL. ABS.		.36-.44
39							COR COEF.		.9995-.9995
40									
41							PRECISION		DIFF %DIFF
42									
43									
44									
45							ACCURACY		%REC 90-110
46									
47									
48									
48							COMMENTS:		
50									
51									
52									
53									
54									
55									

Attachment 22.2

DATE: _____

ANALYST: _____

ANIONS

RUN # _____

#	ORDER #	SAMPLE #	ALK	CL	SO4	COMMENTS	QUALITY CONTROL				
							PRECISION	DIFF	%DIFF		
56							ALKALINITY				
57							PRECISION		DIFF	%DIFF	
58											
59											
60											
61											
62											
63							ACCURACY			%REC 90-110	
64											
65											
66											
67											
68											
69											
70											
71											
72											
73							PRECISION		DIFF	%DIFF	
74											
75											
76											
77											
78											
79							ACCURACY			%REC 90-110	
80											
81											
82											
83											
84											
85											
86											
87											
88											
89							PRECISION		DIFF	%DIFF	
90											
91											
92											
93											
94											
95							ACCURACY			%REC 90-110	
96											
97											
98											
99											
100											
101											
102											
103											
104											
105											
106											
107											
108											
109											
110											
							COMMENTS:				



EFFECTIVE DATE: 11/2006

SOP# 361

REVISION # 0

ABSORBANCE (COLOR) MEASUREMENT BY SPECTROPHOTOMETRY

Table of Contents

1.0	Applicable Analytical Methods.....	1
2.0	Matrix or Matrices.....	1
3.0	Method Detection Limits (MDLs).....	2
4.0	Scope and Application.....	2
5.0	Method Summary.....	2
6.0	Definitions.....	2
7.0	Interferences.....	3
8.0	Safety.....	3
9.0	Equipment and Supplies.....	4
10.0	Reagents and Standards.....	4
11.0	Sample Collection, Preservation, Shipment, and Storage.....	5
12.0	Quality Control (QC).....	5
13.0	Calibration and Standardization.....	6
14.0	Procedure.....	7
15.0	Calculations.....	9
16.0	Method Performance.....	9
17.0	Pollution Prevention.....	9
18.0	Data Assessment.....	10
19.0	Corrective Actions.....	10
20.0	Waste Management.....	10
21.0	References.....	11
22.0	Attachments.....	11
	Signature Page.....	12

1.0 Applicable Analytical Methods

1.1 "204 B Color-Spectrophotometric Method", Standard Methods for Examination of Water and Wastewater, APAA, AWWA, WEF, 14th Edition, 1975, p. 66.

1.2 "NCASI Method Color 71.01 – Color Measurement in Pulp Mill Wastewaters by Spectrophotometry", National Council of the Paper Industry for Air and Stream Improvements, Inc. (NCASI), West Coast Regional Center, Organic Analytical Program, October 1999.

2.0 Matrix or Matrices

- 2.1 Drinking water, surface water, ground water, wastewater and saline water.
- 2.2 Domestic and industrial wastes.
- 3.0 **Method Detection Limits (MDLs)**
- 3.1 The estimated MDL achievable is instrument and light path length dependent.
- 3.2 All MDLs are performed according to the Code of Federal Regulations 40 CFR, Part 136, Appendix B. See SOP 103.
- 3.3 Analytical results for 7 replicates were tabulated statistically. The MDL was calculated using a formula that applies the student t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See section 16.1.
- 3.4 The MDL for this method is determined annually or whenever there is a significant change in the procedure including a change in the analyst.
- 3.5 Reporting limit (RL) – The RL for this method has been set .007 absorbance units.
- 4.0 **Scope and Application**
- 4.1 This method applies to drinking, surface, ground, waste and saline water, domestic and industrial wastes.
- 4.2 The applicable range is .007 - .500 absorbance units. The range can be expanded through dilution of the samples.
- 5.0 **Method Summary**
- 5.1 This procedure utilizes a spectrophotometer to measure the absorbance of light as it passes through a sample at a wavelength set at 400 nm. The color is determined by multiplying the absorbance by 1000. Samples are reported as absorbance and the data user must multiple the results by 1000.
- 5.2 The term "color" represents the true color of an aqueous sample from which turbidity has been removed by centrifuging. Turbidity can cause the color value determined for a sample to be elevated due to an increase in light scattering. In this procedure, centrifuging is used to remove turbidity from the sample.
- 6.0 **Definitions**
- 6.1 Analyte – Absorbance.
- 6.2 Calibration Blank (CB) - Prepared by adding reagents to blank water in the same concentration as the samples and standards. The CB is used to zero the instrument,

for all initial and continuing blank determinations, and to flush the system between samples and standards.

- 6.3 Initial Calibration Blank (ICB) - A CB analyzed at the beginning of the analysis run to demonstrate that the instrument is capable of acceptable performance.
- 6.4 Calibration Standard (CAL) - A solution prepared from the primary standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 6.5 Laboratory Control Sample (LCS) or Second Source Standard (SSS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed and prepared exactly like a sample. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 6.6 Laboratory Duplicates (LD1 and LD2) - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.
- 6.7 MDL - The minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. See internal procedure SOP 103 for details.
- 6.8 Precision Control – A quality control audit consisting of two aliquots of the same sample, taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.
- 7.0 **Interferences**
- 7.1 Since very slight amounts of turbidity interfere with the determination, samples must be filtered or centrifuged prior to analysis.
- 7.2 The absorbance increases as the pH of an aqueous sample increases.
- 8.0 **Safety**
- 8.1 Safety glasses and shoes that cover the feet are required in all designated laboratory areas.
- 8.2 It is recommended that the analyst wear gloves and a lab coat when performing this procedure.
- 8.3 The analyst must be familiar with the Laboratory Chemical Hygiene Plan.
- 8.4 The analyst must be familiar with the Laboratory Safety Policy (SOP 100).

- 8.5 The analyst must be familiar with any material safety data sheets applicable to this method.
- 8.6 The analyst must be familiar with the location of safety equipment including showers, eye wash stations, and spill kits.
- 8.7 The analyst should always thoroughly wash hands in warm soapy water when leaving the work area and before handling food or drink.
- 8.8 The analyst should assume that all samples have the potential to be hazardous and should always exercise caution when transporting, handling, and/or opening any samples.
- 8.9 General good laboratory practices are required. The analyst should take all necessary precautions in order to minimize the potential of exposure to samples and reagents used in this method.
- 9.0 **Equipment and Supplies**
- 9.1 Milton Roy Spectronic 1001 Plus Spectrophotometer
- 9.2 16 x 125 mm Borosilicate disposable culture tubes
- 9.3 Centrifuge
- 9.4 200-1000 μ L pipet with corresponding tips
- 9.5 5-10 mL pipet with corresponding tips
- 9.6 1-5 mL pipet with corresponding tips
- 9.7 Parafilm Laboratory Film
- 9.8 Culture tube racks
- 9.9 50 mL beaker
- 10.0 **Reagents and Standards**
- 10.1 All reagents, solvents, and standards must be traceable to the stock inventory-tracking log.
- 10.2 All reagents, solvents, and standards must be labeled with the date received, date opened, expiration date, tracking number, and receiver's initials.
- 10.3 All prepared reagents and standards must be labeled with the date prepared, expiration date, preparer's initials, tracking number, diluent, and description.

- 10.4** All standard logbooks must be completely filled out.
- 10.5** All certificates of analysis must include the stock inventory tracking number that was assigned to the standard. Original certificates are kept by the Laboratory's Quality Assurance/Quality Control Officer.
- 10.6** All reagents are prepared with DI water. DI water is normal tap water that has been passed through a Millipore, Super Q™ water purification system and has an industry standard resistivity of 18MΩ.
- 10.7** Stock Platinum Cobalt Solution (PCS) (.500 absorbance units @ 400 nm) – purchased. Stock solutions for absorbance do not need to be refrigerated, but care should be taken to protect the standards from evaporation, light and contamination. Check for signs of concentration or formation of precipitates prior to analysis. Replace the stock solution if a change in concentration is indicated by the inability to meet the criteria specified in the quality control section (section 12).
- 10.8** Detection Verification Standard (DVS) .010 absorbance units: Dilute 2 mL of the .500 PCS (section 10.7) to 100 mL with deionized water. Standard solutions for absorbance do not need to be refrigerated, but care should be taken to protect the standards from evaporation, light and contamination.
- 10.9** Second Source Standard - .250 absorbance units @ 400 nm – purchased. Standard solutions for absorbance do not need to be refrigerated, but care should be taken to protect the standards from evaporation, light and contamination.
- 11.0** **Sample Collection, Preservation, Shipment, and Storage**
- 11.1** Samples are collected in 500 mL high-density polyethylene screw cap bottles or equivalent. The bottles should be filled completely. The proper bottle code is GN.
- 11.2** Samples are stored at 4°C. Avoid freezing. No chemical preservation is necessary.
- 11.3** The recommended maximum holding time is 48 hours. The absorbance should be read as soon as possible following sample collection.
- 12.0** **Quality Control (QC)**
- 12.1** The minimum QC for this method includes an initial demonstration of capability (IDOC), and ongoing analyses of standards and blanks as a test of continued performance.
- 12.2** IDOC
- 12.2.1** Prior to analyzing samples by this method, the analyst must analyze 4 samples that are homogeneous and of known concentration. All 4 samples must be from the same known source. Test the 4 samples according to the procedure stated in 14.0 –

14.5.9. The results are statistically tabulated to obtain the average percent recovery (X) and the standard deviation (s) of the percent recoveries. Obtained values for s and X are compared to the criteria in Section 15.3.1 – 15.5. If both s and X are acceptable, this method may be used to generate data. If s or X fails, the analyst must take corrective action and repeat the IDOC. The analyst must repeat the above steps until acceptable values for s and X are obtained.

12.3 System audits are checked at a frequency of one for every 15 samples or at a minimum once per analytical batch and are in control if the following criteria are met:

12.3.1 Blanks

12.3.1.1 Demonstrate that the analytical system is free of absorbance by preparing and analyzing a blank with each sample set (15 samples or less). Prepare a method blank using the same procedure used for samples.

12.3.1.2 If absorbance of the blank is between -.001 and .001 it is in control and the analysis may continue. If the absorbance of the blank is not in control analysis is halted until the source of contamination is eliminated and a blank shows no evidence of contamination.

12.3.2 Sample and duplicate precision

12.3.2.1 Analyze a sample and duplicate with each sample set (15 samples or less) to assess the precision of the analyses. Calculate the relative percent difference (RPD) in absorbance for each sample and duplicate pair. The calculated RPD should be less than 20%.

12.3.3 Verification audits

12.3.3.1 Analyze a .250 PC second source standard prior to the analysis of each set of samples. If the absorbance of the .250 PC second source standard is between .225 and .275 it is in control and the analysis may continue. If the absorbance of the .250 PC second source standard is not in control analysis is halted until the standard is in control.

12.3.3.2 Demonstrate that the absorbance is detectable at the reporting limit using the detection verification standard (DVS). The DVS is in control if the absorbance is between .005 and .015. If the absorbance of the DVS is not in control analysis is halted until the standard is in control.

13.0 Calibration and Standardization

13.1 Pipet Calibration:

13.1.1 All pipets are calibrated on a quarterly basis and documented in a maintenance log that contains tolerance ranges of the pipets.

13.2 Spectrophotometer Calibration:

- 13.2.1** Fill the auto flow cell with DI water. Verify zero after every four to six samples using the same process.
- 13.2.2** Determine that the spectrophotometer system is operating within acceptable parameters by conducting standard checks before each set of analyses. The percent recovery determined for the standard check should be within the calculated warning limits. The absorbance determination may be sensitive to spectrophotometer and cell conditions. If the calibration check fails to meet the acceptance criterion, be sure the auto-pump is operating correctly and/or perform appropriate maintenance and reanalyze the standard check sample. If this fails to correct the calibration verification difficulties, prepare new standard and re-analyze.
- 13.2.3** Verify that the spectrophotometer is operating properly by periodically measuring an independent standard check sample. If all checks and adjustments fail to correct the problem, place a service call or electronically calibrate the instrument. To electronically calibrate the instrument first select the transmittance option and set the wavelength to 450 nm. With the 100% T/Zero control, set the display to read 100.0, insert an occluder in the sample well manually, and close the cover. Adjust the %T adjustment knob to read exactly 0.0 and remove the occluder. Re-measure independent standard check sample.

14.0 Procedure

- 14.1** Complete batch sheet in the SCN Color Book by writing sample identification numbers and QC parameters.
- 14.2** Obtain a 50 mL beaker and fill with deionized water and then fill a labeled 16 X 125 test tube approximately 2/3 full for a blank.
- 14.3** Label 16 X 125 test tubes to correspond to sample laboratory identification numbers. Turn spectrophotometer on to warm up for at least 30 minutes. Be sure the wavelength is set at 400 nm. If not, press "400" then "Go To λ ". Obtain all samples from GN storage refrigerator.
- 14.4 Preparation of samples:**
- 14.4.1** Pour enough of the sample from the sample bottle to fill a 16 X 125 test tube approximately 2/3 full. All sample tubes should be the same level. At least one sample per 15 samples must be poured off and analyzed in duplicate.
- 14.4.2** Place samples into the centrifuge; balance the centrifuge. Lock the centrifuge, set timer for 15 minutes, set speed at between 8 – 8.5 to give 2500 rpm. Press the start button. Once the timer has gone off and the red button is on to indicate the centrifuge has stopped spinning, you may open the centrifuge and remove the tubes.
- 14.4.3** Check samples to ensure they are clear; if not centrifuge again.
- 14.5** Analysis by Spectrophotometer:

- 14.5.1** Place sample collection tube into the blank. Gently pull up on arm to initiate pumping sample into the instrument's auto cell. Introduce air into the sample line by pulling inlet tube in and out of blank water, this allows for a smoother flow of sample. Once the spectrophotometer stabilizes, push "Second function" followed by "Zero" in order to zero the instrument. Next push "Print". Place sample collection tube into the blank once more and pull up on the arm to verify the blank is zeroed. Evacuate the water from the tubes by pulling up the arm two times.
- 14.5.2** Move the two waste tubes from the "Color Waste" bottle to the "Waste Platinum Cobalt Standard" bottle and secure. Fill a labeled test tube 2/3 full of the Stock Platinum Cobalt Solution .500 absorbance units. Place sample collection tube into the standard solution test tube. Gently pull up on the arm to initiate pumping the solution into the instrument's auto cell. Introduce air into the sample line by pulling the inlet tube in and out of the solution, this allows for a smoother flow. Once the spectrophotometer stabilizes, push "Print". Return the .500 concentration standard to the test tube rack.
- 14.5.3** Fill a labeled test tube 2/3 full of the Second Source Standard .250 absorbance units. Place sample collection tube into the standard solution test tube. Gently pull up on the arm to initiate pumping the solution into the instrument's auto cell. Introduce air into the sample line by pulling the inlet tube in and out of the solution, this allows for a smoother flow. Once the spectrophotometer stabilizes, push "Print". Return the .250 concentration standard to the test tube rack.
- 14.5.4** Fill a labeled test tube 2/3 full of the DVS .010 absorbance units. Place sample collection tube into the standard solution test tube. Gently pull up on the arm to initiate pumping the solution into the instrument's auto cell. Introduce air into the sample line by pulling the inlet tube in and out of the solution, this allows for a smoother flow. Once the spectrophotometer stabilizes, push "Print". Return the .010 concentration standard to the test tube rack. Evacuate the instrument by pulling up the arm two times. Return the waste tubes to the container titled "Color Waste" and the test tube containing the standard to the test tube rack.
- 14.5.5** Place sample collection tube into one of the samples. Gently pull up on the arm to initiate pumping sample into the instrument's auto cell. Introduce air in to the sample line by pulling inlet tube in and out of the sample, this allows for a smoother flow. Once the spectrophotometer stabilizes, push "Print" and return the sample to test tube rack. Record the absorbance in the SCN Color Book to the corresponding sample number. If any of the samples have an absorbance higher than that of the 500 µg/L absorbance, then a dilution is required to bring the sample into the operating range. The lowest dilution that brings the sample into the operating range, should be used. Dilutions should be made at 1:2, 1:5, 1:10, 1:100, 1:1000 etc.
- 14.5.6** Repeat 14.5.3 for all sample tubes.
- 14.5.7** Once all samples are read, evacuate the instrument by pulling up the arm two times.
- 14.5.8** Change the waste lines from the "Color Waste" container to the "Waste Platinum Cobalt Standard" container and secure. Place sample collecting tube into the test tube with the .500 Platinum Cobalt Standard. Gently pull up on the arm to initiate pumping standard into the instrument's auto cell. Introduce air into the sample line by pulling the inlet tube in and out of the standard, this allows for a smoother flow. Once the spectrophotometer stabilizes, push "Print" and dump the remaining standard from the test tube into the "Waste Platinum Cobalt Standard" container.

Evacuate the instrument by pulling up the arm two times. Return the waste lines to the "Color Waste" container.

- 14.5.9** Place sample collecting tube into the blank test tube containing deionized water. Gently pull up on the arm to initiate pumping water into the instrument's auto cell. Introduce air into the sample line by pulling the inlet tube in and out of the water, this allows for a smoother flow. Once the spectrophotometer stabilizes, push "Print".
- 14.5.10** Purge the instrument with deionized water 3 - 4 times, allowing blank water to remain in the auto cell. Turn off spectrophotometer and cover.
- 14.5.11** Dump sample tube contents into sink making sure to rinse with copious amounts of water. Dispose of tubes into glass waste. Calculate results (Section 15) and enter results into computer software.

15.0 Calculations

- 15.1** Absorbance units are read directly from the spectrophotometer, no calculations are required unless a dilution was used. If a dilution was used the absorbance unit from the spectrophotometer is multiplied by the dilution factor (i.e. if 1:2 dilution absorbance unit is multiplied by 2). Record this value.
- 15.2** Results less than .007 absorbance units are reported as "ND" indicating not detected.
- 15.3** Calculate %RPD for the LD1/LD2 samples as follows:

$$\%RPD = \frac{|LD1 - LD2|}{(LD1 + LD2)/2} \times 100\%$$

Where: LD1 is the sample and LD2 is the sample duplicate

16.0 Method Performance

- 16.1** MDL – A current MDL was determined using 7 replicate analyses of a diluted standard with a mean concentration of .0037 absorbance units resulting in a standard deviation of 0.0005 and an MDL of .0015 absorbance units at 95% confidence. MDL studies are determined annually for this method using the Code of Federal Regulations 40 CFR, Part 136, Appendix B and SOP 103.
- 16.2** RL – After examining several factors such as normal precision of samples near the RL, normal blank levels, and the MDL, the RL has been set at .007 absorbance units.

17.0 Pollution Prevention

- 17.1** Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Whenever feasible, staff should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

- 17.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.
- 17.3 For information concerning pollution prevention which may be applicable to laboratory operations, consult Less is Better: Laboratory Chemical Management for Waste Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N. W., Washington, DC 20036.
- 18.0 **Data Assessment**
- 18.1 Data is reported to a maximum of two significant figures and as follows: .0XX, .XX0, X.X, or XX.
- 18.2 Appropriate laboratory reporting codes for dilutions, interferences, holding times, improper preservation, etc., are entered into the qualifier field in the laboratory information management system for the sample according to laboratory policy. See SOP 106.
- 18.3 Precision and accuracy data for an analytical batch must be within the acceptance criteria stated in Section 12 before the data can be reported. Standards and controls must be within the acceptance criteria stated in Section 12 before the data can be reported.
- 18.4 The Lead-worker, Laboratory Scientist or Unit Manager reviews all data before the final results are reported.
- 19.0 **Corrective Actions**
- 19.1 A maintenance logbook is kept with the instrument to document any issues that occur.
- 19.2 Any sample not analyzed within the 48 hour hold time is coded "H." See SOP 106.
- 19.3 If the quality control audits set in section 12 are not met, the analysis is repeated.
- 20.0 **Waste Management**
- 20.1 Liquid waste that is generated by the assays includes platinum cobalt acidic standards and sample waste. The sample waste can be disposed of down the drain with copious amounts of water. Any platinum cobalt acidic standards waste should be disposed of in a one-gallon waste container specifically for acidic metals waste. Once the container is nearly full it is transported in a safe manner (SOP 100) to the basement and placed in the hazardous waste storage room for proper disposal.

- 20.2 Broken/waste glass is collected at the bench in a plastic pail until transferred to a collection barrel for disposal.
- 20.3 Excess samples can be disposed of down the drain with copious amounts of water if they do not contain identified hazardous material (i.e., samples from an industrial site, etc.) that requires handling and proper disposal as hazardous waste.
- 21.0 **References**
- 21.1 "204 B Color-Spectrophotometric Method", Standard Methods for Examination of Water and Wastewater, APAA, AWWA, WEF, 14th Edition, 1975, p. 66.
- 21.2 "NCASI Method Color 71.01 – Color Measurement in Pulp Mill Wastewaters by Spectrophotometry", National Council of the Paper Industry for Air and Stream Improvements, Inc. (NCASI), West Coast Regional Center, Organic Analytical Program, October 1999.
- 22.0 **Attachments**
- 22.1 Sample batch sheet.

Signature Page

APPROVED BY _____ DATE _____
CHIEF, LABORATORY SERVICES SECTION

APPROVED BY _____ DATE _____
COMPLIANCE OFFICER

APPROVED BY _____ DATE _____
QA OFFICER

APPROVED BY _____ DATE _____
UNIT MANAGER

APPROVED BY _____ DATE _____
ANALYST