Appendix C

QAPP
White Pond Watershed Management Plan

Quality Assurance Project Plan

White Pond Watershed Management Plan
Concord, Massachusetts

PREPARED FOR:
Town of Concord
Division of Natural Resources
141 Keyes Road
Concord, Massachusetts 01742

PREPARED BY:
ESS Group, Inc.
401 Wampanoag Trail, Suite 400
East Providence, Rhode Island 02915

ESS Project No. C596-000

Revised September 26, 2013

QUALITY ASSURANCE PROJECT PLAN
White Pond Watershed Management Plan
Concord, Massachusetts

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PROJECT MANAGER/QA OFFICER

9/27/2013
DATE

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Abbreviation	Definition
CLM	Certified Lake Manager
cm	Centimeter
GPS	Global Positioning System
ESS	ESS Group, Inc.
g	Gram
L	Liter
MassDEP	Massachusetts Department of Environmental Protection
MassDOT	Massachusetts Department of Transportation
mg	Milligram
mL	Milliliter
PE	Professional Engineer
PG	Professional Geologist
Premier	Premier Laboratory
PWS	Professional Wetland Scientist
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
SOGs	Standard Operating Guidelines
SOPs	Standard Operating Procedures
TKN	Total Kjeldahl nitrogen
TSS	Totals suspended solids
Town	Town of Concord, Massachusetts
µg	Microgram
µS	Microsiemen
USEPA	United States Environmental Protection Agency

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APPENDICES

1.0 DISTRIBUTION LIST AND PROJECT PERSONNEL SIGN-OFF SHEET

The distribution list and project personnel sign-off sheet is encompassed on the Title and Approval Page, located at the front of this document.

2.0 PROJECT ORGANIZATION

ESS Group, Inc. has been contracted by the Town of Concord to assist with the development of a watershed management plan. Carl Nielsen will be the ESS Project Manager and also serve as the project internal Quality Assurance (QA) Officer. The Project Manager will be responsible for coordinating all field and laboratory efforts as well as serving as a direct contact for all parties involved with the project. Responsibilities of the QA Officer will be primarily associated with ensuring that personnel serving the project are properly trained in all appropriate procedures relating to sample collection and data generation. The QA Officer will regularly verify that the items described in this QAPP are being followed. Additionally, the QA Officer will verify conformance with project reporting deadlines and data quality objectives, and ensure that project deliverables satisfy contract provisions.

This QAPP will direct field and laboratory activities for the White Pond Watershed Management Plan. ESS will conduct all field sample collection activities, as appropriate. Premier Laboratory, a Massachusetts certified laboratory, will provide analytical services for all sediment and water quality parameters (except those analyzed in the field by ESS personnel).

The project organizational chart (Figure 1) describes the principal officials and investigators associated with the project and illustrate the pathways of communication that will be utilized.

2.1 Communication Pathways

Carl Nielsen of ESS will serve as Project Manager and will coordinate all field and office work to ensure that it meets the standards established for the project and that work is performed in a timely manner. Mr. Nielsen will also act as QA Officer and will review fieldwork, lab reports, and client deliverables for acceptability. He will ensure that all involved personnel are properly trained in appropriate protocols and will review reports for accuracy and completeness. In addition, Mr. Nielsen will provide regular progress updates to Delia Kaye, the Project Supervisor from the Town, for the duration of the project.

Field data collection will be primarily conducted by the following key personnel: Matt Ladewig, Dan Herzlinger, Eliza Moore, and Alex Patterson. They will be responsible for conducting field work at White Pond and developing project deliverables. These staff will report directly to Mr. Nielsen.

Senior ESS staff including Jeffrey Hershberger and Lauren Caputo may assist the Project Manager with reporting oversight and engineering feasibility on the project. They will coordinate with the field data collection team, as needed, and report to Mr. Nielsen.

GIS data management and mapping will be conducted by Collin Smythe and overseen by Gordon Perkins. Mr. Perkins will ensure that all GIS work completed is accurate and appropriately presented.

In the event that the QAPP requires substantial modification, Carl Nielsen will contact the Project Supervisor from the Town before proceeding with any further project activities.

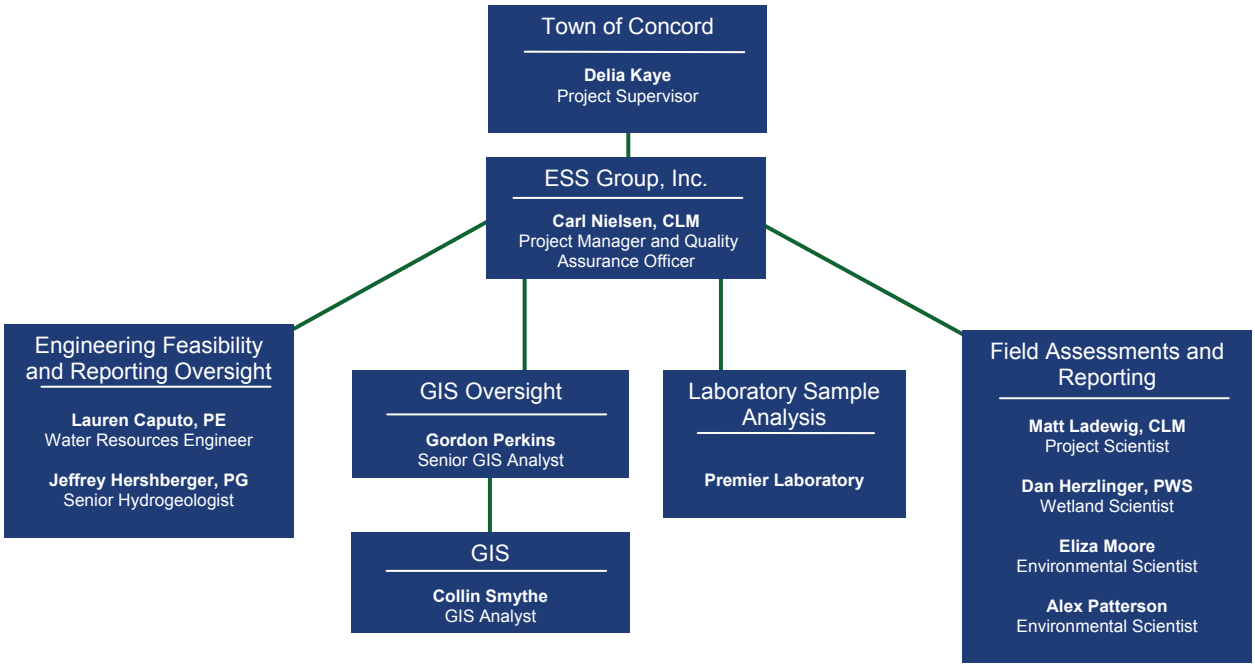


Figure 1. Organizational Chart for the Project

2.2 Personnel Responsibilities and Qualifications

A summary of personnel responsibilities and qualifications for key members of the ESS project team is presented below.

Carl Nielsen, CLM, Project Manager/Quality Assurance Officer and Primary Contact Person. Mr. Nielsen is a Certified Lake Manager and has an MS degree in Fisheries and Wildlife. Mr. Nielsen has over 23 years of experience in aquatic ecosystem assessment and management. Mr. Nielsen has been personally responsible for conducting over 60 similar lake or pond diagnostic and feasibility assessments, many of which he has used to develop comprehensive lake and watershed management plans. Mr. Nielsen has also specialized in the investigation and management of algal and water quality related problems and nuisance aquatic vegetation. Mr. Nielsen has been a Senior Water Resource Scientist for more than 175 aquatic resource studies ranging in size from small pond and stream systems to analyses of entire watershed systems. For this project, Mr. Nielsen will prepare for and attend all project meetings and presentations, manage and oversee all fieldwork and be responsible for preparing the draft and final reports. He will also be the quality assurance officer and serve as the primary point of contact for the project.

Matt Ladewig, CLM, Project Scientist. Mr. Ladewig is a Certified Lake Manager and holds an MS degree in Aquatic Resource Ecology and Management. He has 10 years of experience in the monitoring, modeling, and management of aquatic ecosystems. Mr. Ladewig has completed studies on over 50 lakes and ponds for water suppliers, lake associations, and state and municipal governments. He has also developed and implemented numerous surface water sampling, sediment testing, and biomonitoring programs (including those targeting macroinvertebrates and cyanobacteria). Mr. Ladewig also maintains current macroinvertebrate taxonomic certifications with the Society for Freshwater Science. On this project, he will serve as Project Scientist leading field surveys and assisting Mr. Nielsen with project implementation and reporting.

***Jeffrey Hershberger, PG, Senior Hydrogeologist*.** Mr. Hershberger is a Professional Geologist with over 22 years of experience and an MS degree in Geology. Mr. Hershberger's professional experience emphasizes aquifer hydraulics as related to groundwater flow, analysis of the fate and transport of nutrients and other contaminants in the subsurface, aquifer remediation, aquifer yield, capture zone modeling for remedial design and wellhead protection, groundwater/surface water interactions and development of conceptual site models of hydrogeology and subsurface transport. Related field experience includes performance and field management of subsurface investigations, multi-media sampling events, and water supply exploration and aquifer testing programs. Project management experience includes site investigations under various state regulations, complex field sampling programs, water supply development and water resource evaluation and assessment. For this project, Mr. Hershberger will work to evaluate the hydrology of the White Pond watershed and determine how management actions in White Pond may be impacted by these systems.

Lauren Caputo, PE, Water Resources Engineer. Ms. Caputo is a licensed professional engineer with eight years of experience in water resources, specializing in surface water modeling, watershed management, and stormwater management. Her experience includes hydrologic and hydraulic modeling, surface water quality modeling, flood mapping studies, stormwater management design, NPDES compliance, and strategy development. She has project management experience in assisting MassDOT in the implementation of the Impaired Waters Program to help determine if stormwater runoff from MassDOT roads impacts impaired water bodies across the state. Ms. Caputo is well-versed in AutoCAD and GIS as well as P8 Urban Catchment Model, Interconnect Channel and Pond Routing Model (ICPR), Stormwater Management Model (SWMM), Hydraflow Storm Sewers, and HEC-RAS. She will be responsible for making recommendations regarding management options for improving the storm water drainage issues associated with White Pond and providing cost estimates for any watershed BMPs or other structural restoration efforts.

Dan Herzlinger, PWS, Environmental Scientist. Mr. Herzlinger is a Professional Wetland Scientist with over nine years of experience conducting ecological field studies, wetland delineations, environmental permit review/preparation, natural resource site assessments, environmental inspection/construction oversight, wildlife habitat evaluations and rare species surveys. Mr. Herzlinger's range of project experience includes the siting and permitting of energy generation facilities and infrastructure, commercial development, lake management and watershed assessments for non-point source pollution. He has expertise in the use of GIS, sub-meter accuracy GPS, laser rangefinder and methodology for conducting visual assessments. Mr. Herzlinger has a strong working knowledge of the Massachusetts Wetlands Protection Act and its implementing regulations, and as the Conservation Agent for the Town of Acushnet, Massachusetts, he oversaw the administration and enforcement of the Act. Mr. Herzlinger will be responsible for assisting with field assessments associated with the White Pond project, particularly wetland analysis, water quality data collection and the identification of aquatic plants and organisms.

Gordon Perkins, Senior GIS Analyst. Mr. Perkins has more than 10 years of experience in site design, GIS, and visualization. He has developed and applied several methodologies in project visualization and GIS that have successfully endured rigorous peer review. In addition, Mr. Perkins is experienced in site design, and permitting in support of restoration projects. He specializes in design communication through the creative use of 2D and 3D computer applications to create perspective renderings, site plans and animations. With a strong background in Landscape Architecture and permitting, he successfully integrates site solutions that are functional, environmentally conscious, and aesthetically pleasing. On this project, Mr. Perkins will be responsible for producing high-quality GIS-based graphics to support the project report.

Alex Patterson, Environmental Field Scientist. Mr. Patterson has a BS in Wildlife & Conservation Biology and over four years of professional experience. He has conducted ecological field studies throughout

the eastern United States and abroad. He has worked on numerous lake and pond projects throughout southern New England, which have included bathymetry surveys, water quality monitoring, sediment mapping and sampling, wetland delineation, aquatic plant mapping, benthic invertebrate sampling, wildlife habitat evaluations, stream flow monitoring, and spatial analysis of data using GIS. On this project, he will be an Environmental Field Scientist responsible for collecting water quality and sediment samples, collecting plankton samples, and completing other biological sampling in accordance with field collection protocols.

Eliza Moore, Environmental Scientist. Ms. Moore has a BS degree in Biology and an MS degree in Marine Zoology and over three years of experience conducting biological assessments in freshwater and marine ecosystems. Ms. Moore is experienced in the collection of field data including aquatic plant mapping and bathymetry. For this project Ms. Moore will assist with field investigations and the creation of data tables.

Collin Smythe, GIS Analyst. Mr. Smythe has a degree in Geography and six years of professional experience. Mr. Smythe worked extensively for Vermont Department of Environmental Conservation evaluating watersheds using a combination of field work and GIS software to site stormwater BMPs for over 8 different municipalities. Mr. Smythe will be applying those skills to the White Pond Watershed project.

2.3 Special Training Requirements/Certification

The Project Team has extensive experience in water quality and sediment sampling, aquatic plant and bathymetry mapping, watershed water quality modeling, and pond and watershed management. Carl Nielsen and Matt Ladewig are both Certified Lake Managers (CLMs) and have extensive years of experience in limnology and lake management. Additionally, Dan Herzlinger is a Professional Wetland Scientists (PWS) with training in identification and mapping of aquatic and emergent vegetation.

No special training or certification courses were specifically attended in preparation for this project. However, ESS staff have received training in limnological field methods, including water quality sampling, bathymetry mapping, sediment sampling, and taxonomic identification from previous academic study, routine participation at conferences on the subject of lake management, as well as during informal ESS in-house training associated with a variety of similar projects throughout New England. Additional in-house training will be provided for ESS staff, as necessary, to meet project requirements.

3.0 PLANNING/PROJECT DEFINITION

3.1 Project Planning Meetings

Initial scoping of this project was defined by the Town in its Request for Proposals for this project. A project “kick-off” meeting was held on August 15, 2013 in order to clarify project goals and contract details.

3.2 Problem Definition/Site History and Background

White Pond is a relatively deep, 43-acre kettle pond. The pond has a small surface watershed of only approximately 158 acres. Watershed land use ranges from forest (including conservation land) to residential areas. As with all kettle ponds, these systems generally age over time, but this aging process can be accelerated by increased sediment and nutrient inputs from their surrounding watershed due to development. Over time, these systems become susceptible to algal blooms as nutrients accumulate within the pond.

This study has been designed to help identify the likely primary source(s) of nutrient and sediment inputs and develop a set of prioritized management actions to reduce or eliminate these sources, with the goal of improving water quality, preventing algal blooms, and ensuring that the pond’s many resources can be enjoyed by current and future generations of residents and visitors.

Work will be conducted under the guidance of this QAPP, which is compatible with US EPA and MassDEP guidelines and developed specifically for the White Pond project. All laboratory water quality and sediment analysis will be performed by Premier Laboratory, a Massachusetts certified laboratory.

4.0 PROJECT DESCRIPTION AND SCHEDULE

This project is designed to document key physical, chemical and biological aspects of White Pond and its watershed. These data will be used to develop a watershed management plan to ensure the future protection of the pond. Development of the White Pond Watershed Management Plan will be partially supported by existing data. The primary data gaps requiring project-specific data acquisition include the following:

1. **Conduct a Bathymetric Survey –** Determine the pond's water depth contours.
2. **Conduct Sediment Sampling –** Determine the contribution of internal recycling to nutrient loading at White Pond.
3. **Document Nutrient and Sediment Loading in the White Pond Watershed** – Sample water quality in White Pond and its watershed for nutrients and TSS.
4. **Sample Point Source Water Quality** – Identify and sample point sources discharging to the pond, if present.
5. **Assess Biological Resources –** Conduct an assessment of aquatic macrophytes.

In order to successfully achieve the goals and objectives stated above, ESS will complete project tasks according during the seasonal and weather conditions appropriate to each. The project began August 15, 2013 and will be completed within one year.

5.0 TECHNICAL DESIGN FOR FIELD SAMPLING

5.1 Bathymetry

White Pond will be surveyed via sonar, marked rod, and/or weighted line at a minimum of 50 points along appropriately spaced transects to determine the lake's maximum depth and define the water depth contours (bathymetry) (Figure 2). Measurements will be made at points along appropriately spaced transects and data will be recorded using a Trimble GeoXT GPS (or similar device) with sub-meter accuracy. Information generated will be used to produce a figure depicting the water depth contours. This information will be incorporated into the assessment of White Pond's hydrologic and nutrient budgets and be used to determine the area of pond bottom that becomes anoxic during summer stratification. ESS personnel will follow the SOGs for the creation of a bathymetry map (Appendix A), to conduct an assessment of the bathymetry of White Pond.

5.2 Sediment Sampling

Sediment samples will be collected from areas likely to be contributing to internal nutrient recycling within the pond (i.e., soft sediments located in hypoxic or anoxic waters below the thermocline). A single sample for laboratory analysis will be composited from three sediment grabs. The proposed location for collection of the sediment sample is shown in Figure 3.

Sediment grabs will be collected with an Ekman stainless steel dredge sampler that samples an area of approximately 0.025 m^2. ESS will transfer the sediment sample to Premier for analysis of nutrients (total phosphorus and total nitrogen). Analyses will also be completed for selected metals (iron, aluminum, calcium, and magnesium) known to bind phosphorus.

Path: G:\GIS-Projects\Concord - Whites Pond\Bathymetry.mxd

Drawing Date: 2013/08/29

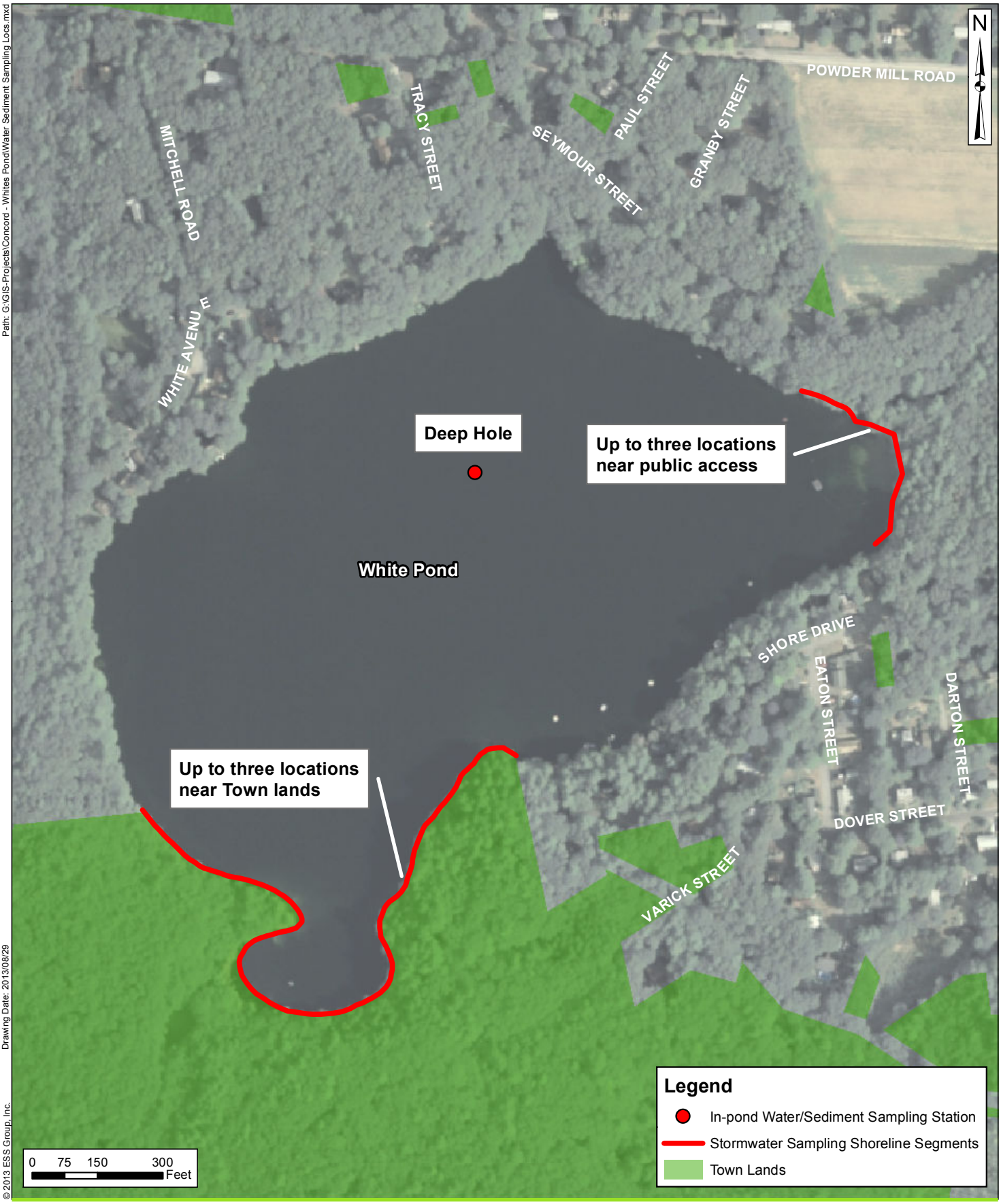
White Pond
Concord, Middlesex County, Massachusetts

1 inch = 300 feet

Source: 1) MassGIS, Landuse Data, 2005
2) USGS Topography

Proposed Bathymetry Transects

Figure 2



Path: G:\GIS-Projects\Concord - Whites Pond\Water Sediment Sampling Locs.mxd

Drawing Date: 2013/08/29

ess group
environmental consulting & engineering services

White Pond
Concord, Middlesex County, Massachusetts

1 inch = 300 feet

Source: 1) MassGIS, Orthos, 2009
2) Town of Concord, Town Lands, 2013

Proposed Water Quality and Sediment Sampling Locations

Figure 3

5.3 Water Quality

Water quality sampling at White Pond will consist of surface and groundwater phases. Surface water quality will be measured or analyzed from White Pond and selected watershed sources. Groundwater quality will be measured or analyzed from samples collected within sediments along the shoreline of the pond.

(a) **In-pond Nutrient Water Quality:** ESS will collect one round of samples at two in-pond locations, including the surface and bottom of the deepest part of White Pond (Figure 3). The following parameters will be measured in the field in accordance with the SOGs outlined in Appendix A: dissolved oxygen, water temperature, specific conductance, pH, turbidity, and Secchi transparency. Water quality samples will also be sent to Premier and analyzed for nutrients (total phosphorus, nitrate nitrogen, and TKN). As a QA/QC measure of field sampling activities, duplicate samples will be incorporated into the sampling program at random to represent at least 5% of the total number of samples.

(b) **Point Source and Shoreline Erosion Water Quality Sampling:** No point sources of nutrients and sediment to the pond are currently documented. However, if storm water discharge pipes or other point sources are located during this study, the locations of each outfall will be recorded using a Trimble GeoXT GPS unit with sub-meter accuracy.

Given the heavy foot traffic through Town lands on the southwestern end of the pond and at the public access area on the eastern end of White Pond, it is likely that some portion of total nutrient and sediment loading may be generated from these priority areas. Therefore, watershed water quality sampling will focus on collecting runoff from eroded footpaths near the pond shoreline.

Example of GKY FirstFlush sampler installed for collection of road runoff.

Up to six locations will be selected for point source and/or shoreline erosion water quality sampling. Of these, up to three locations will be targeted at each of the priority shoreline areas (Figure 3). Sample volume from shoreline erosion locations will be collected using GKY FirstFlush samplers (see inset and specifications in Appendix B). These samplers can be installed prior to a storm and retrieved during or just after the storm. The flush design allows these samplers to sample shallow overland sheet flows that would be difficult to sample using standard grab sampling methodologies. Sample volume from any identified point sources would be collected using standard techniques consistent with ESS SOGs (Appendix A). The positions of each sampling location will be recorded using a Trimble GeoXT GPS unit with sub-meter accuracy. Sampling will be conducted following an antecedent period of at least 72 hours with less than 0.10 inches of precipitation.

Water quality parameters to be assessed by Premier will include total phosphorus, nitrate nitrogen, total Kjeldahl nitrogen, and TSS. ESS will also measure specific conductance, salinity, turbidity, temperature, dissolved oxygen and pH in the field.

(c) **Groundwater Input Sampling:** Groundwater is likely to be a significant source of flows, and possibly nutrients, through White Pond. Understanding the quantity and quality of these flows can be critical toward understanding why the system is no longer meeting its water quality goals.

Shallow groundwater seepage can be measured by installing devices called seepage meters. These devices are installed in pond shoreline sediments and closed to all surface inputs and outputs of water by sealing the top bung with a rubber stopper. A bag holding a known volume of water (typically 250 mL) is connected to seepage meter with a tube. The bag will take on or lose water based on the movement of groundwater into (inseepage) or out of (outseepage) the system. The area of pond bottom sealed by the meter is measured and, with the change of water volume in the bag, used to calculate the rate of shallow groundwater seepage.

ESS will deploy up to twelve seepage meters at six shoreline segments to measure the rate of in or out seepage. Shoreline segments were chosen to represent developed and forested land uses from both sides of the pond and provide information on how groundwater flows into and out of the pond (Figure 4). Two meters will be deployed in each shoreline segment: one to measure shallower groundwater seepage and one to measure deeper seepage rates. Seepage meters will be deployed for sufficient time to allow for measurable groundwater movement into or out of the meters.

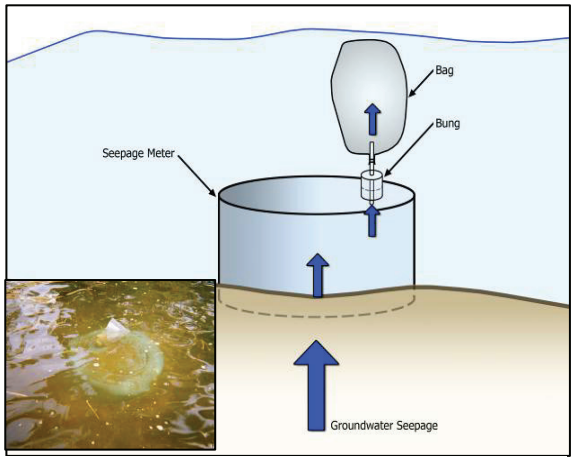


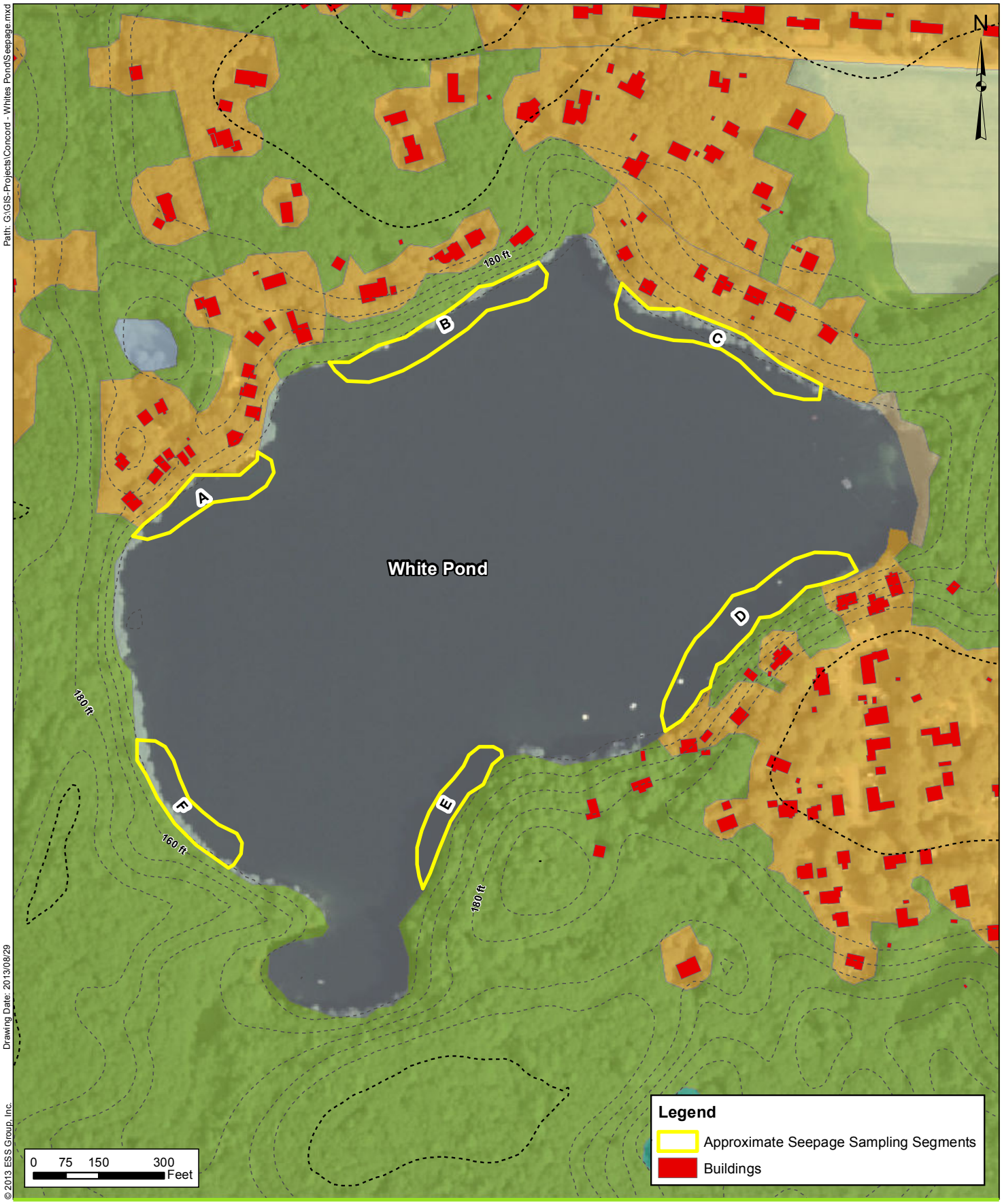
Illustration of seepage meter

ESS will also collect shallow groundwater samples from shoreline segments showing net groundwater inseepage. In addition to screening for septage in the groundwater, this will provide nutrient concentrations data that can be paired with seepage rates to estimate nutrient loading via groundwater. A stainless steel littoral interstitial porewater sampler, which is essentially a mini-well, will be used to extract samples from shoreline sediments for water quality testing. A minimum of three samples will be extracted from each shoreline segment and composited. Composite samples will be measured in the field for temperature, pH, and specific conductance. One composite sample from each shoreline segment will be sent to Premier for dissolved phosphorous, ammonia, and nitrate analysis.

5.4 Biological Assessments

An inventory of the aquatic plant community will be conducted for the purpose of describing species composition and abundance.

ESS will assess aquatic macrophyte cover and community composition in the pond from a boat, using plant rakes and direct observation. Plant species encountered will be identified using the most current



ess group
environmental consulting & engineering services

White Pond
Concord, Middlesex County, Massachusetts

1 inch = 300 feet

Source: 1) MassGIS, Landuse Data, 2005
2) USGS Topography
3) Town of Concord, Buildings, 2013

Proposed Seepage Sampling Segments

Figure 4

taxonomic keys. Taxonomic keys used to identify plants include: *A Guide to Aquatic Plants in Massachusetts* (New England Aquarium, 1999), *Aquatic and Wetland Plants of Northeastern North America* (Crow and Hellquist, 2000) and a series produced by the New Hampshire Agricultural Experiment Station (Crow and Hellquist, 1982).

If conditions warrant, ESS will also employ the use of an underwater video camera to aid in underwater plant mapping. This approach achieves results similar to the results that may be obtained by a diver. The data collected from this study will an update to conditions previously documented in the pond and evaluate the potential costs of various plant management techniques for White Pond. In the completion of this macrophyte survey, ESS personnel will follow a streamlined approach comparable to that outlined in the SOGs for the creation of an aquatic plant map (Appendix A).

Maps depicting the distribution of plant cover and plant biovolume will be created in GIS format. Locations of any exotic aquatic invasive species will also be noted.

6.0 ANALYTICAL PROCEDURES

Water quality samples (in-pond, shallow groundwater and storm water) and sediment samples will be collected in the field by ESS personnel using the appropriate containers and preserved as required by the lab. All field sampling will follow a streamlined approach comparable to that outlined in the appropriate SOGs (Appendix A).

Physical and chemical water quality parameters to be tested by ESS personnel in the field will include the following: flow rate, pH, specific conductance, turbidity, dissolved oxygen, clarity (Secchi disk depth), and temperature. All field meters will be calibrated in accordance with their respective operator's manual prior to fieldwork and as needed while in the field. In order to avoid cross-contamination, field equipment will be rinsed prior to each measurement using de-ionized water or thorough rinsing with surface water from the next station. Shallow groundwater flow rates will be measured using seepage meters. Stormwater flows will be measured by time of travel or volumetric (time to fill a known volume) methods, as dictated by the nature of the observed flow. Water quality and flow will be assessed in the field using instrumentation in accordance with the SOGs provided in Appendix A.

Surface water quality analytical parameters to be tested by Premier will include: nitrate nitrogen, total Kjeldahl nitrogen, total phosphorus, and TSS.

Groundwater quality analytical parameters to be tested by Premier will include dissolved phosphorus, nitrate nitrogen, and ammonia.

Sediment quality parameters to be tested by Premier will include total nitrogen, total phosphorus, iron, aluminum, calcium, and magnesium.

The laboratory testing programs for sediment quality and water quality are summarized in Table A below.

Table A. Water and Sediment Quality Sampling/Laboratory Parameters

Parameter	Sample Matrix	Number of Samples	Volume Needed	Sample Container	Sample Preservation	Maximum Hold Time	EPA #
Total Phosphorus *	Water	2 (dry)/as appropriate (wet)	250ml	Plastic	H_2SO_4, Ice	28 days	365.2
TKN *	Water	2 (dry)/as appropriate (wet)	250ml	Plastic	H_2SO_4, Ice	28 days	353.3
Nitrate nitrogen *	Water	2 (dry) as appropriate (wet) 6 (groundwater)	250ml	Plastic	Ice	28 days	353.2
TSS *	Water	2 (dry)/as appropriate (wet)	1000ml	Plastic	Ice	7 days	160.2

Parameter	Sample Matrix	Number of Samples	Volume Needed	Sample Container	Sample Preservation	Maximum Hold Time	EPA #
Dissolved Phosphorous[1]	Water	6	250 ml	Plastic	Ice (unfiltered) H_2SO_4 (filtered)	24 hours (unfiltered) 28 days (filtered)	365.2
Ammonia	Water	6	250 ml	Plastic	H_2SO_4, Ice	28 Days	350.1
Iron	Sediment	1	100g	Amber Glass	Ice	6 months	6010B
Aluminum	Sediment	1	100g	Amber Glass	Ice	6 months	6010B
Calcium	Sediment	1	100g	Amber Glass	Ice	6 months	6010B
Magnesium	Sediment	1	100g	Amber Glass	Ice	6 months	6010B
Total Phosphorous	Sediment	1	4 oz	Amber Glass	Ice	28 days	SM4500P-E
Total Nitrogen (TKN and Nitrite/Nitrate-nitrogen)	Sediment	1	4 oz	Amber Glass	Ice	28 days	SM4500NO_3-F, SM4500N_{org}-C

*Does not include field duplicates or dry-weather point source measurements.
[1] Samples will be laboratory filtered.

Table B summarizes the parameters to be measured in the field with respective EPA methods. Specific conductance, dissolved oxygen, temperature, pH and flow rate will be measured directly in the water column, where possible. Turbidity samples will be collected in glass or plastic containers and measured immediately in the field. Duplicate measurements will be collected at a 5% rate for quality control (QC) purposes.

Table B. Description of Field-measured Water Quality Parameters, Including Precision and Accuracy

Parameter	Flow Rate	Specific Conductance	Dissolved Oxygen	Turbidity	pH	Temperature
Sample Matrix	Water	Water	Water	Water	Water	Water
Number of Samples*	As appropriate	As appropriate	As appropriate	As appropriate	As appropriate	As appropriate
Sample Container	Instrument	Instrument	Instrument	Instrument	Instrument	Instrument
Hold Time	In Field	In Field	In Field	In Field	In Field	In Field
EPA Number	-	120.1	360.1	180.1	150.1	170.1
Expected Range of Field Measurements	0.3 – 100 cfs	0 to 1,500 µS	0 to 15 mg/L 0 to 150 % Sat.	0 to 1000 NTU	4 - 10 SU	-2 to 30 °C
Precision	0.1 cfs (Expected)	1% full scale	0.01 mg/L 0.1 % Sat.	0.01 NTU (Expected)	0.1 SU	0.1 °C
Accuracy	± 0.1 cfs (Expected)	± 1 % full scale	± 0.3 mg/L ± 2 % Sat.	± 2 %	± 0.1 SU	± 0.2 °C

*Does not include field duplicates or dry-weather point source measurements.

7.0 QUALITY CONTROL REQUIREMENTS

QC requirements are the system of technical activities that measure the performance of a process and will be utilized for field and laboratory analysis. Information on QC protocols followed in this project is provided in previous sections. A summary of quality controls to be utilized in the present study is provided in the following sections.

7.1 Bathymetry Mapping

By ensuring that the field bathymetry mapping plan is followed and creating GIS figures using SOGs (Appendix A), ESS will be certain to collect and report bathymetry data that are representative of the actual water depths in White Pond.

7.2 Sediment Sampling

By ensuring that the field sampling plan is followed, proper sampling techniques are used, proper analytical procedures are followed, and that sample holding times are not exceeded, ESS will be certain to collect and report water quality data that are representative of actual sediment conditions.

7.3 Water Quality Sampling

By ensuring that the field sampling plan is followed, proper sampling techniques are used, proper analytical procedures are followed, and sample holding times are not exceeded, ESS will be certain to collect and report water quality data that are representative.

The in-pond water sampling program has been designed to provide data representative of TKN, nitrate nitrogen, and total phosphorus in the pond. In addition, water quality parameters including temperature, Secchi disk depth, turbidity, pH, specific conductance, and dissolved oxygen will be measured in the field.

The storm water sampling program has been designed to provide data representative of TKN, nitrate nitrogen, total phosphorus and TSS being generated from the watershed and transported into the pond.

All equipment used in the field efforts will be calibrated, and data will be recorded in a consistent fashion. Duplicate field measurements of a single sample will be performed at a rate of approximately 5% and should agree within 10%. In general, if a discrepancy of greater than 10% is observed between the sample and its duplicate, the piece of equipment will be recalibrated and the sample will be reassessed.

7.4 Biological Assessments

Best efforts will be made to identify organisms in the field. However, plants that cannot be easily identified within the field due to either condition or development stage will be sampled and transported back to the ESS office in plastic bags for identification and/or verification using appropriate taxonomic keys, dissecting microscopes, and consultation with other in-house plant experts. This will ensure that identifications made are as accurate as possible.

7.5 Laboratory Analyses

The accuracy, precision, and sensitivity of laboratory analytical data are critical to achieving the QC acceptance criteria of the analytical protocols. With respect to parameters tested in the laboratory, QC requirements for precision, accuracy, and measurement range will be implemented according to Premier Lab's Quality Systems Manual and individual SOPs (Appendix C).

Duplicate water quality samples for lab analysis will be collected at a rate of 5% and should agree within 20%. In general, if a discrepancy of greater than 20% is observed between the sample and its duplicate, ESS will request that the lab reanalyze the sample for the analyte in question. ESS will contact the lab immediately to inquire about questionable data and determine whether the problem is due to a transcription error, equipment failure, or other issue. If necessary (and remaining sample volume, hold times, etc. allow), ESS will request that sample be reanalyzed.

8.0 DATA VALIDATION AND MANAGEMENT

Carl Nielsen, the Project Manager, will be in charge of ensuring the proper collection of data and preparation of tables and figures for the entirety of the project. The data will be compiled in Microsoft Excel and the narrative will be written in Microsoft Word format. Other data files (e.g., photos) will also be made available to the Town. GIS data will be managed in ESRI ArcMap 10.2.

8.1 Field Data

A permanently bound notebook with waterproof pages will be maintained for field sampling. All entries into the notebook will be made with indelible ink or pencil. Corrections will be made using a single line through the mistake with the initials of the individual who made them. Entries will include sampling location, time, date, weather conditions, personnel, parameters to be measured and associated data, as well as any problems encountered during sampling. Copies of data sheets will be checked regularly by the Project Quality Assurance Officer and will be made available for review upon request.

8.2 Laboratory Data

Analytical results will be recorded in a laboratory notebook, specific for each instrument and method. The automated analytical equipment will have computer generated analytical runs and any problems associated with the analytical runs will be flagged and noted. If any corrective action is taken, it will be noted in narrative in the instrument notebook.

The laboratory will provide ESS with the following deliverables:

- Sample data results for all field samples
- Internal and field duplicate sample results, as applicable
- A case narrative of any deviations from QA/QC criteria and observations about the samples that potentially affect sample or data quality (i.e., missed holding times, broken or leaking bottles, and reference standards or check standards outside criteria, etc.).

The following deliverables will not be required, but will be maintained by the laboratory as applicable and will be made available upon request:

- All raw data
- Duplicate laboratory recoveries and acceptance limits
- Matrix spike/matrix spike duplicate results and acceptance limits
- Method/reagent blank results
- Calibration standards/reference standards/LFB reports
- Copies of instrument logbooks
- Copies of internal chains of custody

All reports will be generated in digital form and will be available in hard copy format, as needed.

9.0 REPORTING

ESS will submit hard and electronic copies of the draft and final Watershed Management Plan report. GIS data and laboratory reports will also be provided.

10.0 DATA ACQUISITION REQUIREMENTS

This section describes protocols associated with data obtained from external sources (i.e., not collected during sampling). A range of readily available data and reports will be used to create a summary of the White Pond's historical and current condition. This will include review of reports as well as information

compiled by the White Pond Action Committee and external GIS data layers available through MassGIS and the Town to describe and summarize current and historical recreational use, community use, and ecological conditions. These data will supplement data collected by direct field-based sampling and will be used to help develop recommendations for the management of White Pond.

External qualitative data may be accepted for use if they provide useful contextual information about White Pond or its watershed. At the discretion of the QA Officer, external quantitative data collected under unknown or undocumented protocols may also be used to supplement project data but will not be relied upon solely to drive the modeling, analyses, or management recommendations of the White Pond Watershed Management Plan. External quantitative data clearly collected under inappropriate or erroneous protocols will not be used to develop the White Pond Watershed Management Plan.

11.0 ASSESSMENT AND RESPONSE ACTIONS

The QA Officer will provide oversight for each field data collection effort to ensure that protocols described in this QAPP are being followed. This duty includes ensuring that field equipment is properly calibrated, data are recorded in a consistent manner, and samples arrive at laboratories in a timely fashion.

The Project Manager will review the final report to ensure that appropriate methodology is adhered to and reported data is within the accepted range for each parameter. Any “outlier” data discovered will be reported in the final report, and potential sources of error will be described.

12.0 QUALITY MANAGEMENT REPORTS

Quality management reports serve to ensure that ESS and the review agency Town are regularly informed on the project status. To accomplish this goal, ESS will maintain regular contact with the Town, subconsultants and vendors, either through telephone, email, or in-person meetings.

13.0 VERIFICATION AND VALIDATION REQUIREMENTS

Data review, validation, and verification provide methods for determining the usability and limitations of data, as well as a standardized data quality assessment. ESS will be responsible for reviewing laboratory reports for completeness, correctness, and adherence to QC requirements. The Project Manager from ESS will review data received from the laboratories, to assess the data against applicable acceptance criteria. The laboratories conducting the analyses will conduct internal data verifications before submitting the data to ESS.

14.0 VERIFICATION AND VALIDATION PROCEDURES

All field notebook entries, chain-of-custody forms, and other records will be reviewed by the ESS Project Manager for completeness and correctness. Analytical data provided by the laboratories will be reviewed and validated internally to provide information on whether data are acceptable. The ESS Project Manager will be responsible for reviewing the laboratory reports and data packages, as well as data entries and transmittals, for completeness and adherence to QC requirements.

Results of the verification and validation processes will be presented in the project’s final report.

15.0 LITERATURE CITED

Crow, G.E. and Hellquist, C.B. 1982. Aquatic Vascular Plants of New England. New Hampshire Agricultural Experiment Station, University of New Hampshire, Durham, New Hampshire.

Crow, G.E. and Hellquist, C.B. 2000. Aquatic and Wetland Plants of Northeastern North America. University of Wisconsin Press, Madison, Wisconsin.

New England Aquarium, 1999. A Guide to Aquatic Plants In Massachusetts. New England Aquarium, Central Wharf, Boston, Massachusetts.

Appendix A

ESS Standard Operating Guidelines

STANDARD OPERATING GUIDELINESFOR THE CREATION OF A BATHYMETRY MAP

1.0 INTRODUCTION

1.1 Purpose and Applicability

This Standard Operating Guideline (SOG) provides basic instructions for the mapping of depth contours within standing waterbodies. The methods outlined below are intended (1) to standardize depth measurement techniques used by ESS Group field personnel; (2) to standardize the recording of depth measurements to ensure the creation of an accurate bathymetry map.

2.0 RESPONSIBILITIES

2.1 Project Manager

The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.

2.2 Field Personnel

The field personnel are responsible for taking accurate depth measurements at documented locations throughout the waterbody. The field personnel are also responsible for recording the number of depth measurements that will best characterize the bathymetric contours of the waterbody, i.e. steep contour areas with coves will be more thoroughly characterized than shallow contour areas with no coves.

3.0 REQUIRED MATERIALS

- The following materials are necessary for the creation of a bathymetry map:
- Boat
- Depth Probe
- Measuring Pole 10ft in length. Marked off in 1ft increments
- Enlarged outline of the waterbody on write-in-the-rain paper
- Global Positioning System (GPS) unit (optional)
- Field note book
- Historical bathymetric maps for the waterbody (optional)

4.0 METHOD

4.1 Depth Measurement Procedure

- A number of transects will be drawn on the map of the waterbody to act as a guide in the collection of depth measurements. The number and location of transects selected will depend on the size and shape of the waterbody, with the aim of thoroughly characterizing the bathymetric contours within it. Historical bathymetric maps can be used (if available) to guide in the selection of transect locations so that areas requiring more thorough characterization can be identified.
- The boat will be driven along each transect, at appropriately spaced points along the transect the boat will be stopped and a measure of the depth of the water at that point will be recorded.
- The number of depth measurement points will depend on the rate of change in depth as the boat is moved along each transect, i.e. the steeper the slope of the waterbody bottom, the more depth measurements will be taken in order to illustrate incremental changes in depth (i.e. 1ft, 2ft or 5ft increments).

- Each depth measurement point along the transect will be numbered and marked onto the map in order to later link depth data with location information. Locations may be estimated based on landmarks and shoreline morphometry or more precisely mapped using a Global Positioning Systems (GPS). The depth at each point will also be noted with its associated transect and point number in the field note book.
- At each measurement point when the depth is 10ft or less, a measuring pole will be used to measure the exact depth of the water in feet. At depths greater than 10ft a sonar depth probe will be used. This approach minimizes the possibility of plant growth interfering with sonar measurements.

4.2 Creation of Bathymetry Maps

- In the office, depth measurements recorded from throughout the waterbody will be linked with the transects and measurement point locations drawn onto the outline map.
- The known depths at known locations throughout the water body will then be used as a guide (or base) for the drawing of contour lines onto the outline map, thus illustrating incremental changes in water depth either in 1ft, 2ft or 5ft increments depending on the overall depth of the water body.

5.0 QUALITY CONTROL

At each depth measurement point, no matter which depth equipment is being used, a couple of measurements will be taken in very close proximity to each other to make sure the readings are the same, in case of rocks, plants, or other obstacles on the bottom are affecting the measurement at one specific point. In instances where the the measurements are slightly different, the average depth will be recorded.

6.0 DOCUMENTATION

Depth measurements will be recorded in field note books associated with location information in the form of transect numbers and depth measurements points, by ESS personnel. The locations of transect lines and depth measurement points will be recorded on a write-in-the-rain map outline of the waterbody. Any unanticipated site specific information, which requires ESS field personnel to deviate from the above SOG will be reported in an ESS field notebook. Documentation for recorded data must include a minimum of the following:

- Date of survey
- Weather conditions
- Signature or initials of person performing the survey
- Depth measurement point locations
- Comments/Observations

7.0 TRAINING/QUALIFICATIONS

To properly complete an assessment of depth contours within a waterbody, the analyst must be familiar with the measurement and data collection protocols as stated within this SOG and must have confidence in the use of depth measurement equipment.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF SPECIFIC CONDUCTANCE

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine calibration and operation of a variety of specific conductance meters. Although this meter measures additional parameters (e.g., temperature, TDS), this SOG addresses specific conductance measurement only (other capabilities are outlined in the appropriate SOG and manufacturer's individual instrument manuals). This SOG is designed specifically for the measurement of specific conductance in accordance with EPA Method 120.1 and Standard Method 2510 B which address specific conductance measurements of drinking, surface, and saline waters, domestic and industrial wastes, and acid rain.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (OAM) and may include duplicate or replicate measurements or confirmatory analyses.

2.0 RESPONSIBILITIES

The analyst is responsible for verifying that the specific conductance meter is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- Specific conductance meter
- Specific conductance meter manufacturer's instruction manual
- Deionized water
- KCI standard at concentration that approximates sample concentrations
- Lint-free tissues
- National Institute of Standards and Technology (NIST)-traceable thermometer
- Calibration sheets or logbook
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

- Specific conductance measurements should be taken soon after sample collection since temperature changes, precipitation reactions, and absorption of carbon from the air can affect the specific conductance. If specific conductance measurements cannot be taken immediately (within 24 hours), samples should be filtered through a 0.45 μm filter, stored at 4°C and analyzed within 28 days.
- Report results as specific conductance, μmhos/cm at 25°C.

- As temperature can affect the specific conductance measurements obtained, record both the specific conductance and the temperature of the sample. The Cole-Parmer Portable Conductivity Meter and YSI Model 85 have the ability to compensate for temperature.
- Secondary standards may be purchased as a solution from commercial vendors. These standards should not be used after their expiration dates as provided by the manufacturer. An expiration date of one year should be used if the manufacturer does not supply an expiration date or if the standards are prepared from various salts (e.g., KCI).

4.2 Calibration and Measurement Procedures

- The specific conductance meter must be calibrated daily (or the calibration checked) before any analyses are performed.
- Set up the instrument according to the manufacturer's instructions.
- Rinse the probe with deionized water and dry with a lint-free tissue.
- Dip the probe into the calibration standard. Immerse the probe tip beyond the upper steel band. Stir the probe gently to create a homogenous sample.
- Record the stabilized specific conductance reading of the standard and the temperature. Enter the calibration mode (according to manufacturer's instructions) and change the value on the primary display to match the value of the calibration standard. The meter can be adjusted to $\pm$ 20% from the default setting. If the measurement differs by more than $\pm$ 20%, the probe should be cleaned or replaced as needed. If the meter does not have automatic temperature compensation (ATC), correct all measurements to 25°C by adding 2% of the reading per degree if the temperature is below 25°C or by subtracting 2% of the reading per degree if the temperature is above 25°C.
- An additional check may be performed, if required by the project plan, by placing the probe into an additional KCI standard. This standard should be from a different source than the standard used for the initial calibration. This standard should read within 5% of the true value.
- Verify the calibration every 15 samples and at the end of the day. Recalibrate or replace the instrument if the check value is not within 15% of the true value.
- The probe will be rinsed with deionized water and wiped gently with a lint-free tissue between sample analyses.
- The meter must be recalibrated following any maintenance activities and prior to the next use.
- Conductivity data may be post calibrated using any of a variety of calibration data including, but not limited to field calibration points, manufacturer calibration data, and analytical results from samples collected during field deployment of the sensors. The decision criteria for post calibration, and the technique used will be specified in the project plan, and will be consistent with the manufacturer's recommendations.

4.3 Troubleshooting Information

If there are any performance problems with any of the specific conductance meters which result in inability to achieve the acceptance criteria presented in Section 5.0, consult the appropriate section of the meter instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department immediately for further instructions.

4.4 Maintenance

- Instrument maintenance should be performed according to the procedures and frequencies required by the manufacturer.
- The probe must be stored and maintained according to the manufacturer's instructions.
- If an instrument with ATC is being used, the meter should be checked annually for accuracy with an NIST thermometer.

5.0 QUALITY CONTROL

- The meter must be calibrated daily before sampling and recalibrated every 12 hours, and will not be used for sample determinations of specific conductance unless the initial check standard value is within 5% of the true value.
- Duplicate measurements of a single sample will be performed at the frequency specified in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within 10%.
- The temperature readout of the meter will be checked against an NIST traceable thermometer at least quarterly. If the difference is greater than 0.2°C, the instrument manufacturer will be consulted for instructions. Temperature measurements will be compensated for any difference with the reference thermometer.
- Some agencies may require the analysis of USEPA Water Pollution (WP) performance evaluation samples. These performance evaluation samples will be analyzed as required.

6.0 DOCUMENTATION

- All specific conductance meter calibration, temperature check, and maintenance information will be recorded on the daily calibration sheet (an example is presented as Figure 1). Specific conductivity data may be recorded on the appropriate laboratory or field data sheets or logbooks.
- Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:
    - Date and time of calibration
    - Signature or initials of person performing the measurement
    - Instrument identification number/model
    - Expiration dates and batch numbers for all standards
    - Reading for standard before and after meter adjustment
    - Readings for all continuing calibration checks
    - Temperature of standards (corrected for any difference with reference thermometer)
    - Comments
- Documentation for recorded data must include a minimum of the following:
    - Date and time of analysis
    - Signature or initials of person performing the measurement
    - Instrument identification number/model
    - Sample identification/station location

- Temperature (corrected for any difference with reference thermometer) and conductance of sample (including units and duplicate measurements) Note: show all calculations for converting instrument reading to μmhos/cm if the instrument provides readings in any other units. Useful conversions are: 1 mS/m = 10 μmho/cm or 1 μmho/cm = 0.1 mS/m.
- Comments

7.0 TRAINING/QUALIFICATIONS

To properly perform specific conductance measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.

Certain state certification programs require that specific conductance measurements be taken in the field by, or in the presence of, personnel that are qualified under the certification program.

8.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF DISSOLVED OXYGEN

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine measurement of dissolved oxygen using a polarographic sensor equipped dissolved oxygen meter with a digital read-out such as the YSI Model 55 Handheld Dissolved Oxygen System. Measurements are made in accordance with EPA Standard Methods that addresses dissolved oxygen measurement of drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory measurements.

2.0 RESPONSIBILITIES

The analyst is responsible for verifying that the dissolved oxygen measuring device is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- Dissolved oxygen meter with digital read-out device
- Manufacturer's instruction manual for the instrument
- YSI Model 5775 Standard Membrane Kit with KCl solution and O-rings
- NIST-traceable thermometer

Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

To achieve accurate dissolved oxygen measurements, samples should be analyzed *in situ*. Measurements in flowing waters should be made in relatively turbulent free areas. Measurements in standing waters will require probe agitation to create water movement around the probe.

4.2 Calibration and Measurement Procedures

To accurately calibrate the YSI Model 55, you will need to know the approximate altitude of the region in which you are located and the approximate salinity of the water you will be analyzing. Fresh water has a salinity of approximately zero. Seawater has an approximate salinity of 35 parts per thousand (ppt). If uncertain, measure salinity with an appropriate device.

- Ensure that the sponge inside the instrument’s calibration chamber is wet then insert the probe into the chamber. Turn the instrument on and wait for readings to stabilize (approximately 15 minutes).

- To calibrate, enter the calibration menu by pressing and releasing both the up and down arrow keys at the same time. Enter the altitude (in hundreds of feet) at the prompt by using the arrow keys to increase or decrease the altitude (example: 12 = 1,200 feet). Press enter when correct altitude is shown.
- The meter should display CAL in the lower left of the display with the calibration value in the lower right of the display and the current D.O. reading (before calibration) should be on the main display. Once the D.O. reading is stable, press ENTER. Enter the salinity at the prompt by using the arrow keys. Press ENTER when finished and the instrument will return to normal operation.
- Calibration should be performed at a temperature within ± 10°C of the sample temperature. Verify the calibration every 15 samples and at the end of the day.
- If erratic readings occur, replace membrane as per the manufacturer's manual. The average replacement interval is two to four weeks.
- Replace the membrane as per the manufacturer's manual if bubbles appear (>1/8 inch diameter), or if the membrane becomes damaged, wrinkled, or fouled.
- Avoid contact with any environment which contains substances that may attack the probe materials (e.g. acids, caustics, and strong solvents).
- The meter must be re-calibrated following any maintenance activities and prior to the next use.

4.3 Troubleshooting Information

If there are any performance problems with the dissolved oxygen-measuring device, consult the appropriate section of the instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department immediately for further instructions.

4.4 Maintenance

Instrument maintenance for meter-type dissolved oxygen measuring devices should be performed according to the procedures and frequencies required by the manufacturer.

5.0 QUALITY CONTROL

Duplicate measurements of a single sample will be performed at the frequency specified in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within ± 0.2 mg/L.

The temperature readout of the meter will be checked regularly (at least weekly) against a NIST-traceable thermometer. If the difference is greater than 0.5°C, the instrument manufacturer will be consulted for instructions. Temperature measurements will be compensated for any difference with the reference thermometer.

6.0 DOCUMENTATION

All dissolved oxygen meter calibration, checks, and maintenance information will be recorded on the daily calibration sheet or logbook. Dissolved oxygen data may be recorded on the appropriate laboratory or field data sheets or logbooks.

- Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:
    - Date and time of calibration
    - Signature or initials of person performing the measurement
    - Instrument identification number/model

- Expiration dates and batch numbers for all standard solutions
- Readings for all continuing calibration checks
- Comments

- Documentation for recorded data must include a minimum of the following:
  - Date and time of analysis
  - Signature or initials of person performing the measurement
  - Instrument identification number/model
  - Sample identification/station location
  - Dissolved oxygen, both in mg/L and percent saturation (corrected for any difference with reference thermometer) and temperature of sample (including units and duplicate measurements)
  - Comments

7.0 TRAINING/QUALIFICATIONS

To properly perform dissolved oxygen measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.

Certain state certification programs require that dissolved oxygen measurements in the field be taken by, or in the presence of, personnel that are qualified under the certification program.

8.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF FLOW RATE

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine measurement of flow rate in bodies of running water. The two techniques under consideration are the Time of Travel Method and the Global Flow Probe Procedure.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory measurements.

2.0 RESPONSIBILITIES

The analyst is responsible for verifying that the instrumentation is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for the Global Flow Probe Procedure:

- Global Flow Probe FP101, Global Water, Gold River, CA
- LCD computer display
- Radio Shack 675 HP or equivalent batteries
- Manufacturer's instruction manual for the instrument
- Laboratory or field data sheets or logbooks

The following materials are necessary for the Time of Travel Method:

- A neutral buoyancy floating object, such as a cracked ping-pong ball
- Twine or other heavy-duty string material
- Water proof yard-stick to measure stream depth
- Stop-watch
- Permanent marker (e.g., sharpie)
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 General Measurement Procedures For Global Flow Probe Procedure

To achieve accurate flow measurements samples must be analyzed in the field. Flow measurements may be taken in small and large streams, rivers and within pipes.

- The average velocity of stream flow multiplied by the cross-sectional area is equal to the flow rate (Q=VxA). The cross sectional area is determined manually by measuring the depth of the water at

several points across the channel. The cross section in square feet times the average velocity in feet per second gives the cubic feet per second (c.f.s.).

- When sampling within round pipes, one needs only to measure the water depth and then refer to the tables in the Global Flow Probe Instruction Manual to determine the cross-sectional area.

4.2 Calibration and Measurement Procedures for Global Flow Probe Procedure

The Flow Probe is set up and calibrated at the factory. The calibration sequence is entered automatically when the batteries are changed or by holding down both Right and Left buttons simultaneously for 8 seconds. Calibration should be checked annually.

- To change between English and Metric units and to enter the calibration sequence, hold down both Left and Right buttons simultaneously for 8 seconds. The Left button scrolls between English “mi” and Metric “km”.
- To check the calibration push the Right button to “CAL”. For “mi” calibration set Probe calibration to 33.31. For “km” calibration set Probe calibration to 1603. The Left button increases the number when the arrow points up and decreases the number when the arrow points down.
- The Flow Probe computer has a simple 2 – button operation. The Right button changes between Function and the Left button picks the Option. Pushing both buttons simultaneously for 1 second zeros the displayed value.
- By pushing the Right button you may scroll through the following functions. Velocity Function: “V” is instantaneous velocity to the nearest 0.1 feet per second. Push the Left button to scroll between “AV” (average velocity) and “MX” (maximum velocity) which reads out to the nearest 0.01 feet per second. Stop Watch / Clock Function: Push the Left button to start and stop watch.
- Make sure the prop turns freely and point the prop directly into the flow with the arrow on the bottom of the probe pointing down-stream.
- Press the Right button until the “V” for velocity appears and select the desired velocity parameters to be measured by pushing the Left button. Average velocity readings “AV” must be collected for flow rate measurements (c.f.s.).
- Put the probe at your measuring point and press both Right and Left buttons simultaneously and release to re-zero and begin recording. Hold in the flow for several seconds until you have steady average velocity.
- When sampling in small streams and within pipes, the probe should be moved slowly and smoothly along a vertical plane throughout the flow to ensure that the probe evenly samples the cross-sectional area of the flow.
- When sampling larger streams and rivers divide the stream into subsections (e.g. 2-3 feet in width). At the center of each subsection, insert the probe and sample vertically from the surface to the bottom smoothly to obtain a vertical average velocity profile. The Average Velocity times the Area of the subsection is the Flow for the subsection. Add all the subsection flows to obtain the Total Stream Flow.
- Repeat procedure three times in at least three different locations, recording data in field notebook. The flow rate should be calculated as an average of the three measurements taken at different locations within the channel or pipe.
- Calculate discharge (Q) from the measured data, as follows:

- Measure and calculate the cross-sectional area of your flow stream in square feet and multiply this by the average velocity in feet / second to obtain discharge in cubic feet per second (c.f.s.).
- Cross-sectional area (ft^2) x AV (ft/sec) = Q (ft^3/sec)

4.3 Calibration and Measurement Procedures for the Time of Travel Method

To measure travel time, the length of time taken for the floating object to travel 3 feet will be measured as follows:

1. Select an appropriate stream cross section with relatively uniform and uninterrupted flow
2. Securely attach 3 feet of string to floating object (i.e., cracked ping-pong ball)
3. Release floating object in the water and activate timer
4. Record time (T) from when the floating object is released to the time when the string goes taut, indicating that the object has traversed 3 feet
5. Repeat procedure three times at three different locations, recording data in a field notebook. The flow rate should be calculated as an average of the three measurements taken at different locations within the stream channel. Flow rate = 3 feet/T (seconds) = X feet / second
6. Measure stream average width and average depth at sampling location

- Calculate discharge (Q) from the measured data, as follows:

1. Calculate cross-sectional area (A) of the stream, by multiplying average width and average depth
2. Select a coefficient or correction factor (C): 0.8 for rocky bottom streams, 0.9 for muddy bottom streams. The coefficient allows correction for the fact that water travels faster at the surface than at the stream bottom, due to resistance from bottom materials
3. $Q = \frac{A*C*L}{T}$ Where L= 3 feet and T= time of travel (seconds)

   Units of Q are typically cubic feet per second

4.4 Troubleshooting Information for Global Flow Probe Procedure

If there are any performance problems with the Global Flow Probe, consult the appropriate section of the instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department at (916) 638-3429 immediately for further instructions.

4.5 Maintenance for Global Flow Probe Procedure

Instrument maintenance for the Global Flow Probe should be performed according to the procedures and frequencies required by the manufacturer.

5.0 QUALITY CONTROL

5.1 Quality Control for Global Flow Probe Procedure

The Global Flow Probe calibration should be checked annually to ensure that the Flow Probe is operating up to factory specifications.

5.2 Quality Control for the Time of Travel Method

To ensure a quality measurement, a minimum of three times of travel measurements will be obtained and recorded at each sampling point. An average value will be used to measure flow rate / discharge.

6.0 DOCUMENTATION

6.1 Documentation for Global Flow Probe Procedure

All Global Flow Probe calibration, checks, and maintenance information will be recorded on the daily calibration sheet or logbook. Flow data may be recorded on the appropriate laboratory or field data sheets or logbooks.

- Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:
  - Date and time of calibration
  - Signature or initials of person performing the measurement
  - Instrument identification number/model
  - Readings for all continuing calibration checks
  - Comments
- Documentation for recorded data must include a minimum of the following:
  - Date and time of analysis
  - Signature or initials of person performing the measurement
  - Instrument identification number/model
  - Sample identification/station location
  - Flow Rate in cubic feet per second (c.f.s.), average water velocity and maximum water velocity
  - Comments

6.2 Documentation for the Time of Travel Method

All data will be recorded in a field logbook. Documentation for recorded data must include a minimum of the following:

- Date, time and location of measurement
- Time of travel and distance traveled
- Comments, if any

7.0 TRAINING/QUALIFICATIONS

- To properly perform Global Flow Probe measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.
- Certain state certification programs require that flow measurements in the field be taken by, or in the presence of, personnel that are qualified under the certification program.
- No special training is required to implement the Time of Travel Method; however, the analyst must be familiar with the calibration and measurement techniques stated in this SOG.

8.0 REFERENCES

Volunteer Stream Monitoring: A Methods Manual. EPA 841-B-97-003, November 1997.

Global Flow Probe Instruction Manual.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF PH

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine calibration and operation of a variety of pH meters, including the YSI Model 55, Hydac Multimeter Probe and the pHep pH Testers. Although these meters may measure additional parameters (e.g., temperature, specific conductivity, etc.), this SOG addresses pH measurement only (other capabilities are outlined in the appropriate SOG and manufacturer's individual instrument manuals). This SOG is designed specifically for the measurement of pH in accordance with EPA Method 150.1 and Standard Method 4500-H B which address electrometric pH measurements of drinking, surface, and saline waters, domestic and industrial wastes, and acid rain.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory analyses.

2.0 RESPONSIBILITIES

- The analyst is responsible for verifying that the pH meter is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.
- The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials may be necessary for this procedure:

- pH meter
- pH meter manufacturer's instruction manual
- Deionized water
- 4.0, 7.0, and 10.0 buffer solutions
- Lint-free tissues
- Mild detergent
- 10% hydrochloric acid
- National Institute of Standards and Technology (NIST)-traceable thermometer
- Calibration sheets or logbook
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

4.1.1 To achieve accurate pH measurements, samples should be analyzed in the field (preferably within 15 minutes), or as soon as possible after collection. Sample should be collected in plastic or glass containers.

4.1.2 After measuring a sample containing oily material or particulate matter, the electrode must be cleaned by carefully wiping with a lint-free cloth, or washing gently in a mild detergent, followed by a deionized water rinse. If this does not suffice, an additional rinse with 10% hydrochloric acid (followed by deionized water) may be needed.

4.1.3 As temperature can affect the pH measurements obtained, both the pH and the temperature of the sample must be recorded. Both the Hydac Multimeter and the pHep Tester that will be used in this study have the ability to compensate for temperature.

4.1.4 Calibration must include a minimum of two points that bracket the expected pH of the samples to be measured. Calibration measurements must be recorded in logbook.

4.1.5 Primary standard buffer salts available from NIST can be purchased and are necessary for situations where extreme accuracy is required. Secondary standard buffers may be purchased as a solution from commercial vendors and are recommended for routine use. Buffers should not be used after their expiration dates as provided by the manufacturer. An expiration date of one year should be used if the manufacturer does not supply an expiration date or if the buffers are prepared from pH powder pillows, etc.

4.1.6 When using the meter in the laboratory, always place the buffer/sample beaker on the magnetic stirrer, and make sure the stirring bar is rotating during measurements. Rinse the stirring bar as well as the beaker between buffers/samples.

EXCEPTION: Do not use the magnetic stirrer for acid rain samples. It is crucial not to induce dissolved gases into the sample to be absorbed or desorbed, as this will alter the pH. Stir the sample gently for a few seconds after introducing the electrode, then allow the electrode to equilibrate prior to recording temperature and pH readings.

4.1.7 When the meter is being used in the field, move the probe in a way that creates sufficient sample movement across the sensor; this insures homogeneity of the sample and suspension of solids. If sufficient movement has occurred, the readings will not drift (<0.l pH units). Rinse the electrode with deionized water between samples and wipe gently with a lint-free tissue.

4.1.8 When measuring the pH of hot liquids, wait for the liquid to cool to 160°F or below.

4.1.9 Fluctuating readings may indicate more frequent instrument calibrations are necessary.

4.2 Calibration and Measurement Procedures

4.2.1 The pH meter must be calibrated daily before any analyses are performed. The meter should be re-calibrated every 12 hours or at the frequency specified in the project plan.

4.2.2 Connect the electrode to the meter. Choose either 7.0 and 10.0 (high range) or 4.0 and 7.0 (low range) buffers, whichever will bracket the expected sample range. Place the buffer in a

clean glass beaker. If the pH is being measured in a laboratory, place the beaker on the magnetic stirrer and place the stirring bar in the beaker. Measure and record the temperatures of the buffers using a calibrated thermometer or automatic temperature compensation (ATC).

4.2.3 Place the electrode into the 10.0 buffer or into the 7.0 buffer.

4.2.4 Adjust the instrument calibration according to the manufacturer's instructions. Discard the buffer and rinse the beaker and stirring bar thoroughly with deionized water.

4.2.5 Refill the beaker with the 7.0 buffer or the 4.0 buffer. Rinse the electrode, gently wipe with a lint-free tissue, and place it in the selected buffer solution. If the pH is being measured in a laboratory, place the beaker on the magnetic stirrer and place the stirring bar in the beaker. Continue adjusting the instrument calibration according to the manufacturer's instructions. Record the electrode slope (if provided by the instrument) on the calibration sheet (an acceptable slope is between 92 and 102 percent). Measure and record the temperature of the buffer using a calibrated thermometer or ATC. Discard the buffer and rinse the beaker and stirring bar thoroughly with deionized water.

4.2.6 An additional check may be performed, if required by the project plan, by placing the electrode into an additional buffer solution. This buffer should be from a different source than the buffers used for the initial calibration. This buffer should read within +0.2 pH units of the buffer's true pH value.

4.2.7 Verify the calibration every 15 samples and at the end of the day. Recalibrate the instrument if the check value varies more than 0.2 pH units from the true value.

4.2.8 The electrode will be rinsed with deionized water and wiped gently with a lint-free tissue between sample analysis.

4.2.9 Recalibrate the instrument if the buffers do not bracket the pH of the samples.

4.2.10 The meter must be re-calibrated following any maintenance activities and prior to the next use.

4.3 Troubleshooting Information

If there are any performance problems with any of the pH meters which result in the inability to achieve the acceptance criteria presented in Section 5.0, consult the appropriate section of the meter instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department immediately for further instructions.

4.4 Maintenance

4.4.1 Instrument maintenance should be performed according to the procedures and frequencies required by the manufacturer.

4.4.2 The electrode must be stored and maintained according to the manufacturer's instructions.

4.4.3 If an instrument with ATC is being used, the device should be checked on a quarterly basis for accuracy with an NIST thermometer.

5.0 QUALITY CONTROL

5.1 Duplicate measurements of a single sample will be performed at the frequency specified in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within ±0.l pH units.

5.2 The temperature readout of the meter will be checked annually against an NIST-traceable thermometer. If the difference is greater than 0.2°C, the instrument manufacturer will be consulted for instructions. Temperature measurements will be compensated for any difference with the reference thermometer.

5.3 Some regulatory agencies may require the analysis of USEPA Water Supply (WS) or Water Pollution (WP) performance evaluation samples. These performance evaluation samples will be analyzed as required.

6.0 DOCUMENTATION

6.1 All pH meter calibration, temperature check, and maintenance information will be recorded on the daily calibration sheet (Figure 1). pH data may be recorded on the appropriate laboratory or field data sheets or logbooks.

6.2 Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:

- Date and time of calibration
- Signature or initials of person performing the measurement
- Instrument identification number/model
- Expiration dates and batch numbers for all buffer solutions
- Reading for pH 7.0 buffer before and after meter adjustment
- Reading for pH 4.0 or 10.0 buffer before and after meter adjustment
- Readings for all continuing calibration checks
- Temperature of buffers (corrected for any difference with reference thermometer), including units
- Comments

6.3 Documentation for recorded data must include a minimum of the following:

- Date and time of analysis
- Signature or initials of person performing the measurement
- Instrument identification number/model
- Sample identification/station location
- Temperature (corrected for any difference with reference thermometer) and pH of sample (including units and duplicate measurements)
- Comments

7.0 TRAINING/QUALIFICATIONS

To properly perform pH measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.

Certain state certification programs require that pH measurements in the field be taken by, or in the presence of, personnel that are qualified under the certification program.

8.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

STANDARD OPERATING GUIDELINES FOR THE CREATION OF AN AQUATIC PLANT MAP

1.0 INTRODUCTION

1.1 Purpose and Applicability

This Standard Operating Guideline (SOG) provides basic instructions for the mapping of aquatic plants present within standing waterbodies. The methods outlined below are intended to, (1) standardize plant mapping techniques used by ESS Group, Inc. (ESS) field personnel; and (2) standardize recording of field data to assure the creation of an accurate plant map.

2.0 RESPONSIBILITIES

2.1 Project Manager

The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the survey in accordance with this SOG and the project plan.

2.2 Field Personnel

The surveyors are responsible for identifying dominant aquatic plant beds within the waterbody, establishing the locations of the beds using GPS, noting the percentage of plant cover and biovolume throughout the waterbody, keeping a species list of all plants identified within the waterbody and collecting clearly marked samples of all those plants unidentifiable in the field.

3.0 REQUIRED MATERIALS

The following materials are necessary (unless otherwise noted) for the creation of a plant map:

- Boat
- Long handled grappling rake
- Throw grappling rake (for deeper waters)
- Aquascope
- Plant keys
- Enlarged outline of the waterbody on water resistant paper
- Water resistant field notebook
- Small see-through plastic bags
- Indelible marker
- Cooler
- Ice
- GPS unit (Trimble GeoExplorer 2005 series recommended)
- Underwater camera (Optional – useful in deeper waters)

4.0 METHOD

4.1 Aquatic Plant Survey and Sample Collection

A number of transects will be drawn on the map of the waterbody to act as a guide for the survey. The number and location of transects selected will depend on the size and shape of the waterbody, with the aim of thoroughly characterizing the plants within it.

The boat will be driven along each transect; at pre-determined points along each transect, anchor will be dropped and a detailed survey of the aquatic plants will be carried out in the immediate area. The number

of points surveyed along each transect will depend on the bathymetry and plant diversity in the survey area, with the aim of characterizing changes in the composition, cover and biovolume of plant beds. Each point sampled along each transect will be numbered and recorded on the site map in order to link plant survey data with location information. Alternatively, records may be added electronically in the field, if this function is supported by the GPS unit used.

At each survey point a grappling rake will be used to sample aquatic plants from within the water column and the floor of the waterbody for closer identification.

Each plant present within each sample will be identified *in situ* (using keys if necessary) and recorded in the species list for the waterbody. The dominant plant at each transect point will be noted with its associated transect and point number in the field notebook.

If identification of certain plants is not possible in the field, a generous sample of these plants will be stored with a little water in a plastic bag clearly labeled with the associated transect and point number in indelible ink. All such sample bags will be stored in a cooler filled with ice to preserve the quality of the samples, and transported back to the lab for identification using a dissecting microscope, if necessary. Unknown plants will be assigned a code number (e.g. UK1) to use as species identification for future transects and sampling locations.

4.2 Assessment of Percentage Plant Cover and Percentage Plant Biomass

At each survey point ESS field personnel will use general observation as well as an Aquascope to estimate the percentage plant cover (i.e. the percentage of the bottom covered by plants, which is a factor of plant density). A simple code system will be used whereby percentage "ranges" are assigned an integer: i.e. 0 = 0%; 1 = 1%-25%; 2 = 26%-50%; 3 = 51%-75%; 4 = 76%-100%. At each survey point the estimation of plant cover will be recorded with the associated transect and point number in the field notebook. All estimations of plant cover and biomass are made by the same field personnel to ensure consistency.

In addition to plant cover, biovolume will be estimated by ESS field personnel at each survey point, using both general observation as well as an Aquascope (or underwater camera for deeper water). The percentage of biovolume represents that percentage of the water column that is occupied by plants; biovolume is a factor of water depth, plant height, and plant density. As noted above, a simple code system will be used to assign integers as estimations of percent biovolume. At each survey point the estimation of biovolume will be recorded with the associated transect and point number in the field notebook. All estimations of plant cover and biomass are made by the same field personnel to ensure consistency.

Assessment of both plant cover and biovolume will be made along the length of each transect with general observation and an Aquascope. In increased water depths or under turbid conditions, the grappling rake will be used to assess these measurements. The bottom of the waterbody will be scraped in order to estimate plant cover and biovolume. At depths greater than 16ft, the grappling rake will not be effective and the plant cover and biovolume will be assumed to be 0%.

4.3 Creation of Plant Maps

Upon completion of the field survey, dominant plant beds identified within the waterbody will be linked with associated transects and survey point locations to create a dominant aquatic plant distribution map.

Percentage plant cover and plant biovolume "code numbers" will be linked with the transects and survey point locations drawn onto the outline map to create maps that illustrate the percentage cover and percentage biomass of aquatic plants in every part of the waterbody.

5.0 QUALITY CONTROL

Dominant species as well as unidentifiable plants (unknowns) will be sampled *in situ* and transported back to the lab in plastic bags. Identification checks with other plant keys and consultations with ESS plant experts will be made to confirm species identification.

6.0 DOCUMENTATION

All observed and sampled plants will be recorded by ESS personnel in field notebooks in the form of a species list. Dominant plants will be also be associated with location information in the form of transect numbers and survey points. Transect lines and survey points will be recorded on a map outline of the waterbody that has been printed on water resistant paper (e.g. Rite-in-the-Rain). Any unanticipated site-specific information, which requires ESS field personnel to deviate from the above SOG will be reported in an ESS field notebook. Documentation for recorded data must include a minimum of the following:

- Survey date
- Weather conditions
- Signature or initials of person performing the survey
- Plant survey transect and point locations
- Comments/observations

Additionally, survey point data may be added electronically in the field using a GPS unit.

7.0 TRAINING/QUALIFICATIONS

To properly complete an assessment of plants within a waterbody, the analyst must be familiar with the sampling protocols as stated in this SOG, must have confidence in the use of plant keys and must have familiarity with the aquatic plants of the area in question.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF WATER CLARITY WITH A SECCHI DISC

1.0 INTRODUCTION

This Standard Operating Guideline (SOG) provides basic instructions for the routine measurement of water clarity in lakes and ponds with a Secchi disc. Water clarity is a function of the number of particles in the water (algae, sediment, etc) and the color of the water, which both have an impact on the depth of light penetration. The transparency of the water column can be used as an indicator of water body productivity, with certain exceptions (e.g., naturally sediment laden waterbodies). Generally, the more productive a system is the more algae in the water column, and the lower the transparency. Water transparency can also be affected by erosionally suspended particles which are related to water depth and wave action. Thus on any given day the turbidity of a water body may be affected by its productivity, the season, wind speed and level of sunlight. The methods outlined below are intended (1) to standardize the use of a Secchi disc in the measurement of turbidity; (2) to standardize recording of field data to assure proper documentation of weekly, monthly and seasonal patterns in turbidity.

2.0 REQUIRED MATERIALS

The following materials are necessary for the measurement of turbidity with a Secchi disc:

- Weighted Secchi disc with attached length of rope marked off in one tenth of a meter increments with indelible ink.
- Field data sheets

3.0 METHODS

- A location will be selected from which to measure turbidity. This location will stay constant throughout the study.
- The date, weather conditions, and personnel conducting the measurement will be recorded on the field sheet.
- The Secchi disc will be lowered slowly into the water by the rope so that the weight enters the water first and the disc follows, flat side parallel to the water surface.
- The disc will continue to be lowered through the water column until it is no longer visible.
- A note will be made of the depth of the disc at this point in tenths of a meter by reading where the surface of the water touches the rope.
- The disc will then be slowly raised until it is just visible again.
- Once again a note will be made of the depth of the disc at this point.
- An average of these two depths will be calculated to give the “Secchi depth”, i.e. a measure of the turbidity of the water.

4.0 DOCUMENTATION

Secchi depth data will be reported on field data sheets for every day that a measurement is taken. Documentation for recorded data must include a minimum of the following:

- The date
- The time
- Weather Conditions
- Signature or initials of person performing the measurement
- Depth measurements and average Secchi depth
- Field comments/observations on anything that may influence the Secchi depth measurement that day.

5.0 QUALITY CONTROL

- Duplicate measurements of a single sample will be performed at the frequency specified in the project plan. In the absence of project specific criteria, duplicate measurements should agree within ± 0.25 meters.
- The Secchi disk rope should be checked at least annually against a tape measure to ensure the units of measurement are accurate.

STANDARD OPERATING GUIDELINES FOR COLLECTION OF SEDIMENTS FROM FRESHWATER ENVIRONMENTS

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOGs) provide basic instructions for the collection of bottom sediments from freshwater environments. Collections are to be performed in accordance with methodologies generally accepted by the Massachusetts Department of Environmental Protection (MADEP). Laboratory analysis of sediment samples should be performed by a state certified laboratory with the detection limits for analysis specified on the project's Chain of Custody as per MADEP's Interim Policy # COMM-94-007 and their subsequent Technical Update for freshwater sediment screening (May 2002).

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements may be defined in a site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) and may include duplicate or replicate measurements or confirmatory measurements.

2.0 RESPONSIBILITIES

Field personnel are responsible for verifying that all sampling equipment is in proper operating condition prior to use and for implementing the sampling procedures in accordance with this SOG and any specific project plan.

The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials may be necessary for this procedure:

- Sediment coring or grab sampling device
- Stainless steel mixing bowl
- Stainless steel mixing spoon or tool
- Nitrile gloves
- Alconox
- Pre-cleaned sample jars provided by laboratory
- Pencil and labeling marker or pen
- Field data sheets or logbooks
- GPS receiver and/or map of target waterbody to record sample locations

4.0 METHOD

Field personnel are to collect sediment cores or grabs in accordance with the instructions provided with each specific sampling device deployed. Nitrile gloves should be worn at all times during these procedures. At each sampling location, a pre-cleaned grab sample dredge or corer is to be deployed, typically from a boat. All equipment is to be decontaminated using alconox and fresh water before the collection of each discrete sample. If specified by the project plan, samples may be composited in a pre-cleaned stainless steel mixing bowl and mixed thoroughly with a pre-cleaned stainless steel spoon before being transferred to the glass sampling jars provided by the laboratory. However, volatile organic compound (VOC) samples should be collected from cores prior to compositing.

The sample jar should be labeled with the sample identification, date, and any other project specific requirements. This information should be recorded in a field book at the time of sampling along with other essential information such as water depth, sample coordinates (or the location should be mapped on a figure at the time of sampling), and any other general notes on the nature of the sediment collected.

5.0 QUALITY CONTROL

Duplicate field samples or split samples may be collected if specified by the project plan. Once samples have been retrieved and placed into jars, the samples should be kept on ice or refrigerated until the laboratory can analyze them. Specific sample volumes, holding times, and detection limits for each parameter to be analyzed (Table 1) should be adhered to unless the project plan has outlined project-specific requirements.

TABLE 1. SEDIMENT ANALYSIS

PARAMETER	Volume Needed (ml)	Sample Container	Sample Preservation	Maximum Hold Time (hours)	Detection Limits (mg/Kg)	EPA #
Arsenic	100 g	Amber Glass	Ice	6 months	0.5	200.7
Cadmium	100 g	Amber Glass	Ice	6 months	0.1	200.7
Chromium	100 g	Amber Glass	Ice	6 months	1.0	200.7
Copper	100 g	Amber Glass	Ice	6 months	1.0	200.7
Lead	100 g	Amber Glass	Ice	6 months	1.0	200.7
Mercury	100 g	Amber Glass	Ice	6 months	0.02	245.1
Nickel	100 g	Amber Glass	Ice	6 months	1.0	200.7
Zinc	100 g	Amber Glass	Ice	6 months	1.0	200.7
PCBs	100 g	Amber Glass	Ice	7 days	0.01	8082
PAHs	100 g	Amber Glass	Ice	7 days	0.02	8270
EPH	100 g	Amber Glass	Ice	14 days	25	418.1
VOCs	100 g	Amber Glass	Methanol, Ice	7 days	0.1	EPA/ACE 8260
% Organic Content	100 g	Amber Glass	Ice	7 days	1.0%	160.4
% Ash Content	100g	Amber Glass	Ice	7 days	1.0%	160.4
Grain Size Analysis (Sieve and Hydrometer)	1,000g	Plastic Bag/Glass	None Required	Indefinite	0.1%	ASTMD 2216
% Water	100g	Amber Glass	Ice	14 days	1.0%	160.3

6.0 DOCUMENTATION

Documentation for recorded data must include a minimum of the following:

- Date and time of collection and analysis
- Signature or initials of person performing the collection or measurement
- Sample identification/station location
- Pertinent comments

7.0 TRAINING/QUALIFICATIONS

To properly perform sediment collections, the field personnel must be familiar with the techniques stated in this SOG and experienced in the operation of the sampling equipment.

8.0 REFERENCES

MADEP Interim Policy # COMM-94-007

MADEP 2002. Technical Update: Freshwater Sediment Screening Benchmarks for Use under the Massachusetts Contingency Plan. May 2002.

STANDARD OPERATING GUIDELINES FOR THE ACQUISITION OF SURFACE WATER

1.0 INTRODUCTION

1.1 Purpose and Applicability

This Standard Operating Guideline (SOG) provides basic instructions for the routine acquisition of surface water. The methods outlined below are intended (1) to standardize water sample collection methods used by ESS Group, Inc. (ESS) field personnel; (2) to ensure that samples delivered to the laboratory represent field conditions as accurately as possible; (3) to standardize recording of field data to assure proper documentation of sample collection; (4) to minimize cross contamination between sampling sites.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory analyses.

2.0 RESPONSIBILITIES

2.1 Project Manager

The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.

2.2 Field Personnel

The analyst is responsible for verifying that the sampling bottles are appropriately sanitized and contain the appropriate preservative for the desired laboratory analyses. Sample bottle caps should be securely in place to ensure that no contamination has occurred and that preservative has not been released.

3.0 REQUIRED MATERIALS

The following materials are necessary for the acquisition of surface water:

- Nitrile gloves
- Labeled sampling container provided from contracted laboratory, which is appropriately sanitized and contains the appropriate preservative for the desired analyses
- Laboratory or field data sheets or logbooks
- List of sites or locations of each site to be sampled

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

- Unless noted otherwise, surface water samples will be collected via direct grab methods.
- Upon entering a sampling location, ESS field personnel shall minimize disturbance to upstream waters and shall always sample water from the undisturbed upstream region. In addition, when wading in waterbodies, field personnel will try and disturb as little bottom sediment as possible.
- Sample collection shall precede the measurement of physical field parameters (such as turbidity, conductivity, dissolved oxygen, etc.) in order to minimize the risk of sediment disturbance and/or contamination.

- Clean rubber gloves shall be worn at each sampling location. Gloves shall be rinsed with distilled water prior to subsequent sample collection. When sampling multiple sites on the same date, gloves may be rinsed in the immediate downstream reaches of the waterbody to be sampled, before sample collection, in order to minimize the risk of cross-contamination. When warranted by the sensitivity of the laboratory analyses under investigation or at the Clients request, new, sterile rubber gloves shall be worn at each different sampling location.
- In absence of a project specific sampling protocol, grab samples are to be collected from beneath the water surface (at approximately 8 to 12 inches beneath the surface or mid-way between the surface and the bottom if the waterbody is shallow, (EPA 1997)). Samples will be collected at an appropriate distance from the stream bank or lake shoreline and away from submerged obstacles. For small streams (i.e., 10-20 feet wide with a maximum depth of less than 2 feet) the appropriate distance to collect a sample would be the center, while within larger streams the sample would be taken at a location where water depth is 2-3 feet.
- When collecting samples, ESS field personnel shall stand downstream of the desired sampling location, hold the bottle near its base and plunge it below the water surface with the opening (mouth) downward. The opening of sample bottles shall always be directed away from field personnel in an upstream direction.
- Sample containers with preservatives should not be used to collect surface water samples. If using containers with preservatives, a pre-cleaned container of similar type should be used to collect the sample with subsequent transfer to the preserved container.
- ESS personnel shall leave an approximate 1-inch air space (except for dissolved oxygen and BOD samples) in sample bottles, so that bottles may be shaken (if needed) before analyses (EPA, 1997).
- ESS personnel shall place sample bottles and temperature blanks (if required by QAPP or QAM) in a cooler filled with ice (if required by QAPP or QAM).
- The testing or analytical method and sample containers, preservation technique, and sample volumes should be selected in consultation with the laboratory to ensure that the samples obtained will provide the desired results.

5.0 QUALITY CONTROL

5.1 Field Duplicates

Field duplicate measurements of a single sample will be performed at the frequency specified in the project plan. Collection of duplicates will adhere to the surface water acquisition methods described above. Field duplicates will be collected immediately following initial sample collection.

6.0 DOCUMENTATION

Surface water quality field data will be reported in field notebooks by ESS personnel. Surface water quality laboratory data will be reported by contracted laboratories on official laboratory letterhead. Any unanticipated site-specific information, which requires ESS field personnel to deviate from the above SOG will be reported in an ESS field notebook. Documentation for recorded data must include a minimum of the following:

- Date and time of analysis
- Signature or initials of person performing the measurement
- Sample identification/station location
- Comments/observations

7.0 TRAINING/QUALIFICATIONS

To properly perform the acquisition of surface water, the analyst must be familiar with the sampling protocols as stated in this SOG.

8.0 REFERENCES

EPA, 1997. Volunteer Stream Monitoring: A Methods Manual. United States Environmental Protection Agency. Office of Water. EPA 841-B-97-003.

STANDARD OPERATING GUIDELINES FOR MEASUREMENT OF TEMPERATURE

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine measurement of temperature using any high quality mercury-filled thermometer or thermistor with analog or digital read-out device such as the Hydac Multimeter Probe and YSI Model 55. Multimeter instruments used for temperature measurement may measure additional parameters (e.g., dissolved oxygen, conductivity, pH, etc.). This SOG addresses temperature measurement only (other capabilities are outlined in the appropriate SOG). This SOG is designed specifically for the measurement of temperature in accordance with EPA Method 170.1 and Standard Method 2550 B which address thermometric temperature measurement of drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory measurements.

2.0 RESPONSIBILITIES

2.1 The analyst is responsible for verifying that the temperature measuring device is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

2.2 The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- Thermometer or thermistor with analog or digital read-out device
- Manufacturer's instruction manual for the instrument
- National Institute of Standards and Technology (NIST)-traceable thermometer
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

To achieve accurate temperature measurements, samples should be analyzed immediately upon collection (preferably within 15 minutes). Samples should be collected in glass or plastic containers.

4.2 Calibration and Measurement Procedures

4.2.1 ESS-owned temperature measuring devices will, at a minimum, be checked annually as described in Section 5.0. The device will be checked against an NIST-traceable thermometer

and the necessary compensation made for the difference in temperature between the two. Rental equipment will be checked by the manufacturer and documentation provided to ESS.

4.2.2 Immerse the thermometer or temperature measuring device into the sample.

4.2.3 Swirl and take a reading when the value stabilizes.

4.2.4 Record the temperature reading to the nearest 0.50 for a thermometer or 0.10 for digital meter-type instruments. Compensate for any difference with the NIST-traceable thermometer.

4.2.5 Temperature data may be post-calibrated using any of a variety of calibration data including, but not limited to, field calibration points, manufacturer calibration data, and analytical results from samples collected during field deployment of the sensors. The decision criteria for post calibration, and the technique used, will be specified in the project plan, and will be consistent with the manufacturer's recommendations.

4.3 Troubleshooting Information

If there are any performance problems with any of the meter-type temperature measuring devices, consult the appropriate section of the meter instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department immediately for further instructions. If a performance problem exists with the thermometer, discard the thermometer and replace it.

4.4 Maintenance

Instrument maintenance for meter-type temperature measuring devices should be performed according to the procedures and frequencies required by the manufacturer.

5.0 QUALITY CONTROL

5.1 The temperature measuring devices will, at a minimum, be checked against an NIST-traceable thermometer at the frequency stated in Section 4.2.1. This verification procedure will be performed as follows:

- Immerse the thermometer or temperature sensor and the NIST-traceable thermometer into a sample.
- Allow the readings to stabilize.
- Record the readings and document the difference.
- Label the thermometer or temperature sensor with the correction value/adjustment and the date the accuracy check was performed.
- Compensate for the difference when sample measurements are taken.

5.2 Duplicate measurements of a single sample will be performed at the frequency stated in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within $\pm$ 0.50C or approximately $\pm$ 1.00F.

6.0 DOCUMENTATION

6.1 Records for checking the accuracy of the thermometer or temperature measuring device (where applicable) will include:

- Date
- Thermometer or meter-type temperature measuring device checked
- Reference thermometer number
- Readings for reference thermometer and thermometer being checked
- Adjustment made for difference in readings
- Initials of analyst

6.2 Documentation for recorded data must include a minimum of the following:

- Date and time of analysis
- Signature or initials of person performing the measurement
- Thermometer ID # or instrument identification number/model
- Sample identification/station location
- Temperature of sample (including units and duplicate measurements) compensated for any difference with the reference thermometer if applicable
- Comments

7.0 TRAINING/QUALIFICATIONS

To properly perform temperature measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.

Certain state certification programs require that temperature measurements in the field be taken by, or in the presence of, personnel that are qualified under the certification program.

8.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

STANDARD OPERATING GUIDELINESFOR MEASUREMENT OF TURBIDITY

1.0 INTRODUCTION

1.1 Purpose and Applicability

These Standard Operating Guidelines (SOG) provide basic instructions for routine measurement of turbidity using a nephelometric turbidity meter with a digital read-out device such as the LaMotte 2020 Turbidimeter. Measurements are made in accordance with EPA Method 180.1 that addresses nephelometeric turbidity measurement of drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory measurements.

2.0 RESPONSIBILITIES

2.1 The analyst is responsible for verifying that the turbidity measuring device is in proper operating condition prior to use and for implementing the calibration and measurement procedures in accordance with this SOG and the project plan.

2.2 The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- Turbidity meter with digital read-out device
- Manufacturer's instruction manual for the instrument
- Turbidity tubes
- Mild detergent
- Lint-free cloth
- Distilled water
- Nephelometric Turbidity Unit (NTU) calibration standards (1.00 NTU and 10.0 NTU)
- Laboratory or field data sheets or logbooks

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

To achieve accurate turbidity measurements, samples should be analyzed immediately upon collection (preferably within 15 minutes). Samples should be collected in glass or plastic containers.

4.2 Calibration and Measurement Procedures

4.2.1 Select a turbidity standard in the range of the samples to be tested (1.00 NTU or 10.0 NTU). Fill a turbidity tube with the standard, cap, and wipe the tube with the clean lint-free cloth.

4.2.2 Place the sample into the turbidity meter such that the indexing arrow on the turbidity tube is aligned with the indexing arrow on the meter face. Close the lid and press the "READ" button. If the displayed value is not the same as the value of the standard (within 2%), continue with the calibration procedure.

4.2.3 Follow the calibration procedures outlined by the manufacturer's manual.

4.2.4 Verify the calibration every 15 samples and at the end of the day. Recalibrate the instrument if the check value varies more than 2% from the true value.

4.2.5 The turbidity tubes will be rinsed with deionized water and wiped gently with a lint-free tissue between sample analysis.

4.2.6 Recalibrate the instrument with the appropriate NTU standard if the standard is not of the same order of magnitude as the samples being tested.

4.2.7 The meter must be re-calibrated following any maintenance activities and prior to the next use.

4.2.8 Record the turbidity reading to the nearest 0.01 NTU for measurements less than 11 NTU and to the nearest 0.1 for measurements greater than 11 NTU but less than 110 NTU. For values greater than 110 NTU record to the nearest 1 NTU.

4.3 Troubleshooting Information

If there are any performance problems with any of the meter-type turbidity measuring devices, consult the appropriate section of the meter instruction manual for the checkout and self-test procedures. If the problem persists, consult the manufacturer's customer service department immediately for further instructions.

4.4 Maintenance

Instrument maintenance for meter-type turbidity measuring devices should be performed according to the procedures and frequencies required by the manufacturer.

5.0 QUALITY CONTROL

5.1 The turbidity measuring tubes will, at a minimum, be checked against NTU calibration standards at the frequency stated in Section 4.2.1. This verification procedure will be performed as follows:

- Insert the turbidity tube with distilled water into the turbidity meter.
- Press "READ".
- Record the readings and document the difference.
- Label each turbidity tube with its corresponding turbidity correction value.
- Record the adjustment and the date the accuracy check was performed in a logbook.

- Compensate for the difference when sample measurements are taken.

5.2 Duplicate measurements of a single sample will be performed at the frequency stated in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within ± 2% for readings below 100 NTU and ± 3% for readings above 100 NTU.

6.0 DOCUMENTATION

All turbidity meter calibration, checks, and maintenance information will be recorded on the daily calibration sheet or logbook. Turbidity data may be recorded on the appropriate laboratory or field data sheets or logbooks.

6.1 Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:

- Date and time of calibration
- Signature or initials of person performing the measurement
- Instrument identification number/model
- Expiration dates and batch numbers for all standard solutions
- Reading for 1.00 NTU standard before and after meter adjustment
- Reading for 10.0 NTU standard before and after meter adjustment
- Readings for all continuing calibration checks
- Comments

6.2 Documentation for recorded data must include a minimum of the following:

- Date and time of analysis
- Signature or initials of person performing the measurement
- Instrument identification number/model
- Sample identification/station location
- Turbidity of sample (including units and duplicate measurements)
- Comments

7.0 TRAINING/QUALIFICATIONS

To properly perform turbidity measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOG. The analyst must also be experienced in the operation of the meter.

Certain state certification programs require that turbidity measurements in the field be taken by, or in the presence of, personnel that are qualified under the certification program.

8.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

STANDARD OPERATING GUIDELINES FOR STORM WATER SAMPLING

1.0 INTRODUCTION

1.1 Purpose and Applicability

This Standard Operating Guideline (SOG) provides basic instructions for the routine acquisition of storm water. The methods outlined below are intended (1) to standardize storm water sample collection methods used by ESS Group, Inc. (ESS) field personnel; (2) to ensure that samples delivered to the laboratory represent field conditions as accurately as possible; (3) to standardize recording of field data to assure proper documentation of sample collection; (4) to minimize cross contamination between sampling sites.

1.2 Quality Assurance Planning Considerations

The end use of the data will determine the quality assurance requirements that are necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan or Quality Assurance Project Plan (QAPP) (hereafter referred to as the project plan) or laboratory Quality Assurance Manual (QAM) and may include duplicate or replicate measurements or confirmatory analyses.

2.0 RESPONSIBILITIES

2.1 Project Manager

The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOG and the project plan. The project manager will directly coordinate storm water sampling events or designate a task coordinator on the project team.

2.2 Field Personnel

Field personnel are responsible for obtaining a correct bottle order from the laboratory and verifying that the sampling bottles are appropriately sanitized (or new) and contain the appropriate preservative for the desired laboratory analyses. Sample bottle caps should be securely in place to ensure that no contamination has occurred and that preservative has not been released. Field staff must completely fill out all required chains of custody and observe proper hold times for all samples.

Field personnel are also responsible for ensuring that all meters and equipment are functional and calibrated prior to use.

Field personnel are responsible for communicating with the project manager or task coordinator to confirm that an event will be sampled prior to departure for the project site. They are also responsible for documenting precipitation extent, intensity, and total amounts through photographs, field notes, and/or online weather reports and maps.

3.0 REQUIRED MATERIALS AND EQUIPMENT

The following equipment and materials are required for storm water sampling:

- Nitrile gloves
- Labeled sampling container provided from contracted laboratory, which is appropriately sanitized and contains the appropriate preservative for the desired analyses
- Appropriately maintained and calibrated meters (see individual SOGs for water quality measurements)

- Weatherproof field data sheets or field books
- Weatherproof pen
- List of sites or locations of each site to be sampled

Additionally, the following equipment and materials may be necessary for certain projects:

- Stopwatch
- Collapsible ruler
- Extendible grab sampler
- Cut off bottle or cup (for collecting overland runoff samples)
- DGPS (pre-loaded with sampling locations, if necessary)
- Pry bar, hook, shovel, or other tools (for opening manhole covers, grates, etc.)
- Loppers or other pruning tool (for clearing vegetation)
- Waders or hip boots

4.0 METHOD

4.1 Sample Handling, Preservation, and General Measurement Procedures

4.1.1 Selecting the Storm

- The target of storm water sampling is typically the "first flush" of a storm event. To obtain a sample representative of this first flush, sampling should only be conducted after a significant dry period, typically 72 hours (although the recommended dry period may be more or less depending on the project and/or state). Dry weather is usually defined as a period of 0.1 inch of precipitation or less and no measurable snow cover. Storm water sampling events may require a minimum storm event size of at least 0.5 inches of precipitation. Compliance with the minimum period of antecedent dry weather and storm event size is especially important on projects where sampling needs to be conducted in accordance with state regulations. Other regulations may also apply and field personnel should check with the project manager prior to sampling if the requirements of the storm water sampling program are unclear.
- Storms should be screened for a high probability of producing a sufficient amount of rain over the entire watershed area. Storms that meet this criterion should be tracked on a daily basis until the day of the storm. On the day of the storm, the storm watcher will use radar, precipitation total maps, forecast discussions, and any other evidence that is available and useful to track the storm. Remember that forecast and radar ***trends*** are at least as important as the latest forecast or radar map. Declining probabilities of precipitation or forecasted storm amounts are generally signs of a storm that is not likely to produce satisfactory results. It is important to check the scientific forecaster discussion (available as a link from most weather websites), which provides background information on the forecast reasoning. Changes to the going forecast may emerge in this discussion several hours before the daily or hourly forecasts for individual locations are altered.

- The project manager should track storm systems to assess the potential of each storm to produce conditions adequate for storm water sampling and communicate expectations to field personnel. Field staff should be notified as far in advance as possible, preferably two to five days, that sampling may be necessary for a particular event. This will reduce the number of missed events.
- Field personnel should have all equipment and materials (including bottles) prepped well in advance of the targeted storm event. Prior to leaving for the project site, field personnel should confirm with the project manager that storm water sampling is authorized. This will minimize the number of false starts. Field personnel should also notify the analytical laboratory of the sampling schedule for the day to ensure that samples will be received within holding times and that lab personnel will be available to log samples in a timely manner. This is particularly important when collected samples with short hold times, such as bacteria.
- See Figure 1 for a flow chart of project manager and field personnel responsibilities during the storm selection and sampling process.

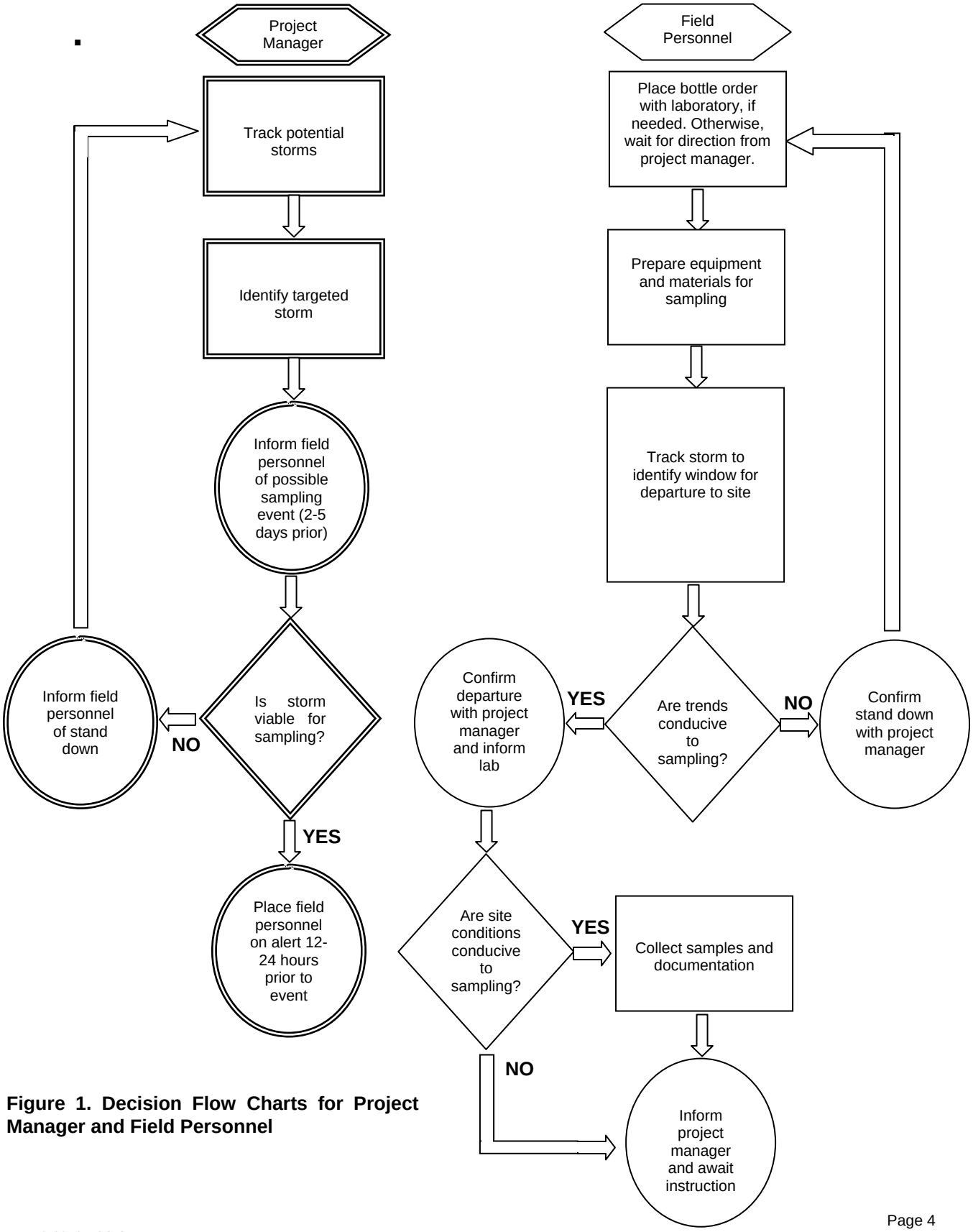


Figure 1. Decision Flow Charts for Project Manager and Field Personnel

4.1.2 Field Methods

General Guidelines

- The testing or analytical method and sample containers, preservation technique, and sample volumes should be selected in consultation with the laboratory to ensure that the samples obtained will provide the desired results.
- Unless noted otherwise, storm water samples will be collected via direct grab methods.
- New disposable gloves shall be worn at each sampling location to prevent cross-contamination.
- The opening of sample bottles shall always be directed away from field personnel in an upstream direction.
- Sample containers with preservatives should not be used to collect storm water samples. If using containers with preservatives, a pre-cleaned container of similar type should be used to collect the sample with subsequent transfer to the preserved container.
- Field personnel shall leave an approximate one-inch air space in sample bottles (except for dissolved oxygen, BOD, and alkalinity samples, unless otherwise directed by the lab), so that bottles may be shaken (if needed) or frozen before analyses.
- Field personnel shall place sample bottles and temperature blanks (if required by QAPP or QAM) in a cooler filled with ice.

Guidelines for Stream Sampling

- Sample once the duration and amount of rain is sufficient to produce runoff.
- Field personnel shall minimize disturbance to upstream waters and shall always sample water from the undisturbed upstream region. In addition, when wading in waterbodies, field personnel will try and disturb as little bottom sediment as possible.
- Sample collection shall precede the measurement of physical field parameters (such as turbidity, conductivity, dissolved oxygen, etc.) in order to minimize the risk of sediment disturbance and/or contamination.
- In absence of a project specific sampling protocol, stream grab samples are to be collected from beneath the water surface (at approximately 8 to 12 inches beneath the surface or mid-way between the surface and the bottom if the waterbody is shallow, (EPA 1997)). Samples will be collected at an appropriate distance from the stream bank (generally midstream) and away from submerged obstacles. Field personnel shall stand downstream of the desired sampling location, hold the bottle near its base, and plunge it below the water surface with the opening (mouth) downward.

5.0 QUALITY CONTROL

5.1 Field Duplicates

Field duplicate measurements of a single sample will be performed at the frequency specified in the project plan. Collection of duplicates will adhere to the methods described above. Field duplicates will be

collected immediately following initial sample collection. Not all projects require field duplicates. If unsure, check with the project manager prior to placing a bottle order.

6.0 DOCUMENTATION

Storm water field data will be reported on field sheets or in field notebooks by ESS personnel. Laboratory data will be reported on official laboratory letterhead. Any unanticipated site-specific information, which requires field personnel to deviate from the above SOG will be reported on field sheets or in a field notebook. Documentation for recorded data must include a minimum of the following:

- Date and time of analysis
- Name or initials of person conducting the measurement or collection
- Sample identification/station location
- Comments/observations

Photographic evidence of storm water flows is also desirable and may be required for certain projects. Additionally, storm total maps and/or hourly precipitation records should be saved to the project folder for a period extending from 72 hours prior to end of the selected storm event.

7.0 TRAINING/QUALIFICATIONS

To properly perform the storm water sampling, the analyst must be familiar with the sampling protocols as stated in this SOG.

8.0 REFERENCES

EPA, 1997. Volunteer Stream Monitoring: A Methods Manual. United States Environmental Protection Agency. Office of Water. EPA 841-B-97-003.

Appendix B

GKY First Flush Sampler Fact Sheet

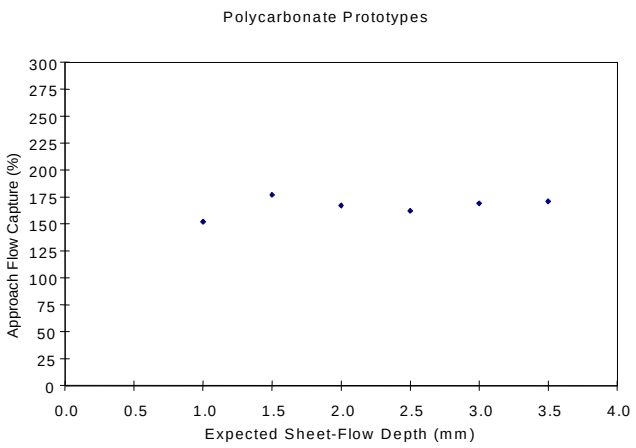
GKY FirstFlush *Sampler*

U.S. Patent Number 5,847,292 dated December 8, 1998

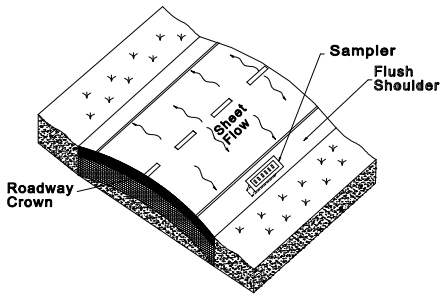
Inventors: G. Ken Young, Frank R. Graziano, Stuart M. Stein

Developed under the Small Business Innovative Research Program (SBIR) in conjunction with the Federal Highway Administration (FHWA), the **GKY FirstFlush Sampler** will make compliance with NPDES regulations easier and at much less expense than current sampling methods. Consider the following advantages of the **GKY FirstFlush Sampler**:

- It's small (roughly 230 mm x 430 mm x 150 mm), inexpensive, and expendable;
- It can be easily configured to capture different runoff volumes that are *exactly representative* of the entire pavement section (not a sample of the runoff);
- It captures runoff at a relatively constant rate regardless of the sheetflow depth (within expected ranges);
- Because of the constant rate of capture, our sampler also provides a theoretical estimate of the rainfall depth based on the captured volume;
- It is unobtrusive and entirely passive;
- The collection vessel is itself the sample container for shipment to the lab for analysis; and
- It requires no calibration or special skills to install and maintain.



Measured Capture Efficiency



Typical Application

The **GKY FirstFlush Sampler** is made entirely of plastic, keeping costs low. The grate and insert sections are manufactured from glass-filled polycarbonate (strong and durable) and the sample receptacle from high-density polyethylene (HDPE), a chemically compatible material that will not compromise the analytical results.

The principle of operation is simple; the constant capture efficiency (developed through extensive laboratory testing), allows the volume of the captured sample to be easily estimated:

$$Vol. = 6.35 D_{Runoff} L_{Flow} N_{Ports} Eff_{Ports}$$

Where :

Vol. = Required volume of sample, ml

D_{runoff} = Desired runoff capture depth, mm (i.e. 13 mm)

L_{Flow} = Runoff flow length, m

N_{ports} = Number of sample-ports

Eff_{Ports} = Sample-port capture efficiency

6.35 = Conversion factor

Given the length of the roadway section, you can simply select the number of sample-ports to leave open (maximum of 5) to tailor the sampling to meet your specific requirements. The included look-up charts will enable you to quickly and easily approximate how much volume is captured for a given rainfall depth and length of roadway.

For pricing or more information, call **(703) 870-7000** or e-mail **scoldren@gky.com**

Appendix C

Premier Laboratory Standard Operating Protocols

Total Suspended Solids
SM 2540D

Prepared by: **Melisa Montgomery**
Quality Assurance Officer

Approved by: **Gregory Plante**
Laboratory Manager

Reviewed and Implemented by: **Ronald Warila**
General Manager/Technical Director

Reference:

Standard Methods, 20th Edition, 1998, Method 2540D

I. Applicability

1.1 Analyte: Total suspended solids

1.2 Matrix: Water, wastewater

1.3 Regulation: NPDES, CWA

II. Important Notes

2.1 Perform analysis on an unpreserved sample. A well mixed sample is filtered through a pre-weighed glass fiber filter, and dried to a constant weight at 103-105^{0}C. The increase in the filter weight equals the total suspended solids (TSS).

2.2 **Shake sample vigorously** and rapidly transfer an aliquot to graduated cylinder.

2.3 Limit sample volume to obtain no more than 200 mg of final residue but not less than 2.5 mg.

2.4 The Practical Quantitation Limit (PQL) is 5 mg/L.

III. Procedure

3.1 Prepare a glass fiber filter by placing the disk in the vacuum filter apparatus with the wrinkled side up.

3.1.1 While vacuum is applied, wash the disk with three successive 20 mL volumes of reagent water.

3.1.2 Remove all traces of water by continuing to apply vacuum for 30 seconds after water has passed through. Discard the washings.

3.2 Remove the filter from the vacuum filter apparatus and transfer to a drying pan. Dry in an oven at 103-105°C for one hour.

3.2.1 If total volatile solids is also required on the sample, ignite at 550 +/-50°C for 15 minutes. Cool in a desiccator and weigh to the nearest 0.0001 g.

3.2.2 Repeat the cycle of drying, igniting (if applicable), cooling, and weighing until a constant weight is obtained or until weight loss is less than 0.5 mg.

3.2.3 Store in a desiccator until needed. Weigh immediately before use.

3.3 Re-assemble the vacuum filter apparatus and begin suction. Shake the sample vigorously and rapidly transfer 500 mL of sample to the filtration funnel by means of a 500 mL graduated cylinder.

3.4 Filter the sample through the glass fiber filter, rinse with three 10 mL portions of reagent water, and continue to apply vacuum for 3 minutes after filtration is complete.

3.5 Dry the filter with residue for at least one hour at 103°C-105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg. Record all weights.

3.6 If the residue is greater than 0.2 g, repeat the analysis with a smaller volume.

IV. Calculations

$$\textbf{Total suspended solids mg/L} = \frac{1{,}000{,}000 \times (A - B)}{C}$$

where: A = weight of filter plus residue, g
B = weight of filter, g
C = volume of sample used, mL

Record results to two significant figures.

V. Quality Assurance

5.1 All quality control data should be maintained and available for easy reference or inspection.

5.2 Analyze a reagent blank with each batch of samples analyzed. The result for the reagent blank must be less than the quantitation limit.

5.3 Analyze sample duplicates at a minimum frequency of one per 10 samples or two per month, whichever is more frequent. Duplicates %RPD should agree within 10%.

5.4 If the duplicate RPD is > 10% and ≤ 20%, note in report narrative.

5.5 If the duplicate RPD is > 20%, reanalyze the sample.

VI. Reagents and Materials

6.1 Desiccator

6.2 Drying Oven: Capable of maintaining a temperature of 103-105^{o}C

6.3 Analytical balance: Capable of reading to 0.0001 g

6.4 Graduated cylinder, 100 mL

6.5 Glass fiber filter, 47, 70, or 90 mm diameter, without organic binder

SOP Revision History

Revision No.	Description of Changes	Effective Date	Initiated by
1.2	Added revision history table Changed format	9/23/11	LM
2	Changed header Changed approval signatures	10/23/12	LM
3	Changed minimum residue requirements in Section 2.3 Changed PQL in Section 2.4 Changed volume filtered in Section 3.3 Changed wording in Section 5.4 Added Section 5.5	11/1/12	DD, LM

Next review: 11/2013

ICP Metals

Method 200.7

Prepared by: **Melisa Montgomery**
Quality Assurance Officer

Approved by: **Gregory Plante**
Laboratory Manager

Reviewed and Implemented by: **Ronald Warila**
General Manager/Technical Director

Reference

Methods for Chemical Analysis of Water and Wastes, EPA-600/r-94/111, May 1994, Method 200.7, revision 4.4 (Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes)

I. Applicability

1.1 Analyte: Refer to ICP manual for installed spectral lines

1.2 Matrix: Digestates from all approved procedures

1.3 Regulation: NPDES, CWA

II. Important Notes

2.1 As with all metals analysis, the equipment and glassware used must be free of any contamination.

III. Interference

3.1 The proper identification of interferences encountered while performing ICP analysis is vital to producing sound analytical data. The following is a brief summary of some of the major interferences that may produce either false positive or false negative results.

3.2 Spectral interferences are caused by (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomenon and (4) stray light from the line emission of high-concentration elements. Computer-correcting the raw data after monitoring and measuring the interfering element can compensate for spectral overlap. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

3.3 Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interference can be assumed.

3.4 The interference is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that arsenic is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc.

3.5 Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.6 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

3.7 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

3.8 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

3.9 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU at the time of the analysis.

IV. Procedure

4.1 Preliminary treatment of most matrices is necessary due to the complexity of sample matrices. The use of an internal standard or matrix matching must be used to determine concentrations of unknowns. Refer to the appropriate digestion SOP according to the matrix of the samples to be analyzed as shown in the table below:

Document No.	Title
MD-02	Acid Digestion of Aqueous Samples and Extracts for Total Metals for ICP Analysis
MD-03	Acid Digestion of Soils, Sediments, and Sludges for ICP-MS, ICP, GFAA and FLAA

4.1.1 For the "direct analysis" of total recoverable analytes in drinking water samples containing turbidity <1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure described in Section 3.1 of the aqueous sample acid digestion SOP (Doc. No. MD-02) while making allowance for sample dilution in the data calculation.

4.2 Set up the instrument with proper operating parameters established by the instrument manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

4.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Table 3. Flush the system with a reagent blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

4.3.1 **Note:** For boron concentrations greater than 500 mg/L, extended flush times >1 minute may be required.

4.4 The validity of the calibration standards must be verified by analyzing a second source standard with concentrations of all elements of interest at or near the midpoint of the calibration.

4.5 Flush the system with the calibration blank solution for at least 1 minute before the analysis of each sample. Rinse time may be reduced if data will support the absence of analytes above the stated MDLs. Analyze the instrument performance check and the calibration blank after every 10 samples.

4.6 An Interference Check solution (ICS) must be run prior to analysis of samples. An ICSA and ICSAB must be analyzed at the beginning of each analytical sequence, and an ICSAB must be analyzed end of each analytical sequence. The ICSA solution contains parts A (major interferences) only. The ICSAB contains A (major interferences) plus B (elements of interest).

V. Standards Preparation

Blank – This standard serves as the CCB/ICB		
Vol. HNO_3, mL	**Vol. Reagent H_2O, mL**	**Total Vol., mL**
10	490	500

Trace 1 – This standard serves as the initial calibration standard for the analytes below

Stock Solution	Concentration, ppm	Amount, mL	Stock Standard	Concentration, ppm	Amount, mL
Ag	1000	1.0	Mo	1000	1.0
As	1000	1.0	Ni	1000	1.0
B	1000	1.0	Pb	1000	1.0
Ba	1000	5.0	Sb	1000	1.0
Be	1000	1.0	Se	1000	1.0
Cd	1000	1.0	Sn	1000	2.0
Co	1000	1.0	Ti	1000	1.0.
Cr	1000	1.0	Tl	1000	1.0
Cu	1000	1.0	V	1000	1.0
Mn	1000	1.0	Zn	1000	1.0

Volume HNO_3, mL = 20 **Volume reagent H_2O, mL = 955**

Total Vol., mL = 1000

Trace 2 – This sample serves as an initial calibration standard for the analytes in the Trace 3 Standard:

1:2 dilution of Trace 3 standard

Trace 3 – This standard serves as the initial calibration standard for the analytes below.

Stock Solution	Concentration, ppm	Amount, mL
Al	10,000	1.0
Ca	10,000	1.0
Fe	10,000	2.0
Mg	10,000	1.0
Na	10,000	10.0
K	10,000	10.0

Vol. HNO_3, mL = 20 **Vol. reagent H_2O, mL = 955**

Total Vol., mL = 1000

QCS – This sample serves as the quality control sample for the analytes below. All stock solutions used must be from a source independent of the calibration standards.

Stock Solution	Concentration, ppm	Amount, mL	Stock Standard	Concentration, ppm	Amount, mL
Ag	1000	0.25	Mg	10,000	0.50
Al	10,000	0.20	Mn	1000	0.50
As	1000	0.50	Mo	1000	0.50
B	1000	0.50	Na	10,000	0.50
Ba	10,000	0.20	Ni	1000	0.50
Be	1000	0.05	Pb	1000	0.50
Ca	1000	0.50	Sb	1000	0.50
Cd	1000	0.25	Se	1000	0.50
Co	1000	0.50	Sn	1000	0.50
Cr	1000	0.50	Ti	1000	0.50
Cu	1000	0.25	Tl	1000	0.50
Fe	1000	0.50	V	1000	0.50
K	10,000	0.50	Zn	1000	0.50

Volume HNO_3, mL = 20 **Volume reagent H_2O, mL = 968.8**

Total Vol., mL = 1000

ICV/CCV
1:1 solution of Trace 1 and Trace 3

ICSAB			
Stock Solution	**Concentration, ppm**	**Element(s)**	**Amount, mL**
**CLPP-ICS-A	2500	Al, Ca, Mg	10
	1000	Fe	
**CLPP-ICS-B	100	Cd, Pb, Ni, Ag, Zn	2.5
	50	Ba, Be, Cr, Co, Mn, V	
As	1000		0.5
B	1000		0.25
Mo	1000		0.25
Sb	1000		0.25
Se	1000		0.25
Sn	1000		0.25
Ti	1000		0.25

Vol. HNO_3, mL = 20 **Vol. reagent H_2O, mL = 965.5**

Total Vol., mL = 1000

****(Certified Vendor)**

Yttrium/Lithium Internal Standard

Yttrium Stock Solution

*Yttrium Solid, g	Vol. HNO_3, mL	Vol. Reagent H_2O, mL
0.39	2	98

*Yttrium nitrate tetrahydrate, 99.999%, or Yttrium Oxide, 99.9999%
The use of yttrium oxide requires the solution be gently heated to dissolve.

Internal Standard

Vol. Yttrium Stock Solution, mL	Amt. $LiNO_3$, g	Vol. HNO_3, mL	Approx. Vol H_20, mL	Total Vol., mL
100 uL	0.5	20	980	1000

This solution is not used to determine a specific concentration but a constant absorbance. Therefore, the final solution concentrations may be carried for conditions.

Tuning Solution

*Vol. 1000 ppm Mn Stock, mL	Vol. HNO_3, mL	Vol. Reagent H_2O, mL	Total Vol., mL
0.5	**2.0**	**97.5**	**100**

Trace Table 1

Element	Concentration in Standards, ppb								
	Trace 1	Trace 2	Trace 3	ICV	QCS	ICSAB	LFB	PQL	Linearity Check
Ag	1000	---	---	500	250	250	500	2	5,000
Al	---	5000	10000	5,000	2,000	25,000	10,500	50	50,000
As	1000	---	---	500	500	500	500	5	50,000
B	1000	---	---	500	500	250	500	5	50,000
Ba	5000	---	---	2,500	2,000	125	500	10	50,000
Be	1000	---	---	500	50	125	500	1	50,000
Ca	---	5000	10000	5,000	5,000	25,000	10,500	50	100,000
Cd	1000	---	---	500	250	250	500	2	50,000
Co	1000	---	---	500	500	125	500	2	50,000
Cr	1000	---	---	500	500	125	500	2	50,000
Cu	1000	---	---	500	250	125	500	2	50,000
Fe	---	10000	20000	10,000	5,000	10,000	2,500	50	200,000
K	---	50000	100000	50,000	5,000	---	7,000	200	500,000
Mg	---	5000	10000	5,000	5,000	25,000	10,500	50	100,000
Mn	1000	---	---	500	500	125	500	2	10,000
Mo	1000	---	---	500	500	250	500	2	50,000
Na	---	50,000	100,000	50,000	5,000	---	10,500	1000	500,000
Ni	1000	---	---	500	500	250	500	2	50,000
Pb	1000	---	---	500	500	250	500	2	100,000
Sb	1000	---	---	500	500	250	500	3	50,000
Se	1000	---	---	500	500	250	500	5	50,000
Sn	2000	---	---	1000	500	250	250	5	50,000
Ti	1000	---	---	500	500	250	500	2	10,000
Tl	1000	---	---	500	500	250	500	5	50,000
V	1000	---	---	500	500	125	500	2	50,000
Zn	1000	---	---	500	500	250	500	2	50,000

VI. Quality Assurance

6.1 All quality control data should be maintained and available for easy reference or inspection.

6.2 Calibration Solutions

6.2.1 The calibration solutions are made using the same or similar acid matrix as the samples to be analyzed.

6.3 Quality Control Sample (QCS)

6.3.1 The QCS must be made from an outside second source different from that of the calibration standards' stock solutions.

6.3.2 The QCS is used to verify initially and periodically calibration standards or stock solutions. The QCS must be run once per day or with the introduction of a newly prepared calibration standard or stock solution, whichever is more frequent. The QCS recovery must be within ± 5% of the true value for each analyte of interest.

6.4 Initial Calibration Verification (ICV)

6.4.1 The ICV must be run immediately following the daily calibration. The ICV is made from the same source as the calibration standards.

6.4.2 Initially the recovery must be ± 5% of the true value. The ICV may be run one additional time if the specified recoveries are not met, however if the second analysis fails, corrective action must be taken and any samples analyzed after the previous valid ICV must be re-analyzed.

6.5 Continuing Calibration Verification (CCV)

6.5.1 The CCV must be run periodically after every 10 samples and at the end of each analytical sequence. The CCV is made from the same source as the calibration standards.

6.5.2 The recovery must be ± 10% of the true value. The CCV may be run one additional time if the specified recoveries are not met, however if the second analysis fails, corrective action (re-calibrate) must be taken and any samples analyzed after the previous valid CCV must be re-analyzed.

6.6 Calibration Blank

6.6.1 The calibration blank contains the same acid matrix as the calibration standards and is run with each ICV/CCV. The calibration blank is also used as the Continuing Calibration Blank (CCB) solution. See note 1.

6.6.2 The results of the calibration blank are to agree within two standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, re-calibrate, and reanalyze the previous 10 samples.

6.7 Laboratory Reagent Blank (LRB)

6.7.1 The LRB is a reagent blank carried through the entire sample preparation process.

6.7.2 Employ a minimum of one laboratory reagent blank with each batch of 20 or fewer samples of the same matrix, to verify the absence of contamination. The LRB must be less than the reported detection limit for each analyte of interest.

6.8 Laboratory Fortified Blank (LFB)

6.8.1 A laboratory fortified blank (LFB) must be run with each sample batch of 20 or fewer samples. If the recovery falls outside the control limit of 85-115% *or established control limits, the problem is to be identified and resolved before continuing. *The more restrictive limits prevail. The LFB is spiked, from a source independent of both the calibration standards and QCS, prior to digestion and brought through the entire process.

6.9 Spectral Interference Check (SIC)

6.9.1 The SIC is analyzed in order to validate inter-element and background corrections applied to the samples.

6.9.2 The spectral interference check solution is prepared by combining known concentrations of interfering elements that will provide an adequate test of the correction factors, the "A fraction". Fortify the SIC solutions with the elements of interest in the 1mg/L range, known as the "B fraction". In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

6.9.3 Analyze the ICSA and the ICSAB at the beginning of each analytical run and the ICSAB at the end of a run, or twice during every 8-hour work shift, whichever is more frequent. Recoveries of elements of interest should be within ± 20% of the true values in the ICSAB and less than 2 times the reporting limit in the ICSA.

6.10 Sample Duplicate

6.10.1 Analyze one duplicate sample for every 20 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process. A control limit of ± 20% for RPD shall be used for sample values greater than 10 times the instrument detection limit.

6.11 Laboratory Fortified Matrix (LFM)

6.11.1 An LFM must be run with each batch of 10 or less samples of the same matrix.

6.11.2 The LFM is prepared from a fresh sample aliquot, spiked in the same manner as the LFB and carried through the entire preparation process.

6.11.3 The matrix spike recovery should be within ± 30% of the true value, or documented control limits. Recovery calculations are not made if the spike concentration is less than 30% of the sample concentrations.

6.12 Inter-element Corrections (IECs)

6.12.1 IECs are determined by analyzing a solution that contains an individual interfering element and is free of all other contaminates.

6.12.2 The positive or negative effects on the elements of interest are corrected by the following:

6.12.3 Correction value = true value of interfering element / concentration of the element of interest

6.12.4 IECs must only be evaluated and applied by analyst trained in there application.

6.12.5 IEC determination must be verified annually (at least) and updated, if necessary.

6.12.6 When inter-element corrections are not used, on-going SIC solutions must be analyzed to verify the absence of inter-element spectral interference.

6.13 Linearity (L)

6.13.1 Linearity is established by calibrating with a blank plus the linearity standard shown in Trace Table 1.

6.13.2 Dilute and reanalyze samples that are >90% of the established linear calibration limit or use an alternate, less sensitive line for which quality control data is established.

6.13.3 Linearity for all analytes must be updated quarterly.

6.14 Method Detection Limit (MDL)

6.14.1 MDLs must be maintained for each analyte of interest and updated once every year.

6.14.2 The determination of MDLs must be made in accordance with the following:

a. Fortify reagent water at a concentration of 2 to 3 times the estimated instrument detection limit.

b. Take seven replicate aliquots of the fortified reagent water and process through the entire analytical method.

6.14.3 Perform all calculations defined in the method and report the concentration values in the appropriate units.

6.14.4 Calculate the MDL as follows:

$$\mathbf{MDL = (t) \times (s)}$$

where: t = students t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.143 for seven replicates].

S = standard deviation of the replicate analyses.

6.14.5 The final calculated MDL must be less than the original analyte spike level and greater than 10% of the original level.

6.15 Matrix Evaluation

6.15.1 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values. They are as follows:

6.15.2 Serial dilution

6.15.2.1 If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

6.15.3 Post (digestion) Spike

6.15.3.1 An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 70% to 130% of the known value or the established control limits. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The use of a standard-addition analysis procedure may be used to compensate for this effect.

6.15.4 **Caution**: The standard-addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation (IECs), an alternate wavelength, or comparison with an alternate method is recommended.

6.16 Method of Standard Additions

6.16.1 The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_X, are taken. To the first (labeled A) is added a small volume V_S of a standard analyte solution of concentration C_S. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_X is calculated

$$C_X = \frac{S_B * V_S * C_S}{(S_A - S_B) * V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix.

6.16.2 If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

a. The analytical curve must be linear, the correlation coefficient must be >0.995.

b. The chemical form of the analyte must respond the same way as the analyte in the sample.

c. The interference effect must be constant over the working range of concern.

d. The signal must be corrected for any additive interference.

6.16.3 The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

VII. Calculations

7.1 Results are read in ug/L directly from the ICP. Take into account any dilutions preformed during the digestion process for total metals.

7.2 The recoveries of spikes and relative percent difference between duplicate determinations are to be calculated as follows:

$$\mathbf{RPD} = \frac{|C_S - C_D|}{((C_S + C_D) / 2)}$$

$$\mathbf{\%\ Recovery} = \frac{(C_M - C_S)}{C_T}$$

where: RPD = relative percent difference, %
Recovery = matrix spike recovery, %
C_S = unspiked sample concentration, mg/L
C_D = duplicate sample concentration, mg/mL
C_M = matrix spike concentration, mg/L
C_T = theoretical spike concentration, mg/L

7.3 Report recovery and RPD to the nearest 1 %.

VIII. Reagents and Materials

8.1 Varian 720-ES Axial ICP – capable of trace analysis and background correction for multi-element analysis

8.2 Argon gas supply – high purity, liquid or high pressure cylinders

8.3 Concentrated hydrochloric acid – metals analysis grade

8.4 Hydrochloric acid, 1:1 dilution – add 500 mL concentrated hydrochloric acid to 400 mL reagent water and dilute to 1 liter

8.5 Concentrated nitric acid – metals analysis grade

8.6 Nitric acid, 1:1 dilution – add 500 mL concentrated nitric acid to 400 mL reagent water and dilute to 1 liter

8.7 Standard stock solutions – purchased from commercial suppliers

8.8 Second source solutions – purchased from commercial suppliers

8.9 Mixed calibration standard solutions

8.9.1 Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric.

8.9.2 Add the appropriate types and volumes of acids to match sample matrix.

8.9.3 Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together.

8.9.4 Transfer the mixed standard solutions to PFE fluorocarbon or previously unused polyethylene or polypropylene bottles for storage.

8.9.5 Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging.

8.9.6 Calibration standards must be initially verified using a quality control sample and monitored daily for stability.

8.9.7 **Important:** If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. Cool and dilute to 100 mL with reagent water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional hydrochloric acid.

8.9.8 **Note 1:** If the sample analysis solution has a different acid concentration from that given, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

Potential Interferences
Analyte Concentration Equivalents Arising from Interferences at the 100 mg/L Level[a]

Analyte	Wavelength, nm	Interferent[a,b]									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al -	1000 mg/L	Mg -	1000 mg/L
Ca -	1000 mg/L	Mn -	200 mg/L
Cr -	200 mg/L	Tl -	200 gm/L
Cu -	200 mg/L	V -	200 mg/L
		Fe -	1000 mg/L

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentrations to the interferent figure.
[c] Interferences will be affected by background choice and other interferences that may be present.

IX. Sample Collection, Preservation and Storage

9.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples **must** be tested immediately prior to aliquoting for processing or "direct analysis" to ensure the

sample has been properly preserved. If properly acid preserved, the sample can be held up to six months before analysis.

9.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.

9.3 For the determination of total recoverable elements in aqueous samples, samples are **not** filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection; however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until verified to be pH <2.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.

9.4 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

9.5 For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

Appendix A

Metals Department Glossary

1. **Quality Control Sample (QCS):** The QCS must be made from an outside second source different from that of the calibration standards' stock solutions. It is used to verify the calibration.
2. **Initial Calibration Verification (ICV):** The ICV is made from the same source as the calibration standards and is used to verify the calibration standards or stock solutions used to calibrate the instrument.
3. **Continuing Calibration Verification (CCV):** The CCV is made from the same source as the calibration standards at mid-level of the calibration.
4. **Calibration Blank:** The calibration blank contains the same acid matrix as the calibration standards. The calibration blank is also used as the Continuing Calibration Blank (CCB) solution.
5. **Laboratory Reagent Blank (LRB):** The LRB is a reagent blank carried through the entire sample preparation process.
6. **Laboratory Fortified Blank (LFB):** A laboratory fortified blank (LFB) is reagent water fortified with the elements of interest
7. **Sample Duplicate:** A duplicate sample is a second aliquot of a sample that is carried through the entire sample preparation and analytical process.
8. **Laboratory Fortified Matrix / Duplicate (LFM/LFMD):** The LFM/LFMDs are prepared from fresh sample aliquots, spiked in the same manner as the LFB and carried through the entire preparation process.
9. **Linear Dynamic Range (LDR) or Linearity (L):** The linear dynamic range is established by calibrating with a blank plus the linearity standard in Table 1.
10. **Method Detection Limit (MDL):** MDLs is a statistical evaluation of seven (non zero) readings of samples produced in the application of a method.
11. **Serial dilution:** An analysis of a 1:4 dilution that should agree within 10% of the original determination.
12. **Post (digestion) Spike**: An analyte spike added to a portion of a prepared sample, or its dilution.
13. **Practical Quantitation Limit (PQL):** The lowest concentration that can be accurately measured rather than just detected.
14. **Contract Required Detection Limit check standard (CRI):** A standard analyzed to verify the linearity of the ICP instrument near the contract required detection limit. This term is found in the ICP software, but it is not used by Premier Laboratory.

SOP Revision History

Revision No.	Description of Changes	Effective Date	Initiated by
3.2	Added revision history table, deleted Trace 5 standard from standards list and from Table1.	12/1/09	LM
3.3	Changed format	9/26/11	LM
4	Changed header Added number of exposures to be used in Section 4.3 Changed the requirements for the analysis of ICSA and ICSAB in the analytical sequence in Section 4.6 Corrected concentrations and amounts in tables for: Trace 1, Trace 3, ICSAB, Yttrium Working Solution and Trace Table 1 Deleted Trace 4 standard Corrected ICP model number in Section 8.1 Added Metals Department Glossary in Appendix A	10/3/12	NB, LM
5	Added definition of CRI in glossary.	10/26/12	LM
6	Added Section 3.9 for drinking water direct analysis Added table of digestion SOPs to Section 4.1 Added Section 4.1.1 for direct analysis sample prep Changed frequency of LFM in Section 6.11 Added Section IX	4/25/13	LM

Total Kjeldahl Nitrogen

EPA 351.2

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Approved by: **Gregory Plante**
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Reviewed and Implemented by: **Ronald Warila**
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Reference

Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, method 351.2 and 351.1

Determination of Total Kjeldahl Nitrogen by Flow Injection Analysis, Method 10-107-06-2-D, Lachat Instruments, Inc

Technical Report EPA/ CE-81-1, Procedures for Handling and Chemical Analysis of Sediment and Water Samples, May 1981

I. Applicability

1.1 Analyte: Total Kjeldahl Nitrogen

1.2 Matrix: Water, wastewater, soil, sludge, and waste extracts

1.3 Regulation: NPDES, CWA

1.4 The applicable range is 0.5 to 20.00 mg N/L.

1.5 The method detection limit is 0.5 mg N/L.

1.6 The method throughput is 60-80 injections per hour.

II. Method Summary

2.1 The sample is heated in the presence of sulfuric acid (H_2SO_4) for two and one half hours. The residue is cooled, diluted with water and analyzed for ammonia. This digested sample may also be used for phosphorus determination.

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2.2 Total Kjeldahl nitrogen is the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of the digestion described.

2.3 Organic Nitrogen may be reported by subtracting the ammonia results (determined by method 350.1) in mg/L from the TKN results in mg/L for a sample.

2.4 Total Nitrogen may be reported by adding the TKN results in mg/L to the combined Nitrate and Nitrite results in mg/L (determined by method SM4500-NO_3F).

2.5 Approximately 0.3 ml. of the digested sample is injected onto the chemistry manifold where its pH is controlled by raising it to a known, basic pH by neutralization with a concentrated buffer. This in-line neutralization converts the ammonium cation to ammonia, and also prevents undue influence of the sulfuric acid matrix on the pH-sensitive color reaction that follows.

2.6 The ammonia thus produced is heated with salicylate and hypochlorite to produce blue color which is proportional to the ammonia concentration. The color is intensified by adding sodium nitroprusside. The presence of potassium tartrate in the buffer prevents precipitation of calcium and magnesium.

III. Interferences

3.1 Samples must not consume more than 10% of the sulfuric acid during the digestion. The buffer (reagent 3) will only accommodate 4.5-5.0% sulfuric acid without any significant change in signal intensity.

3.2 High nitrate concentrations >10 times the TKN level will suppress the TKN results. A dilution must be performed prior to digestion to eliminate the effect.

3.3 All final digestates must be free of turbidity, filter if necessary.

IV. Definitions

4.1 **Calibration Blank (CB)** -- A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

4.2 **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 response with respect to analyte concentration.

4.3 **Instrument Performance Check Solution (IPC)** - A solution of one or more method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria.

4.4 **Laboratory Fortified Blank (LFB) --** an aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

4.5 **Laboratory Fortified Matrix (LFM)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like sample, and 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 LFM corrected for background concentrations.

4.6 **Laboratory Reagent Blank (LRB)**—An aliquot of reagent water or other blank matrices that is digested exactly as a sample in including exposure to all glassware, equipment, and reagents that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

4.7 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

4.8 **Method Detection Limit (MDL)** — The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

4.9 **Quality Control Sample (QCS)** -- A solution of method analytes of known concentrations that is used to spike an aliquot of LRB. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards.

4.10 **Stock Standard Solution (SSS)** -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

V. Procedure for Distillation

5.1 **Important:** If the block digester tubes are not completely dry and have water droplets on them, there exists the possibility of ammonia contamination in the water droplets. Ensure the tubes are completely dry before beginning the digestion procedure.

5.2 To 20.0 mL of sample or QC standard, add 5 mL digestion solution and mix thoroughly.

5.3 The following QC standards must be digested with each batch of 20 samples or less:

20 mg/L standard
10 mg/L standard
5 mg/L standard
0.5 mg/L standard
Method blank
10mg/L QCS

5.4 Add 2 - 4 Alundum granules or 5-6 Teflon stones to each tube for smooth boiling

5.5 Verify that boiling stones have been placed in each tube. Place tubes in the preheated digestion block for one hour at 160 °C. Water from the sample should have boiled off before increasing the temperature.

5.6 Ramp the digestion block up to 380 °C and set the timer at 90 minutes. The typical ramp time is 50 - 60 minutes. **The temperature must be maintained at 380 °C for 30 minutes.**

5.7 Before removing samples, gather the necessary supplies to dilute the samples with water.

5.7.1 Remove the samples from the block and **allow only *5* minutes cooling**.

5.7.2 Add water to the samples rapidly so that all samples are diluted within 10 minutes of removal from the block.

5.8 Add 20.0 mL DI water to each tube and vortex to mix. The longer the samples have been allowed to cool, the longer the samples should be vortexed.

5.9 Transfer sample to a polypropylene snap-cap vial. Filter out any turbidity, if applicable, only after being vortexed.

VI. Colorimetric Analysis Procedure

6.1 Setup the manifold as shown in diagram 1.

6.2 Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

6.3 Verify input peak timing and integration window parameters using the green dye provide by the manufacturer if necessary followed by DI water flush.

6.4 Place standards in the autosampler, and fill the sample tray. Input the information required

by data system, such as concentration, replicates and QC scheme.

6.5 **Add buffer line first, pump for *5* minutes before adding the rest of the reagents.**

6.6 Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with responses for each standard.

6.7 After the calibration has been established, it must be verified by the analysis of a suitable quality control sample (QCS).

6.7.1 If measurements exceed +/-10% of the established QCS value, the analysis should be terminated and the instrument re-calibrated.

6.7.2 The new calibration must be verified before continuing analysis. Periodic reanalysis (every 10 samples or less) of the QCS can be substituted for continuing calibration check.

6.8 After a stable baseline has been obtained, start the sampler and perform analysis.

6.9 Important Notes

6.9.1 Allow at least 15 minutes for the heating unit to warm up to 60 °C.

6.9.2 If sample concentrations are greater than the high standard the digested sample should be diluted with Reagent 7. When the auto diluter is used, Reagent 7 should be used as diluent. **Do not dilute digested samples or standards with DI water.**

6.9.3 If the salicylate reagent is merged with a sample containing sulfuric acid in the absence of the buffer solution, the salicylate reagent will precipitate. If this occurs all Teflon manifold tubing should be replaced, alternately if flow is only partially restricted, flush the system with 50% sodium hydroxide to dissolve the blockage.

6.9.4 In normal operation nitroprusside gives a yellow background color, which combines with the blue indosalicylate to give an emerald green color. This is the normal color of the solution in the waste.

6.9.5 If baseline drifts, peaks are too wide, or other problems with precision arise, clean the manifold by the following procedure:

1) Place transmission lines in water and pump to clear reagents (2-5 minutes).
2) Place reagent lines in 1 M hydrochloric acid (1 volume of HCl added to 11 volumes of water) and pump for several minutes.
3) Place all transmission lines in water and pump for several minutes.
4) Resume pumping reagents, starting again with the buffer only.

VII. Calibration Standards

7.1 **Standard 1:** Stock Standard 1000 mg N/L

7.1.1 In a 1 L volumetric flask, dissolve 3.819 g ammonium chloride (NH_4Cl) that has been dried for two hours at 110 °C in about 800 mL DI water. Dilute to the mark and invert to mix.

7.2 **Standard 2:** Intermediate Stock Standard 20 mg N/L

7.2.1 To a 1 L volumetric flask, add 20 mL of Standard 1 and dilute to the mark with DI water. Invert to mix.

Working Standards (Prepared Daily)	**A**	**B**	**C**	**D**	**E**
Concentration in mg/L of N	20.0	10.0	5.00	0.50	0.0
Volume of Standard 2 digested and diluted to 20mL with DI water.	Use Std #2 as is	10	5	0.5	0

VIII. Calculations

8.1 Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration.

8.2 Sample concentration is calculated from the regression equation and reported in mg/L directly from the instrument.

8.3 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

8.4 For solids or sediments calculate using the following:

$$\textbf{Total Kjeldahl Nitrogen mg/kg (dry weight)} = \frac{(x)(y)(1000)}{(g)(\%S)}$$

where: x = TKN concentration in sediment digest, mg/L
y = final volume of sediment digest, L
g = wet weight of sample digest, g
%S = percent of solids in sediment sample as a decimal fraction

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IX. Sample Collection, Preservation and Storage

9.1 Samples should be preserved to pH <2 with H_2SO_4 and cooled to 4 °C when collected.

9.2 The maximum holding time is 28 days when properly preserved and stored at 4 °C.

9.3 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water.

9.4 Volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

9.5 The Federal Register entry which defines standard EPA NPDES and NPDWR methods states that "Manual Distillation is NOT required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies".

9.5.1 Studies which show that the non-distilled samples give the same recoveries as the manually distilled samples must be documented and updated regularly.

X. Quality Assurance

10.1 The minimum requirements for this method consists of an initial demonstration of laboratory capability, and the analysis of laboratory distilled reagent blanks, fortified blanks and a mid-level CCV in order to evaluate performance.

10.2 Initial Demonstration of Performance

10.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

10.2.2 The linear calibration range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected.

10.2.2.1 The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear.

10.2.2.2 The verification of linearity must use a minimum of a blank and three standards.

10.2.2.3 If any verification data exceeds the initial values by 10%, linearity must be reestablished.

10.2.2.4 If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

10.2.3 Immediately following the calibration, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a quality control sample (QCS).

10.2.3.1 If the determined concentrations are not within 10% of the stated values, performance of the determinative step of the method is unacceptable.

10.2.3.2 The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

10.2.4 Method detection limits (MDLs) must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.

10.2.4.1 To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method.

10.2.4.2 Perform all calculations defined in the method and report the concentration values in the appropriate units.

10.2.4.3 Calculate the MDL as follows:

$$\mathbf{MDL = (t) \times (S)}$$

where: t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]

S = standard deviation of the replicate analyses

10.2.4.4 MDLs should be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response.

10.3 Laboratory Reagent Blank (LRB)

10.3.1 The laboratory must analyze at least one LRB with each batch of 20 samples or less.

10.3.2 Data produced are used to assess contamination from the laboratory environment.

10.3.3 Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

10.4 Laboratory Fortified Blank (LFB)

10.4.1 Prepare and analyze at least one LFB with each batch of 20 samples or less and calculate accuracy as percent recovery.

10.4.2 If the recovery of any analyte falls outside the required control limits of **90-110%,** that analyte is out of control, and the source of the problem should be identified and resolved before continuing analyses. The LFB analyses data must be used to assess performance against the required control limits of 90-110% or laboratory established control limits.

10.4.3 The control limits must be equal to or better than the required control limits of 90-110%. New control limits can be calculated using the most recent 20-30 data points. This data must be kept on file and be available for review.

10.4.4 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

10.5 Instrument Performance Check Solution (IPC)

10.5.1 For all determinations the IPC (a mid-range check standard) and a calibration blank must be analyzed 1) immediately following daily calibration, 2)after every tenth sample (or more frequently, if required) and 3)at the end of the sample run.

10.5.2 Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within 10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within 10%.

10.5.3 If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated.

10.5.4 All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

10.6 Laboratory Fortified Sample Matrix (LFM)

10.6.1 The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The added analyte concentration should be the same as that used in the laboratory fortified blank.

10.6.2 If the concentration of fortification is less than 25% of the background concentration of the matrix the matrix recovery should not be calculated.

10.6.3 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 75-125%.

10.6.4 Percent recovery may be calculated using the following equation:

$$\mathbf{R = \frac{C_s - C}{S} \times 100}$$

where: R = percent recovery
C = fortified sample concentration
C_s = sample background concentration
S = concentration equivalent of analyte added to sample

10.6.5 Until sufficient data becomes available (usually a minimum of 20-30 analysis), assess laboratory performance against recovery limits of 75-125%. When sufficient internal performance data becomes available, develop control limits from percent mean recovery.

10.6.6 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

XI. Reagents and Materials

11.1 Balance—analytical, capable of accurately weighing to the nearest 0.0001g.

11.2 Glassware Class A volumetric flasks and pipettes or plastic containers as required Samples may be stored in plastic or glass.

11.3 Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios, including the following:

a. Autosampler
b. Multichannel proportioning pump
c. Reaction unit or manifold
d. Colorimetric detector
e. Data system
f. Heating Unit
g. Vortex stirrer
h. Use deionized water (10 mega ohm) for all solutions.

11.4 Degassing with helium

11.4.1 To prevent bubble formation, degas the carrier and buffer with helium. Use He at 140 kPa (20 lb/in^2) through a helium degassing tube. Bubble helium through one liter of solution for one minute.

11.4.2 **All reagents used in heated chemistry must be degassed.**

11.5 **Reagent 1 - Mercuric Sulfate Solution**

11.5.1 By Volume: Add approximately 40.0 mL water and 10 mL concentrated sulfuric acid (H_2SO_4) to a 100 mL volumetric flask. Then add 8.0 g red mercuric oxide (HgO). Stir until dissolved, dilute to the mark and invert to mix. Warming the solution while stirring may be required to dissolve the mercuric oxide.

11.6 **Reagent 2 - Digestion Solution**

11.6.1 By Volume: In a 1 L volumetric flask, add 133.0 g potassium sulfate (K_2SO_4) and 200 ml concentrated sulfuric acid (H_2SO_4) to approximately 700 ml water. Add 25.0 mL Reagent 1. Dilute to the mark with water and invert to mix. **Prepare fresh monthly.**

11.7 **Reagent 3 - Buffer**

11.7.1 **Important:** To reduce the possibility of the potassium tartrate being contaminated it is recommended that the tartrate buffer is boiled for 10 minutes. To verify that the tartrate buffer is pure enough compare the

reagent baseline to the DI baseline. The baseline, with all reagents flowing should not be greater than 0.15mV difference from just the DI water pumping in all the lines.

11.7.2 By Volume: In a 1 L container add 900 ml water, 50 g potassium tartrate (or potassium sodium tartrate, D, L-$NaKC_4H_4O_6 \bullet 4H_2O$), 50 g sodium hydroxide (NaOH), and 26.8 g sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \bullet 7\ H_2O$) mix until dissolved. Boil for 10 minutes. Cool to room temperature and transfer to a 1 L volumetric flask. Dilute to the mark and invert to mix.

11.8 **Reagent 4 - Sodium Hydroxide (0.8 M)**

11.8.1 By Volume: In a 1 L volumetric flask dissolve 32 g sodium hydroxide (NaOH) in about 800 mL of water. Invert to mix and dilute to the mark.

11.8.2 By Weight: In a 1 L container dissolve 32 g sodium hydroxide (NaOH) in 985g of water.

11.9 **Reagent 5 - Salicylate Nitroprusside**

11.9.1 By Volume: In a 1 L volumetric flask dissolve 150.0 g sodium salicylate [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$], and 1.0 g sodium nitroprusside [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \bullet 2H_2O$] in about 800 mL water. Invert to mix and dilute to the mark. **Store in a dark bottle and prepare fresh monthly.**

11.9.3 By Weight: To a tared 1 L dark container, add 150.0 g sodium salicylate [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$], 1.0 g sodium nitroprusside [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO \bullet 2H_2O$] and 908g water. Stir or shake until dissolved. **Store in a dark bottle and prepare fresh monthly.**

11.10 **Reagent 6 - Hypochlorite Solution**

11.10.1 By Volume: In a 250 mL volumetric flask, dilute 13.1 mL Regular Clorox Bleach, 6.0% sodium hypochlorite, The Clorox Company, Oakland, CA, (**do not substitute with any other brand of bleach**) to the mark with water (236.9 ml). Invert to mix. **Prepare fresh daily.**

11.10.2 By Weight: To a tared 250 mL container, add 16 g of Regular Clorox Bleach and 234 g DI water. Invert to mix. **Prepare fresh daily.**

11.11 **Reagent 7 - Diluent**

11.11.1 **Important:** Diluent is used to prepare the carrier and for off line dilutions. The

sulfuric acid concentration in the carrier needs to match the digestion matrix.

11.11.2 By Volume: In a 2 L volumetric flask, add in the following order: approximately 1800 ml of DI water, 100 mL of concentrated H_2SO_4 and 63.4g of Potassium sulfate (K_2SO_4). Invert to mix and bring to volume. **Prepare fresh weekly.**

XII. Pollution Prevention

12.1 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.

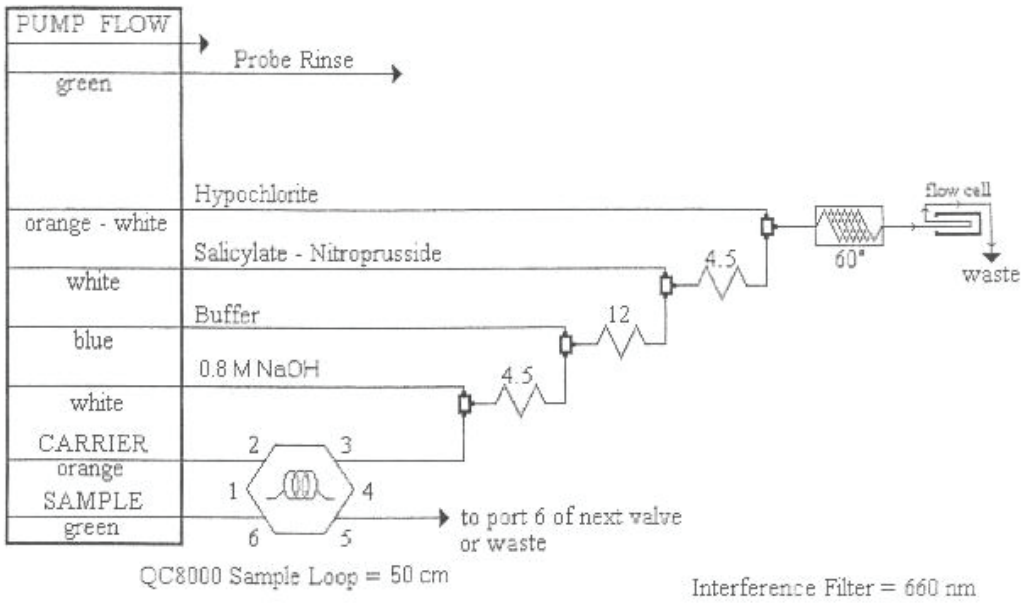
12.3 Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation.

12.4 Quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIII. Waste Management

13.1 All waste is handled in accordance with Premier Laboratory's Chemical Hygiene Plan, which is available to all employees and interested parties.

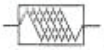
Diagram 1: TKN Manifold Setup



CARRIER is Diluent (reagent 7).

All manifold tubing is **0.8 mm (0.032 in) i.d**. Lachat Part No. 50028. This is **5.2 uL/cm**.

4.5	is	**70**	cm of tubing on a 4.5 cm coil support
12	is	**255**	cm of tubing on a 12 cm coil support

APPARATUS: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  indicates 650 cm of tubing wrapped around the heater block at the specified temperature.

SOP Revision History

Revision No.	Description of Changes	Effective Date	Initiated by
1.1	Added revision history table Changed the amount of bleach used to make 6% sodium hypochlorite from 15ml to 13.1ml in Section X.	4/14/09	LM
1.2	Section V: changed 2ml digestion solution to 5ml and changed concentration of 2ppm QC standard to 5ppm	4/17/09	LM
1.3	Changed format Added Section 5.3	9/22/10	LM
2	Changed header Changed approval signatures Corrected units for standard in 7.1 Corrected distilled standards in Section 7.2	10/4/12	DD, LM

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Phosphorus Automated (All Forms)
Method 365.1

Prepared by: Melisa Montgomery, Quality Assurance Officer
Approved by: Robert Stevenson, Laboratory Director
Reviewed and Implemented by: Ronald Warila, General Manager

Reference:

Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 365.1

Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, Method 4500P-F

Technical Report EPA/ CE-81-1, Procedures for Handling and Chemical Analysis of Sediment and Water Samples, May 1981

QuikChem® Method 10-1 15-01-1-A, Lachat Instruments, Milwaukee, WI, August, 2000

I. Applicability

1.1 This method covers the determination of all forms of phosphorus in drinking water, surface water and domestic and industrial wastes. It is also modified to perform soil analysis with a pre-digestion. The applicable range of this method is 0.01 to 2.0 mg/L Phosphate as P.

II. Important Notes

2.1 Sample containers may be of plastic material, such as a cubitainer, or of Pyrex glass.

2.2 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 mL of conc. H_2SO_4 per liter and refrigeration at 4°C.

2.3 Ortho phosphate is **never preserved**.

2.4 Concentrations of ferric iron (Fe^3-) greater than 50 mg/L will cause a negative error due to precipitation of, and subsequent loss, of orthophosphate. Samples high in iron can be pretreated with sodium bisulfite to eliminate this interference. Treatment with bisulfite will also remove the interference due to arsenates.

2.5 Glassware contamination is a problem in low level phosphorus determinations. Glassware should be washed with 1:1 HC1 and rinsed with deionized water.

Commercial detergents should rarely be needed but, if they are used, use special phosphate-free preparations for lab glassware.

2.6 All quality control samples are digested.

2.7 All glassware is cleaned with 1:1 HCl.

III. Definitions

3.1 Calibration Blank (CB) – A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

3.2 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 response with respect to analyte concentration.

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3.5 Laboratory Fortified Matrix (LFM) – An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LSM is analyzed exactly like sample, and 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 LFM corrected for background concentrations.

3.6 Laboratory Reagent Blank (LRB) – An aliquot of reagent water or other blank matrices that is digested exactly as a sample in including exposure to all glassware, equipment, and reagents that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

3.7 Linear Calibration Range (LCR) – The concentration range over which the instrument response is linear.

3.8 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.9 Quality Control Sample (QCS) – A solution of method analytes of known concentrations that is used to spike an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.10 Stock Standard Solution (SSS) – A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

IV. Procedure for Ortho Phosphorus

4.1 Analyze unfiltered, with no digestion or hydrolysis. Holding time is 48 hours with no preservative. Proceed to calibration section.

V. Procedure for Total Phosphorus

5.1 Digestion of Aqueous samples

5.1.1 To 50 mL of sample, add 1 drop phenolphthalein indicator solution. If a red color appears, add H_2SO_4 solution dropwise until color is discharged.

Then add 1 mL H_2SO_4 solution to all samples, blanks and QC samples.

5.1.2 Add 0.4 g of ammonium persulfate.

5.1.3 Boil gently on a preheated hot plate for approximately 30-40 minutes or until a final volume of about 10 mL is reached, or if grey smoke fills the flask. Do not allow sample to go to dryness. Redigest if sample goes to dryness.

5.1.4 Cool sample and dilute to approximately 30 mL with distilled water. Add 1 mL 6N NaOH then dilute to a final volume of 50mL.

5.1.5 If samples are not clear at this point, filter the sample and an aliquot of both the LFB and LRB to be run as filter QC samples.

5.2 Procedures for Sediment Samples

5.2.1 Persulfate digestion

5.2.1.1 Weigh 0.5-1.0g dry weight equivalent of the sample and transfer to a 150-mL beaker.

5.2.1.2 Add 10 mL 30 percent H_2SO_4 and 2 g potassium persulfate.

5.2.1.3 Mix the suspension and heat on a hot plate for 1 hr.

5.2.1.4 Filter with a pre-rinsed paper filter (Watman 41 or equivalent) into a l00-mL volumetric flask and dilute to volume.

5.2.1.5 Prepare a separate LFB, LRB and LFM/LFMD for sediments.

VI. Calculations

6.1 Report only the values that are less than 90% of the highest standard in the calibration. Dilute appropriately and re-analyze samples that do not meet this criteria

6.2 Aqueous Samples

6.2.1 Direct reading in mg/L from the Lachat

6.3 Solid Samples

6.3.1 Calculate the phosphate concentration on a dry weight basis as follows:

$$\textbf{Total phosphate mg/kg (dry weight)} = \frac{(x)(y)(1000)}{(g)(\%S)}$$

where: x = phosphate concentration in sediment digest, **mg/L**
y = final volume of sediment digest, **L**
g = wet weight of sample digest, **g**
%S = percent of solids in sediment sample, **as a decimal fraction**

VII. Standards and Reagent Preparation

7.1 Preparation of Reagents

7.1.1 Use deionized water for all solutions.

7.1.2 Degassing with helium

7.1.2.1 To prevent bubble formation, degas the carrier solution with helium. Use He at 5-20 psi through a disposable narrow tip pipette. Bubble He vigorously through the solution for one minute. Dispose of the pipette after each use.

7.1.3 **Reagent 1 – Stock Ammonium Molybdate Solution**

7.1.3.1 In a 1 L volumetric flask dissolve 40.0 g ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in approximately 800 mL DI water.

7.1.3.2 Dilute to the mark and stir for four hours.

7.1.3.3 Store in plastic and refrigerate.

7.1.3.4 May be stored up to two months when kept refrigerated.

7.1.4 **Reagent 2 – Stock Antimony Potassium Tartrate Solution**

7.1.4.1 In a 1 L volumetric flask, dissolve 3.0 g antimony potassium tartrate (potassium antimony tartrate hemihydrate $K(SbO)C_4H_4O_6\cdot \frac{1}{2}H_2O$) or dissolve 3.22 g antimony potassium tartrate (potassium antimony

tartrate trihydrate $K_2(C_4H_2O_6Sb)_2 \cdot 3H_2O$) in approximately 800 mL of DI water.

7.1.4.2 Dilute to the mark and invert three times.

7.1.4.3 Store in a dark bottle and refrigerate.

7.1.4.4 Maybe stored up to two months when kept refrigerated.

7.1.5 **Reagent 3 – Molybdate Color Reagent**

7.1.5.1 To a 1 L volumetric flask add about 500 mL DI water.

7.1.5.2 Add 35.0 mL concentrated sulfuric acid and swirl to mix.

(CAUTION: The reaction is exothermic; it will get warm!)

7.1.5.3 When it can be comfortably handled, add 72.0 mL Stock Antimony Potassium Tartrate Solution (Reagent 2) and 213 mL Stock Ammonium Molybdate Solution (Reagent 1).

7.1.5.4 Dilute to the mark and invert three times.

7.1.5.5 Degas with helium.

7.1.5.6 Prepare fresh weekly.

7.1.6 **Reagent 4 – Ascorbic Acid Reducing Solution, 0.33 M**

7.1.6.1 In a 1 L volumetric flask dissolve 60.0 g granular ascorbic acid in about 700 mL of DI water.

7.1.6.2 Dilute to the mark and invert to mix.

7.1.6.3 Add 1.0 g dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$).

7.1.6.4 Prepare fresh weekly.

7.1.6.5 Discard if the solution becomes yellow.

7.1.7 **Reagent 5 – Sodium Hydroxide - EDTA Rinse**

7.1.7.1 Dissolve 65 g sodium hydroxide (NaOH) and 6 g tetrasodium ethylenediamine tetraacetic acid (Na_4EDTA) in 1.0 L DI water.

7.1.8 **Reagent 6 – Sulfuric Acid Solution, 11 N**

7.1.8.1 Carefully add 300mL concentrated H_2SO_4 to approximately 600mL of distilled water and dilute to 1L with distilled water.

7.2 Preparation of Standards

7.2.1 **Stock Standard Solution #1: 250.0 mg/L of Phosphate as P**

7.2.1.1 In a 500 mL volumetric flask dissolve 0.5495 g primary standard grade anhydrous potassium phosphate monobasic (KH_2PO_4) that has been dried for one hour at 105 ^oC in approximately 400 mL water.

7.2.1.2 Dilute to the mark with DI water and invert to mix.

7.2.2 **Stock Standard Solution #2: 50.0 mg/L of Phosphate as P**

7.2.2.1 In a 200 mL volumetric flask, dilute 40.0 mL Stock Standard Solution #1 to the mark with DI water.

7.2.2.2 Invert to mix.

7.3 Working Standards

7.3.1 Prepare fresh daily using deionized H_2O as shown below:

Standard	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**Blank**
Concentration, mg/L	2	1	0.5	0.2	0.05	0.02	0.01	--
mL of Solution #2	10	5	2.5	1.0	0.25	0.1	--	--
mL of Standard A	--	--	--	--	--	--	1	--
Final Volume, mL	250 mL							

VIII. Instrumental Analysis

8.1 pH Adjustment of Samples

8.1.1 Test the pH of all samples submitted for orthophosphate analysis using the pH test strip method.

8.1.2 If samples have a pH >8, add 1 drop of phenolphthalein indicator to a 50 mL aliquot of sample. If a red color develops, add 11 N sulfuric acid (310 mL concentrated H_2SO_4/L) drop-wise to just discharge the color. Acidic samples (pH<4) must be neutralized with 1 N NaOH (40 g NaOH/L).

8.2 Prepare reagent and standards as described.

8.3 Set up manifold as shown in Diagram 1.

8.4 Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

8.5 Prime the auto diluter pump with the carrier reagent.

8.6 Input the sample data into the sample tray application.

8.7 Calibrate using the prepared standards to create a curve with a correlation coefficient of 0.995 or better.

8.8 Analyze the samples and QC in the established sequence.

IX. Quality Assurance

9.1 The minimum requirements for this method consists of an initial demonstration of laboratory capability, and the analysis of laboratory distilled reagent blanks, fortified blanks and a mid-level CCV in order to evaluate performance. Undigested reagent blanks, fortified blanks and mid level CCV may be used when digestion of the analyzed samples in not required.

9.2 Initial Demonstration of Performance

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Linear Calibration Range (LCR)

9.2.2.1 The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected.

9.2.2.2 The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear.

9.2.2.3 The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3 Quality Control Sample (QCS)

9.2.3.1 Immediately following the calibration, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS.

9.2.3.2 If the determined concentrations are not within 10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4 Method Detection Limit (MDL)

9.2.4.1 MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.

9.2.4.2 To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units.

9.2.4.3 Calculate the MDL as follows:

MDL= (t) x (S)

where: t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t= 3.14 for seven replicates]
S = standard deviation of the replicate analyses

9.2.4.4 MDLs should be determined every year, when a new operator begins work or whenever there is a significant change in the background or instrument response.

9.3 Laboratory Reagent Blank (LRB)

9.3.1 The laboratory must analyze at least one LRB with each batch of 20 samples or less.

9.3.2 Data produced are used to assess contamination from the laboratory environment.

9.3.3 Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.4 Laboratory Fortified Blank (LFB)

9.4.1 At least one LFB must be analyzed with each batch of 20 samples or less.

9.4.2 Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses. The LFB analyses data must be used to assess performance against the required control limits of 90-110% or laboratory established control limits.

9.4.2.1 The control limits must be equal to or better than the required control limits of 90-110%. New control limits can be calculated

using the most recent 20-30 data points. This data must be kept on file and be available for review.

9.4.3 Prepare a 1.25 ppm LFB by adding 0.5 mL of 250 ppm phosphate stock solution to 100 mL of distilled water. Digest with the sample batch for total phosphate.

9.4.4 An orthophosphate LFB is an aliquot of the 1.0 ppm standard that has been diluted from the stock with DI water.

9.4.5 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

9.5 Instrument Performance Check Solution (IPC)

9.5.1 For all determinations the IPC (a mid-range check standard) must be analyzed and a calibration blank immediately following daily calibration, and after every tenth sample (or more frequently, if required) and at the end of the sample run.

9.5.2 Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within 10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within 10%.

9.5.3 If the calibration cannot be verified within the specified limits, reanalyze the IPC solution.

9.5.4 If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated.

9.5.5 All samples following the last acceptable IPC solution must be reanalyzed.

9.5.6 The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.6 Laboratory Fortified Sample Matrix (LFM)

9.6.1 The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples.

9.6.2 In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis.

9.6.3 The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.6.4 For total phosphate, the LFM undergoes the digestion process.

9.6.5 The LFM is prepared by adding 0.5 mL of 250 ppm stock to 100 mL of sample. This will result in a 1.25-ppm spike.

9.6.6 If orthophosphate is needed, add 0.1 mL of 250-ppm stock to 25 mL of sample. This will result in a 1.0-ppm spike. The orthophosphate LFM is not digested.

9.6.7 If the concentration of fortification is less than 25% of the background concentration of the matrix the matrix recovery should not be calculated.

9.6.8 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 75-125%. Percent recovery may be calculated using the following equation:

$$\mathbf{R = \frac{C_s - C}{s} \times 100}$$

where: R = percent recovery
C = fortified sample concentration
C_s = sample background concentration
s = concentration equivalent of analyte added to sample

9.6.9 Until sufficient data becomes available (usually a minimum of 20-30 analysis), assess laboratory performance against recovery limits of 75-125%.

9.6.10 When sufficient internal performance data becomes available, develop control limits from percent mean recovery. If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

X. Pollution Prevention

10.1 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 the laboratory. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice.

10.2 Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation by the following means:

10.2.1 Insure that the quantity of the chemicals purchased is based on expected usage during its shelf life and the disposal cost of unused material.

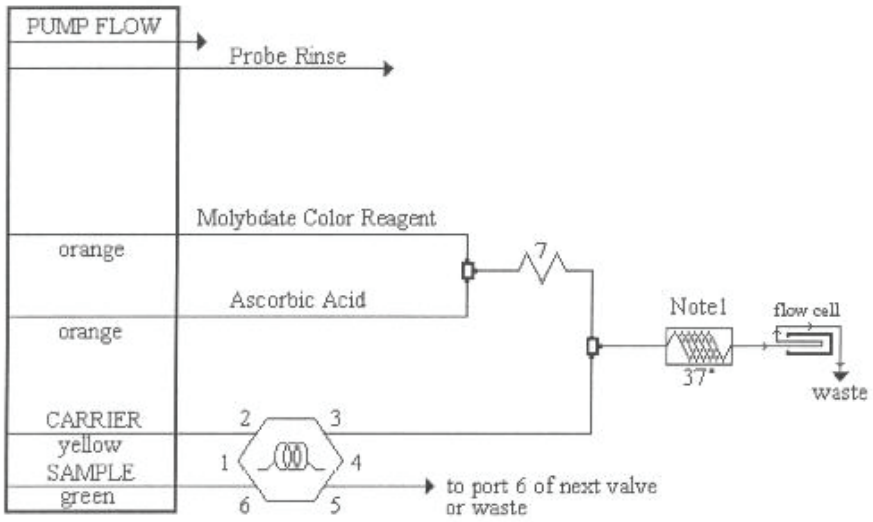
10.2.2 Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

10.2.3 Control the usage by closely monitoring the instrument operation to avoid pumping reagents through after sample run has completed.

XI. Waste Management

11.1 All waste is handled in accordance with Premier Laboratory's Chemical Hygiene Plan, which is mandatory reading for all employees and is readily available for any interested parties.

Diagram 1: Phosphate Manifold Setup



Carrier: DI water
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2 µL/cm.
AE Sample Loop: 70 cm x 0.8 mm i.d.
QC8000 Sample Loop: 75.5 cm x 0.8 mm i.d.
Interference Filter: 880 nm

Apparatus: An injection valve, a 10 mm path length flow cell , and a colorimetric detector module is required. The  shows 175 cm of tubing wrapped around the heater block at 37°C.

7: 135 cm of tubing on a 7 cm coil support

Note 1: 175 cm of tubing on the heater.

SOP Revision History

Date	Previous Revision No.	New Revision No.	Description of Changes	Effective Date	Initiated by
6/8/09	2.2	2.3	Added revision history table	6/8/09	LM
2/22/11	2.3	2.4	Clarified addition of H_2SO_4 in Section 5.1.1 Clarified filtration requirement in Section 5.1.5 Added requirement to prepare LFB, LRB, and LFM/LFMD for sediments in Section 5.2.1.5 Changed standards preparation instructions for smaller amounts in Section 7.2	2/25/11	BS, LM

Determination of Nitrate & Nitrite
SM4500 NO_3 -F

Prepared by: **Melisa Montgomery**
Quality Assurance Officer

Approved by: **Gregory Plante**
Laboratory Manager

Reviewed and Implemented by: **Ronald Warila**
General Manager/Technical Director

Reference

Methods and Guidance for Analysis of Water, EPA 821-C99-004, Method 353.2, 1978

Standard Methods for the Examination of Water and Wastewater, SM4500 NO_3 F, 20th Edition, 1998

Determination of Nitrate and Nitrite by Flow Injection Analysis, Method 10-107-04-1-A, Lachat Instruments, Inc

I. Scope and Application

1.1 Matrix: Drinking water, surface water, mixed domestic and industrial wastewaters.

1.2 Regulation: NPDES, RCRA, SDWA, CWA

1.3 The applicable range is 0.2 to 20.0 mg N/L as NO_3 or NO_2. The method throughput is 55 injections per hour.

II. Summary of Method

2.1 Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water-soluble dye has a magenta color that is read at 520 nm. Nitrite alone also can be determined by removing the cadmium column.

III. Definitions

3.1 Calibration Blank (CB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.

3.2 Calibration Standard (CAL) – A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 Field Duplicates (FD) – Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.3.1 Sample Duplicates (DUP) – A duplicate sample is a second sample aliquot brought through the entire sample preparation and analytical process.

3.4 Instrument Performance Check Solution (IPC) – A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.5 Laboratory Fortified Blank (LFB) – An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.6 Laboratory Fortified Sample Matrix (LFM) – An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and 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 LFM corrected for background concentrations.

3.7 Laboratory Reagent Blank (LRB) – An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.8 Linear Calibration Range (LCR) – The concentration range over which the instrument response is linear (correlation coefficient >0.995).

3.9 Material Safety Data Sheet (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.10 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.11 Performance Evaluation Sample (PE) – A solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), U. S. Environmental Protection Agency, Cincinnati, Ohio,

to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.12 Quality Control Sample (QCS) – A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.13 Stock Standard Solution (SSS) – A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

IV. Interferences

4.1 Residual chlorine can interfere by oxidizing the cadmium column.

4.2 Low results would be obtained for samples that contain high concentrations of iron, copper, or other metals. In this method, EDTA is added to the buffer to reduce this interference.

4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

4.4 Sample turbidity may interfere. Turbidity can be removed by filtration through a 0.45 pore diameter membrane filter prior to analysis.

V. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for know extremely hazardous materials.

5.2 The following chemicals have the potential to be highly toxic or hazardous. For detailed explanations, consult the MSDS.

a. Cadmium granules- **highly toxic!** Always wear protective clothing, gloves, and eyewear.
b. Ammonium hydroxide
c. Sodium hydroxide
d. Phosphoric acid
e. Sulfanilamide

VI. Equipment and Supplies

6.1 Balance – analytical, capable of accurately weighing to the nearest 0.0001 g

6.2 Glassware – Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3 Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

6.3.1 Lachat 8000

6.3.1.1 Autosampler

6.3.1.2 Colorimetric detector

6.3.1.3 Data system

6.3.1.4 10 nm band pass, 80 µL, glass flow cell

6.3.1.5 520 nm interference filter

6.4 Special Apparatus

6.4.1 Cadmium, (Copper Sulfate activated) Reduction Column (Lachat part #50237)

VII. Reagents and Standards

7.1 Preparation of Reagents

7.1.1 Use deionized water (10 megohm) for all solutions.

7.1.2 Degassing with helium

7.1.2.1 To prevent bubble formation, degas all solutions, except the standards, with helium. Use He at 140 kPa (20 lb/in2) through a helium degassing tube (Lachat part #50100). Bubble He through one liter of solution for one minute.

7.1.3 Reagent 1, 15N Sodium Hydroxide

7.1.3.1 By Volume: Add 150 g NaOH very slowly to 250 mL or g of water. CAUTION: The solution will get very hot! Swirl until dissolved. Cool and store in a plastic bottle.

7.1.4 Reagent 2, Ammonium Chloride buffer, pH 8.5

7.1.4.1 By Volume: In a 1L volumetric flask, dissolve 85.0 g ammonium chloride (NH_4Cl) and 1.0 g disodium ethylenediamine tetra-acetic acid dihydrate ($Na_2EDTA{\cdot}2H_2O$) in about 800 mL water. Dilute to the mark and invert to mix. Adjust the pH to 8.5 with 15 N sodium hydroxide solution.

7.1.4.2 ACS grade ammonium chloride has been found occasionally to contain significant nitrate contamination. USP grade is the only grade to be used. (VWR # EM-AX1277-1, 500g bottle or equivalent)

7.1.5 Reagent 3, Sulfanilamide color reagent

7.1.5.1 By Volume: In a 1L volumetric flask, add approximately 600 mL DI water. Then add 100 mL 85% phosphoric acid (H_3PO_4), 40.0 g sulfanilamide, and 1.0 g N-(1-naphthyl) ethylenediamine dihydrochloride (NED). Shake to wet, and stir to dissolve for 30 minutes. Dilute to the mark, and invert to mix. Store in a dark bottle.

7.1.5.2 This solution is stable for one month.

7.2 Preparation of Standards

7.2.1 NOTE: Following are standards preparation instructions for a 1-channel system determining NO_2 + NO_3 or NO_2 alone and instructions for a 2-channel system where one channel is used for NO_2^- + NO_3^- and the other channel is used for determining NO_2^-. For the 1-channel system, either NO_2 or NO_3 standards may be used. The use of NO_3^- standards is recommended when running a 1-channel method for NO_2 + NO_3. For the 2-channel system, the use of separate NO_2 + NO_3 standard sets is recommended.

7.2.2 Standard 1. Stock Nitrate Standard 200 mg N/L as NO_3

7.2.2.1 By Volume: In a 1L volumetric flask, dissolve 1.444 g potassium nitrate (KNO_3) into approximately 600 mL water. Dilute to the mark and invert to mix.

7.2.2.2 This solution is stable for six months.

7.2.3 Standard 2, Stock Nitrite Standard, 200 mg N/L as NO_2

7.2.3.1 By Volume: In a 1L volumetric flask, dissolve 0.986 g sodium nitrite ($NaNO_2$) or 1.214 g potassium nitrite (KNO_2) in approximately 800 mL water. Dilute to the mark and invert to mix. This solution is stable for 3-5 days.

7.2.4 Working standards are prepared daily as shown in the following charts.

Nitrate Standards						
Standard	**A**	**B**	**C**	**D**	**E**	**F**
Concentration mg N/L as NO_3	20.0	10.0	5.0	2.0	0.5	0.1
Volume (mL) of **Stock Standard 1** diluted to 250 mL with **DI water**	25.0	10.0	5.0	---	---	---
Volume (mL) of **Standard A** diluted to 250 mL with **DI water**	---	---	---	12.5	5.00	2.50

Nitrite Standards						
Standard	**A**	**B**	**C**	**D**	**E**	**F**
Concentration mg N/L as NO_3	20.0	8.0	4.0	1.00	0.4	0.2
Volume (mL) of **stock standard 2** diluted to 250 mL with **DI water**	25.0	10.0	5.0	---	---	---
Volume (mL) **standard A** diluted to 250 mL with **DI water**	---	---	---	12.5	5.00	2.50

VIII. Sample Collection, Preservation and Storage

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample.

8.2 Samples for nitrate-nitrite (combined) may be preserved with H_2SO_4 to a pH<2 and cooled to 4 ºC at the time of collection. Preservation should be avoided in order to minimize premature breakdown of the cadmium column.

8.3 Samples should be analyzed as soon as possible after collection. If storage is required, preserved samples are maintained at 4 ºC and may be held for up to 28 days.

8.4 Samples to be analyzed for nitrate or nitrite only should be cooled to 4 ºC and analyzed within 48 hours.

8.5 **Caution:** Samples must not be preserved with mercuric chloride or thiosulfate because this will degrade the cadmium column.

8.6 All samples analyzed must be free of suspended matter that will clog the reduction column and restrict sample flow. The samples must be pre-filtered if any suspended matter is present.

IX. Quality Control

9.1 The minimum requirements for this method consists of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.2 Initial Demonstration of Performance

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Linear Calibration Range (LCR) – The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3 Quality Control Sample (QCS) – When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within 10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4 Method Detection Limit (MDL) – MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units.

9.2.5 Calculate the MDL as follows:

$$\mathbf{MDL = (t) \times (S)}$$

where: t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t= 3.14 for seven replicates]
S = standard deviation of the replicate analyses

9.2.6 MDLs should be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response.

9.3 Assessing Laboratory Performance

9.3.1 Laboratory Reagent Blank (LRB) – The laboratory must analyze at least one LRB with each batch of 20 samples or less. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.3.2 Laboratory Fortified Blank (LFB) – At least one LFB with each batch of 20 samples or less. Calculate accuracy as percent recovery (Section 9.4.2). If the recovery of any analyte falls outside the required control limits of 90-110%, that

analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The LFB analyses data must be used to assess laboratory performance against the required control limits of 90-110%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x - 3S

9.3.3.1 The optional control limits must be equal to or better than the required control limits of 90-110%. After each five to 10 new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. This data must be kept on file and be available for review.

9.3.3.2 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

9.3.4 Instrument Performance Check Solution (IPC) – For all determinations the IPC (a mid-range check standard) must be analyzed and a calibration blank immediately following daily calibration, and after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within 10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within 10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.4 Assessing Analyte Recovery and Data Quality:

9.4.1 Laboratory Fortified Sample Matrix (LFM) – Prepare and analyze one LFM for every batch of 20 or less samples.

9.4.1.1 In each case, the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.1.2 If the concentration of fortification is less than 25% of the background concentration of the matrix, the matrix recovery should not be calculated.

9.4.2 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%.

9.4.2.1 Percent recovery may be calculated using the following equation:

$$R = \frac{C_s - C}{S} \times 100$$

where: R = percent recovery
C = fortified sample concentration
C_s = sample background concentration
s = concentration equivalent of analyte added to sample

9.4.3 Until sufficient data becomes available (usually a minimum of 20-30 analysis), assess laboratory performance against recovery limits of 90-110%. When sufficient internal performance data becomes available, develop control limits from percent mean recovery and the standard deviation of the mean recovery.

9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

9.4.5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

9.4.6 Sample Duplicate – Analyze one duplicate sample for every 20 or less samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process. A control limit of ± 20% for RPD shall be used for sample values greater than 5 times the instrument detection limit. A difference of detection limit is to be used to evaluate samples below 5 times the detection limit.

X. Calibration and Standardization

10.1 Prepare reagents and standards.

10.2 Set up manifold as shown in Figure 1.

10.3 Input data system parameters.

10.4 Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

10.5 Place standards in the autosampler. Input the information required by the data system.

10.6 Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the peak area for each standard to determine the calibration curve.

10.7 Verify calibration using a midrange calibration standard every ten samples or every analytical batch. Compute the percent recovery using the following equation:

$$\% \text{ recovery} = \frac{D}{K} \times 100$$

where: D = Determined concentration of analyte in the calibration standard
K = Actual concentration of the analyte in the calibration standard

10.8 If the % recovery exceeds ±10%, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the analytical batch re-analyzed.

X. Procedure

11.1 Prepare reagents and standards.

11.2 Set up manifold as shown in Figure 1.

11.3 Input data system parameters.

11.4 Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

11.5 Adjust samples to pH between 5 and 9 before analysis with either concentrated HCl or NaOH for preserved samples.

11.6 Place samples in the autosampler. Input the sample identification required by the data system.

11.7 Trouble-shooting Guide is in the System Operation Manual along with instructions for repacking a cadmium column.

XI. Data Analysis and Calculations

12.1 Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting peak area versus standard concentration. Sample concentration is calculated from the regression equation.

12.2 Report only those values that fall between the lowest and the highest calibration standards. Samples greater than 90% of the highest standard must be diluted and re-analyzed.

12.3 Report sample results for nitrate/nitrite in ug N/L as NO_3 or NO_2 to two significant figures for samples above the MDL. Enter results below the MDL as zero in the LIMS system.

XII. Pollution Prevention

13.1 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.

13.2 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.

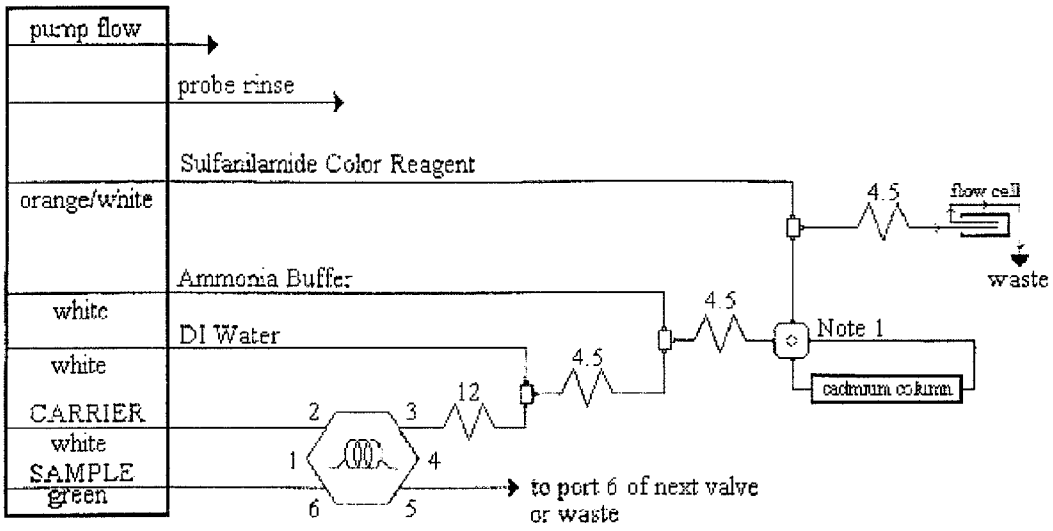
13.3 Quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

13.4 Cadmium waste must be disposed of in strict accordance with Premier Laboratory's Chemical Hygiene Plan requirements for hazardous solid waste. See the laboratory safety officer for detailed instructions if necessary.

XIII. Waste Management

14.1 All waste is handled in accordance with Premier Laboratory's Chemical Hygiene Plan, which is made available to all employees and interested parties.

Figure 1.



QC8000 Sample loop = 13 cm x 0.5 mm i.d. Interference filter = 520 nm
AE sample loop = 7.5 cm x 0.5 mm i.d.

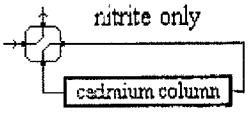
CARRIER is helium degassed DI water

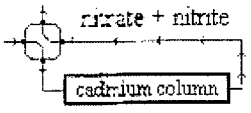
Manifold tubing is **0.5 mm (0.022 in)** i.d. This is 2.5 uL/cm.

4.5	is	**70**	cm of tubing on a 4.5 cm coil support
12	is	**255**	cm of tubing on a 12 cm coil support

APPARATUS: An injection valve, a 10 mm path length flow cell , and a colorimetric detector module is required..

Note 1: This is a two state switching valve used to place the cadmium column in-line with the manifold.





SOP Revision History

Revision No.	Description of Changes	Effective Date	Initiated by
1.2	Added revision history table	6/8/09	LM
1.3	Changed format	2/3/12	LM
2	Changed approval signatures Changed header	12/6/12	LM
3	Changed frequency of LFM in Section 9.4.1 Changed frequency of sample duplicates in Section 9.4.6 Changed "nitrate only" to "nitrate-nitrite (combined)" in Section 8.2	4/25/13	LM