Quality Assurance Project Plan

Santuit Pond Water Quality Monitoring Program

Prepared For:

Mashpee Wampanoag Tribe and
Southeast New England Program Network

Prepared By:

TRC Environmental Corporation

March 13, 2026



Disclaimer

The SNEP Network is administered by: New England Environmental Finance Center at the University of Southern Maine, UMaine System.

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1.0 Project Management

1.1 Title Page (A1)

Quality Assurance Project Plan for Santuit Pond Water Quality Monitoring

Prepared by:

TRC Environmental Corporation

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Prepared for:

Southeast New England Program Network

Mashpee Wampanoag Tribe

Version Date: March 13, 2026

Revision: 0

Estimated Project Start and End Dates: March 2026 – February 2031

EPA Grant: 00A01232

EPA QA Tracking: 26019

1.2 Approval Page (A2)

Project name: Santuit Pond Water Quality Monitoring
Version date: March 13, 2026
Plan Prepared by: TRC Environmental Corporation

Brian Weeden, Chairman, Mashpee Wampanoag Tribe	4/22/2026 Date
Kimberly Groff – SNEP Network Massachusetts Liaison	3/24/2026 Date
Matt Ladewig – TRC Project Director	3/24/2026 Date
Stephanie L. Martin – TRC Project Manager	3/24/2026 Date
Anna Chase – TRC Quality Assurance Officer	3/24/2026 Date
Jessica Iverson – EPA Region 1 Quality Assurance Reviewer	JESSICA IVERSON Digitally signed by JESSICA IVERSON Date: 2026.05.19 14:38:08 -04'00' Date
Matt Stamas – EPA Project Officer	MATTHEW STAMAS Digitally signed by MATTHEW STAMAS Date: 2026.05.28 08:42:06 -04'00' Date
Jasper Sha, Quality Assurance Analyst, MassDEP	4/29/26 Date

This QAPP was developed in general accordance with the following guidance documents: EPA Quality Program Directive CIO 2105-S-02 Quality Assurance Project Plan Standard (QAPP Standard) (EPA 2024) and EPA Region 1 Quality Assurance Project Plan Program Guidance (EPA 2024). This QAPP is formatted based on the R1 Optional QAPP Template prepared by the EPA R1 Quality Assurance Branch, May 2024.

1.3 Distribution List (A7)

See **Table 1** for a list of individuals who will receive a copy of the Quality Assurance Project Plan (QAPP) and any subsequent revisions. Refer to **Figure A** for an organizational chart that outlines the roles and responsibilities of the individuals involved in the project.

1.4 Project Organization and Personnel (A8, A9, A10)

Project organization and key personnel for this Quality Assurance Project Plan (QAPP) are summarized in **Table 1** and **Figure 1**.

Table 1: Distribution List & Project Organization, Personnel, and Responsibilities

Organization	Personnel and Title	Responsibilities
Mashpee Wampanoag Tribe	Jason Steiding Natural Resource Director Jason.Steiding@MWTribe-nsn.gov	Grant Recipient / Lead Project Partner
Town of Mashpee	Ashley Fisher Water Quality Coordinator / Grant Administrator afisher@mashpeema.gov	Project Partner
Kimberly Groff Consulting	Kimberly Groff Consultant KimberlyGroffMA@gmail.com	Project Liaison
TRC Environmental Corporation	Matt Ladewig Principal Water Resource Scientist MLadewig@TRCCompanies.com	Project Director
TRC Environmental Corporation	Stephanie L. Martin Environmental Scientist Stephanie.Martin@TRCCompanies.com	Project Manager
TRC Environmental Corporation	Anna Chase Project Manager AChase@trccompanies.com	TRC Quality Assurance Officer

Organization	Personnel and Title	Responsibilities
MassDEP	Malcolm Harper Massachusetts 319 Grant Coordinator malcolm.harper@mass.gov	Funding Agency Representative
MassDEP	Jasper Sha Quality Assurance Analyst jasper.sha@mass.gov	MassDEP Quality Assurance
US EPA Region 1	Matt Stamas Environmental Engineer Stamas.Matthew@epa.gov	EPA Program Officer
US EPA Region 1	Jessica Iverson Quality Assurance Reviewer iverson.jessica@epa.gov	EPA Quality Assurance

Mashpee Wampanoag Tribe (MWT) and Town of Mashpee (Project Partners)

The Mashpee Wampanoag Tribe manages 321 acres of Tribal lands in Mashpee, Middleborough, and Taunton, Massachusetts. Known as “People of the First Light,” they aim to live in harmony with their abundant natural resources, having earned a livelihood from the land and the sea for thousands of years.

Since July 2021, the SNEP Network has provided technical assistance to MWT to address nutrient pollution in Santuit Pond and help manage water quality issues related to stormwater on a watershed scale. Santuit Pond is a 176-acre freshwater Great Pond with public access at the Town Landing and a maximum depth of about 9 ft. It forms the headwaters of the Santuit River, which flows into Popponesset Bay. River herring, alewives, brook trout, and American eel swim up the stream to the pond via the fish ladder, rebuilt with federal wildlife funds in 2013. Under the Final Massachusetts Integrated List of Waters for the Clean Water Act 2022 Reporting Cycle, the Pond is listed as a Category 5 water body (meaning it needs a TMDL) and is impacted by several impairments: 1. Fish passage barrier; 2. Abnormal fish deformities, erosions, lesions, tumors; 3. Chlorophyll-a; 4. Harmful algal blooms; 5. Nutrient/eutrophication biological indicators; 6. High pH; 7. Total phosphorus; 8. Transparency/clarity.

On its end, the Town of Mashpee is making progress in addressing runoff from septic systems and residential landscapes near the pond. Mashpee Wampanoag Tribe (MWT) has been collaborating with the Town of Mashpee (Town) to explore opportunities to reduce watershed sources and directly tackle in-pond management issues.

With SNEP Network assistance, the Town and Tribe jointly developed the Santuit Pond Learning Hub, which serves as a communication tool for the public and other interested community organizations. The partnership has been successful to date in engaging stakeholders and identifying, designing, and implementing projects to improve water quality in Santuit Pond, including the development of a MassDEP-approved Watershed Based Plan for Santuit Pond.

The Massachusetts Department of Environmental Protection (MassDEP) recently awarded the MWT a Clean Water Act (CWA) §319 Nonpoint Source Program Grant to undertake in-lake alum treatments at Santuit Pond over the course of two years. As part of the grant, the MWT intends to conduct water quality monitoring before, during, and following the treatments. The existing 2022 QAPP for the *Santuit Pond Baseline Monitoring and Sediment Coring Program* addressed some parameters that will be sampled as part of the alum treatment monitoring program. Still, it is not sufficient on its own to support the more robust water quality sampling anticipated. Additionally, the MWT anticipates that water quality monitoring may continue indefinitely following the final alum treatment. Therefore, expansion and approval of a new, broader QAPP will provide ongoing benefits to the MWT and Santuit Pond.

Kimberly Groff Consulting

Kimberly Groff Consulting will act as the SNEP Network liaison between the Project Partners, TRC Environmental Corporation (TRC), and the New England Environmental Finance Center at the University of Southern Maine. In this role, Dr. Groff will manage the project on behalf of the SNEP Network and assist the Project Partners in reviewing TRC's project deliverables, which currently consist of this QAPP.

TRC Environmental Corporation

TRC previously developed the 2022 *Santuit Pond Baseline Monitoring and Sediment Coring Program QAPP* and is the primary environmental contractor responsible for developing and implementing the Santuit Pond Water Quality Monitoring Program QAPP. Project Director, Matthew Ladewig, will provide high-level oversight of project execution and creation of project deliverables. Project Manager, Stephanie Martin, will serve as TRC's primary point of contact with the SNEP Network and Project Partners. TRC Quality Assurance Officer, Anna Chase, will be responsible for quality assurance/quality control review of TRC deliverables.

Pace Analytical Services

Pace Analytical Services (Pace) of Westborough and Mansfield, Massachusetts, will provide laboratory support and analysis as a subcontractor of TRC. Pace will provide the analysis of chlorophyll a in surface water samples and is also capable of analyzing for alkalinity, aluminum, iron, oxidation-reduction potential, total dissolved phosphorus, total phosphorus, total nitrogen (including nitrate, nitrite, and total Kjeldahl nitrogen), and total suspended solids. The MassDEP lab certification IDs for Pace's laboratories are M-MA086 and M-MA030.

Phoenix Environmental Laboratories, Inc.

Phoenix Environmental Laboratories, Inc. (Phoenix) of Manchester, Connecticut, will provide laboratory support and analysis as a subcontractor of TRC. Phoenix will provide analysis of

alkalinity, aluminum, iron, oxidation-reduction potential, total dissolved phosphorus, total phosphorus, total nitrogen (including nitrate, nitrite, and total Kjeldahl nitrogen), and total suspended solids in surface water samples. The MassDEP lab certification ID is M-CT007.

Aquatic Analysts

Aquatic Analysts of Friday Harbor, Washington, will provide laboratory support and analysis as a subcontractor of TRC. Aquatic Analysts will provide algal identification and enumeration in surface water samples. Although this type of analysis is not certifiable in Massachusetts, Aquatic Analysts is included on MassDEP's contract services list for algal enumeration.

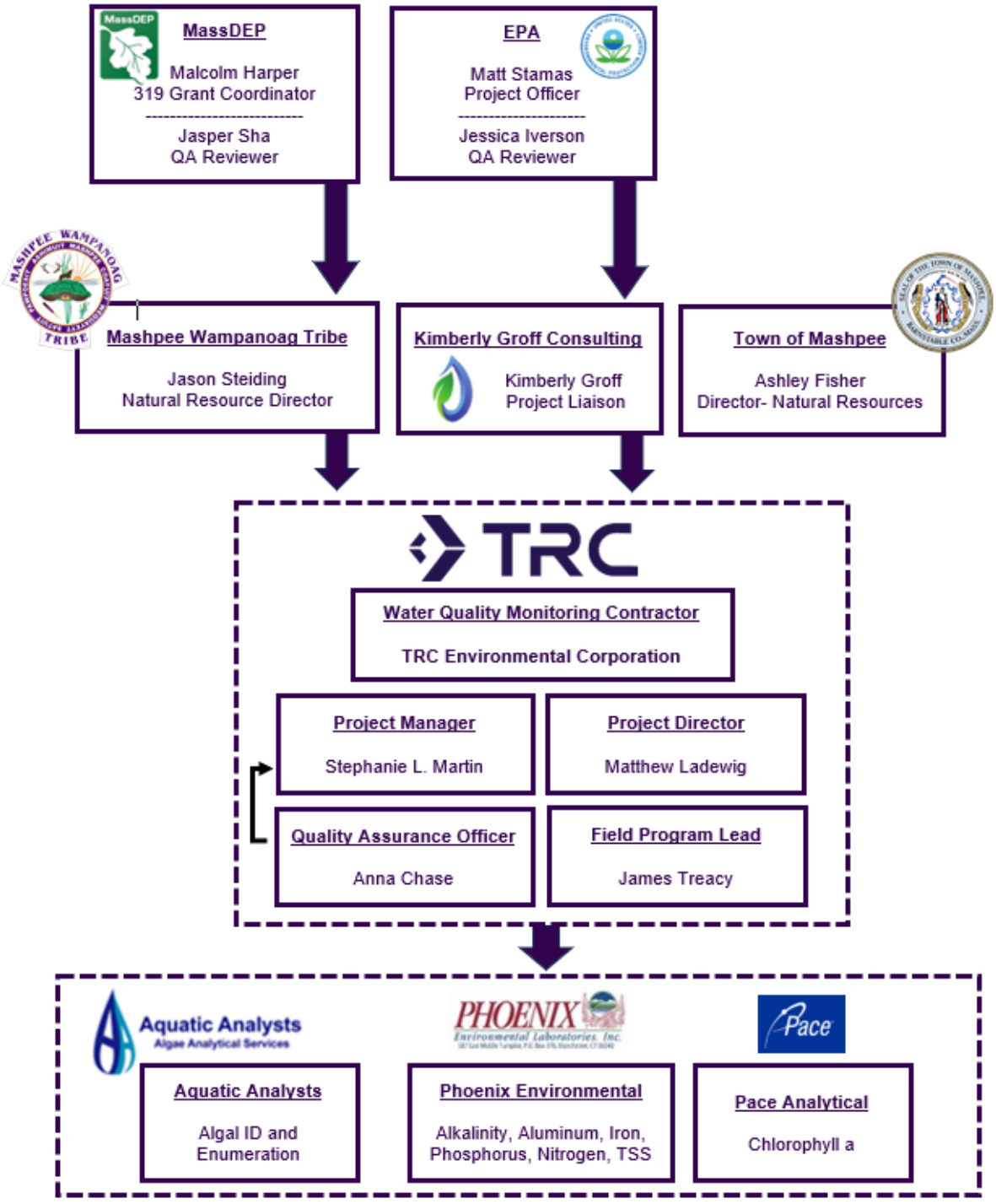

Figure 1: Project Organization Chart

→ Indicates a direct line of communication between the QA Officer and Project Manager.

1.5 Project Quality Assurance Officer Independence (A9)

TRC's QA Officer, or their designee, shall remain independent of environmental information operations while providing oversight authority for the project and have a direct line of contact to the Project Manager. Responsibilities of TRC's QA Officer include assessing and documenting project compliance with the QAPP, verifying the implementation of procedures outlined in the QAPP, and confirming that quality issues and deviations are identified and communicated in accordance with the QAPP.

1.6 Personnel Training/Certification (A11)

No special training or certification courses were specifically attended in preparation for this project.

Personnel involved in this project have received education and training in water quality sampling and measurement. Knowledge and skills have been acquired from previous academic study, routine conference participation, external training courses, and in-house training associated with similar projects throughout New England. Additional in-house training will be provided to sample collection personnel as needed to meet project requirements. Documentation of field staff training and experience will be stored in a designated folder within the project folder and will be maintained by the Project Manager.

At a minimum, all personnel involved in field sample collection or data analysis will be provided with a copy of this QAPP and attachments.

Analytical laboratories responsible for producing chemistry data for tests listed under MassDEP's laboratory certification program will maintain certification through MassDEP or an equivalent agency in other states for the analysis of water samples, as applicable to the analytes processed under this QAPP.

1.7 Project Purpose, Background, and Problem Definition (A4)

Santuit Pond is a publicly accessible 176-acre freshwater Great Pond and serves as a recreational, aesthetic, and cultural resource to communities in and around the Town of Mashpee, Massachusetts. Santuit Pond forms the headwaters of the Santuit River and is situated within an approximately 1,400-acre watershed that extends from the pond outlet northwest to Mashpee-Wakeby Pond and north into the Town of Sandwich, primarily comprising forested and residential land use. Shoreline development is present along much of the western edge of the pond, with some residential areas also present along the east-central shoreline. The northern and southern ends of the pond remain undeveloped, although a few inactive cranberry bogs are present.

The name "Santuit" originates from the Wampanoag word "Sachem," meaning spiritual leader, and the land and water resources in the Town of Mashpee have been home to the Mashpee Wampanoag Tribe (MWT) for 12,000 years. The Mashpee Wampanoag Tribe (legally known as the Mashpee Wampanoag Indian Tribal Council, Inc.) is one of two federally recognized tribes of Wampanoag people in Massachusetts. Recognized in 2007, they are headquartered in Mashpee on Cape Cod. Within Mashpee, 170 acres of MWT lands taken into trust are distributed over 11 independent parcels. The Tribal Trust Lands and the associated water resources are sacred and

culturally essential to the Tribe, and as such, the environmental health of these lands is critical to MWT life and culture.

As with most of Cape Cod, Santuit Pond is located in an area of thick glacial outwash deposits. As a result, the pond is primarily groundwater-fed and has no permanent surface tributaries, although surface flows may reach the pond in the form of stormwater runoff. The Santuit Pond dam was built in the mid-1800s but was rehabilitated and outfitted with an improved fish ladder to aid the passage of anadromous river herring in 2013. Additionally, a historical diversion to Lovell's Pond in Barnstable was closed off following the cessation of active cranberry operations in the early 2000s, Although some seepage from Santuit Pond may still flow toward Lovell's Pond, the Santuit River now effectively serves as the only surface outlet of the pond.

Santuit Pond is classified by MassDEP as a Class B freshwater body. Pursuant to 314 CMR 4.02, these waters are "designated as a habitat for fish, other aquatic life, and wildlife, including for their reproduction, migration, growth and other critical functions, and for primary and secondary contact recreation. Class B waters shall be suitable for irrigation and other agricultural or process related uses when applicable. These waters shall have consistently good aesthetic value."

Under the Final Massachusetts Integrated List of Waters for the Clean Water Act 2022 Reporting Cycle (MassDEP 2023), Santuit Pond is listed as a Category 5 water body (i.e., needing a TMDL) and is impacted by the following impairments:

1. Fish passage barrier
2. Abnormal fish deformities, erosions, lesions, tumors
3. Chlorophyll-a
4. Harmful algal blooms
5. Nutrient/eutrophication biological indicators
6. High pH
7. Total phosphorus
8. Transparency/clarity

Most of Santuit Pond's impairments are highly interrelated. Most notably, excessive total phosphorus has caused eutrophication biological indicators, including harmful algal blooms, which likewise result in high concentrations of chlorophyll a. These impairments, in turn, reduce transparency and have led to high pH levels and low dissolved oxygen. This suggests that the reduction of phosphorus concentrations in Santuit Pond could have cascading benefits.

Various other studies also demonstrate that Santuit Pond has and continues to suffer from poor water quality due to eutrophication (i.e., overabundant nutrient levels, specifically phosphorus in freshwater) and the pond does not fully support the designated water uses including contact recreation and aquatic life support (e.g., the Clean Water Act fishable swimmable goals). The incidence of harmful algal blooms (HABs) in Santuit Pond during both winter and summer has increased dramatically since the late 1990's early 2000's. The pond remains under a swimming advisory due to HABs. Sources of phosphorus pollution have been documented in previous studies (e.g., AECOM 2010) and include septic inputs, cranberry bogs, stormwater runoff and the historic accumulation of phosphorus in sediment that is now cycling to the water column. A number of recent studies (USACE, 2021; ESS, 2022; MWT, 2022; and TRC, 2022) concluded that internal cycling of phosphorus from the sediment is the major source of nutrient pollution and

needs to be addressed as part of a larger, watershed-wide effort to reduce nutrient loading to Santuit Pond. These studies and the outcome are further described below.

Summary of Prior Recent Studies

In 2010, a comprehensive study of the pond and its watershed was performed, and findings were presented in the *Santuit Pond Diagnostic Study*. This study involved sampling of surface water, stormwater, cranberry bog flood water, groundwater, and sediments and biological surveys of aquatic macrophytes and waterfowl, as well as incorporating historical data of the pond. The study identified Santuit Pond as a eutrophic system with the major source of excessive phosphorus coming from internal loading.

Then in 2021, ESS Group, Inc. conducted a *Focused Feasibility Study of Santuit Pond*, which evaluated a number of management options to improve water quality, with the long-term goal of reducing nutrients in the pond. The primary recommendation from that study was nutrient inactivation (e.g., alum treatment) to target internal release of phosphorus from the sediments. However, prior to moving forward with nutrient inactivation, it was recommended that additional baseline water quality and sediment data be collected to develop a better understanding of internal phosphorus recycling and to develop an appropriate dose to address internal nutrient cycling.

In 2022, TRC further analyzed the management method of nutrient inactivation and provided an updated field study to the current conditions in the pond in the *Santuit Pond Baseline Monitoring, Sediment Coring, and Nutrient Inactivation Dosing Study*. The 2022 pond study recommended use of nutrient inactivation through application of a phosphorus-binding agent, like aluminum sulfate (alum). The goal of the proposed alum treatment is to reduce the available phosphorus within the surficial sediments to improve water quality conditions for fish and wildlife, prevent harmful blooms of potentially toxic cyanobacteria, and improve recreational opportunities in the pond.

TRC noted that following AECOM's 2010 study, SolarBee solar-powered surface circulators were installed in the pond to improve dissolved oxygen conditions within the pond. However, the seasonal and diel depletion of dissolved oxygen in bottom waters appears to continue, despite years of operation. This is reflected in the water column's excessive phosphorus concentrations, which appear not to have meaningfully decreased since 2010 based on TRC's 2022 *Santuit Pond Baseline Monitoring, Sediment Coring, and Nutrient Inactivation Dosing Study*. If the aeration promoted by the SolarBee circulators were fully capturing the internal phosphorus load, in-pond concentrations should now be close to 0.015 mg/L, based on the pond water quality response modeling completed by AECOM. However, in-pond concentrations are roughly three to five times higher than the AECOM study predicted value. The lack of success with increased circulation highlights the importance of the use of alum treatments to manage internal loading.

A nine-element watershed-based plan (WBP) for Santuit Pond was completed by the SNEP Network and local project partners in 2022 and subsequently approved by MassDEP. The plan identifies the controllable sources of phosphorus in the pond along with the management actions that are necessary to address external and internal loads of phosphorus. Watershed or external source of phosphorus account for 21% of the controllable load while sediment cycling (internal load) accounts for 76% of the controllable load. Under this plan, watershed management actions

to address external loads that will provide long-term improvement of water quality in Santuit Pond are currently in progress. These include enforcement of septic system Title 5 regulatory requirements, planned enhancements in wastewater collection and treatment at the community level, and a variety of green infrastructure and retrofit projects to address stormwater runoff from housing developments and roads abutting the pond. Although these actions are anticipated to result in the reduction of external pollutant loading to Santuit Pond over time, the gains will take years to realize and will only address a minor fraction of the total phosphorus load. In the case of septic loading, the extended time of travel for groundwater movement means that full benefits may take five years or more, after implementation, to reach the pond.

Given these limitations and public safety concerns, in-pond management actions to address internal loads are necessary to significantly improve water quality in Santuit Pond in the interim, until watershed source controls are fully online. Additionally, watershed management alone cannot produce the nutrient reductions needed to address impairments and fully restore Santuit Pond; in-pond intervention is a critical element to achieve the desired water quality improvements. Therefore, Project Partners have pursued and obtained funding to conduct alum treatments over a two-year period in Santuit Pond.

Project Description

The Santuit Pond Water Quality Monitoring Program aims to track and measure changes in water quality throughout Santuit Pond before, during, and after alum treatments, while ensuring each treatment is implemented in a manner that minimizes impacts on protected resources. At a minimum, the monitoring program includes water quality monitoring associated with two alum treatments anticipated to occur in fall 2026 and fall 2027. Based on monitoring results and pond management needs, extended post-treatment monitoring and/or additional alum treatment and monitoring may be conducted. These activities will be implemented in accordance with the procedures and requirements established in this QAPP or through approved amendments, as needed.

In addition to the water quality parameters that have been collected under the 2022 Santuit Pond Baseline Monitoring and Sediment Coring Program QAPP, the Santuit Pond Water Quality Monitoring Program also seeks to monitor algae (identification and enumeration), alkalinity, aluminum, iron, oxidation-reduction potential (ORP), total dissolved phosphorus, total nitrogen, and total suspended solids (TSS). The Scope of Work associated with the alum treatments and monitoring is documented in MassDEP's Final Scope of Services – Santuit Pond Nutrient Reduction Project Number 24-01/319 (Appendix A).

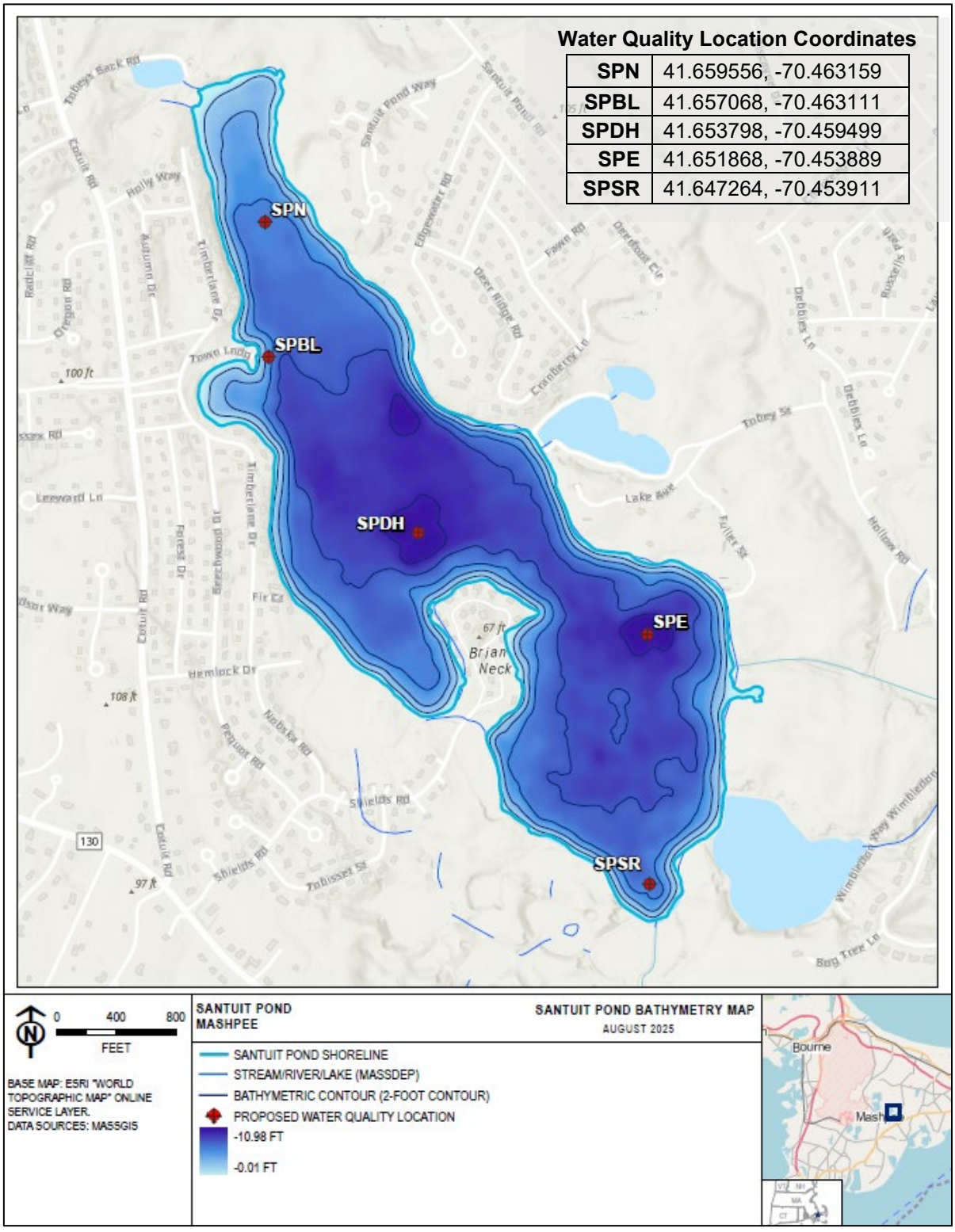

Figure 2: Santuit Pond Water Quality Monitoring Sample Locations

1.8 Project Task Description (A5)

This QAPP covers quality assurance elements applicable to each task associated with Santuit Pond's Water Quality Monitoring Program, which shall be implemented before, during, and after each alum treatment.

At a minimum, the monitoring program includes water quality monitoring associated with two alum treatments, which are anticipated to take place in fall 2026 and fall 2027. Based on monitoring results and management needs, extended post-treatment monitoring and/or additional alum treatments and monitoring may be conducted. These activities will be implemented in accordance with the procedures and requirements established in this QAPP or through approved amendments. A general project schedule is presented in **Table 2**.

Table 2: Project Schedule

	2025			2026																								2027												2028
	Q4			Q1			Q2			Q3			Q4			Q1			Q2			Q3			Q4			Q1			Q2			Q3			Q4			Q1
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan
QAPP Development	x	x	x	x																																			
Design and Permitting			x	x	x	x	x																																
Alum Treatments Sampling and Monitoring													x	x	x																					x	x	x	
Data Analysis and Reporting													x	x	x	x																					x	x	x	x

1.8.1 Field Data Collection

The following sections provide an overview of the task-related parameters or samples that will be collected from Santuit Pond. Alum treatments and associated water quality monitoring are expected to take place in the fall, when water temperatures are cool but not cold, and the water column is fully mixed, allowing for good flocculent formation while also avoiding periods when ambient water quality puts undue stress on aquatic life. However, water quality monitoring conducted under this monitoring program may occur at any time of year.

1.8.1.1 In-Pond Water Quality Monitoring

Water quality monitoring will take place before, during, and after each alum treatment. This will allow changes in water quality to be documented and quantified, while ensuring that the treatment is implemented to avoid or minimize impacts on protected resources.

Santuit Pond water quality monitoring locations are presented in **Figure 2** and listed below:

- Santuit Pond - Deep Hole (SPDH-S and SPDH-B)
    - Sample Collection and In-Situ Measurements
- Santuit Pond – North (SPN)
    - In-Situ Measurements

- Santuit Pond – Boat Launch (SPBL)
    - Sample Collection and In-Situ Measurements
- Santuit Pond – East (SPE)
    - In-situ Measurements
- Santuit Pond – Santuit River (SPSR)
    - Sample Collection and In-Situ Measurements

The SPDH monitoring location is just north of Briant's Neck, in the pond's deepest point, where water depth is up to approximately 10 feet. Water quality samples and measurements will be obtained from both surface (SPDH-S) and bottom (SPDH-B) waters at this monitoring location, as this may reveal changes in water quality with depth. The SPN monitoring location is in the northernmost portion of the pond, with depths ranging from 6 to 8 feet. The SPBL monitoring location adjacent to the Santuit Pond Town Landing holds high public interest and visibility. It is currently undergoing construction to reduce stormwater loading and erosion into the pond. Monitoring at this location will document water quality adjacent to the separately funded Stormwater and Water Quality Improvement Project at the Town Landing. The SPE monitoring location is approximately 8 feet deep and located east of Briant's Neck. The SPSR monitoring location is near the outlet to capture the quality of water discharging into the Santuit River.

Water quality monitoring will be conducted at approximately the following intervals for each alum treatment:

- Pre-Alum Treatment
    - Approximately 1 week before treatment.
    - On the day of treatment, immediately before the treatment begins.
- During the Alum Treatment
    - On each day of the treatment, while the treatment is in progress. (Rotating pH measurements each treatment day)
- Post-Alum Treatment
    - One post-treatment event

During each pre- and post-alum treatment water quality monitoring event, water transparency will be measured using a Secchi disk, and vertical water quality profiles will be measured in-situ within the water column at each monitoring location. Profile measurements will be recorded at 0.3-meter (1-foot) intervals along a vertical profile in the water column and will include water temperature, dissolved oxygen, specific conductance, and pH. Turbidity and ORP will be measured in both surface and bottom waters of monitoring location SPDH, as well as from the surface waters of monitoring locations SPN, SPBL, SPE, and SPSR.

The following parameters will be field measured at each monitoring location during each pre- and post-alum treatment water quality monitoring event:

- Secchi Disk Transparency
- Oxidation Reduction Potential (ORP)

- Turbidity
- Vertical Profile at 0.3-meter (1-foot) intervals from the surface to the bottom
    - Water Temperature
    - Dissolved Oxygen
    - Specific Conductance
    - pH

Additionally, during each alum treatment, pH will be measured at 0.3 m (1 ft) intervals at each monitoring location on a rotating basis throughout each day of treatment. It is anticipated that each alum treatment will take place over a minimum of four days, so at least four (4) days of treatment monitoring are expected.

Samples will be collected from select monitoring locations for laboratory analysis during both the pre- and post-alum treatment water quality monitoring events. Because the SPDH is deep relative to the other monitoring locations and has the most potential for water quality to vary with depth, grab samples will be collected from within 0.3 meters (1 foot) of the surface and bottom. Only surface samples will be collected from monitoring locations SPBL and SPSR. Grab samples for laboratory analysis will not be obtained from the SPN and SPE monitoring locations.

Water quality samples collected throughout the water quality monitoring program will be sent to the laboratory for analysis of the following:

- Algal Identification and Enumeration
- Alkalinity
- Aluminum
- Chlorophyll a
- Iron
- Total Dissolved (Soluble) Phosphorus
- Total Phosphorus
- Total Nitrogen (Total Kjeldahl Nitrogen, Nitrate, and Nitrite)
- Total Suspended Solids

1.8.2 Documentation

The approach and results for the field data collected will be detailed in monitoring reports. At a minimum, these reports will be maintained and issued annually and at the conclusion of the §319 Nonpoint Source Grant by the Project Manager or their designee. The reports will detail any deviations from this QAPP.

1.9 Data Quality Objectives and Acceptance Criteria (A6)

1.9.1 Field Data DQOs

The data quality objectives (DQOs) specific to field-collected data, as described in this QAPP, will be met if the collected data can be used to assess or determine the value or change in each water

quality measurement. These DQOs can be described using the following performance criteria: precision, accuracy, bias, representativeness, comparability, completeness, and sensitivity.

1.9.1.1 Precision

Water quality samples and field measurement results will be sufficiently precise to ensure reliable detection of each analyte or parameter within its expected environmental range.

Field duplicates will be collected at a 10% rate and submitted as blind duplicates (i.e., not labeled as “duplicate”) for quality control purposes. Laboratory duplicates will be tested in accordance with the requirements of the contract laboratories' SOPs and/or Quality Manual/Quality Assurance Manual. Precision will be measured using the Relative Percent Difference (RPD) between duplicates.

The precision objectives for field parameters are presented in **Table 3**. The precision objective for laboratory samples is presented in **Table 4**. The Project Manager, Quality Assurance Officer, or their designee will review the collected data to ensure it is accurate, unbiased, and meets data quality objectives.

1.9.2 Accuracy and Bias

Water quality laboratory samples and field measurement results will be sufficiently accurate and unbiased to ensure the results reflect the true value of the analyte or parameter being measured.

Where applicable, laboratory accuracy will be measured using Percent Recovery of one or more of the following quality control samples: laboratory control samples (LCS) and matrix spikes (MS). Method blanks and other checks on accuracy may also be used. Additionally, field blanks will be sampled at a 5% rate to quantify potential bias due to field contamination.

The pre- and post-calibration of field sensor equipment will be performed immediately before and after each sampling event (**Section B5**). Additionally, field blanks will be sampled at a 5% rate to quantify potential bias due to field contamination.

The accuracy objectives for this project are presented in **Table 3** for field parameters and **Table 4** for laboratory analysis. These tables also include performance objectives for the water quality data. The Project Manager, Quality Assurance Officer, or their designee will review the collected data to ensure that it is adequately precise to meet the data quality objectives.

Table 3: Field Parameter Performance Objectives

Parameter	SOP	Units	Resolution	Expected Range	Precision* Objective	Accuracy Objective**
Water Depth	TRC SOP No. 904	Ft	0.1	0 - 11	+/- 10%	+/- 0.5
Transparency (Secchi Depth)	TRC SOP No. 915	m	0.1	0 - 10	+/- 0.25	N/A
ORP	TRC SOP No. 917	mV	0.1	-500 - 500	+/- 20%	+/- 20
pH	TRC SOP No. 902	SU	0.01	5-9	+/- 0.2	+/- 0.2
Turbidity	TRC SOP No. 905	NTU	0.01	0.1-50	+/-5%	+/-10% of Standard <0.1 for 10 NTU
Water Temperature	TRC SOP No. 904	°C	0.01	0-30	+/-0.2	+/-0.15
Specific Conductance	TRC SOP No.900	µS/cm	4 digits	25-500	+/-10%	+/-5% of Standard <70 for 1,400 µS/cm
Dissolved Oxygen	TRC SOP No. 907	mg/L	0.01	0-14	+/-0.2	+/-0.2

*The relative percent difference (RPD) between primary and duplicate measurements will be used to determine precision.
**Where applicable, pre- and post-calibration and verification, using the manufacturer's recommended instrumentation standards, will be used to determine accuracy. The accuracy of water depth will be determined based on the accuracy of the instrument used, as tested by the manufacturer.

Table 4: Laboratory Performance Objectives

Analyte	SOP*	Units	Expected Range	Laboratory Minimum Detection Limit	Laboratory Reporting Limit (MRL)	Accuracy Objective**	Precision Objective***
Alkalinity	Phoenix SOP No. 305.2320B - Total Alkalinity Effective: 01/23/25	mg/L	2.5-25.0	5.00	5.00	+/-15% or <MDL (field blanks)	+/-20%
Aluminum	Phoenix SOP No. 506 - Determination of Trace Elements by Inductive Coupled Argon Plasma (ICP) Spectroscopy Effective: 03/31/20	mg/L	0.01-5.0	0.010	0.010	+/-15% or <MDL (field blanks)	+/-20%
Iron	Phoenix SOP No. 506 - Determination of Trace Elements by Inductive Coupled Argon Plasma (ICP) Spectroscopy Effective: 03/31/20	mg/L	0.005-5.0	0.005	0.005	+/-15% or <MDL (field blanks)	+/-20%
Total Phosphorus	Phoenix SOP No. 321.4500PE - Phosphorus, All Forms Effective:7/12/2022	mg/L	0.01-0.1	0.01	0.01	+/-15% or <MDL (field blanks)	+/-20%

Table 4: Laboratory Performance Objectives

Analyte	SOP*	Units	Expected Range	Laboratory Minimum Detection Limit	Laboratory Reporting Limit (MRL)	Accuracy Objective**	Precision Objective***
Total Dissolved (Soluble) Phosphorus	Phoenix SOP No. 321.4500PE - Phosphorus, All Forms Effective:7/12/2022	mg/L	0.01-0.1	0.01	0.01	+/-15% or <MDL (field blanks)	+/-20%
TKN	Phoenix SOP No. 304.NH3/TKN - Ammonia/TKN Phenate Method Effective: 11/06/23	mg/L	0.2-2.0	0.1	0.10	+/-15% or <MDL (field blanks)	+/-20%
Nitrate-Nitrogen	Phoenix SOP No. 336.353.2 - Total Nitrite as Nitrogen / Total Nitrate as Nitrogen Effective: 7/26/2022	mg/L	0.02-1.0	0.01	0.02	+/-15% or <MDL (field blanks)	+/-20%
Nitrite-Nitrogen	Phoenix SOP No. 336.353.2 - Total Nitrite as Nitrogen / Total Nitrate as Nitrogen Effective: 7/26/2022	mg/L	0.005-0.02	0.01	0.01	+/-15% or <MDL (field blanks)	+/-20%

Table 4: Laboratory Performance Objectives

Analyte	SOP*	Units	Expected Range	Laboratory Minimum Detection Limit	Laboratory Reporting Limit (MRL)	Accuracy Objective**	Precision Objective***
Total Suspended Solids	Phoenix SOP No. 324.2540D - Total Suspended Solids (TSS) dried at 103°-10S°C Effective: 1/10/2022	mg/L	1-100	1.0	2	+/-15% or <MDL (field blanks)	+/-20%
Algal Identification and Enumeration****	Algae Analytical and Quality Assurance Procedures Effective: 1/15/2021	Units/mL and $\mu m/mm^3$	Not Applicable	1	1	Not Applicable	Not Applicable
Chlorophyll a	Alpha SOP No. SM10200H - Standard Methods for the Examination of Water and Wastewater, 18th Edition Effective 8/6/2015	mg/m^3	1-150	N/A	2	+/-15% or <MDL (field blanks)	+/-35%

*The laboratory manager or their designee is responsible for updating SOPs.

**Accuracy will be measured using Percent Recovery of one or more of the following quality control samples: laboratory control samples (LCS) and matrix spikes (MS). Method blanks and other checks on accuracy may also be used.

***The relative percent difference (RPD) between primary and duplicate laboratory samples will be used to determine precision.

****Enumerated units may be cells, colonies, or filaments, depending on the taxon. See Aquatic Analysts' QA Procedures for performance objectives.

1.9.2.1 Representativeness

Water quality samples will be collected at locations selected to be representative of the different areas of the pond.

Sample results are expected to be representative, providing that the samples are collected in accordance with relevant SOPs and analytical laboratory sampling protocols, including the use of appropriate containers, collection of sufficient volume, use of preservatives as directed, and adherence to sample times. Deviations from the established protocols will be noted on the chain-of-custody (COC) form or field books by field personnel and included in the data reporting.

1.9.2.2 Comparability

Water quality samples collected from different monitoring locations and events will be sufficiently comparable to each other, provided that the samples are collected in accordance with relevant SOPs and analytical laboratory sampling protocols, including the use of appropriate containers, collection of sufficient volume, use of preservatives as directed, and adherence to sample times. Deviations from the established protocols will be noted by field personnel and included in data reporting. The Project Manager, Quality Assurance Officer, or their designee will review the data to ensure it is sufficiently comparable to meet data quality objectives.

1.9.2.3 Completeness

Water quality data will be considered complete if water quality samples are collected from the proposed sample locations during each sampling event and analyzed for the intended analytes. If data cannot be obtained (e.g., due to lack of access), this will be promptly reported to the Project Manager to determine whether this is likely to affect the completeness of the dataset in a substantive way. If the effect is determined to be substantive, the Project Manager will consider alternatives to improve the completeness of the dataset, potentially including, but not limited to, additional sampling events. The sample completeness goal for the Santuit Pond Monitoring Program is 90 percent.

1.9.2.4 Sensitivity

The selected method for water quality analysis will be considered sufficiently sensitive if it can reliably detect concentrations within the expected environmental range, discriminate between measurement responses representing different levels of the variable of interest, and provide meaningful data suitable for comparison between sample locations.

1.10 Documents and Records (A12)

The Project Manager will maintain the current approved version of the QAPP. Should any change to the QAPP be necessary, the current version of the QAPP will be saved in the Project Manager's electronic archive folder for the project before any changes are made, and the updated version will be assigned the next consecutive version number. The Project Manager will distribute the new version of the QAPP to the individuals listed on the Approvals page in **Section A2** of this QAPP for approval before distributing the new version of the QAPP to the individuals identified on the Distribution List in **Section A7**.

The following data will be included as part of a final project report:

- Chain-of-custody forms, laboratory analytical reports, and electronic data deliverables for samples analyzed in the laboratory;
- Tabular data for field-measured parameters;
- GIS data created to support the development of map figures.

The Project Manager or Quality Assurance Officer will review analytical reports for accuracy and completeness and contact the party responsible for completing the form or report in the event that any omissions or suspected inaccuracies are found. In the event that any corrections are made, they will be written on the form, dated, and initialed by the party responsible for completing the form, or a new report will be issued with a new version number and date. All project data will be retained in the Project Manager's electronic files for this project for a period of at least five years following project completion in the electronic records for the project.

2.0 Implementing Environmental Information Operations

2.1 Sampling Design and Rationale (B1)

The sampling design and rationale for planned environmental information operations tasks associated with water quality monitoring before, during, and after each alum treatment are described in the following sections.

2.1.1 Field Data Collection – In-Pond Water Quality Monitoring

Water quality monitoring will take place before, during, and after each alum treatment. This will allow changes in water quality to be documented and quantified while also ensuring that the treatment is implemented in a way that avoids or minimizes impacts on protected resources.

A minimum of two pre-alum treatment monitoring events and one post-alum treatment monitoring event shall be conducted for each alum treatment. Additionally, pH monitoring shall be conducted on a rotating basis throughout the day during alum treatment days. In anticipation that each treatment will occur over a minimum of four days, it is expected that the number of measurements will be higher for pH than for any other parameter.

During each pre- and post-alum treatment water quality monitoring event, water transparency will be measured using a Secchi disk, and vertical water quality profiles will be measured in-situ within the water column at each monitoring location. Profile measurements will be recorded at 0.3-meter (1-foot) intervals along a vertical profile in the water column and will include water temperature, dissolved oxygen, specific conductance, and pH. Turbidity and ORPwill be measured in both surface and bottom waters of monitoring location SPDH, as well as from the surface of the waters of monitoring locations SPN, SPBL, SPE, and SPSR. Additionally, during each alum treatment, pH will be measured at 0.3 m (1 ft) intervals at each monitoring location on a rotating basis throughout each day of treatment. All other parameters will only be measured once before treatment for each treatment event, unless permit requirements or environmental conditions warrant more, as determined by MWT and the Project Manager.

Samples will be collected from select monitoring locations for laboratory analysis during both the pre- and post-alum treatment water quality monitoring events. Because the SPDH is deep relative to the other monitoring locations and has the most potential for water quality to vary with depth, grab samples will be collected from within 0.3 meters (1 foot) of the surface and bottom. Only surface samples will be collected from monitoring locations SPBL and SPSR. Grab samples for laboratory analysis will not be obtained from the SPN and SPE monitoring locations. Field measurements and water quality samples will be collected at the same in-pond monitoring locations during each water quality monitoring event.

Surface water quality analysis and water quality field parameters to be monitored are listed in **Tables 5** and **6**, respectively. The values presented in **Tables 5** and **6** represent the minimum number of measurements and samples to be collected for the fall 2026 and fall 2027 alum treatments. Should extended post-treatment monitoring and/or additional alum treatments be deemed necessary, these activities will be implemented in accordance with the procedures and requirements established in this QAPP or through approved amendments.

Table 5: In-Pond Sample Collection and Analysis

Analyte/ Parameter	Sampling Position(s)	Min. Number of Visits	Number of Samples per Visit	Minimum Total Number of Samples	Laboratory
Alkalinity	SPDH: Surface and Bottom SPBL and SPSR: Surface	6	4	24	Phoenix
Aluminum	SPDH: Surface and Bottom SPBL and SPSR: Surface	6	4	24	Phoenix
Iron	SPDH: Surface and Bottom SPBL and SPSR: Surface	6	4	24	Phoenix
Total Phosphorus (Total and Soluble)	SPDH: Surface and Bottom SPBL and SPSR: Surface	6	4	24	Phoenix
Total Nitrogen (TKN, Nitrate, Nitrite)	SPDH: Surface and Bottom SPBL and SPSR: Surface	6	4	24	Phoenix
Total Suspended Solids	SPDH: Surface and Bottom SPBL and SPSR: Surface	6	4	24	Phoenix
Algal Identification and Enumeration	SPDH: Surface and Bottom SPBL and SPSR: Surface	6	4	24	Aquatic Analysts
Chlorophyll a	SPDH: Surface and Bottom SPBL and SPSR: Surface	6	4	24	Pace

Table 6: Measurement of In-Pond Water Quality Field Parameters

Analyte	Sampling Position(s)	Minimum Number of Visits	Minimum Number of measurements per Visit	Minimum Total Number of Measurements
Secchi Disk Transparency	All Monitoring Locations	8	5	40
ORP	SPDH: Surface and Bottom SPN, SPBL, SPE, SPSR: Surface	6	6	36
pH (pre- and post-)	SPDH: Surface and Bottom SPN, SPBL, SPE, SPSR: Surface	6	36	216
pH (during)	All Monitoring Locations 0.3-meter (1-foot) intervals	8	144	1,152
Turbidity	SPDH: Surface and Bottom SPN, SPBL, SPE, SPSR: Surface	6	6	36
Water Temperature	All Monitoring Locations 0.3-meter (1-foot) intervals	6	36	216
Specific Conductance	All Monitoring Locations 0.3-meter (1-foot) intervals	6	36	216
Dissolved Oxygen	All Monitoring Locations 0.3-meter (1-foot) intervals	6	36	216

2.2 Methods for Environmental Information Acquisition (B2)

During each water quality monitoring event, in-pond water quality measurements and sampling will follow the Standard Operating Procedures identified in **Table 7** and **Table 8**, respectively.

Laboratory sample containers, preservation methods, and hold times applicable to the analytes being sampled as part of the Santuit Pond Water Quality Monitoring Program are summarized in **Table 9.**

Table 7: Field Method SOPs

Parameter	Matrix	Instrument	SOP References**	Date
Secchi Disk Transparency	Water	Secchi Disk	TRC SOP No. 915 Secchi Disk Transparency Measurement SOP	6/30/2024
ORP	Water	YSI EXO pH & ORP Smart Sensor or similar	TRC SOP No. 917 ORP Calibration and Measurement SOP	10/15/2025
pH	Water	Oakton Waterproof Pocket Tester,YSI EXO pH & ORP Smart Sensor, or similar	TRC SOP No. 902 pH Calibration and Measurement SOP	6/13/2024
Turbidity	Water	LaMotte 2020we Turbidimeter or similar	TRC SOP No. 905 Turbidity Calibration and Measurement SOP	6/13/2024
Water Temperature	Water	YSI Pro 2030 or similar	TRC SOP No. 904 Surface Water Sampling SOP	6/13/2024
Specific Conductance	Water	YSI Pro 2030 or similar	TRC SOP No. 900 Specific Conductance Calibration and Measurement SOP	6/13/2024
Dissolved Oxygen	Water	YSI Pro 2030 or similar	TRC SOP No. 907 Surface Water Sampling SOP	6/13/2024
Sample Collection	Water	N/A	TRC SOP No. 904 Surface Water Sampling	6/13/2024

*See **Appendix A** for SOP documents, where applicable.
**Technical review personnel are responsible for updating SOPs.

Table 8: Laboratory Analytical Methods

Parameter	Matrix	Laboratory	Analytical Method
Alkalinity	Water	Phoenix	SM 2320B
Aluminum	Water	Phoenix	200.7/6010
Iron	Water	Phoenix	200.7/6010
Phosphorus (Total and Total Dissolved)	Water	Phoenix	SM 4500PE
Total Kjeldahl Nitrogen	Water	Phoenix	351.1
Nitrate-Nitrogen	Water	Phoenix	353.2
Nitrite-Nitrogen	Water	Phoenix	353.2
Total Nitrogen	Water	Phoenix	Calculation: TKN + Nitrate-Nitrogen + Nitrite-Nitrogen
Total Suspended Solids	Water	Phoenix	SM 2540D
Algal Identification and Enumerations	Water	Aquatic Analyst	SM 10200 F
Chlorophyll a	Water	Pace	SM 10200 H

2.2.1 Procedure for In-Pond Water Quality Monitoring

Preserve all samples collected for laboratory analysis using the appropriate method for each sample container. Laboratory sample containers, preservation methods, and holding times applicable to the analytes being sampled are summarized in **Table 9.**

2.2.1.1 Procedure for In-Pond Oxygen, Temperature, and Conductance Profiles

Use a multi-parameter water quality meter (multi-probe or sonde) to measure DO, temperature, and specific conductance at one-meter depth intervals. Lower the multi-probe sonde into the water and record the vertical profile of DO, temperature, and specific conductance at each meter. Avoid putting the sonde into contact with the bottom sediments, as this will likely result in inaccurate measurements. An accurate measure of the site depth using sonar will help prevent this from occurring. Record field measurements and any on-site calibrations in a field notebook or in an electronic field form.

2.2.1.2 Procedure for In-Pond Analyte Sampling

Collect in-pond grab samples for nutrients using a Van Dorn sampler or equivalent (e.g., Kemmerer). This type of sampler allows the collection of water from the water column at discrete depths. The Van Dorn sampler is an open tube with spring-loaded seals and valves on both ends of the tube. The sampler is lowered to the desired depth in the water column, and a weight or messenger is sent down the line holding the sampler to trigger the spring mechanism that shuts the end seals. The sampler is retrieved, and its contents are dispensed into the appropriate sample containers.

Pre-rinse the Van Dorn sampler and unpreserved sample containers with pond water from the collection depth prior to collecting samples. Set the spring-loaded end seals on the Van Dorn sampler and lower it to collect the surface sample (0.5 meter), trigger the end seals, and retrieve the sampler. Dispense the contents into the appropriate sample containers for storage. While maintaining the same depth, take additional samples as necessary to achieve the needed volume of water. Repeat this process to collect additional samples at each of the required depths, as identified in **Table 6**. Use caution to avoid lowering the sampler into the bottom sediments or sediment/water interface which could contaminate the sample and cause inaccurate results.

2.2.1.3 Procedure for In-Pond Chlorophyll a Samples

Surface grab samples have the potential to either overestimate or underestimate phytoplankton populations during calm days (e.g., phytoplankton settling) or during blooms with a surface concentration of upwardly buoyant cyanobacteria. Therefore, surface sampling should be conducted using a two-meter sampling tube to obtain a depth-integrated sample. The field methodology for obtaining a chlorophyll a sample with an integrated sampling tube should be consistent with the NLA Field Operations Manual (US EPA 2022), except that samples do not need to be filtered in the field if the filtration can be completed by the analytical laboratory within the method hold time.

To collect samples, first open the valve at the bottom of the tube and rinse the integrated sampler three times in the water. Rinsing activities should be performed on the opposite side of the boat from where the sampling will occur. Once ready to sample, lower the sampler to a depth of two meters (if the euphotic zone is less than two meters deep, lower the sampler only to the depth of the euphotic zone). Cap the upper end of the sample with the rubber stopper and slowly raise it up. Dispense contents of the sampler into the laboratory-provided sampling bottles.

Table 9: Laboratory Sample Containers, Preservation Methods, and Hold Times

Analyte	Media	Required Container and Volume Required	Hold Time	Preservation	Comments
Alkalinity	Water	(1) 120 mL Plastic	14 days	As is	Sample bottles must be full and contain no headspace. Samples must be stored at 4 °C until analysis.
Aluminum	Water	(1) 250 mL Plastic	6 months	HNO_3	Samples must be stored at 4 °C until analysis.
Iron	Water	(1) 250 mL Plastic	6 months	HNO_3	Samples must be stored at 4 °C until analysis.
Total Phosphorus	Water	(1) 250 mL Plastic	28 days	H_2SO_4	Samples must be stored at 4 °C until analysis.
Total Dissolved Phosphorus	Water	(1) 50 mL Plastic	15 minutes (filtration) 28 days, once filtered and preserved	H_2SO_4	Field-filter with 45-micron filter. *If field filtering is not possible, collect in an unpreserved bottle and submit the sample to the laboratory as soon as possible. Samples must be stored at 4 °C until analysis.
Total Kjeldahl Nitrogen	Water	(1) 250 mL Plastic	28 days	H_2SO_4	Samples must be stored at 4 °C until analysis.
Nitrate-Nitrogen	Water	(1) 250 mL Plastic	48 hours	As Is	Samples must be stored at 4 °C until analysis.
Nitrite-Nitrogen	Water	(1) 250 mL Plastic	48 hours	As Is	Samples must be stored at 4 °C until analysis.

Analyte	Media	Required Container and Volume Required	Hold Time	Preservation	Comments
Total Suspended Solids	Water	(1) 500 mL Plastic	7 days	As Is	Samples must be stored at 4 °C until analysis.
Algal Identification and Enumerations	Water	(1) 125 mL Opaque Plastic	>1 year	1% Lugol's	Avoid exposure to light. Stable at room temperature.
Chlorophyll a	Water	(2) 1 L Opaque Plastic	48 hours	As Is	Samples must be stored at 4 °C until analysis.

2.3 Integrity of Environmental Information (B3)

Water quality measurements and samples will be collected in accordance with relevant procedures or SOPs for water quality field sampling and handling (**Appendix A**). Sample collection personnel will wear unused nitrile gloves when collecting and handling samples. Permanent markers will be used to label all sample bottles with project ID, sample ID, date and time sampled, analyses requested, and initials of the sampler, at a minimum. Samples will be placed on ice or in a dedicated refrigerator to maintain sample temperature between 0°C and 4°C until transfer to the analytical laboratory's custody. Samples will be transferred to the laboratory as soon as possible to allow for processing and analysis before the analytical hold time is exceeded.

All samples transferred to laboratory custody will be accompanied by a completed COC form. Personnel transferring samples to the laboratory will sign the COC and indicate the date and time of sample transfer.

2.4 Environmental Information Management (B7)

2.4.1 Field Data Collection and Records

Field notes, forms, and other documentation (e.g., photographs) will be saved for each round of water quality monitoring. A copy of each will be retained by the Project Manager for at least five years following project completion in the electronic records for the project.

Information to be recorded for each laboratory analytical sample will include the following: the individual performing the sample collection, date and time of sample collection, and laboratory analysis requested. This information will be recorded on a laboratory COC form. All original COC forms will accompany samples for laboratory analysis and a copy of each will be retained by the Project Manager for at least five years following project completion in the electronic records for the project.

2.4.2 Analytical Laboratory Data

All electronic data deliverables, laboratory reports, case narratives, QC reports, email correspondence, or other information generated by an analytical laboratory will be retained by the Project Manager for at least five years following project completion in the electronic records for the project. This will include preliminary or draft data, in addition to any revisions.

2.5 Quality Control (B4)

Laboratory analytical SOPs and quality control information relevant to each analyte are provided in **Appendix B**.

Field duplicates will be collected for water quality samples, field water quality measurements, and discharge measurements at an overall 10% rate. These field duplicates will be used expressly for quantifying the Relative Percent Difference (RPD) between samples collected or measurements taken at the same location. To avoid biasing the dataset, duplicate sample data will not be included in the final data analyses.

The minimum field duplicate sampling rate for each laboratory analyte is summarized in **Table 10, and** the minimum field duplicate sampling rate for each field parameter is summarized in **Table 11**. Since the minimum duplicate goal is an overall 10% rate, at least one in every ten samples or measurements will have a field duplicate.

Field blanks will also be sampled at an overall 5% rate to assess bias due to sample contamination. The minimum field blank sampling rate for each applicable laboratory analyte is summarized in **Table 10**. Since the minimum field blank goal is an overall 5% rate, at least 1 in every 20 samples will have a field blank.

Table 10: Analytical Sample Field Duplicates and Field Blanks

Analyte	Minimum Number of Samples	Minimum* Number of Field Duplicate Samples	Minimum* Number of Field Blank Samples
Alkalinity	24	3	2
Aluminum	24	3	2
Iron	24	3	2
Phosphorus (Total and Total Dissolved)	24	3	2
Total Kjeldahl Nitrogen	24	3	2
Nitrate-Nitrogen	24	3	2
Nitrite-Nitrogen	24	3	2
Total Suspended Solids	24	3	2
Algal Identification and Enumerations	24	3	2
Chlorophyll a	24	3	2

*Assumes two alum treatments, with water quality samples collected for laboratory analysis during pre-treatment and post-treatment monitoring events. Should extended post-treatment monitoring and/or additional alum treatments be deemed necessary, additional field duplicate and field blank samples shall be collected at a rate of 10% and 5%, respectively.

Table 11: Field Parameter Duplicates*

Parameter	Minimum Total Number of Measurements**	Minimum Number of Field Duplicate Measurements*
Secchi Disk Transparency	40	4
ORP	36	4
pH (pre- and post-)	216	22
pH (during)***	1,152	116
Turbidity	36	4
Water Temperature	216	22
Specific Conductance	216	22
Dissolved Oxygen	216	22

*Assumes two alum treatments. Should extended post-treatment monitoring and/or additional alum treatments be deemed necessary, additional field duplicate measurements shall be collected at a rate of 10%.
**With the exception of pH, assumes a minimum of 6 water quality monitoring events.
***During each alum treatment, pH will be measured at 0.3 m (1 ft) intervals at each monitoring location on a rotating basis throughout each day of treatment. It is anticipated that each alum treatment will take place over a minimum of four days, so at least four (4) days of treatment monitoring are expected.

2.6 Instruments/Equipment Calibration, Testing, Inspection, and Maintenance (B5)

The laboratory manager or their designee is responsible for maintaining all instrumentation and supplies. Laboratory analytical equipment calibration, testing, and maintenance protocols are provided in **Appendix B**.

The Project Manager, Field Lead, or their designee is responsible for maintaining field equipment and supplies. Field instrumentation will be cleaned, stored, and serviced in accordance with manufacturer recommendations.

Field instrumentation will be calibrated and/or checked in accordance with manufacturer recommendations immediately before and following a sampling event or in accordance with relevant SOPs. Where applicable, pre- and post-field checks will be conducted against the appropriate calibration standard for data validation/verification purposes in accordance with existing SOPs (**Appendix A**). Although not specified in the SOPs, dissolved oxygen, specific conductance, and pH instruments will also include a pre- and post-field calibration check immediately before and after each sampling event. These activities will be the responsibility of the sample collection personnel.

2.7 Inspection/Acceptance of Supplies and Services (B6)

Sample collection personnel will complete a bottle order request form with each analytical laboratory to ensure that the number, type, and condition of sample containers are appropriate for the analysis to be conducted. Additionally, sample collection personnel will be responsible for visually inspecting sample containers and verifying their cleanliness, integrity, and consistency

with this QAPP before collecting samples for laboratory analysis. Sample containers that are visibly damaged, soiled, or inappropriate for the required analysis will not be used for sample collection or storage.

3.0 Assessments, Response Actions, and Oversight (C)

This section outlines the activities for evaluating the effectiveness of implementing quality assurance and quality control measures. The purpose of the assessment is to ensure that QAPP is implemented as described.

3.1 Assessments, Response Actions, and Oversight (C1/C2)

The Project Manager or Quality Assurance Officer will provide oversight for field data collection to ensure that the protocols described in this QAPP are being followed.

The Project Manager or Quality Assurance Officer will review each batch of reported data to ensure that appropriate protocols are being followed and that the data are within the accepted range for each parameter or analyte. Any “outlier” data discovered will be identified, and potential sources of error will be assessed to determine possible causes and avoid or minimize those going forward.

The Project Manager or Quality Assurance Officer will conduct audits after each water quality monitoring event and may also request additional data audits or reviews to assess conformance and compliance with the QAPP.

4.0 Environmental Information Review and Usability Determination for Field Collected Data

This section addresses the Quality Assurance activities that occur after the project's data collection has been completed. The implementation of these elements ensures that the data conforms to the specified criteria and achieves the project's objectives.

4.1 Environmental Information Review (D1)

Contract laboratories will use the control limits set forth in **Section B5** to accept analytical data generated under conditions that meet the control limits for instrument precision and accuracy and reject or qualify analytical data generated under conditions that do not meet these control limits.

The Project Manager, Quality Assurance Manager, or their designee will review analytical reports to verify and validate the completeness and reasonableness of laboratory results using the record of samples submitted for analysis on the completed COC forms and the anticipated environmental range of values for the selected parameter and sample matrix.

Data will be considered complete when analytical values are reported for all analyses requested for all samples submitted to the laboratory. Data will be considered reasonable when all values measured for the sample and all values generated by the same analytical procedure fall within the expected range of values for that sample or that parameter.

Field-measured data will be reviewed against the control limits provided in this document. The Project Manager, Quality Assurance Manager, or their designee will review field-measured data to verify and validate the completeness and reasonableness of field-measured results using the anticipated environmental range of values for the selected parameter and sample matrix.

Field-measured data will be considered complete when values are reported for all parameters measured. Data will be considered reasonable when all values measured and all values generated by the same method fall within the expected range of values for that parameter.

Data that does not meet completeness or reasonableness criteria will be evaluated for rejection (if unusable) or qualification (if usable) and flagged accordingly.

4.2 Project Evaluation – Usability Determination (D2)

Project evaluation and data usability determinations will be made as follows:

- The Project Manager, Quality Assurance Manager, or their designee will be responsible for verifying that all water quality samples collected are completely and accurately represented on COC forms prior to transfer to the laboratory for analysis. If there are data gaps or inaccuracies on COC forms, the forms will be corrected immediately upon noticing the error, and the revised information will be communicated to the laboratory.

- Additionally, Contract laboratory technicians will be responsible for validating instrument calibration by measuring the calibration standards for the selected parameter after accepting a new calibration and recalibrating if the measurements do not meet established control limits for accuracy and precision.

- Analytical data provided by the laboratories will also be reviewed and validated by the Project Manager, Quality Assurance Manager, or their designee to provide information on whether data are acceptable for use in developing project conclusions and deliverables. The results of the verification and validation processes will be addressed in the project deliverables. The Project Manager will be responsible for the final review of deliverables for completeness and adherence to method and quality control requirements.

- The Project Manager will provide updates related to data usability, as directed.

5.0 References

AECOM. 2010. Santuit Pond Diagnostic Study; Mashpee, Massachusetts. Prepared for Town of Mashpee.

ESS Group, LLC. 2022. Santuit Pond Focused Feasibility Study: Interim Recommendations for Water Quality Improvement. Prepared for Kimberly Groff, Massachusetts Liaison, SNEP Network.

Howes, B., R. Samimy, D. Schlezinger, S. Kelley, J. Ramsey, J. Wood, and E. Eichner. 2004. Linked Watershed-Embayment Model to Determine Critical Nitrogen Loading Thresholds for Popponesset Bay, Mashpee and Banstable, MA. Commonwealth of Massachusetts, Department of Environmental Protection, Estuaries Project.

MassDEP. 2023. Final Massachusetts Integrated List of Waters for the Clean Water Act 2022 Reporting Cycle. CN 568.1, Massachusetts Department of Environmental Protection, Bureau of Water Resources, Division of Watershed Management, Watershed Planning Program. Worcester, MA.

TRC. 2022. Santuit Pond Baseline Monitoring, Sediment Coring, and Nutrient Inactivation Dosing Study; Mashpee, Massachusetts. Prepared for the Southeast New England Program Network, Mashpee Wampanoag Tribe, Town of Mashpee.

US Army Corps of Engineers (USACE). 2021. Santuit Pond – Section 206 Aquatic Ecosystem Restoration Project. Mashpee, MA. September 2021. USACE, New England District.

Water Resource Services, Inc. (WRS). 2014. Investigation of Algal Blooms and Possible Controls for Lovell's Pond, Barnstable, Massachusetts, 2013.

Appendix A: Scope of Services, Santuit Pond Nutrient Reduction Project, Project Number 24-01/319

Attachment A: Scope of Services

Santuit Pond Nutrient Reduction Project

Project Number 24-01/319

Introduction:
Santuit Pond (MA96277) is a publicly accessible 176-acre freshwater Great Pond located in Mashpee. Santuit Pond, and is listed on MassDEP's 2022 Integrated List of Waters as Category 5 for Phosphorus, Harmful Algal Blooms, transparency, Cholorophyll-a and other impairments. Recent studies concluded that internal cycling of the phosphorus from the sediment is the major source of nutrient pollution and needs to be addressed as part of a larger, watershed-wide effort to reduce nutrient loading to Santuit Pond. The Grantee is the Mashpee Wampanoag Tribe.

Project Goals:
The goal of this project is to reduce the impact of phosphorus on Santuit Pond and improve water quality conditions and prevent harmful algal blooms through alum application and education of local residents. The project will significantly reduce internal phosphorus loading to protect the pond from further water quality degradation due to internal recycling of nutrients. Treatment of phosphorus in the surficial sediment will lead to decreased phosphorus in the water column, cyanobacteria abundance, preventing or minimizing the formation of cyanobacteria blooms and improved habitat. Improved water clarity and dissolved oxygen levels are also expected.

Strategy:
The grantee will conduct an alum treatment in Santuit Pond to reduce internal phosphorus loading and to reduce the available phosphorus within the sediment to improve water quality conditions for fish and wildlife, prevent harmful blooms of potentially toxic cyanobacteria, and improve recreational opportunities in the pond. This will also benefit the Santuit River and Shoestring Bay downstream of Santuit Pond.

The objective is to reduce internal loading by at least 249 kg/year (over 65% of the annual load) which will lead to decreased phosphorus recycling, reduced cyanobacteria abundance, and increased water clarity and improved deep water oxygen levels. Aluminum compounds will be applied to an area of approximately 145-acre area of sediments where anoxia occurs most frequently, at a dose of approximately 42-80 g/m^2 to remove phosphorus from the water column and improve fish and wildlife habitat and reduce public health risk from harmful algal blooms. Treatments will be applied to the pond with application rates and timing to be determined following review by local and state government staff.

Targeted Pollutants and Waterbodies:
The pollutant of concern: phosphorus. The waterbody of concern is Santuit Pond (MA96277) in the Cape Cod Watershed.

Scope of Services:
The scope of services for this contract shall consist of the following tasks and deliverables as

outlined below, consistent with the Grantee's technical proposal received on May 24, 2024 and as outlined in the RFR of March 15, 2024. In order for a deliverable to be considered complete under the contract, the deliverable must be completed in accordance with the contract specifications and the contract schedule must be approved by MassDEP.

Task 1: Quality Assurance and Project Evaluation
Revision of Quality Assurance Project Plan (QAPP) for Mashpee Wampanoag Tribe to provide details about the quality assurance/quality control requirements and technical activities for collection of water quality data associated with the planned alum treatments at Santuit Pond, including ongoing water quality monitoring post-treatment.

The revised and expanded QAPP will add content regarding additional water quality measures, which is anticipated to include algal identification and enumeration, alkalinity, aluminum, iron, oxidation-reduction potential, total dissolved phosphorus, total nitrogen, and total suspended solids. Additionally, the QAPP will be reorganized to improve alignment with EPA Region 1's May 2024 Optional QAPP Template.

Deliverables 1:
- MassDEP and EPA-approved revised QAPP for the collection of water quality data, to be approved prior to the commencement of any sampling.
- Using an appropriate method to determine results of anticipated pollutant load reductions achieved by alum treatment implemented under this project.
- Documentation of the BMP implementation work. Information to be supplied for each BMP includes BMP type, date(s) of completion, targeted pollutant(s), size of targeted treatment area, and site maps.

Task 2: Permitting
The Grantee will prepare and file a Notice of Intent with the Mashpee Conservation Commission and apply for License to Apply Chemicals from MassDEP. The Grantee will obtain additional permits as required including those from the Division of Maine Fisheries, NHESP, etc.

Deliverable 2: Approved Orders of Conditions, License to Apply Chemicals, and additional permits as required

Task 3: Alum Treatment
The Grantee will apply aluminum compounds to an area of at least 145 acres, in areas where the phosphorus levels are known to be most elevated and where the sediment is impacted by anoxic conditions which releases phosphorus from the sediment contributing to internal loading of the lake, at a dose of approximately 42-80 g/m^2 of aluminum compounds. Application and timing of treatment will be as the issued permits and specifications.

Additionally, environmental monitoring data will be collected prior to, during, and after treatment. The data to be collected is anticipated to include algal identification and enumeration, alkalinity, aluminum, chlorophyll a, dissolved oxygen, iron, oxidation-reduction potential, pH, temperature,

Secchi disk transparency, total phosphorus, total dissolved phosphorus, total nitrogen, and total suspended solids as well as any additional data that may be required as part of permit conditions.

Deliverable 3:
Summarize and report on the results of the treatment and monitoring results (if required as part of permit conditions). Estimate amount of phosphorus removed from the water column. Complete treatment and provide treatment report, detailing amounts applied, locations, treatment conditions, and initial results.

Task 4. Training and Monitoring
Provide training of MWT staff in water quality monitoring field sampling and data management techniques. This will improve the capacity of MWT staff to continue ongoing monitoring of water quality in Santuit Pond after Project completion.

Deliverable 4:
Summary of training and electronic copies of training materials, as appropriate
Copies of water data collected uploaded to the MassDEP water quality data portal, as appropriate

Task 5: Outreach and Education
Conduct a workshop to educate area residents on best property management for minimizing impact on the pond, discuss the project, and explain how the alum treatment works. Report on project progress during televised select board meetings and post information on the Santuit Pond Learning Hub webpage.

Present the project and its benefits to the public in the form of its newsletter and facilitate a meeting between consultant(s), the public, members of the Mashpee Wampanoag Tribal and other watershed stakeholders on how local residents can help to prolong the benefits of the project through local landscaping practices and other improvements such as rain gardens, shoreline buffers, and other means for encouraging infiltration. Please note, all public outreach and education materials, etc. developed as part of the grant or match must be approved by the MassDEP Project Officer before distribution, posting etc.

Deliverable 5:
Conduct one workshop
MassDEP-approved newsletter(s), handout materials, and postings

Task 6: Reporting and Project Oversight
The Grantee will submit the following deliverables to MassDEP in accordance with the Milestone Schedule in Attachment C:

- *Invoices* and supporting documentation will be emailed to the 319 Project Officer monthly or as appropriate.
- *Quarterly Progress Reports* must be emailed in a format compatible with the Department's software (MS Word unless otherwise specified). These reports must contain a summary of all

work completed, by task and as a percentage of each task completed, during the reporting period, and planned activities for the next quarter. *Quarterly Progress Reports* described above must be submitted to the Department within 15 days following the end of the reporting quarter (i.e., by January 15th, April 15th, July 15th, and October 15th of each year).
- The *Invoice* and *Attachment for Match Certification forms* should be signed by the authorized signatory, scanned, and submitted via email to the Department's Contract Manager.
- A draft *Final Report* shall be submitted to the 319 Project Officer for review and comment at least two (2) months prior to the contract end date. This report must include a description of all activities undertaken as part of the project and a summary of the project.
- One electronic version of the final report with photographs and supporting documentation, and other project deliverables as appropriate will be submitted to the Department by the project end date. The **electronic report shall be authored in MS Word** and then converted to tagged PDF files for compatibility with the Department's internet web site.

Any files that are intended for publication on the MassDEP web site must comply with accessibility guidelines found at www.mass.gov/accessibility.

Deliverable 6:
- Quarterly progress and fiscal reports.
- Draft Final Report at least two months prior to the contract end date.
- Final Report.

Additional Contract Conditions

- Work undertaken as part of this grant project must exceed the requirements of the NPDES MS4 permit and cannot be credited toward meeting the requirements of that permit.
- All materials, software, maps, reports and other products produced through this contract shall be considered in the public domain and thus available at the cost of production. If GIS products are produced, a copy of any spatial data developed and full meta-data documentation must be provided as part of the project deliverables. A template for meta-data documentation is available from MassGIS. Data should be provided in either an ESRI file geo-database or shapefile.
- During the project, title to any and all real and personal property, equipment and accessories purchased and used for the project scope of work and funded in whole or part by this contract shall be in the name and control of the Grantee.
- After termination of the project, the manner of use and disposition of any equipment and accessories purchased and used for the project and funded in whole or part under this contract shall be determined by the Department.
- Grantees must immediately notify the Department of the loss or reassignment of any key employee or subcontractor identified in the proposal, and the Department requires that a replacement employee or subcontractor be assigned within 60 days. The Department reserves the right to terminate the contract if the Grantee fails to replace a key employee or subcontractor within this time frame or to substitute appropriately qualified key employee.

- Any changes to the contract scope of work or budget categories must be approved in writing by the Department. Requests for contract scope or budget modifications must be submitted in writing to the 319 Project Officer for review and approval.
- The award of this Grant by the Department does not constitute a permit or any other approval that may be required for the implementation of the project funded by the Grant. The grantee shall timely obtain, and comply with, all federal, state and local permits and approvals required for the project.
- The Department reserves the right to approve the selection of all consultants or subcontractors.
- For any BMP installation funded under the 319 program, written certification that the system has been installed according to engineering and design specifications will be required from the designer or supplier of the technology. The certification must occur prior to the system being covered, buried, or otherwise made inaccessible, and shall occur in advance of release of payment for the system by the Department.

Public Awareness Terms and Conditions

- Prior written approval from the Department is required before material derived from the deliverables received under this Agreement is presented for publication or posted on the internet. An Acknowledgment of Support must be made in connection with the publishing or Internet posting of any material based on or developed under this Agreement. The acknowledgment will be in the form of a statement substantially as follows:
  "This project has been financed with Federal Funds from the Environmental Protection Agency (EPA) to the Massachusetts Department of Environmental Protection (the Department) under an s. 319 competitive grant. The contents do not necessarily reflect the views and policies of EPA or of the Department, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use."
- Statements to the press are authorized as long as proper acknowledgment is given to the Department and EPA.
- Announcements: The grant recipient agrees that announcements through the web or print materials for Workshop, conference, demonstration days or other events as part of a project funded by a 319 assistance agreement shall contain a statement that the materials or conference has been funded by the Massachusetts Department of Environmental Protection and the United States Environmental Protection Agency.
- Public or Media Events: The Recipient agrees to notify the MassDEP and EPA Project Officers of public or media events publicizing the accomplishment of significant events related to construction projects as a result of this agreement, and provide the opportunity for attendance and participation by state and federal representatives with at least ten working days notice.
- Limited English Proficiency Communities: To increase public awareness of projects serving communities where English is not the predominant language, recipients are encouraged to include in their outreach strategies communication in non-English languages. Translation costs for this purpose are allowable, provided the costs are reasonable.

Attachment B: Budget

Santuit Pond Nutrient Reduction Project

Project Number 24-01/319

Expense Items	319 Amount	Total Amount
Subcontractual Services		
Project Evaluation/QAPP Development	$1,500	$1,500
Design & Permitting	$15,000	$15,000
Alum Treatment	$645,000	$645,000
Training	$9,500	$9,5000
Outreach and Education	$10,000	$10,000
Project Management & Reporting	$18,500	$18,500
Monitoring related supplies and materials	$500	$500
Subtotal	***$700,000***	***$700,000***
Total	**$700,000.00**	**$700,000**

The Department will retain 10% of the total maximum obligation of the 319 grant funds or the final invoice submitted by the Grantee, whichever is greater, until all contract provisions are satisfied and final reports and other products are delivered and accepted. This 10% retainage shall be reflected on each invoice submitted by the Grantee and will be cumulative in the amount of $70,000 (10% of the contract amount).

Attachment C: Milestone Schedule

Santuit Pond Nutrient Reduction Project

Project Number 24-01/319

Month	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**
1: QAPP/Evaluation																						X	X	X
2: Design & Permitting	X	X	X																					
3: Alum Treatment**			X												X									
4. Training & Monitoring	X	X	X	X	X	X									X	X	X	X	X	X	X	X	X	X
5: Outreach & Education	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
6: Project Management and Reporting				X			X			X			X			X			X			X		X
** Fall 2025 Alum Treatment timeline contingent on permit approval.																								

Appendix B: Field Sampling Standard Operating Procedures, Field Data Forms, and Chains of Custody

Title: **Specific Conductance Calibration and Measurement SOP**	Procedure Number: **900**
	Revision Number: **00**
	Effective Date:

Authorization Signatures

Technical Review Anna Chase	Date 6/13/2024
Environmental Sector Quality Director	Date

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1.0 PURPOSE, SCOPE, AND APPLICABILITY

1.1 Purpose and Applicability

This Standard Operating Procedure (SOP) provides basic instructions for routine calibration and operation of a variety of specific conductance meters. This SOP document also addresses estimation of total dissolved solids (TDS) and salinity by direct measurement of specific conductance (specific methods and capabilities for these parameters are outlined in the manufacturer's individual instrument manuals). This SOP is designed to be consistent 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 (QAM) and may include duplicate or replicate measurements or confirmatory analyses.

2.0 RESPONSIBILITIES

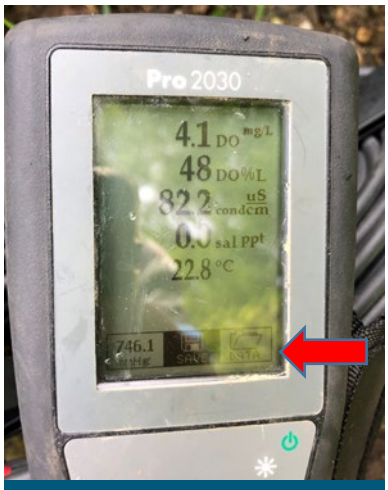
The project manager is responsible for ensuring that project-specific requirements are communicated to the project team and for providing the materials, resources, and guidance necessary to perform the measurements in accordance with this SOP and the project plan.

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 SOP and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- Specific conductance meter (YSI Pro2030 or similar)
- Specific conductance meter manufacturer's instruction manual
- Distilled water
- Conductivity standard at concentration that approximates anticipated range of sample concentrations
- Lint-free tissues
- Calibration sheets or logbook
- Laboratory or field data sheets or logbooks



Handheld YSI 2030 meter, red arrow showing where the specific conductance is measured.

4.0 METHODS

4.1 Sample Handling, Preservation, and General Measurement Procedures

- Specific conductance measurements should be taken in situ or 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, or µS/cm at 25°C.

4.2 Calibration and Measurement Procedures

It is not necessary to calibrate conductivity, specific conductance and salinity. Calibrating one of these parameters will simultaneously calibrate the others. YSI recommends calibrating specific conductance for greatest ease.

When calibrating Specific Conductance, the Pro2030 uses the factory default values for the Specific Conductance Reference Temperature and the Specific Conductance Temperature Coefficient regardless of what is configured in the System Setup Menu. The default value for the Reference Temperature is 25°C and the default value for the Temperature Coefficient is 1.91%/°C. It is important to note that the Temperature Coefficient of a calibration solution is dependent on the contents of the solution. Therefore, YSI recommends using a traceable calibration solution made of KCl (potassium chloride) when calibrating Specific Conductance since these solutions typically have a Temperature Coefficient of 1.91%/°C. Additionally, be sure to enter the value of the solution as it is listed for 25°C when calibrating Specific Conductance.

The specific conductance meter must be calibrated (or the calibration checked) before any analyses are performed.

- 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 from date of purchase should be used if the expiration date is worn or missing.
- Rinse the probe with distilled water prior to use. If necessary, dry with a lint-free tissue or cloth.
- Fill a clean container (i.e. plastic cup or glass beaker) with fresh, traceable conductivity calibration solution and place the sensor into the solution. The solution must cover the holes of the conductivity sensor that are closest to the cable (see photo). Ensure the entire conductivity sensor is submerged in the solution or the instrument will read approximately half or less of the expected value. Gently move the probe up and down to remove any air bubbles from the conductivity sensor.
- Turn the instrument on and allow the conductivity and temperature readings to stabilize. Press the Cal key. Highlight



Solution above two holes near cable

Conductivity and press enter. Next, highlight the desired calibration method, Sp. Conductance or Conductivity, and press enter.

- Highlight the units you wish to calibrate, either uS/cm or mS/cm, and press enter. 1 mS = 1,000 uS. Next, use the up or down arrow key to adjust the value on the display to match the value of the conductivity calibration solution. If calibrating conductivity, it is necessary to look up the value of the solution at the current temperature and enter that value into the Pro2030. Most conductivity solutions are labeled with a value at 25°C. If calibrating specific conductance, enter the value listed for 25°C. Depressing either the up or down arrow key for 5 seconds will move the changing digit one place to the left. The Pro2030 will remember the entered calibration value and display it the next time a conductivity calibration is performed. The meter may be adjusted to ±20% from the default setting. If the measurement differs by more than ±20%, the probe should be cleaned, serviced, or replaced as needed.
- An additional check may be performed, if required by the project plan, by placing the probe into an additional 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.
- Press enter to complete the calibration. Or, press Cal to cancel the calibration and return to the Run screen.
- 'Calibration Successful' will display for a few seconds to indicate a successful calibration and then the instrument will return to the Run screen.
- Verify the calibration at least once a month or whenever the instrument has been moved from freshwater to saltwater environments or vice versa. Recalibrate or service the instrument, as needed, if the check value is not within 15% of the true (calibration standard) value.



Use of YSI handheld multiparameter device and probe in the field

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 or the project-specific acceptance criteria, consult the appropriate section of the meter instruction manual for troubleshooting procedures. If the problem persists, consult the manufacturer's customer service department immediately for further guidance.

4.4 Maintenance

The probe must be stored and maintained according to the procedures and frequencies required by the manufacturer.

5.0 QUALITY CONTROL

The meter must be calibrated (or the calibration checked) before sampling 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%.

It is suggested to develop a calibration check worksheet that accompanies this SOP.

6.0 DOCUMENTATION

Meter calibration, temperature check, and maintenance information will be recorded in a calibration log. Specific conductance data may be recorded on the appropriate laboratory or field data sheets or logbooks.

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

- Date and time of calibration or check
- Person performing the measurement
- Instrument identification number/model
- Expiration dates and batch numbers for all standards
- Reading for standard before and after meter adjustment, if completing a calibration
- 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
- Person performing the measurement
- Sample identification/station location
- Temperature (corrected for any difference with reference thermometer) and conductance of sample (including units and duplicate measurements).
- 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 SOP. 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.

Title: **pH Calibration and Measurement SOP**	Procedure Number: **902**
	Revision Number: **00**
	Effective Date:

Authorization Signatures

Anna L. Chase	
Technical Review Date Anna Chase 6/13/2024	Environmental Sector Quality Director Date

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1.0 PURPOSE, SCOPE, AND APPLICABILITY

1.1 Purpose and Applicability

These Standard Operating Procedures (SOP) provide basic instructions for routine calibration and operation of a variety of pH meters. Measurements are made in accordance with methods that address 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 analyses.

2.0 RESPONSIBILITIES

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 SOP and the project plan.

The analyst is responsible for verifying that the pH meter is in proper operating condition prior to use and for implementing the calibration record check and measurement procedures in accordance with this SOP and the project plan.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- pH meter
- pH meter manufacturer's instruction manual
- Calibration sheets or logbook
- Distilled water
- Calibration standards at concentrations that approximate anticipated range of sample concentrations (generally pH 4, pH 7, and pH 10 but this may vary by manufacturer)
- Field data sheets or logbooks or tablet with electronic field data collection system

4.0 METHODS

4.1 General Measurement Procedures

Measurements of pH should be taken in situ or immediately after sample collection since temperature changes and absorption of carbon dioxide from the air can affect pH.

4.2 Calibration and Measurement Procedures

Calibration instructions for the Oakton EcoTestr pH meter are presented below. If utilizing a different pH meter, please see the manufacturer's instruction manual.

Calibration should be done regularly, preferably once a week during active use. You can calibrate up to three points using either the USA buffers (7.0 pH, 4.0 pH, and 10.0 pH) or NIST buffers (6.9 pH, 4.0 pH, 9.2 pH).

- Press ON/OFF button to switch unit on.
- Submerge electrode in 2 to 3 cm of pH standard buffer solution.
- Press the "cal/esc" button to enter calibration mode. Display will show "CAL" followed by the default pH value.
- After the reading has stabilized a check mark will appear on the display. Do not remove the meter from the buffer. After 3 seconds, the meter will auto accept the calibration and the display will read "donE".
- Repeat the above procedure to calibrate additional points (three-point calibration is recommended).
- To abort calibration press "cal/esc" button at any time.

4.3 Troubleshooting Information

If there are performance problems with any pH meter which result in inability to achieve the acceptance criteria presented in Section 5.0 or the project-specific acceptance criteria, consult the appropriate section of the instruction manual for troubleshooting procedures. If the problem persists, consult the manufacturer's customer service department for further guidance.

4.4 Maintenance

The pH meter must be stored and maintained according to the procedures and frequencies required by the manufacturer. Always keep the sensor electrodes clean. Rinse the electrodes with de-ionized water and wipe them dry with clean cloth before storing with its protective cap.

5.0 QUALITY CONTROL

The meter must be calibrated (or the calibration checked) before sampling and will not be used for sample determinations of pH 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 site specific workplan or QAPP. In the absence of project-specific criteria, duplicate measurements should agree within 10%.

It is suggested to develop a calibration check worksheet that accompanies this SOP.

6.0 DOCUMENTATION

Meter calibration and maintenance information will be recorded in a calibration log. pH data may be recorded on the appropriate laboratory or field data sheets or logbooks.

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

- Date and time of calibration or check

- Person performing the measurement
- Instrument identification number/model
- Expiration dates and batch numbers for all standards
- Reading for standard before and after meter adjustment, if calibrating the instrument
- 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
- Person performing the measurement
- Sample identification/station location
- Comments

7.0 TRAINING/QUALIFICATIONS

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

Title: **Surface Water Sampling SOP**	Procedure Number: **904**
	Revision Number: **00**
	Effective Date:

Authorization Signatures

Anna L. Chase	
Technical Review Date Anna Chase 6/13/2024	Environmental Sector Quality Director Date

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TABLES

Table 1.0 Example Container Types, Preservative Requirements, and Hold Times for Water Quality Samples 3

1.0 PURPOSE, SCOPE, AND APPLICABILITY

This Standard Operating Procedure (SOP) provide basic instructions for the routine acquisition of surface water from lakes, ponds, and streams. The methods outlined below are intended to (1) standardize water sample collection methods; (2) ensure that samples delivered to the laboratory represent field conditions as accurately as possible; (3) assure proper documentation of sample collection; and (4) minimize cross contamination between sampling sites.

2.0 REQUIRED MATERIALS

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

- Nitrile gloves
- Labeled sample bottles provided by contracted laboratory (appropriately sanitized and containing the necessary preservative for desired analyses, see Table 2.0 for examples)
- Field data sheets or logbooks, including list of sites or locations to be sampled, and pencil
- Cooler with ice packs for sample storage
- Van Dorn or Kemmerer sampler is collecting samples at depth
- Integrated depth sampler (if collecting algae sample)
- Secchi disk (if collecting algae samples)
- Zooplankton net (if collecting zooplankton samples)
- Laboratory Chain of Custody

Table 1.0 Example Container Types, Preservative Requirements, and Hold Times for Water Quality Samples.

Analysis	Bottle Type	Preservative	Hold Time
Total Phosphorus	plastic	H_2SO_4	28 days
Dissolved Phosphorus	plastic	As Is	analyze immediately*
Total Suspended Solids (TSS)	plastic	As Is	7 days
Nitrate, Nitrite	plastic	As Is	48 hrs
Total Kjeldahl Nitrogen (TKN)	plastic	H_2SO_4	28 days
Metals - Total	plastic	HNO_3	6 months**
Metals - Dissolved	plastic	As Is	6 months**
Algae	opaque plastic	Lugol's iodine***	>1 year
Chlorophyll-a	opaque plastic	As Is	24 hrs
Bacteria	sterile plastic	As Is	6 hrs

* 28 days with field filtration into an H_2SO_4-preserved bottle, ** 28 days for mercury, *** Some laboratories will not accept preserved samples – check with the laboratory first if unsure.

3.0 METHODS

3.1 General Sampling Instructions

- Testing methods, sample containers, preservation techniques, and sample volumes should be selected in consultation with the laboratory to ensure that samples obtained will provide the desired results.
- Hold times vary considerably between different analytes and must be taken into consideration when planning field sampling efforts and lab courier pickups to assure the validity of analytical results.
- Field filtration of certain samples (dissolved phosphorus) is recommended. The laboratory may supply syringes and filters for use in the field.



Using a pre-cleaned (as is) bottle to fill a sample bottle containing preservative.

- In general, surface water samples should be collected via direct grab methods.
- Sample collection should precede the measurement of physical field parameters (including pH, apparent color, turbidity, conductivity, and dissolved oxygen) in order to minimize the risk of sediment disturbance and/or sample contamination.
- Clean rubber gloves should be worn at each sampling location. When sampling multiple sites on the same day, gloves may be rinsed in the immediate area of the waterbody to be sampled (downstream at flowing sites).
- Approximately 1-inch of air space should be left when filling sample bottles (except for dissolved oxygen, alkalinity, and BOD samples), so that bottles may be shaken (if needed) before analyses (EPA, 1997; Simpson 1991).
- Sample containers with preservatives should not be used directly to collect water samples. If using containers with preservatives, a pre-cleaned container of similar type (an as is bottle) should be used to collect and subsequently transfer the sample to the preserved container.
- Ensure that all sample bottles are correctly and completely labeled before storage. Sample bottles should be stored in a cooler with ice packs (it is best to avoid ice, as meltwater could potentially contaminate samples) or in a refrigerator until they are submitted to a lab courier.

3.1.1 Lake and Pond Sampling

- Grab samples from lakes and ponds should be collected at approximately 8 to 12 inches beneath the water surface or mid-way between the surface and the bottom if the waterbody is shallow (EPA 1997). Samples should not be collected in close proximity to the lake shoreline or submerged obstacles.
- To collect water samples, hold an as is bottle near the base, remove the lid, and plunge it into the water with the opening facing downward. Invert the bottle and allow it to fill before

bringing it to the surface. Decant sufficient water from the bottle to allow for the required headspace and replace the cover, or carefully pour the contents into a bottle containing preservative. Repeat the above process to refill the as is bottle as many times as necessary.

3.1.2 Algae Sampling

- Algae samples should be stored in opaque bottles with a small amount of Lugol's iodine for preservative (~1-2 drops in a 250 mL bottle), unless otherwise directed by the laboratory. Algal taxonomy labs can provide opaque plastic bottles, but standard plastic as is bottles covered in aluminum foil can also be used.
- Algae samples should be collected using an integrated depth sampler. An integrated depth sampler consists of a length of tubing (~1in diameter, at least 2 m long) with a weight attached to one end. Sample collection procedures using the depth sampler should proceeds as follows (procedure adapted from EPA 2012):
- Determine the euphotic zone:
    - Lower the secchi disk over the shaded side of the boat until it disappears. Lower the disk a bit further, then slowly raise the disk until it reappears. Record the reappearance depth. The euphotic zone is calculated by multiplying the reappearance depth by 2.
- Holding onto the non-weighted end of the sampler, lower the tube into the water column. Rinse the sampler by submerging it three times.
- Lower the sampler so that it is submerged to the depth of the euphotic zone, or fully submerged if the euphotic zone is deeper than the length of the sampler. Cover the opening at the non-weighted end with a gloved thumb.
- Lift the sampler completely out of the water and cover the opening at the weighted end with a gloved thumb (both ends should be covered). Repeatedly lift each end of the sampler to mix the water sample within the tube.
- Fill the algae sample bottle with the required volume of water from the sampler (the bottle will contain Lugol's solution as preservative so be careful not to over-fill).
- Unlike samples for most other analytes, preserved algae samples can be stored at room temperature before submission to a lab.

3.1.3 Zooplankton Sampling

Zooplankton samples are collected by towing the zooplankton net a known distance vertically through the water column and preserving the collected organisms in ethanol.

- Prior to zooplankton sampling, collect dissolved oxygen measurements through the water column at the sampling location. Identify the depth at which dissolved oxygen falls below 2 mg/L, which will be the lower cutoff for zooplankton sampling.
- The zooplankton net should be lowered through the water column until the net opening reaches the lower cutoff depth. However, do not allow the net to come in contact with the bottom. Record the length of the zooplankton tow (the depth at which the tow begins).
- Steadily pull the zooplankton net up through the water column until it reaches the surface. Wash collected material off the sides of the net and concentrate organisms in a small amount of water in the collection cup. Pour contents of the collection cup into a sample bottle containing 90% ethanol.

- Return zooplankton samples to the appropriate TRC office for sample processing and organism identification. Preserved samples can be stored at room temperature.

3.1.4 Stream Sampling

- Samples should be collected from the center of small streams (i.e., 10-20 feet wide with a maximum depth of less than 2 feet), and at a location where water depth is 2-3 feet in larger streams.
- Always approach a sampling location from downstream, traveling so as to minimize the disturbance of bottom sediments and upstream waters.
- Stand downstream of the desired sampling location, hold the sample bottle near its base and plunge it below the water surface with the opening (mouth) downward. The opening of sample bottles should always be directed away from the sampler in an upstream direction.
- To inform investigations about nutrient inputs, stream flow should be measured whenever water quality samples are collected (see SOP for Measuring Stream Flow)

4.0 QUALITY CONTROL

Prior to leaving the sampling site, field staff should review field notes, scope documents, or other resources to ascertain that all required samples have been collected. Staff should confirm that sample bottles are appropriately and legibly labeled and stored in accordance with sample handling requirements. Following this check the field crew lead should initial the field notes sheet to indicate that a quality check has been completed.

5.0 DOCUMENTATION

Report surface water field data on sheets or in notebooks. Any unanticipated site-specific information, which requires deviation from the above guidelines, should be recorded. Field notes for surface water sampling should include a minimum of the following:

- Name or initials of person collecting the samples
- Sample identification/station location
- Date and time of sample collection
- Environmental conditions (e.g., wind, weather)
- Other comments or observations about water quality and site conditions (e.g., visible algae bloom, dead fish nearby, sample has noticeable odor or color, etc.)

Photographic evidence of any notable conditions is also desirable.

6.0 TRAINING/QUALIFICATIONS

To properly perform surface water sampling, the analyst must be familiar with the sampling techniques stated in this SOP.

7.0 REFERENCES

EPA, 2012. 2012 National Lakes Assessment Field Operations Manual. Version 1.0, May 15, 2012. United States Environmental Protection Agency. Office of Water. EPA-841-B-11-003. Accessed January 22, 2020 at https://www.epa.gov/sites/production/files/2013-11/documents/nla2012_fieldoperationsmanual_120517_final_combinedqrg.pdf

Title: **Turbidity Calibration and Measurement SOP**	Procedure Number: **905**
	Revision Number: **00**
	Effective Date:

Authorization Signatures

Anna L. Chase	
Technical Review Date Anna Chase 6/13/2024	Environmental Sector Quality Director Date

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APPENDICES

Appendix A: Calibration Visual Manual

1.0 PURPOSE, SCOPE, AND APPLICABILITY

1.1 Purpose and Applicability

These procedures provide basic instructions for routine calibration and measurement of turbidity using a nephelometric turbidity meter with a digital read-out device (e.g., LaMotte 2020we 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.

Only use AMCO or formazin standards with the 2020we/wi. StablCal® standards below 50 NTU should not be used to calibrate the 2020we/wi. The diluent used in the StablCal® standards has a different refractive index than traditional formazin standards and will affect the results. The concentration of the calibration standard should be similar to the expected concentration of sample that will be tested. The following standards are available from LaMotte Company:

1480 0 NTU/FNU Standard, 60 mL (EPA or ISO)
1450 1 NTU Standard, 60 mL (EPA)
1453 1 FNU Standard, 60 mL (ISO)
1451 10 NTU Standard, 60 mL (EPA)
1454 10 FNU Standard, 60 mL (ISO)
1452 100 NTU Standard, 60 mL (EPA)
1455 100 FNU Standard, 60 mL (ISO)

2.0 RESPONSIBILITIES

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 SOP 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 SOP 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/cuvettes
- Mild detergent
- Lint-free cloth
- Distilled water
- Nephelometric Turbidity Unit (NTU) calibration standards cuvettes
- Laboratory or field data sheets or logbooks



Example of a sample cuvette

4.0 METHODS

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

- Select a turbidity standard in the range of the samples to be tested (typically between 1.00 NTU and 100.00 NTU) or as recommended by the manufacturer. Fill a turbidity tube or cuvette with the standard, cap, and wipe the tube with the clean lint-free cloth.
- Place the sample into the turbidity meter such that the indexing arrow or line on the turbidity tube is aligned with the indexing arrow or notch 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 10%), continue with the calibration procedure.
- Follow the calibration procedures outlined by the manufacturer's manual.
- Verify the calibration every 15 samples, mid-day, and at the end of the day. Recalibrate the instrument if the check value varies more than 10% from the true value.
- Rinse cuvettes with distilled water and wipe gently with a lint-free cloth between sample analysis.
- Recalibrate the instrument with the appropriate NTU standard if the standard is not of the same order of magnitude as the samples being tested.
- The meter must be re-calibrated following any maintenance activities and prior to the next use.
- 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.



LaMotte 2020we Turbidimeter

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

The turbidity measuring tubes will, at a minimum, be checked against NTU calibration standards at the frequency stated in Section 4.2. This verification procedure will be performed in accordance with the manufacturer's manual.

Duplicate measurements of a single sample will be performed at the frequency required in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within + 5% for readings below 10 NTU and + 10% 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.

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

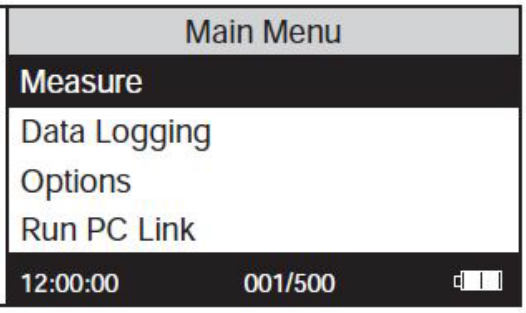
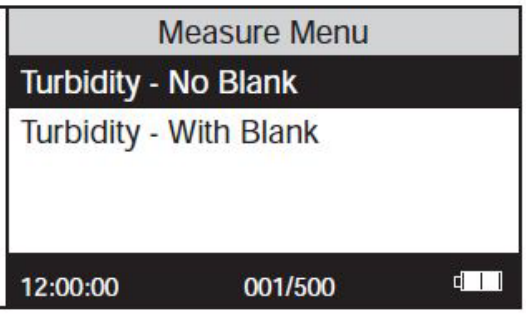
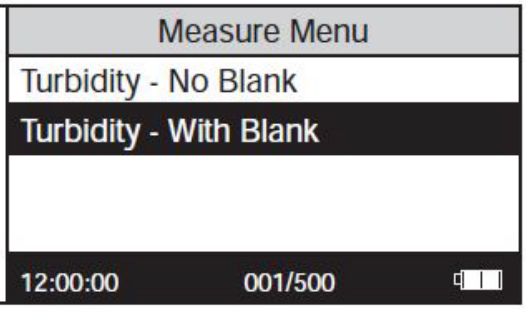
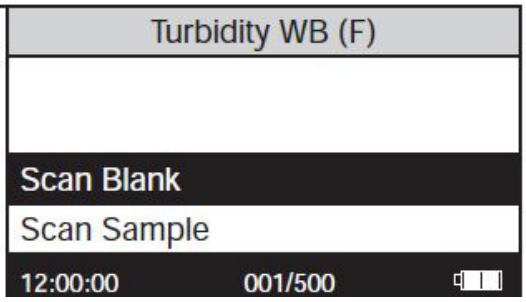
- Date and time of calibration
- Person performing the measurement
- Instrument identification number/model
- Expiration dates and batch numbers for all standard solutions
- Reading for each standard before and after meter adjustment
- Readings for all continuing calibration checks
- Comments
- Documentation for recorded data must include a minimum of the following:
- Date and time of analysis
- Person performing the measurement
- Sample identification/station location
- Turbidity of sample (including units and any duplicate measurements)
- Comments

7.0 TRAINING/QUALIFICATIONS

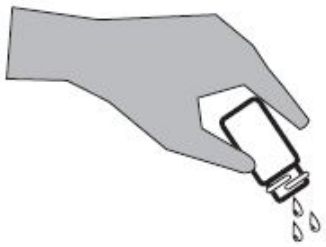
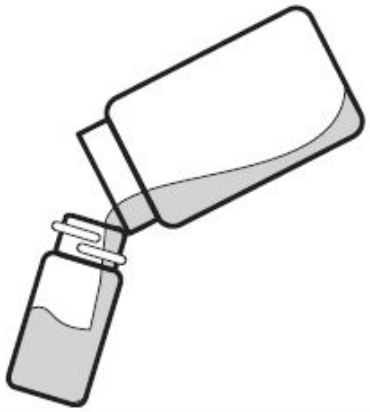
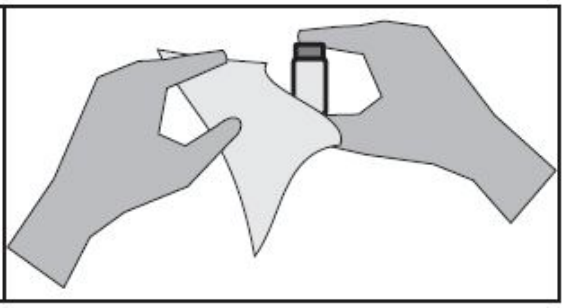
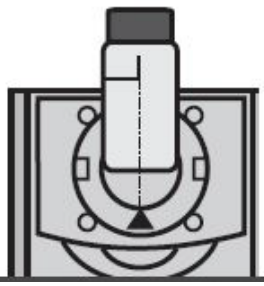
To properly perform turbidity measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOP. The analyst must also be experienced in the operation of the meter.

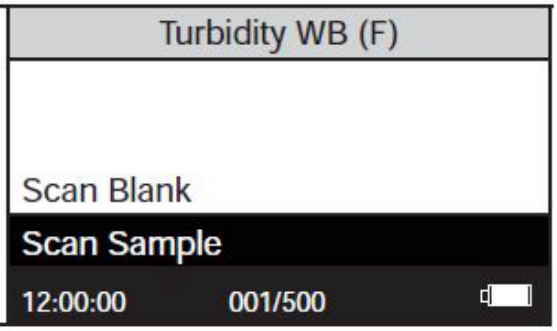
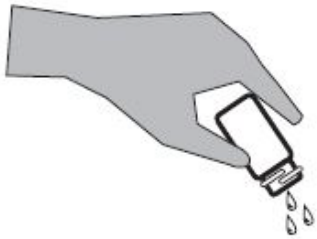
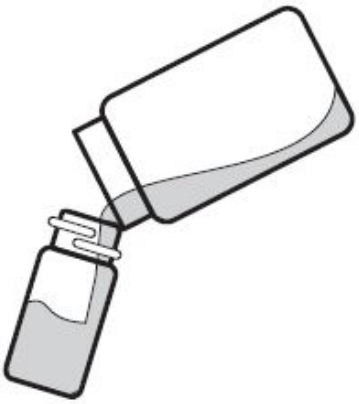
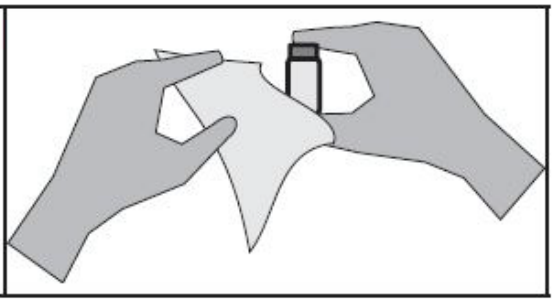
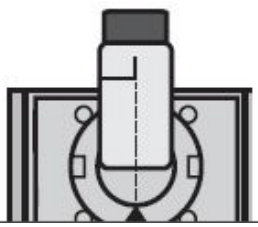
Appendix A:

Calibration Visual Manual

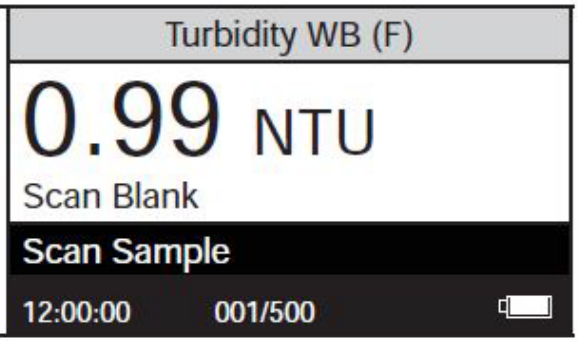
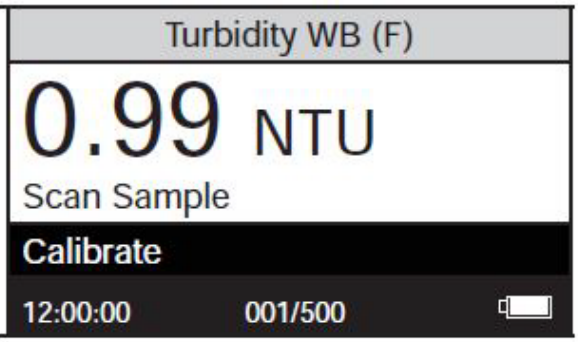
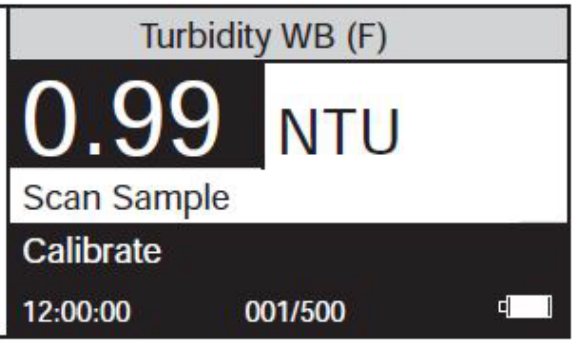
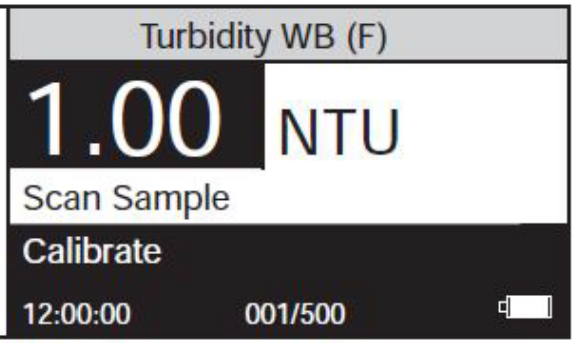
1. Press and briefly hold ⏻ to turn the meter on. The LaMotte logo screen will appear for about 3 seconds and the **Main Menu** will appear.	
2. Press ENTER to select **Measure**.	
3. Press ▼ to scroll to **Turbidity - With Blank**.	
4. Press ENTER to select **Turbidity - With Blank.**	

Calibration

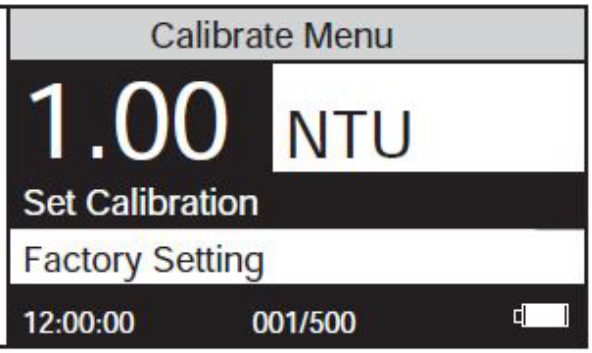
5. Rinse a clean tube (0290) three times with the blank. If samples are expected to read below 1 NTU the meter should be blanked with a 0 NTU Primary Standard or prepared turbidity-free (<0.1 NTU) water. For the most accurate results, use the same tube for the blank and the sample.	
6. Fill the tube to the fill line with the blank. Pour the blank down the inside of the tube to avoid creating bubbles. Cap the tube.	
7. Wipe the tube thoroughly with a lint-free cloth.	
8. Open the meter lid. Insert the tube into the chamber. Align the index line on the tube with the index arrow on the meter. Close the lid.	

9. Press ENTER to scan the blank. The screen will display **Blank Done** for about 1 second and then return to the **Turbidity - With Blank Menu**.	
10. Rinse a clean tube (0290), or the same tube, three times with the standard.	
11. Fill the tube to the fill line with the standard. Pour the standard down the inside of the tube to avoid creating bubbles. Cap the tube.	
12. Wipe the tube thoroughly with a lint-free cloth.	
13. Open the meter lid. Insert the tube into the chamber. Align the index line on the tube with the index arrow on the meter. Close the lid.	

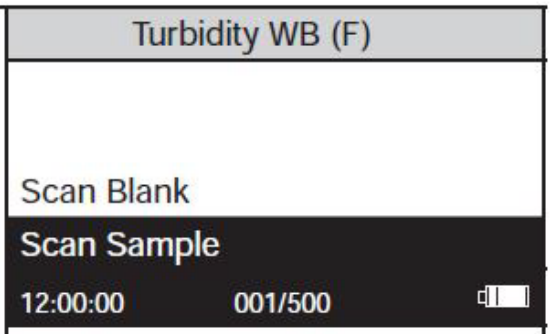
Calibration

14. Press ENTER to scan the standard. The screen will display **Reading** for about 1 second. The result will appear on the screen.	
15. Press ▼ to scroll to **Calibrate**.	
16. Press ENTER to select **Calibrate**. A reverse font (dark background with light characters) will appear to indicate that the reading can be adjusted.	
17. Press ▲ or ▼ to scroll to the concentration of the standard, 1.00 in the example. Note: The allowable adjustment is ±20%.	

18. Press ENTER to select **Caibrate**. Two menu choices will be offered, **Set Calibration** and **Factory Setting**.



19. Press ENTER to select **Set Calibration** and save the calibration. Press ^ or v to scroll and select **Factory Setting** to revert to the factory calibration. The meter will momentarily display **Storing...** and return to the **Turbidity -Without Blank** menu. The calibration has now been saved and the meter can be used for testing.



NOTE: For the greatest accuracy during the calibration procedure, be sure that after the meter is blanked and the blank is scanned as a sample, the reading is 0.00. If not, reblank the meter and scan the blank again until it reads 0.00. When scanning the calibration standards as the sample, scan the calibration standard three times removing the tube from the chamber after each scan and reinserting the tube in the chamber with the same orientation. The readings should be consistent. Use the last consistent reading to calibrate the meter. If the readings are not consistent, avoid using an aberrant reading to calibrate the meter.

Title: **Dissolved Oxygen Calibration and Measurement SOP**	Procedure Number: **907**
	Revision Number: **00**
	Effective Date:

Authorization Signatures	
Anna L. Chase	
Technical Review Anna Chase	Date 6/13/2024
Environmental Sector Quality Director	Date

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1.0 PURPOSE, SCOPE, AND APPLICABILITY

1.1 Purpose and Applicability

These Standard Operating Procedures (SOP) provide basic instructions for routine measurement and calibration of dissolved oxygen using a polarographic sensor-equipped dissolved oxygen meter with a digital read-out (e.g., YSI Pro2030 Dissolved Oxygen, Conductivity, Salinity Instrument). Measurements are made in accordance with methods that address dissolved oxygen measurement of drinking, surface, and saline waters, and 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 measurements.

2.0 RESPONSIBILITIES

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 SOP and the project plan.

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 SOP and the project plan.



Handheld YSI 2030-meter, red arrow showing where the dissolved oxygen is measured.

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- Dissolved oxygen meter with digital read-out device (YSI Pro2030 or similar)
- Clean water
- Manufacturer's instruction manual for the instrument
- Manufacturer's recommended operating solution and replacement membranes or caps
- Laboratory or field data sheets or logbooks

4.0 METHODS

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 may require gentle probe agitation to create water movement around the probe (check instrument manual to confirm).

4.2 Calibration and Measurement Procedures

To accurately calibrate some dissolved oxygen meters, it may be necessary to know the 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 practical salinity units (psu). If uncertain, measure salinity first with an appropriate device. The instructions below are applicable to the YSI Model PRO 2030; for other instruments, consult the instruction manual.

NOTE: It is not necessary to calibrate in both % and mg/L or ppm. Calibrating in % will simultaneously calibrate mg/L and ppm and vice versa. YSI recommends calibrating the dissolved oxygen sensor in % for both ease and accuracy.

Ensure the DO sensor has a good membrane with electrolyte installed.

- A good membrane is free of wrinkles, tears, fouling and air bubbles. Install the sensor guard onto the probe if not already in place.
- Moisten the sponge in the grey calibration/storage sleeve with a small amount of clean water and install the calibration sleeve over the sensor guard. The sponge should only be moistened, and the calibration/storage sleeve should not have excess water in it that could cause water droplets to contact the membrane. The storage sleeve ensures venting to the atmosphere.
- Power the instrument on and, if using a Polarographic sensor, wait approximately 5 to 15 minutes for the storage chamber to become completely saturated and for the sensor to stabilize. If using a Galvanic sensor, wait approximately 5 to 10 minutes for the chamber to become completely saturated. Auto Shutoff should be disabled or set to at least 20 minutes. See System Setup menu for more information on adjusting the Auto Shutoff.
- Ensure the YSI barometer is reading accurately by cross referencing with a separate barometer reading (obtained from a cell phone app or other source). If necessary, perform a barometer calibration.
- Press and hold the Cal key for 3 seconds. Highlight Dissolved Oxygen and press enter.
- "%Local" will automatically be highlighted, press enter. The Pro2030 will display the current DO % and temperature readings along with the % calibration value. The % calibration value will always be 100% for DO Local%.
- Wait at least 3 seconds, then, once the DO% and temperature readings stabilize, press enter to complete the calibration. Or, press the Cal key to cancel the calibration.
- "Calibration Successful" will display for a few seconds to indicate a successful calibration and then the instrument will return to the Run screen.
- Calibration should be performed at a temperature within ± 10°C of the sample temperature. Recalibrate every 15 samples and whenever the unit is turned on.



Use of YSI handheld device and probe

- If calibration is out of range, erratic readings occur, bubbles appear, or if the membrane becomes damaged, wrinkled, or fouled refill the membrane solution and/or replace the membrane, per the manufacturer's manual.
- Avoid contact with environments containing substances that may attack the probe materials (e.g., acids, caustics, and strong solvents).
- DO will now display readings on the Run page that can be recorded in mg/L, mg%, or both.

4.3 Troubleshooting Information

If the calibration is unsuccessful, an error message will display on the screen. Press the "Cal" key to exit the calibration error message and return to the Run screen. See the Troubleshooting guide within the YSI PRO 2030 user manual for possible solutions.

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. Rinsing the probe with distilled or deionized water and preventing exposure of the membrane to drying is typically all that is required on a day-to-day basis.

5.0 QUALITY CONTROL

Duplicate measurements of a single sample should 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.

6.0 DOCUMENTATION

All dissolved oxygen meter calibration, checks, and maintenance information will be recorded in a calibration logbook. Dissolved oxygen data may be recorded on the appropriate field data sheets or field books.

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
- 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

- Person performing the measurement
- Sample identification/station location
- Dissolved oxygen, both in mg/L and percent saturation 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 SOP. 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.

Title: **Secchi Disk Transparency Measurement SOP**	Procedure Number: **915**
	Revision Number: **00**
	Effective Date:

Authorization Signatures

Anna L. Chase	
Technical Review — Anna Chase — Date 6/13/2024	Environmental Sector Quality Director — Date

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1.0 PURPOSE, SCOPE, AND APPLICABILITY

This document provides basic instructions for the routine measurement of water clarity in lakes and ponds with a Secchi disk. 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 waters, stained waters). 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 suspended sediment particles which are related to water depth and wave action. Thus, on any given day the transparency 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 disk in the measurement of transparency; (2) to standardize recording of field data to assure proper documentation of weekly, monthly and seasonal patterns in transparency.

2.0 REQUIRED MATERIALS

The following materials are necessary for the measurement of transparency with a Secchi disk:

- Weighted Secchi disk with attached length of rope marked off in 0.1-meter increments with indelible ink.
- Field data sheets on weatherproof paper or field book
- Viewscope (optional – use if required by project plan or program)

3.0 METHODS

3.1 Sample Handling, Preservation, and General Measurement Procedures

- A location will be selected from which to measure transparency. This location should stay constant throughout the study.
- Orient the vessel to minimize the influence of glare or shadow on the Secchi disk reading.
- The date, weather conditions, and personnel conducting the measurement will be recorded on the field sheet.
- The Secchi disk will be lowered slowly into the water by the rope so that the weight enters the water first and the disk follows, flat side parallel to the water surface.
- The disk 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 disk at this point to the nearest 0.1 meter by reading where the surface of the water touches the rope.
- The disk will then be slowly raised until it is just visible again.
- Once again, a note will be made of the depth of the disk at this point.
- An average of these two depths will be calculated to give the "Secchi depth", i.e. a measure of the transparency of the water.

4.0 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.

5.0 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:

- Date and 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.

6.0 TRAINING/QUALIFICATIONS

To properly use a Secchi disk, the field personnel must be familiar with the techniques stated in this SOP.

Title: **ORP Calibration and Measurement SOP**	Procedure No: **917**
	Revision Number: **00**
	Effective Date:

Authorization Signatures

Technical Review Date Stephanie L. Martin 10/15/2025	Environmental Sector Quality Director Date

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1.0 PURPOSE, SCOPE, AND APPLICABILITY

1.1 Purpose and Scope

This Standard Operating Procedure (SOP) provides basic instructions for routine measurement and calibration of the oxygen reduction potential (ORP) sensor using the YSI Professional Series Digital Handheld Meter with ORP sensor (ProDSS or similar). Measurements are made in accordance with methods that address ORP in 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 necessary to produce data of acceptable quality. These quality assurance requirements will be defined in the site-specific workplan, Quality Assurance Project Plan (QAPP or project plan), Sampling and Analysis Plan (SAP), or laboratory Quality Assurance Manual (QAM), and may include duplicate, replicate, or confirmatory measurements.

2.0 RESPONSIBILITIES

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 SOP and the project plan.

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

3.0 REQUIRED MATERIALS

The following materials are necessary for this procedure:

- YSI Professional Series Digital Handheld Meter equipped with an ORP sensor (ProDSS or similar)
- Manufacturer's instruction manual for the instrument
- YSI Zobell solution. Alternatively, a premixed standard solution that is approved for use with Ag/AgCl ORP sensors or prepare a standard with a known ORP. (Calibration)
- Clean Tap water (Do **NOT** use distilled or deionized water**)**
- Storage bottle containing potassium chloride (KCl) solution. (long-term storage)
- Calibration/storage cup
- Replacement sensor modules
- Laboratory or field data sheets or logbook

4.0 METHODS

4.1 Sampling Handling, Preservation, and General Measurement Procedures

To achieve accurate ORP measurements, samples should be analyzed in situ in a fashion that prevents the addition or loss of any potential oxidants or reductants. Measurements in flowing waters should be made in relatively turbulent free areas.

ORP is a temperature-sensitive measurement and often pH-dependent. Temperature and pH should also be recorded at the time of ORP measurement.

4.2 Calibration and Measurement Procedures

Calibration instructions for the YSI Pro DSS meter equipped with an ORP sensor are presented below. If utilizing a different meter, please see the manufacturer's instruction manual.

Calibration should be done regularly, preferably once a week during active use or in accordance with a project specific QAPP or SAP, as applicable.

- Press ON/OFF button to switch unit on.
- Obtain a premixed standard solution that is approved for use with Ag/AgCl ORP sensors or prepare a standard with a known oxidation reduction potential (ORP) value. Zobell solution is recommended.
- With the probe guard installed, carefully immerse the probe into the standard solution. Make sure both the ORP sensor and temperature sensor are submerged.
- Push the Cal key, then select pH/ORP, then ORP.
- If using YSI Zobell solution, the Calibration value will automatically be adjusted based on the temperature. Otherwise, refer to the table included with the standard solution and enter the mV value that corresponds to the temperature of the solution.
- Wait for the ORP mV and temperature readings to stabilize; the white line on the graph should be flat for about 40 seconds.
- Select Accept Calibration and press the ENTER key. "Calibration successful!" will be displayed in the message area.
- To abort calibration press "cal/esc" button at any time.

4.3 Troubleshooting Information

If there are performance problems with any ORP sensor that result in the inability to achieve the acceptance criteria presented in Section 5.0 or the project-specific acceptance criteria, consult the appropriate section of the instruction manual for troubleshooting procedures. If the problem persists, consult the manufacturer's customer service department for further guidance.

4.4 Maintenance

The ORP sensor must be stored and maintained according to the procedures and frequencies required by the manufacturer. Always keep the sensor modules clean and moist in the clean tap water-saturated air chamber (calibration/storage cap) between

uses - not submerged. Rinse the electrodes with tap water each time it is brought in from the field. If contaminants remain or the sensor exhibits a slow response time, see the user manual for advanced cleaning methods. Replace ORP Sensor Module every 12 months.

Short-term Storage:

When in regular field use, the pH-pH/ORP sensors should remain on the bulkhead with the calibration/storage cup installed. Place a small amount of tap or surface water in the cup prior to storage or transport. The probes should be kept in this water-saturated air chamber between uses; not submerged. Make sure the storage cup makes a tight connection to prevent evaporation.

Long-term Storage:

Remove the sensor from the bulkhead and plug the bulkhead port. Insert the sensor tip into the storage bottle and solution that were originally supplied with the sensor. The storage bottle features an open cap and o-ring to form a tight seal around the sensor tip; the solution contains KCl with potassium phthalate and a preservative. If this original solution is not available, one can prepare a 2 M KCl solution or use pH 4 buffer as an alternative, though these solutions should be monitored for microbial growth and replaced if growth is apparent. Other sensors and system components should not be stored in or exposed to these pH buffers for long periods of time.

Do NOT let the sensor dry out.
Do NOT store the sensor in distilled or deionized water.

5.0 QUALITY CONTROL

Duplicate measurements of a single sample should be performed at the frequency specified in the project plan. In the absence of project-specific criteria, duplicate measurements should agree within ± 2 mV.

6.0 DOCUMENTATION

All ORP sensor calibration, checks, and maintenance information will be recorded in a calibration logbook. ORP data may be recorded on the appropriate field data sheets or field books.

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
- Person performing the measurement
- Instrument identification number/model
- Readings for all continuing calibration checks
- Temperature and pH
- Calibration standard, Lot Number, and expiration date

- Comments

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

- Date and time of analysis
- Person performing the measurement
- Sample identification/station location
- ORP, temperature, and pH measurements (including units and duplicate measurements)
- Comments

7.0 TRAINING/QUALIFICATIONS

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

Date:

Personnel:

Weather:

Objective: Water Quality Monitoring (Pre- and Post- Alum Treatment Monitoring)

Photos:

Waterbody
Santuit Pond Mashpee, MA

PRIMARY: YSI Profile - SPDH (Deep Hole)

Depth (ft)	DO (mg/L)	DO (%)	Spec. Cond. (µS/cm)	Temp (C)	pH	Total Depth (ft)	Secchi Depth (m)
Resolution	two decimal places (Ex. 0.01)	Not Defined in QAPP	4 Digits	two decimal place (Ex. 0.01)	two decimal place (Ex. 0.01)	one decimal place (Ex. 0.1)	once decimal place (Ex. 0.1)
Expected Range	0 - 14		25 - 500	0 - 30		0 - 75	0 - 10
0.5							
1.0							
2.0							
3.0							
4.0							
5.0							
6.0							
7.0							
8.0							
9.0							
10.0							
11.0							
12.0							
13.0							

Lab Samples and Non-YSI WQ Data

Sample ID	Sample Depth	Sample Collection Time	Depth (m)	Turb (NTU)	ORP (mV)	pH
		Resolution	Not Defined in QAPP	two decimal places (Ex. 0.01)	one decimal place	two decimal places
		Expected Range		0.10 NTU - 50.00 NTU	-500 mV - 500 mV	
SPDH-S	Surface					
SPDH-B	Bottom					

Collected samples tested for:
Alpha: Chlorophyll-a (two bottles per sample - SAME DAY SHORT HOLD
Aquatic Analysts: Algal Identification and Enumeration
Phoenix: Alkalinity, Aluminum, Iron, Total Phos, Dissolved Phos, Total Nitrogen (nitrate, nitrite, TKN), TSS

Checklist	Complete? (Yes / No)	Note
In-Pond Samples		
Duplicate		
Field Blank		

Date:

Personnel:

Weather:

Objective: Water Quality Monitoring (Pre- and Post- Alum Treatment Monitoring)

Photos:

Waterbody
Santuit Pond Mashpee, MA

DUPLICATE. YSI Profile - SPDH (Deep Hole)

Depth (ft)	DO (mg/L)	DO (%)	Spec. Cond. (µS/cm)	Temp (C)	pH	Total Depth (ft)	Secchi Depth (m)
Resolution	two decimal places (Ex. 0.01)	Not Defined in QAPP	4 Digits	two decimal place (Ex. 0.01)	two decimal places	one decimal place (Ex. 0.1)	once decimal place (Ex. 0.1)
Expected Range	0 - 14		25 - 500	0 - 30	-	0 - 75	0 - 10
0.5							
1.0							
2.0							
3.0							
4.0							
5.0							
6.0							
7.0							
8.0							
9.0							
10.0							
11.0							
12.0							
13.0							

Lab Samples and Non-YSI WQ Data

Sample ID	Sample Depth	Sample Collection Time	Depth (m)	Turb (NTU)	ORP (mV)	pH
		Resolution	Not Defined in QAPP	two decimal places (Ex. 0.01)	one decimal place	two decimal places
		Expected Range		0.10 NTU - 50.00 NTU	-500 mV - 500 mV	
SPDH-S	Surface					
SPDH-B	Bottom					

Collected samples tested for:
Alpha. Chlorophyll-a (two bottles per sample - SAME DAY SHORT HOLD
Aquatic Analysts: Algal Identification and Enumeration
Phoenix: Alkalinity, Aluminum, Iron, Total Phos, Dissolved Phos , Total Nitrogen (nitrate, nitrite, TKN), TSS

Checklist	Complete? (Yes / No)	Note
In-Pond Samples		
Duplicate		
Field Blank		

	Standard, Batch, Exp. Date	Before Sampling	After Sampling
Turbidity			
pH (___), (___)			
DO			
Conductivity			
ORP			

Date:

Personnel:

Weather:

Objective: Water Quality Monitoring (Pre- and Post- Alum Treatment Monitoring)

Photos:

Waterbody
Santuit Pond Mashpee, MA

YSI Profile - SPBL

Depth (ft)	DO (mg/L)	DO (%)	Spec. Cond. (µS/cm)	Temp (C)	pH	Total Depth (ft)	Secchi Depth (m)
Resolution	two decimal places (Ex. 0.01)	Not Defined in QAPP	4 Digits	two decimal places (Ex. 0.01)	two decimal places	one decimal place (Ex. 0.1)	once decimal place (Ex. 0.1)
Expected Range	0 - 14		25 - 500	0 - 30		0 - 75	0 - 10
0.5							
1.0							
2.0							
3.0							
4.0							
5.0							
6.0							
7.0							
8.0							
9.0							
10.0							
11.0							
12.0							
13.0							

Lab Samples and Non-YSI WQ Data

Sample ID	Sample Depth	Sample Collection Time	Depth (m)	Turb (NTU)	ORP (mV)	pH
		Resolution	Not Defined in QAPP	two decimal places (Ex. 0.01)	one decimal place	two decimal places
		Expected Range		0.10 NTU - 50.00 NTU	-500 mV - 500 mV	
SPBL	Surface					

Collected samples tested for:
Alpha: Chlorophyll-a (two bottles per sample - SAME DAY SHORT HOLD
Aquatic Analysts: Algal identification and Enumeration
Phoenix: Alkalinity, Aluminum, Iron, Total Phos, Dissolved Phos., Total Nitrogen (nitrate, nitrite, TKN), TSS

Checklist	Complete? (Yes / No)	Note
In Pond Samples		
Duplicate		
Field Blank		

	Standard, Batch, Exp. Date	Before Sampling	After Sampling
Turbidity			
pH (___) (___)			
DO			
Conductivity			
ORP			

Date:

Personnel:

Weather:

Objective: Water Quality Monitoring (Pre- and Post- Alum Treatment Monitoring)

Photos:

Waterbody
Santuit Pond Mashpee, MA

YSI Profile - SPSR

Depth (ft)	DO (mg/L)	DO (%)	Spec. Cond. (µS/cm)	Temp (C)	pH	Total Depth (ft)	Secchi Depth (m)
Resolution	two decimal places (Ex. 0.01)	Not Defined in QAPP	4 Digits	two decimal place (Ex. 0.01)	two decimal places	one decimal place (Ex. 0.1)	once decimal place (Ex. 0.1)
Expected Range	0 - 14		25 - 500	0 - 30		0 - 75	0 - 10
0.5							
1.0							
2.0							
3.0							
4.0							
5.0							
6.0							
7.0							
8.0							
9.0							
10.0							
11.0							
12.0							
13.0							

Lab Samples and Non-YSI WQ Data

Sample ID	Sample Depth	Sample Collection Time	Depth (m)	Turb (NTU)	ORP (mV)	pH
		Resolution	Not Defined in QAPP	two decimal places (Ex. 0.01)	one decimal place	two decimal places
		Expected Range		0.10 NTU - 50.00 NTU	-500 mV - 500 mV	
SPSR	Surface					

Collected samples tested for:
Alpha: Chlorophyll-a (two bottles per sample - SAME DAY SHORT HOLD
Aquatic Analysts: Algal Identification and Enumeration
Phoenix: Alkalinity, Aluminum, Iron, Total Phos, Dissolved Phos., Total Nitrogen (nitrate, nitrite, TKN), TSS

Checklist	Complete? (Yes / No)	Note
In Pond Samples		
Duplicate		
Field Blank		

	Standard, Batch, Exp. Date	Before Sampling	After Sampling
Turbidity			
pH (___), (___)			
DO			
Conductivity			
ORP			

Date:

Personnel:

Weather:

Objective: pH Monitoring During Alum Treatment

Photos:

PRIMARY: YSI Profile - Alum Treatment pH Monitoring

Waterbody
Santuit Pond Mashpee, MA

	SPN	SPBL	SPDH	SPE	SPSR	Notes/General Observations
Start Time						
Depth (ft)						
Parameter	pH	pH	pH	pH	pH	
Resolution	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	
0.5						
1.0						
2.0						
3.0						
4.0						
5.0						
6.0						
7.0						
8.0						
9.0						
10.0						
11.0						
12.0						
13.0						

	SPN	SPBL	SPDH	SPE	SPSR	Notes/General Observations
Start Time						
Depth (ft)						
Parameter	pH	pH	pH	pH	pH	
Resolution	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	
0.5						
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						

Date:

Personnel:

Weather:

Objective: pH Monitoring During Alum Treatment

Photos:

Waterbody
Santuit Pond Mashpee, MA

DUPLICATE: YSI Profile - Alum Treatment pH Monitoring

	SPN	SPBL	SPDH	SPE	SPSR	Notes/General Observations
Start Time						
Depth (ft)						
Parameter	pH	pH	pH	pH	pH	
Resolution	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	
0.5						
1.0						
2.0						
3.0						
4.0						
5.0						
6.0						
7.0						
8.0						
9.0						
10.0						
11.0						
12.0						
13.0						

	SPN	SPBL	SPDH	SPE	SPSR	Notes/General Observations
Start Time						
Depth (ft)						
Parameter	pH	pH	pH	pH	pH	
Resolution	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	two decimal places (Ex. 0.01)	
0.5						
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						

Temp ° C Coolant: Cooler: Yes ☐ No ☐ IPK ☐ ICE ☐ No ☐

Pg of

PHOENIX
Environmental Laboratories, Inc.

CT/MA/RI CHAIN OF CUSTODY RECORD

587 East Middle Turnpike, P.O. Box 370, Manchester, CT 06040
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Client Services (860) 645-1102

Data Delivery/Contact Options:
Phone: 401-330-1246
Email(s): Stephanie.Martin@TRCCompanies.com

Customer: TRC ENVIRONMENTAL CORPORATION
Address: 401 WAMPANOAG TRAIL, THIRD FLOOR
EAST PROVIDENCE, RI 02915

Project: SANTUIT POND WATER QUALITY MONITORING **Project P.O:**
Report to (name): STEPHANIE L. MARTIN
Invoice to:
Quote # Project Number: 605177

This section MUST be completed with Bottle Quantities.

Client Sample - Information - Identification

Sampler's Signature _____ Date: _____

Matrix Code:
DW=Drinking Water **GW**=Ground Water **SW**=Surface Water **STW** = Storm Water
WW=Waste Water **RW**=Raw Water **SE**=Sediment **SL**=Sludge **S**=Soil **SD**=Solid
W=Wipe **OIL**=Oil **B**=Bulk **L**=Liquid **X** = Other _____ **(Must be defined)**

Analysis Request

PHOENIX USE ONLY SAMPLE #	Customer Sample Identification	Sample Matrix	Date Sampled	Time Sampled	*MS/MSD (May be billable at analysis unit rate)	ALKALINITY	ALUMINUM	IRON	TOTAL PHOSPHORUS*	DISSOLVED PHOSPHORUS**	TKN	NITRATE-NITROGEN	NITRITE-NITROGEN	TOTAL SUSPENDED SOLIDS			GL Amber ( )oz [ ] H_3PO_4 [ ] NAHSO4 [ ] NH4Cl	Soil VOA Vials [ ] methanol [ ] H_2O	GL Soil container ( )oz	GL Soil container ( )oz	40 ml VOA Vial [ ] As is [ ] HCl [ ] Na2SO3	GL Amber 1000ml [ ] As is [ ] HCL [ ] H_2SO_4	PL As is [x] 120ml [x] 250ml [ ] 500ml	PL H_2SO_4 [x] 150 ml [x] 250 ml	PL HNO_3 [x] 250ml [ ] 1000ml	PL NaOH 250ml	Bacteria Bottle w/thio	Bacteria Bottle as is		
	SPDH-S	SW				x	x	x	x	x	x	x	x	x								4	3	2						
	SPDH-B	SW				x	x	x	x	x	x	x	x	x								4	3	2						
	SPBL	SW				x	x	x	x	x	x	x	x	x								4	3	2						
	SPSR	SW				x	x	x	x	x	x	x	x	x								4	3	2						

Relinquished by:	Accepted by:	Date:	Time:

Comments, Special Requirements or Regulations:

*Low Level

**Field Filtered within 15 minutes of collection

MS/MSD are considered site samples and will be billed as such in accordance with the prices quoted.

Turnaround Time:
☐ 1 Day* ☐ 2 Days* ☐ 3 Days* ☐ 4 Days* ☐ 5 Days*
☑ Standard ☐ Other _____

* SURCHARGES MAY APPLY

RI
☐ RES DEC
☐ I/C DEC
☐ GA Leachability
☐ GB Leachability
☐ GA -GW Objectives
☐ GB -GW Objectives
☐ Other

CT
☐ RCP Cert
☐ GWPC
☐ SWPC
☐ GA PMC
☐ GB PMC
☐ SWPC
RES ☐ DEC ☐ VC
I/C ☐ DEC ☐ VC

MA
☐ MCP Certification
☐ GW-1 ☐ RCS-1 / RCGW-1
☐ GW-2 ☐ RCS-2 / RCGW-2
☐ GW-3
☐ S-1 ☐ S-1 Calc.
☐ S-2
☐ S-3 ☐ _____
☐ SW Protection

State where samples were collected: MA

Data Format
☑ Excel
☑ PDF
☐ GIS/Key
☐ EQuIS
☐ Other

Data Package
☐ Tier II Checklist*
☐ Full Data Package*
☐ Phoenix Std
☐ MAT-212 Form

* SURCHARGE APPLIES

Pace® Location Requested (City/State):

CHAIN-OF-CUSTODY Analytical Request Document

Chain-of-Custody is a LEGAL DOCUMENT - Complete all relevant fields

LAB USE ONLY- Affix Workorder/Login Label Here

Scan QR Code for instructions

Company Name: TRC ENVIRONMENTAL CORPORATION	Contact/Report To: STEPHANIE L. MARTIN
Street Address: 401 WAMPANOAG TRAIL, THIRD FLOOR EAST PROVIDENCE, RI 02915	Phone #: 401-330-1246
	E-Mail: Stephanie.Martin@TRCCompanies.com
	Cc E-Mail: MLadewig@TRCCompanies.com
Customer Project #: 605177	Invoice to:
Project Name: SANTUIT POND WATER QUALITY MONITORING	Invoice E-mail:
Site Collection Info/Facility ID (as applicable): SANTUIT POND MASHPEE, MA	Purchase Order # (if applicable):
	Quote #:
Time Zone Collected: [ ] AK [ ] PT [ ] MT [ ] CT [X] ET	County / State origin of sample(s): MA

Data Deliverables: [ ] Level II [ ] Level III [ ] Level IV [ ] EQUIS [ ] Other_____

Regulatory Program (DW, RCRA, etc.) as applicable: Reportable [ ] Yes [X] No

Rush (Pre-approval required): [ ] Same Day [ ] 1 Day [ ] 2 Day [ ] 3 Day Other _____

Date Results Requested:

DW PWSID # or WW Permit # as applicable:

Field Filtered (if applicable): [ ] Yes [X] No

Analysis:

* Matrix Codes (Insert in Matrix box below): Drinking Water (DW), Ground Water (GW), Wastewater (WW), Product (P), Soil/Solid (SS), Oil (OL), Wipe (WP), Tissue (TS), Bioassay (B), Vapor (V), Surface Water (SW),Sediment (SED), Sludge (SL), Caulk (CK), Leachate (LL), Biosolid (BS), Other (OT)

Specify Container Size **: 1

Identify Container Preservative Type***: 1

Analysis Requested

**Container Size: (1) 1L, (2) 500mL, (3) 250mL, (4) 125mL, (5) 100mL, (6) 40mL vial, (7) EnCore, (8) TerraCore, (9) 90mL, (10) Other

*** Preservative Types: (1) None, (2) HNO3, (3) H2SO4, (4) HCl, (5) NaOH, (6) Zn Acetate, (7) NaHSO4, (8) Sod. Thiosulfate, (9) Ascorbic Acid, (10) MeOH, (11) Other

Lab Use Only: Proj. Mgr: | AcctNum / Client ID: | Table #: | Profile / Template: | Prelog / Bottle Ord. ID:

Customer Sample ID	Matrix *	Comp / Grab	Composite Start Date	Composite Start Time	Collected or Composite End Date	Collected or Composite End Time	# Cont.	Residual Chlorine Result	Residual Chlorine Units	Chlorophyll a	Sample Comment	Preservation non-conformance identified for sample.
SPDH-S	SW	GRAB	n/a	n/a						X		
SPDH-B	SW	GRAB	n/a	n/a						X		
SPBL	SW	GRAB	n/a	n/a						X		
SPSR	SW	GRAB	n/a	n/a						X		

Additional Instructions from Pace® :

Collected By:
Printed Name
Signature

Customer Remarks / Special Conditions / Possible Hazards:

Coolers: | Thermometer ID: | Correction Factor (°C): | Obs. Temp. (°C): | Corrected Temp. (°C): | [ ] On Ice

Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:
Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:
Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:
Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:

Tracking Number:

Delivered by: [ ] In- Person [ ] Courier [ ] FedEx [ ] UPS [ ] Other

Page: of

Submitting a sample via this chain of custody constitutes acknowledgment and acceptance of the Pace® Terms and Conditions found at https://info.pacelabs.com/hubfs/pas-standard-terms.pdf.

Chain of Custody Instructions

***Pace Location Requested**: City and State of Pace Laboratory testing is to be performed at.
***Company Name**: Client's company name
***Street Address**: Client's mailing address
***City, State, Zip**: Client's city, state and zip code for mailing
***Contact/ Report to**: Person to receive results
Customer Project # and Project Name: Client's reference to the project or work involved with these samples.
Site Collection Info/ Facility ID: Client's location of project
Time Zone: Check time zone of sample to ensure proper hold times are met.
Purchase Order #: Client specific number to be listed on project invoice for client billing purposes.
Invoice To: Client contact the project invoice needs to be emailed to.
Invoice Email: Email address that project invoice will need to be emailed to
***Phone #**: Client's contact phone number
E-mail: Client's e-mail for correspondence and final report
Regulatory Program: List the program that is guiding the work to ensure proper regulations are followed: DW, RCRA, etc.
Data Deliverable: Please select or enter required deliverables.
***County/State Origin of Samples**: Enter the county to ensure proper handling of regulated soils. State required to ensure proper reporting.
Field Filtered: Indicate if samples have been filtered in the field. If samples are required to be field filtered and filtering is not indicated, a qualifier will be added to all associated data.

***Customer Sample ID**: The unique sample ID you want to appear on the analytical report
***Collected Date**: Date sample was collected. For composite samples, please fill in both beginning and end date.
***Collected Time**: Time sample was collected. For composite samples, please fill in both beginning and end time.
***Comp/Grab**: Please denote "GRAB" if the sample was collected at one time from one specific location. Please denote "COMP" if the sample is a composite of samples collected at one or more times or locations and combined to make one sample.
***Matrix**: Select from list provided list. If prepopulated chain is provided for you matrix codes may vary.
***Number and Type of Containers**: Total number of containers per container type submitted for the samples
***Container Size:** Specify container size from list.
***Container Preservation Type**: Specify sample preservation from provided list.
***Analysis Requested**: Write the analysis name (or an abbreviation), the name of a group of tests, or the method number you would like us to perform. Examples are BOD, TCLP Metals, PCBs, Method 624, etc. Place a check mark in the small boxes that correspond to the sample(s) on which you want these tests performed.

Sample Comment: List any notes or important information about the individual sample here. Please identify in the sample comment if a sample should be used for MS/MSD.

Customer Remarks/Special Conditions/Possible Hazards: List special instructions about the sample here. If the sample is known or suspected to be hazardous indicate that here and attach SDS if possible. This space can also be used for listing additional analyses, or to request an extra copy of the report to be sent to an alternate person/address, etc.

Rush request: If faster than standard turnaround time results are needed. Circle one of the rush options and note the day the results are requested by. All rush requests require preapproval by the laboratory. Surcharges will apply for non- standard turnaround times. Results will be due by the end of business on the date due based on standard turnaround time unless other arrangements have been made with your Project Manager.

Summarized Sample Acceptance Policy Requirements:

- Proper, full and completed chain-of-custody documentation
- Readable unique sample container identification written in indelible ink
- Appropriate sample container
- Sufficient sample volume to perform requested tests
- Received within required holding time
- Received within temperature preservation requirements
- Sample containers received in good condition (not leaking or broken)
- Any custody seal intact
- Properly preserved
- No headspace in volatile water samples
- **Note:** When sample specific Quality Control is required (e.g. MS/MSD) please ensure necessary sample containers and sample volume is provided.

A data qualifier and/or case narrative will be added to the final test report when the above sample acceptance requirements are not met.

Location Specific Sample Acceptance Policy available from your Project Manager

***Collected By**: Printed name of sample collector
***Collected By Signature**: Signature of sample collector

***Relinquished By/Received By:** This form **must be signed** each time the sample(s) changes hands. Custody seals are available upon request if needed.

***Required field**: Failure to fill in a required field may result in a sample(s) being put on hold until information can be obtained. This may result in a delay in receiving results.

Chain of Custody Form

Client: TRC ENVIRONMENTAL CORPORATION 401 WAMPANOAG TRAIL, THIRD FLOOR EAST PROVIDENCE, RI 02915	Invoice to: (name, email) TRC Project Number: 605177	Shipping Date:
Project: SANTUIT POND WATER QUALITY MONITORING	PO #:	
Contact: (name, email) STEPHANIE L. MARTIN Stephanie.Martin@TRCCompanies.com	Notes: ALGAL IDENTIFICATION AND ENUMERATION ALL SAMPLES PRESERVED IN LUGOL'S SOLUTION NO ICE OR COOLER REQUIRED	

#	Lake/River	√	Date	Site	Depth (m / ft)	Pplk / Peri	**Rush**	**Fast**	**Toxic Only**	Het / Akin	Add'l counts	Comments
1	SANTUIT POND			SPDH-S								
2	SANTUIT POND			SPDH-B								
3	SANTUIT POND			SPBL								
4	SANTUIT POND			SPSR								
5												
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												

Aquatic Analysts… 43 Telegraph Ln, Friday Harbor, WA 98250 (503) 869-5032 jwsweet@aol.com www.AAalgae.com

Appendix C: Laboratory Standard Operating Procedures

PHOENIX
Environmental Laboratories, Inc.
587 East Middle Turnpike, P.O. Box 370, Manchester, CT 06040
Telephone: 860.645.1102 • Fax: 860.645.0823

SOP Number: 304.NH3/TKN

Title: Ammonia/TKN Phenate Method

Scope: This method covers the determination of ammonia, organic nitrogen, and Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes, soils and leachates. The working range for water samples is 0.05-8.0 mg/L, and 2.0-400 mg/kg for solids. Higher concentrations may be determined by sample dilutions.

I. Summary of Method

A. The sample is buffered at a pH of 9.5 with borate buffer in order to decrease hydrolysis of cyanides and organic nitrogen compounds, and then distilled into a sulfuric acid solution. The ammonia ion in the sulfuric acid solution is then determined by colorimetric analysis. This method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction produced is measured at 630nm, and is directly proportional to the original ammonia concentration.

B. The determination of organic nitrogen (ORGN) is based on the ammonia (NH3) and TKN results of a sample. ORGN conc. = TKN conc. – NH3 conc. Using this relationship, it is also possible to determine the concentration of TKN, when the ORGN and NH3 are known.

II. Interferences

A. When present, residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate before distillation. During sample development calcium and magnesium ions may precipitate if present in sufficient concentrations. EDTA is added to the sample in-line in order to prevent this problem. Distillate turbidity may interfere and can be removed by manual filtration.

III. Sample Collection, Preservation and Storage

A. Samples can be collected in plastic or glass. They must be stored at 4°C until time of analysis.

B. Samples must be H_2SO_4 preserved to pH 1.5-2 and analyzed within 28 days of collection.

IV. Equipment and Supplies

A. Kjeldahl tubes.
B. Snap Cap, 70mL with 50mL lines.
C. Graduated cylinders, 50 mL.
D. Lachat QuickChem 8000 autoanalyzer with XYZ autosampler.
E. Digestion heating block with temperature control.
F. Reflux condenser distillation unit with temperature control.

V. Reagents and Standards

(NOTE: Use only reagent grade chemicals for standards and reagents)

A. Ammonia Stock Solution (1.0 ml=1000mg NH3-N): Dissolve 3.819g reagent grade ammonium chloride (NH4CL), that has been oven dried and desiccated, in DI water and bring to volume in a 1 liter volumetric flask.
B. Intermediate Ammonia Standard (1.0 ml=20 mg NH3-N): Dilute 20.0mL ammonia stock solution in 1-liter volumetric flask. Bring up to volume with DI water.
C. Ammonia Spiking Solution (1.0 ml=100 mg NH3-N): Dilute 100mL ammonia stock solution in 1-liter volumetric flask. Bring up to volume with DI water.
D. Ammonia Working Standards:

Std. ID	mL of Inter. Std.	Dilute to	Concentration
A	80	200mL	8.0 mg/L
B	50	250mL	4.00 mg/L
C*	40	500mL	1.60 mg/L
D	5	250mL	0.40 mg/L
E	1.0	200mL	0.10 mg/L
F	0.5	200mL	0.05 mg/L
G	0	250mL	0.00 mg/L

Note: All working standards are to be diluted and taken to volume with DI water. They are to be 1:1 H2SO4 preserved. *Working standard C is the calibration check standard.

E. Sodium hydroxide solution, 6 N: While stirring in a cold water bath, dissolve 240g Sodium Hydroxide (NaOH) in 1 liter of DI water.
F. Sodium hydroxide solution, 0.2 N: In a 1-liter volumetric, dissolve 8g of Sodium Hydroxide (NaOH) in 800mLs of DI water. Dilute to volume and mix.
G. Borate buffer: Add 44mls of 0.2 N NaOH solution to 500 ml of DI water. Add sodium tetraborate (2.5g anhydrous $Na_2B_4O_7$ or 9.50g $Na_2B_4O_7$ *$10H_20$) and dilute to 1 liter.
H. Sulfuric Acid Solution, 1.0N, to about 800mL DI water, add 28mL concentrated H_2SO_4,then bring to a final volume of 1L with DI. Invert 3 times.
I. Sulfuric acid solution, 0.02N: To about 800mL DI water, add 20mL 1.0N H_2SO_4 (see N above). Dilute to 1L with DI water.
J. Phenolphthalein Indicator Solution: Dissolve 5.0g phenolphthalein in 500mL 95% ethyl or isopropyl alcohol and dilute to 1L with DI water.
K. Sodium Phenolate: In a 1 liter volumetric flask, dissolve 88ml of 88% liquefied phenol or 83g crystalline phenol in approximately 600ml of DI water. While stirring, slowly

add 32g sodium hydroxide. Allow to cool, then dilute to volume and mix. **CAUTION: WEAR GLOVES! Phenol causes severe burns and is rapidly absorbed through skin!**

L. Sodium Hypochlorite: In a 500-ml volumetric flask, dilute 250ml "Regular Strength" bleach (5.25% NaOCl) to volume with DI water. (NOTE: DO NOT use "Industrial Strength" or "Ultra Strength" Bleach as they contain higher concentrations of NaOCl.)

M. Buffer Solution: In a 1-liter volumetric flask, dissolve 50.0g disodium ethylenediamine tetraacetate (Na_2EDTA) and 5.5g sodium hydroxide in about 900mls DI water. Dilute to volume and mix.

N. Sodium Nitroprusside: In a 1-liter volumetric flask, dissolve 3.50g sodium nitroprusside (sodium nitroferricyanide) and dilute to volume with DI water. **CAUTION: WEAR GLOVES! Health Hazard -- Affects the Central Nervous System.**

O. Carrier: DI water.

P. TKN Digestion Reagent: Dissolve 134g K_2SO_4 and 7.3g $CuSO_4$ in 500mL DI water. Slowly add 134mL concentrated H_2SO_4. Bring to a final volume of 1L with DI water.

Q. TKN Sodium Hydroxide-thiosulfate reagent: Slowly dissolve 500g NaOH and 25g $Na_2S_2O_3*5H_2O$ in water and dilute to 1 liter with DI water. **Caution: Prepare this reagent in a cooling waterbath, as it is exothermic.**

VI. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.

B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.

C. Calibration standard- A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate instrument response with respect to analyte concentration.

D. Matrix Spike (MS)- An aliquot of environmental sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

VII. Procedure

A. Samples are preserved with H_2SO_4 to pH of <2 at time of sampling, and stored at 4°C until time of analysis. Samples to be determined for ammonia or TKN have a holding time of 28 days from time of collection.

B. Sample screening:

1. Verify pH and record in Ammonia Prep Batching Program.
2. If residual chlorine is present, destroy with Sodium thiosulfate. Record check in Ammonia Prep Batching Program.

C. Ammonia distillation:

1. Rinse Kjeldahl tubes with DI water. Measure 50mL of aqueous sample (or 0.01g of soil diluted to 50mL DI water) into a Kjeldahl tube containing boiling stones. Add 5mL borate buffer, 2-3 drops of phenolphthalein, and enough 6N NaOH to turn the sample light pink. If too much 6N NaOH was added, add 0.02N H_2SO_4 drop-wise until sample is light pink. Phenolphthalein is light pink at a pH of 9.5; this is the pH at which the distillation should occur. Add 1.0mL of Ammonia Spiking Solution to all matrix and blank spike tubes (T.V.= 2.0mg/L). Label the tubes with sample ID number and sample volume using a permanent marker. Record information in the Ammonia - TKN batching program.
2. Place Kjeldahl tubes containing prepared sample onto the distillation heating block, and attach reflux unit. Turn on condenser water.
3. Label clean snap cap tubes with appropriate sample ID number and sample dilution information, and add 10mL 0.02N H_2SO_4 to each tube. Place the snap cap under the condenser, and raise it so that the tip of the condenser is below the surface of the sulfuric acid, but not touching the bottom.
4. Turn on the block and set upper temperature limit to 300°C.
5. Some sample matrices require the addition of an anti-foaming reagent. If a sample begins to bubble and climb up the sides of the tube, add a few drops of antifoam. If a sample is suspected or expected to foam, antifoam may be added as part of sample pretreatment.
6. After 40mL has been distilled, remove snap caps from under the condensers, and bring up to 50mL with DI water. Refrigerate at 4°C until time of color development on Lachat.
7. If sample requires TKN or organic nitrogen determination, save the remainder of sample in the Kjeldahl tube for digestion.

D. Organic Nitrogen/TKN digestion:

1. If samples require NH3 & TKN (or ORGN only), perform ammonia distillation procedure as described in III.B. above, discard distillate, and allow the remainder of the sample in the Kjeldahl tube to cool. If only TKN is requested, place 50mL sample in a clean Kjeldahl tube containing boiling stones.
2. Move to TKN digestion heating block, carefully add 10mL TKN digestion reagent to Kjeldahl tube. Add 1.0mL of Ammonia Spike Solution to all matrix and blank spike tubes (T.V. = 2.0mg/L). Do not attach reflux unit. Turn on block and set upper limit temperature to 400°C. Boil under a ventilation hood until copious white fumes are observed. Continue to digest for another 30 minutes after copious fumes are observed and after the temperature is at least 375°C.
3. Allow samples to cool up to 2 minutes, and dilute with 50mL DI water (NOTE: If samples are allowed to cool longer than 2 minutes, the residue has a tendancy of sticking to the bottom of the tube even with vortexing). Vortex to mix. Make sure that boiling chips are free from the dried slurry in the bottom of the tubes and that the acid residue is dissolved into the water!
4. Move to distillation heating block.

5. Tilt tube away from personnel, towards the back of the hood, and carefully add 10mL sodium hydroxide-thiosulfate reagent to form an alkaline layer at tube bottom. Connect tube to distillation apparatus and swirl tube to insure complete mixing. Do not swirl the tube until the reflux unit is attached. The pH of the solution should exceed 11.0.
6. Label clean snap cap tubes with appropriate sample ID number and sample dilution information, and add 10mL 0.02N H_2SO_4 to each tube. Place the snap cap under the condenser, and raise it so that the tip of the condenser is below the surface of the sulfuric acid, but not touching the bottom.
7. Turn on condenser water. Turn on the block. Make sure the sample ID numbers on the Kjeldahl tubes match the ID numbers on the other end of the condenser.
8. Some sample matrices require the addition of an anti-foaming reagent. If a sample begins to bubble and climb up the sides of the tube, add a few drops of antifoam. If a sample is suspected or expected to foam, antifoam may be added as part of sample pretreatment.
9. After 40mL has been distilled, remove snap caps from under the condensers, and bring up to 50mL with DI water. Refrigerate at 4°C until time of color development on Lachat.

E. Development Procedure on Lachat Autoanalyzer:

1. Refer to SOP #302, Lachat operation, for a more detailed description of instrument use.
2. Turn on power to all modules except pump. Turn on heating unit, set on 65°C, and allow to warm to temperature.
2. Attach ammonia manifold. Be sure to use the 650cm heater block. Refer to manifold diagram if necessary.
3. Load background and generate a sample tray. Be sure to include all sample dilutions and quality control samples (blank, prep blank, LCS, replicates, spikes, check standards, blank spikes) for each form of nitrogen (ammonia, TKN).
4. Use helium to degas all Lachat reagents except for sodium phenolate reagent and sodium nitroprusside.
5. Place feed lines into proper reagent containers. Check that the correct waste container is in place. The sample waste stream is acid waste.
6. Hook pump tubing onto pump tube cassettes, and push into place onto pump. Start pump. Wait while all reagents flow through lines to establish a steady baseline.
9. Place calibration standards in the tray marked S1-S8 in order of descending concentration.
10. Start calibration and samples. The calibration curve correlation coefficient must be 0.9975 or better. If the calibration fails, the standards may have to be remade.
11. Print out calibration statistics and attach it to the last page of the report. Start the run with a free ammonia LCS. Once the run is complete, staple a copy of the lachat run to all associated batch sheets and results sheets. Leave the completed report on the Wet Chemistry supervisor's desk for review.

12. For data transfer, see Appendix A.

VIII. Calculations

A. Calculating RPD:
The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$\text{RPD, \%} = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

B. Calculating the sample spike recovery:
The sample spike is a test if the sample matrix is suitable for accurate testing. To calculate the % recovery, first calculate both the sample and the spiked sample. Then apply the two results to the following calculation:

$$\text{\% Recovery, \%} = \frac{(SR - R)}{STV} \times 100$$

where: SR = value of sample with added spike, mg/L
R = value of sample, mg/L
STV = true value of spike added to sample, mg/L

C. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the value of the LCS sample, and then apply it to the following calculation:

$$\text{\% Recovery, \%} = \frac{(RL)}{(LTV)} \times 100$$

where: RL = value for LCS sample, mg/L
LTV = true value of LCS, mg/L

D. The Phoenix LIMS automatically calculates all recoveries and RPDs.

IX. Quality Control

A. Prep Blank must be analyzed every batch of 20 or fewer samples. This is a DI water aliquot treated like a sample, undergoing all treatments the samples undergo. The prep blank must yield ammonia concentrations below the reporting limit.

B. Laboratory Control Standards must be analyzed every batch of 20 or fewer samples. It must be recovered 90-110%. A failing LCS for a batch of samples requires re-analysis of the batch.

C. Blank spike must be analyzed every batch of 20 or fewer samples. This is a DI water aliquot fortified by the lab with a known quantity of ammonia. The blank spike must be recovered 90-110% for ammonia and 85-115% for TKN.

D. Continuing calibration checks must be analyzed every 10 samples, as is written into the software of the Lachat QuickChem 8000. They must pass within 90-110%. The calibration check for ammonia is the 1.6mg/L standard (Std C) from the calibration curve.

E. Sample replicates must be done every batch of 20 or fewer samples. They must have a RPD of no more than 20%.

F. Sample matrix spikes must be done every batch of 20 or fewer samples. A known amount of ammonia is added to a sample to test the sample matrix. The spike recovery for ammonia 90-110% and 85-115% for TKN, however, if recoveries fall outside of this range, and the LCS and Blank spike are acceptable, it is judged to be sample related and not system related. Report % recovery.

G. MDL studies are performed annually. Seven replicates of a 0.10 mg/L standard are distilled and analyzed for ammonia. Seven replicates of a 0.50 mg/L standard are distilled and analyzed for TKN. Two MDL spikes are performed quarterly to complete a full MDL over the course of a year. An MDL study must also be performed on prep blanks.

H. A Limit of Detection (LOD) study must be analyzed annually. All sample processing steps of the analytical method shall be included in the determination of the LOD. The LOD study is achieved by analyzing a standard at no more than 2-3x the LOD. In many cases, a 1:1 dilution of the lowest calibration standard is prepared and analyzed. LOD recoveries must be 50 – 150%.

I. 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.

J. An initial demonstration of capability (IDOC) must be performed to prove the generation of acceptable data with regard to accuracy and precision. An initial demonstration must be performed by each analyst and consists of analyzing 4 LCS solutions, usually over a series of days.

K. Sample preparations are documented in the Standards Prep Logbook.

L. Reagent preparations are documented in the Reagent Prep Logbook.

M. Lachat use and maintenance is documented in the Lachat Maintenance Logbook.

X. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.
B. Always wear safety glasses for eye protection as well as lab coats.
C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

XI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
B. Standards should be purchased in volumes consistant with laboratory use to minimize the volume of expired standards to be disposed.

XII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

XIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates.
B. See section IX Quality Control in this SOP for acceptable limits.

XIV. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the calibration curve have a correlation coefficient of <0.9975, remake and reanalyze curve before processing samples.
B. Should the preparation blank, LCS or inhouse standard fail acceptance criteria, redistill/redigest and reanalyze batch.
C. Should the matrix spike or sample duplicate analysis fail acceptance criteria, a non-conformance report must be generated or the sample QC must be reanalyzed.

XV. References

A. Method 4500-NH3 B. and G., Standard Methods for the Examination of Water and Wastewater, 2011.
B. Method 4500-Norg D, Standard Methods for the Examination of Water and Wastewater, 2011.
C. USEPA Method 350.1, Determination of Ammonia Nitrogen by Semi-automated Colorimetry, Revision 2, August 1993.
D. USEPA Method 351.1, Determination of Total Kjeldahl Nitrogen by Semi-automated Colorimetry, 1978.
E. Methods for QuikChem Automated Ion Analyzer, Lachat Instruments, Method 10-107-06-1-C, August 1993.

XVI. Appendices and Diagrams

A. Appendix A- Data Transfer

Appendix A: Data Transfer to LIMS

From the Phoenix MDE Icon
Left: Data Transfer
Right: IC/Lachat Data Transfer
File Icon (Browse, Local Disk C Drive, Program Files, Lachat, Data, 2015, Data, All Files)
Select Excel File by Date and Time

Enter Initials
Load and Review Data

Edit Data:
Reject samples not needed by checking them (such as Organic Nitrogen)
Look to reject over-range samples that need a diluted sample reported
Make sure that the diluted sample is there (usually at the end of the batch)

Load Data Tab (if edit changes were made)
Load and Review Data (if edit changes were made)

Process Data
After verifying history issues, select sample by checking it under OK column
History issues include: Minimum, Adjusted Maximum, Number of Samples,
All Time Maximum
Results over the All Time Maximum may have to be prepped
(distilled, digested, etc.) again.
History verification issues can usually be ignored from other laboratories, as their location codes are not historically accurate.
All passing reps and spikes should already be selected with a check

Transfer To Labworks
Print Log

Revision History Log for SOP # 304

Date:	Revision #:	Summary of Changes:	Submitted By:	Approved By:	Effective Date:
2/6/15	8.1	Changed the range in scope to "0.05ppm", section V.D changed 10 ppm std to 6.0 ppm, and changed 0.04 ppm to 0.05ppm, added dechlorination to section VII.B, added sections H, I, & J to IX (LOD, LCR, IDOC), changed acceptance criteria of LCS, blank spike, & MS to 90-110%, added EPA method references to section XV.	Kathy Cressia	Eric Geyer	2/6/15
3/8/17	8.2	Changed "A" standard to 8.0mg/L, fixed typo in borate buffer reagent, added Appendix A on data transfer	William McKernan	Eric Geyer	3/8/17
4/20/17	8.3	Fixed typo in section IX Quality Control- CCC 90-110% recovery, it said 90-100%	Kathy Cressia	Eric Geyer	4/20/17
7/26/17	8.4	During the 8.2 revision, it was missed in the Scope that the range now goes to 8.0 mg/L.	Kathy Cressia	Eric Geyer	7/26/17
7/26/19	8.5	Section IX.C & F – Added spike recovery range for TKN. Section IX.G. – Added information on MDL studies.	Kathy Cressia	Eric Geyer	7/26/19
11/6/23	8.6	Updated SM year in method reference section	Kathy Letourneau	Eric Geyer	11/6/23

Expiration Date

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Effective Date: 01/23/25
Version Number: 6.2
Initiated By:
Approved By:

SOP Number: 305.2320B

Title: Total Alkalinity

Scope: This method covers the determination of alkalinity in drinking, surface, and saline waters, domestic and industrial wastes. Samples with an alkalinity of less than 20mg $CaCO_3$/L need to be titrated by low-level method included in this SOP.

I. Summary of Method

A. The alkalinity of a sample represents the acid-neutralizing capacity of a sample. Strong acid is added to the sample until it reaches a designated pH. The amount of acid added is a function of the alkalinity of the sample.

B. Interferences.

1. Dissolved gases may be lost or gained during sample storage, and can add to or reduce the alkalinity of a sample. Minimize this interference by titrating promptly, by avoiding vigorous shaking, and by keeping the sample at a constant temperature.

II. Sample Collection, Preservation and Storage

A. Samples can be collected in plastic or glass bottles but must be full and contain no headspace. They must be unpreserved and stored at a low temperature.

B. Due to possible microbial action, it is preferred the samples are analyzed within 1 day of collection. Avoid sample agitation and prolonged exposure to air.

III. Reagents and Apparatus

A. Buret capable of reading at 0.1mL increments.

B. pH meter, calibrated.

C. Sulfuric Acid Solution, 0.10N. Dilute 2.8mL reagent grade conc. H_2SO_4 to 1 liter with DI water.

D. Sulfuric Acid Titrant, 0.02N. Dilute 200mL Sulfuric Acid Solution to 1 liter with DI water.

E. Sodium Carbonate Solution, 0.05N. Weigh 0.50g oven-dried and desiccated reagent grade Na_2CO_3 into a 200mL volumetric flask containing 100mL DI water. Dilute to mark with DI water. Prepare fresh weekly.

IV. Procedure

A. Standardization of the titrant:

1. Pipet 10.0 mL Sodium carbonate solution into a rinsed 125mL Erlenmeyer flask.
2. With a calibrated pH meter, titrate with 0.02N H2SO4 titrant to a pH of 4.5.
3. Record the volume of titrant used.
4. Repeat procedure using only DI water (50mL). One drop of titrant should be required to reach the endpoint on this blank DI water sample.
5. Calculate the normality of the titrant.

B. Sample Analysis:

NOTE: If Carbonate, Bicarbonate or Hydroxide Alkalinity is needed, follow steps 1 thru 7. If only Total Alkalinity is needed, omit steps 2-3.

1. Pipet 50.0mL sample into a rinsed 125mL Erlenmeyer flask and gently stir on a stirplate.
2. With a calibrated pH meter, titrate with 0.02N H_2SO_4 titrant to a pH of 8.3.
3. Record the volume of titrant required to reach endpoint (P).
4. Continue to titrate with 0.02N H_2SO_4 titrant to a pH of 4.5.
5. Record the TOTAL volume of titrant (from steps 1-4) required to reach endpoint (T).
6. If less than 1.0mL titrant is required to reach the endpoint, and the client is requesting an MDL of less than 20mg $CaCO_3$/L, then proceed to the IV.C..
7. Calculate the alkalinity of the sample (use Table 1 below for Carbonate, Bicarbonate or Hydroxide Alkalinity relationships).

Table 1. Alkalinity Relationships

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
$P = 0$	0	0	T
$P < \frac{1}{2}T$	0	2P	T − 2P
$P = \frac{1}{2}T$	0	2P	0
$P > \frac{1}{2}T$	2P − T	2(T − P)	0
$P = T$	T	0	0

*Key: P = phenolphthalein alkalinity; T = total alkalinity.

C. Low-level Alkalinity Determination.

1. Pipet 100 to 200mL sample into a rinsed 250mL Erlenmeyer flask.
2. With a calibrated pH meter, measure the pH of the sample. Record this value in logbook.

3. Add 0.02N H_2SO_4 titrant slowly to the sample, while stirring and measuring the pH.
4. Titrate to a pH of 4.5 $\pm$ 0.2. Record the volume of titrant required to reach this pH, and record the exact pH.
5. Carefully add enough 0.02N H_2SO_4 titrant to bring the pH down exactly 0.3 pH units. Record this volume.
6. Calculate the low-level alkalinity of the sample.

V. Calculations

A. Calculating the Normality of the titrant.

$$N = \frac{(A * B)}{53 * C}$$

Where: N = Normality of the titrant
A = grams of Na_2CO_3 weighed into 1L DI water (2.5g)
B = mL $NaCO_3$ solution used (15mL)
C = mL 0.02N H_2SO_4 titrant required to reach endpoint.

B. Calculating the alkalinity of the sample.

$$\text{Alk. (mg } CaCO_3/L) = \frac{(A * N * 50000)}{V}$$

Where: A = Volume of titrant required to reach endpoint. (mL)
N = Normality of the titrant (N)
V = Volume of sample used in titration (mL)

C. Calculating the low-level alkalinity of the sample.

$$\text{Alk. (mg } CaCO_3/L) = \frac{(2B - C) * N * 50000}{V}$$

Where: B = Volume of titrant required to reach first recorded pH (mL)
C = Volume of titrant required to reach second recorded pH (mL)
N = Normality of titrant (N)
V = Volume of sample used in titration (mL)

D. Calculating RPD.
The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$RPD, \% = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

Where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

E. Calculating the LCS:

The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the LCS sample, and then apply it to the following calculation:

$$\% \text{ Recovery}, \% = \frac{(RL)}{(LTV)} \times 100$$

Where: RL = achieved value for LCS sample, mg/L
LTV = true value of LCS, mg/L

VI. Quality Control

A. All reagents and standards are to be labeled with the following information: date prepared, date expires, preparer's initials, analyte, contents, and concentration of contents. Record preparation of all reagents in the reagent prep logbook.

B. A sample prep blank of dilution water must be analyzed with each batch of twenty or fewer samples, as well as at the end of every run. Prep blanks must be determined to be BDL (below detectable level).

C. A bought standard (LCS) is run with each batch of twenty or fewer samples. The acceptable recovery of a LCS is 85-115%.

D. Sample replicates are analyzed every 20 of fewer samples. The RPD must be $\leq$20%, else repeat sample and duplicate analysis to prove matrix effect.

E. The normality of the titrant should be determined daily. Record procedure in sample logbook.

VII. References

A. Standard Methods for the Examination of Waste and Wastewater, Method No. 2320B Alkalinity, 22nd-edition, 1997 (for Potable water)

B. Standard Methods for the Examination of Waste and Wastewater, Method No. 2320B Alkalinity, edition 2011 (for Non-potable water)

Revision History Log for SOP # 305

Date:	Revision #:	Summary of Changes:	Submitted By:	Approved By:	Effective Date:
3/12/18	6.1	MUR revision edition and year change in references	Kathy Cressia	Eric Geyer	3/12/18
1/23/25	6.2	Removed all references to sample dilutions, added Section II, Section IV – deleted all references of titration to a color endpoint, added titration to pH endpoints, deleted IV.D-obsolete, reps every 20 per method, updated method references	Eric Geyer	Kathy Letourneau	1/23/25

Expiration Date

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Effective Date: 03/15/18
Version Number: 5.2
Initiated By: Kathy Cressia
Approved By:

SOP Number: 319.SM4500H$^+$B

Title: pH and Corrosivity

Scope and Application: This method covers the electrometric determination of the pH of both aqueous and solid samples. Corrosivity is then determined as a function of the pH of a sample. The range of this method is from 0 to 14 pH units. A sample is deemed "corrosive" if its pH is less than 2.00 or greater than 12.50 pH units. Ideally, the pH is determined in the field by the sampler. Samples received in the lab should be analyzed as soon as possible, before the sample is submitted to the sample storage refrigerators by the sample receipt department.

I. Summary of Method

A. The pH of the sample is determined electrometrically using a combination electrode. The pH meter is calibrated before each use using a series of standard solutions of known pH.

II. Interferences

A. The electrode is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate salinity.
B. Sodium error at pH levels >10 is reduced or eliminated by using a low-sodium-error electrode.
C. Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gently wiping or detergent washing, followed by rinsing with DI water. An additional treatment with 1:10 HCl may be necessary to remove any remaining film.
D. Temperature effects the electrometric determination of pH. It is important to analyze standards and samples at the same temperature or use an automatic temperature compensation (ATC) probe if the temperatures are different.

III. Sample Collection, Preservation and Storage

A. pH is a field parameter and should be analzyed immediately after sampling.
B. Collect sample in a clean plastic or glass bottle with no preservative.
C. Samples analyzed for pH in the laboratory must be flagged as analyzed past holding time.

IV. Equipment and Supplies

A. pH meter, VWR SCIENTIFIC MODEL B30 PCI.
B. Combination pH Electrode, Orion 8156 NUWP (or equivalent).

C. Temperature Compensation Probe, Mettler Toledo PT1000.
D. Sample vials, 25-50mL.
E. Top loader balance capable of weighing 0.1g.
F. Floats (foam vial holders).
G. Automatic shaker.
H. Kimwipes.

V. Reagents and Standards

A. Primary Standard Buffer, 4.01 pH units; ULTRA #IBF-040-L (or equivalent).
B. Primary Standard Buffer, 7.00 pH units; ULTRA #IBF-070-L (or equivalent).
C. Primary Standard Buffer, 10.01 pH units; ULTRA #IBF-100-L (or equivalent).
D. Primary Standard Buffer, 2.00 pH units; VWR #BDH5010 (or equivalent).
E. Primary Standard Buffer, 12.45 pH units; VWR #BDH5092 (or equivalent).
F. LCS, ULTRA # QCI-713 (or equivalent).

VI. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.
B. Calibration standard- A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate instrument response with respect to analyte concentration.

VII. Procedure

A. The pH meter is left on at all times. The instrument has a sleep mode that is activated when instrument is placed in a water matrix.
B. Pour fresh Primary Standard Buffers 4.01, 7.00 and 10.01 into clean, dry 25mL vials (or equivalent), using sufficient volume to cover the sensing element of the combination electrode. Fresh aliquots of Primary Standard Buffer are required at each calibration.
C. Thoroughly rinse the pH electrode & ATC probe with DI water and blot dry with a Kimwipe.
D. Press the "Calibration" key and select "Ch 1: pH". The meter will perform a 3 buffer calibration with the 4.01, 7.00 and 10.01 buffers.
E. Place the electrode & ATC probe into the vial containing 7.00 Primary Standard Buffer. Stir the electrode in the buffer and press "READ".
F. When the reading stabilizes the instrument will prompt you to put the probe in the second buffer (10.01).
G. Thoroughly rinse the pH electrode & ATC probe with DI water and blot dry with a Kimwipe.
H. Place the electrode & ATC probe into the vial containing 10.01 Primary Standard Buffer. Stir the electrode in the buffer and press "READ".

I. When the reading stabilizes the instrument will prompt you to put the probe in the third buffer (4.01).

J. Thoroughly rinse the pH electrode & ATC probe with DI water and blot dry with a Kimwipe.

K. Place the electrode and ATC probe into the vial containing 4.01 Primary Standard Buffer and stir the electrode in the buffer and press "READ".

L. If the calibration falls within the acceptable 92-102% slope criteria the instrument will display "Calibration OK" and will automatically store the calibration. If the calibration fails repeat steps A-K above.

M. To run samples first go to the LIMS Main Menu and select "QA/QC Batching" / "PREP LOGBOOK".

N. Next select "pH, Corr, Redox" from the Batch pull down menu.

O. Pour fresh aliquots of LCS, 2.00 buffer and 12.45 buffer into clean, dry 25mL vials, using sufficient volume to cover the sensing element of the combination electrode.

P. Thoroughly rinse the pH electrode & ATC probe with DI water and blot dry with a Kimwipe after EVERY buffer/sample reading.

Q. Place the pH electrode & ATC probe into the vial containing LCS and stir the electrode in the LCS.

R. Record the reading in the pH logbook. The LCS is a secondary control standard and must agree within 0.15 pH units of the true value.

S. Thoroughly rinse the pH electrode & ATC probe with DI water and blot dry with a Kimwipe.

T. Analyze the five buffers (4.01, 7.00, 1.01, 2.00 and 12.45) in the same manner as the LCS, recording all readings in the pH logbook including start time of analysis, date, & analyst initials.

U. Analyze soils by weighing 10g into a 25mL vial and making a 1:1 slurry with DI water, and shake on the automatic shaker for 5 minutes. Allow the suspension to settle for 1 hour, then analyze as described above. Record sample preparation in pH logbook.

V. Corrosivity is determined as a function of pH. If a sample has a pH of 2.0 to 12.5 it is not corrosive (report "negative"). If a sample has a pH of less than 2.0 or greater than 12.5 it is corrosive (report "positive").

VIII. Calculations

A. Calculating RPD:

The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$\text{RPD, \%} = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

B. Calculating the LCS:

The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the LCS sample, and then apply it to the following calculation:

$$\% \text{ Recovery, } \% = \frac{(RL)}{(LTV)} \times 100$$

where: RL = achieved value for LCS sample, mg/L
LTV = true value of LCS, mg/L

IX. Quality Control

A. All reagents and standards are labeled with the following information: date received, date expires, date opened, and Phoenix Environmental Lab ID number.
B. A Laboratory Control Standard (LCS) is run every batch of 20 or fewer samples. The derived LCS value must agree within 0.15 pH units of the true value.
C. The instrument is calibrated at every use. The Primary Standard Buffers are poured fresh at each calibration.
D. A Calibration Check is run every 10 or fewer samples, as well as at the end of every batch. The derived Cal. Check value must agree within 0.15 pH units of the true value.
E. A sample replicate is run analyzed every 20 or fewer samples. The replicate value must agree within 0.15 pH units of the sample value.
F. Samples are run as soon as possible, and throughout the workday.

X. Safety

A. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.
B. Always wear safety glasses for eye protection as well as lab coats and gloves.
C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

XI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
B. Reagents and chemicals should be purchased and/or prepared in volumes consistant with laboratory use to minimize the volume of disposal.

XII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

XIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including initial and continuing calibration verifications, blank analysis, laboratory control samples, sample duplicates, inhouse blind samples and proficiency testing.
B. See section IX Quality Control in this SOP for acceptable limits.

XIV. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the slope of the calibration curve be outside of acceptance limits, re-pour buffers and reanalyze curve before processing samples.
B. Should the LCS fail acceptance criteria, re-calibrate instrument.
C. Should a Calibration check standard fail acceptance criteria, reanalyze any samples not bracketed by passing Cal checks.

XV. References

A. Standard Methods for the Examination of Waste and Wastewater, 22nd edition. Method No. 4500-H^+ B, Revised 2011.
B. Test Methods for Evaluating Soil Waste, SW846 Chapter 7, section 7.2, 1996.
C. Test Methods for Evaluating Soil Waste, SW846, Method 9045D, Soil and Waste pH, Final Update IIIB, 11/04.

Revision History Log for SOP # 319

Date:	Revision #:	Summary of Changes:	Submitted By:	Approved By:	Effective Date:
1/17/17	5.1	Section IV- new part numbers for probes, added shaker and took out stirrer, section V- new part numbers for buffers, section VII- updated procedure to reflect shaker	Kathy Cressia	Eric Geyer	1/17/17
3/15/18	5.2	MUR change of reference section	Kathy Cressia	Eric Geyer	3/15/18

Expiration Date

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SOP No.: 321.4500PE

Title: Phosphorus, All Forms

Scope and Application: This method covers the determination of all forms of phosphorus, including o-phosphate, organic phosphate, and total phosphorus. This method is applicable to all drinking water, surface water, ground water, industrial and domestic waste, and soil samples and their leachates. The range for this procedure is 0.010-1.0 mg/L. Samples above 1.0 mg/L can be analyzed by sample dilution prior to digestion. The limit of detection is 0.010 mg/L.

Phosphorus occurs in natural waters and in wastewaters almost solely as phosphates. These are classified as orthophosphates, condensed phosphates, and organically bound phosphates. They occur in solution, in particles or detritus, or in the bodies of aquatic organisms. These forms of phosphate arise from a variety of sources. Small amounts of certain condensed phosphates are added to some water supplies during treatment. Larger quantities of the same compounds may be added when the water is used for laundering or other cleaning, because these materials are major constituents of many commercial cleaning preparations. Phosphates are used extensively in the treatment of boiler waters. Orthophosphates applied to agricultural or residential cultivated land as fertilizers are carried into surface waters with storm runoff and to a lesser extent with melting snow. Organic phosphates are formed primarily by biological processes. They are contributed to sewage by body wastes and food residues, and also may be formed from orthophosphates in biological treatment processes or by receiving water biota.
Phosphorus is essential to the growth of organisms and can be the nutrient that limits the primary productivity of a body of water. In instances where phosphate is a growth-limiting nutrient, the discharge of raw or treated wastewater, agricultural drainage, or certain industrial wastes to that water may stimulate the growth of photosynthetic aquatic micro- and macro-organisms in nuisance quantities.

I. Summary of Method

A. Ammonium molybdate and potassium antimony tartrate react in an acid medium to form a heteropoly acid (phosphomolybdic acid) which is reduced to an intensely blue-colored complex by ascorbic acid. The intensity of the blue color is directly proportional to the concentration of orthophosphate in the sample.

B. Since the above reaction only occurs with the o-phosphate form of phosphorus, pretreatment of condensed and organically bound is required for their

determination. Condensed phosphates must undergo acid hydrolysis at boiling-water temperature. Organically bound phosphates must undergo a digestion using acid, heat, and an oxidizing agent. These treatments transform the bound phosphates to o-phosphate, where they can be quantified.

C. For dissolved phosphate, filter the sample through a 0.45um filter before analysis. If only particulate phosphate is to be determined, analyze for dissolved phosphate and for total phosphate, and subtract dissolved from total.

D. Total Phosphorus (P)- all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure.

1. Total Orthophosphate (P, ortho) or Total Reactive Phosphorus- inorganic phosphorus [$(PO_4)^{-3}$] in the sample as measured by the direct colorimetric analysis procedure.
2. Total Hydrolyzable Phosphorus (P, hydro) – phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. [$(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] plus some organic phosphorus.
3. Total Organic Phosphorus (P, org) – phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate.

E . Dissolved Phosphorus (P-D)- all of the phosphorus present in the filtrate of a Sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure.

1. Dissolved Orthophosphate (P-D, ortho) or Dissolved Reactive Phosphorus- as measured by the direct colorimetric analysis procedure.
2. Dissolved Hydrolyzable Phosphorus (P-D, hydro)- as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates.
3. Dissolved Organic Phosphorus (P-D, org)-as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate.

F. The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

1. Insoluble Phosphorus (P-I) = (P)-(P-D).
2. Insoluble orthophosphate (P-I, ortho)=(P,ortho)-(P-D,ortho).
3. Insoluble Hydrolyzable Phosphorus (P-I,hydro)=(P,hydro)-(P-D,hydro).
4. Insoluble Organic Phosphorus (P-I, org)=(P,org) – (P-D,org).

G. See Appendix B for flow chart.

II. Interferences

A. Glassware must be scrupulously cleaned, as carry over from phosphates is common. Refer to Appendix A in this SOP for the Phosphorus Glassware Cleaning Instructions.

B. Arsenate present in the sample to be tested is a positive interference, as it reacts with the molybdate reagent to produce a blue color similar to the blue formed by o-phosphate. Concentrations as low as 0.1 mg/L are enough to cause interference. By adding sodium bisulfite to the sample, arsenate is reduced to arsenious acid.

C. High concentrations of iron in a sample will give erroneously low results, as it will take away some of the reducing agent. Sodium bisulfite treatment will eliminate this interference.

D. Hexavalent chromium and nitrite interfere to give low results. Concentrations of these ions need to be at least 10.0 mg/L to interfere signifcantly.

E. Particulates may interfere with spectrophotometric analysis by absorbing light. Samples may be filtered after hydrolysis or digestion but not once the color reagent is added.

F. In the determination of orthophosphate, color can interfere. A color blank may be performed.

III. Sample Collection, Preservation and Storage

A. Samples can be collected in plastic or glass. They must be stored at 4°C until time of analysis.

B. Orthophosphate samples must be unpreserved and analyzed within 48 hours from time of collection.

C. Total Phosphorus samples must be H_2SO_4 preserved to pH<2 and analyzed within 28 days of collection.

IV. Equipment and Supplies

A. Spectophotometer, 880nm.

B. Environmental Express 54-position Hot Block with custom glass digestion vials.

C. Pro Clean Environmental Containers glass 60mL vials, P/N GV60/PCLB-72.

D. Graduated cylinder, 50mL.

E. Volumetric flasks, 50mL.

F. Class "A" volumetric pipets; assorted.

G. Hengar granules, boiling stones

V. Reagents and Standards

A. Sulfuric Acid, 5N. Dilute 139mL conc H_2SO_4 to 1000mL with DI water.

B. Potassium antimony tartrate solution. Dissolve 1.3715 g $K(SbO)C_4H_4O_6$ 1/2 H_2O in 400 mL DI water in a 500ml volumetric flask and dilute to volume. Store in a plastic, stoppered bottle.

C. Ammonium molybdate solution. Dissolve 20 g $(NH_4)_6\ Mo_7O_{24}*4H_2O$ in 500ml DI water. Store in plastic, stoppered bottle.

D. Ascorbic acid solution, 0.01M. Dissolve 3.52g ascorbic acid, reagent grade, in 200mL DI water. Make fresh daily.

E. Combined color reagent. Mix 100mL 5N H_2SO_4, 10mL potassium antimony tartrate, 30mL ammonium molybdate, and 60mL ascorbic acid solution in a clean 200mL erlynmeyer flask. If more reagent is needed, increase volumes of each solution proportionally. **Add reagents in the order given, and mix after the addition of each reagent.** Combined reagent is only stable for 4 hours.

F. Sulfuric acid, 11N. Slowly add 300mL conc. H_2SO_4 to 600mL DI water. Cool in a water bath, and dilute to 1 liter. Alternatively, make from 18N (1:1) H_2SO_4 by diluting 600mL to 1 liter of DI water.

G. Ammonium persulfate $(NH_4)_2\ S_2O_8$ solid, reagent grade. Potassium persulfate may be used as an oxidizing reagent.

H. Sodium bisulfite solution. Dissolve 5.2 g of $NaHSO_3$ in l00mL of l N H_2SO_4.

I. Sodium hydroxide solution, 2N. Dissolve 80 g NaOH into 1 liter DI water.

J. Phenolphthalein indicator solution, alcohol-based. Dissolve 5g of phenolphthalein in approximately 500mL 95% ethyl or isopropyl alcohol. Dilute to 1 L with DI water.

K. Stock phosphorus solution. Dissolve 0.4393g of oven-dried and desiccated KH_2PO_4 in 1L DI water. 1.0mL = 100ug P. Record preparation of standards in standards logbook.

L. Standard phosphorus solution. Dilute 100mL of stock phosphorus solution to 1L with DI water. 1.0mL= 10ug P. Record preparation of standards in standards logbook.

M. Nutrients in Soil, ERA #542 or equivalent. Use approximately 1g for PHOS-SM LCS.

N. Simple Nutrients Stock Solution, ERA #505 or equivalent.

O. Simple Nutrients LCS Working Solution. Dilute 2.5mL of simple nutrients stock solution to 1L with DI water. Record preparation of standards in standards logbook. Use 5mL to 25mL DI water for simple LCS.

P. Complex Nutrients Stock Solution, ERA #525 or equivalent.

Q. Complex Nutrients LCS Working Solution. Dilute 5mL of complex nutrients stock solution to 1L with DI water. Resord preparation of standards in standards logbook. Use 5mL to spike. Use 5mL to 50mL DI water for simple LCS.

VI. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.

B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.

C. Calibration standard- A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate instrument response with respect to analyte concentration.

D. Matrix Spike (MS)- An aliquot of environmental sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

VII. Procedure

A. Determination of total phosphorus (TP-WM), all forms of phosphate.

1. Check pH of the sample and record in Phos batching program.
2. Into a digestion vessel, measure 50mL sample or an aliquot diluted to 50mL, hengar granules, and add a drop of phenolphthalein solution. If it turns pink, add 11N H_2SO_4 drop-wise until color disappears.
3. Add 0.4g solid ammonium or potassium persulfate.
4. Add lmL 11N H_2SO_4. Use disposable pipets to reduce chances of contamination.
5. Set the Hot Block to approximately 140°C, enough to get the samples to 100°C. Boil gently under a ventilation hood until a final volume of less than 10mL is achieved. Do not allow sample to go to dryness.
6. For samples suspected to contain iron interference, add 5mL of sodium bisulfite and mix. continue heating for 20 min. Do not allow sample to go to dryness.
7. Cool, dilute to 30mL in the digestion vessels (filter sample, if needed), add 1 drop phenolphthalein solution, and neutralize to a faint pink color using 2N NaOH solution. *Do not filter while sample is neutral, as phosphate-containing precipitates form that will dissolve under acid conditions.*
8. Bring sample up to 50 mL volume with DI water in digestion vessel and mix well. Transfer a 25 mL aliquot to 60 mL glass vessel. If a larger dilution is necessary, transfer a small volume to glass vial and bring to 25 mL final volume with DI water.
9. Determine phosphorus as outlined in the determination of orthophosphate, C.2. and C.3. below.

B. Determination of total phosphorus (TP-SM), all forms of phosphate.

1. Into a digestion vessel, measure 0.5-0.6g of sample and bring to 50mL with DI water. Add hengar granules and add a drop of phenolphthalein solution. If it turns pink, add 11N H_2SO_4 drop-wise until color disappears.
2. Add 0.4g solid ammonium or potassium persulfate.
3. Add lmL 11N H_2SO_4. Use disposable pipets to reduce chances of contamination.

4. Set the Hot Block to approximately 140°C, enough to get the samples to 100°C. Boil gently under a ventilation hood until a final volume of less than 10mL is achieved. Do not allow sample to go to dryness.
5. For samples suspected to contain iron interference, add 5mL of sodium bisulfite and mix. continue heating for 20 min. Do not allow sample to go to dryness.
6. Cool, dilute to 30mL in the digestion vessels (filter sample, if needed), add 1 drop phenolphthalein solution, and neutralize to a faint pink color using 2N NaOH solution. *Do not filter while sample is neutral, as phosphate-containing precipitates form that will dissolve under acid conditions.*
7. Bring sample up to 50 mL volume with DI water in digestion vessel and mix well. Transfer a 25 mL aliquot to 60 mL glass vessel. If a larger dilution is necessary, transfer a small volume to glass vial and bring to 25 mL final volume with DI water.
8. Determine phosphorus as outlined in the determination of orthophosphate, C.2. and C.3. below.

C. Determination of total phosphates (code "TPFATE") hydrolyzable and condensed phosphates.

1. Into a digestion vessel, measure 50mL sample or an aliquot diluted to 50mL and add a drop of phenolphthalein solution. If it turns pink, add 11N H_2SO_4 drop-wise until color disappears. Record pH of original sample in Phos Batching sheet.
2. Add 1 mL of H_2SO_4 to sample. Use a disposable pipet to reduce risk of contamination.
3. Set the Hot Block to approxiamately 140°C, enough to get the samples to 100°C. Boil gently with hengar granules under a ventilation hood until a final volume of less than 10mL is achieved. Do not allow sample to go to dryness.
4. Treat samples containing interferences, as above.
5. Cool samples, filter if needed, then add 1 drop phenolphthalein solution, and neutralize to a faint pink color using 6N NaOH solution. *Do not filter while sample is neutral, as phosphate-containing precipitates from that will dissolve under acid conditions.*
6. Bring sample up to 50 mL volume with DI water in digestion vessel and mix well. Transfer a 25 mL aliquot to 60 mL glass vessel. If a larger dilution is necessary, transfer a small volume to glass vial and bring to 25 mL final volume with DI water.
7. Determine phosphorus as outlined in the determination of orthophosphate, C.2. and C.3. below.

D. Determination of orthophosphate (OP-WM).

1. Decant 25mL of unpreserved sample or an aliquot diluted to 25mL into a glass vial, add 1 drop of phenolphthalein solution. If a pink color appears, add 5N H_2SO_4 drop-wise until color disappears.
2. Add 4 mL combined color reagent and mix thoroughly.
3. After 10 (but before 30) minutes, measure the absorbance of each sample at 880nm, using DI water as the reference solution. The absorbance is correlated to a point on a linear regression which correlates to a concentration of phosphorus.

E. For other forms of Phosphorus, see Section 1.C – 1.F.

VIII. Calculations

A. Refer to the Standards Logbook for the most current calibration curve. To generate a new calibration curve, use phosphorus standard solution. Make the following dilutions: blank (DI water), 0.01mg/L, 0.025 mg/L, 0.05 mg/L, 0.10 mg/L, 0.20 mg/L, 0.50 mg/L and 1.0 mg/L. Add phenolphthalein and 5N H_2SO_4 to each, as you would a sample. Add 8 mL combined color reagent, and read at 880 nm after 15 minutes. Record absorbances, and plot them on the x-axis against the corresponding concentrations. Follow with a linear regression, and use the following calculation:

$Y = (MX + B) * DF$, where: Y = concentration (mg/L)
M = slope of the linear regression
X = absorbance at 620nm
B = y-intercept of linear regression
DF = dilution factor, if any

Note that M and B values will differ with each calibration.

B. Calculating RPD:

The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$RPD, \% = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

C. Calculating the sample spike recovery:

The sample spike is a test if the sample matrix is suitable for accurate testing. To calculate the % recovery, first calculate both the sample and the spiked sample. Then apply the two results to the following calculation:

$$\% \text{ Recovery}, \% = \frac{(SR - R)}{STV} \times 100$$

where: SR = value of sample with added spike, mg/L
R = value of sample, mg/L
STV = true value of spike added to sample, mg/L

D. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the LCS sample, and then apply it to the following calculation:

$$\% \text{ Recovery}, \% = \frac{(RL)}{(LTV)} \times 100$$

where: RL = achieved value for LCS sample, mg/L
LTV = true value of LCS, mg/L

E. Calculating poly-phosphate, as P is done during data transfer, automatically, when needed.

IX. Quality Control

A. All reagents and standards are to be labelled with the following information: date prepared, date expires, preparer's initials, analyte, contents, and concentration of contents. Record preparation of all reagents in the reagent prep logbook.

B. A sample prep blank of dilution water must be analyzed with each batch of twenty or fewer samples. Prep blanks must be determined to be BRL (below reportable level).

C. Two purchased, second source, laboratory control standards (LCS) are run with each batch of twenty or fewer samples. One is a "complex" solution, which goes through the digestion process, while the other is a "simple" solution, which is not digested. The acceptable recovery of a LCS is 85-115%.

D. An in-house standard (CC) made from the standard solution used to calculate the curve is run after every ten samples. The true value of the CC is 0.25mg/L. The acceptable recovery of an in-house standard is 90-110%.

E. A DI water blank, (CB), is analyzed after the CC every ten samples. The CB must be BRL (below reportable level).

F. A sample spike and a sample duplicate are run with every batch of twenty or fewer samples. The acceptable recovery for a sample spike is 75-125%. The acceptable relative percent difference (RPD) for a sample duplicate is less than or equal to 20%.

G. A new calibration curve must be analyzed annually or whenever a new stock solution is made. The correlation coefficient of the curve must be >0.9975.

H. Samples labeled as trip blanks, field blanks, or equipment blanks are ineligible samples for spiking and duplicating.

X. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.

B. Always wear safety glasses for eye protection as well as lab coats.

C. When diluting H_2SO_4, always add acid to water.

D. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

XI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.

B. Reagents and chemicals should be purchased and/or prepared in volumes consistant with laboratory use to minimize the volume of disposal.

XII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

XIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates.

B. See section IX Quality Control in this SOP for acceptable limits.

XIV. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the calibration curve have a correlation coefficient of <0.9975, remake and reanalyze curve before processing samples.

B. Should the preparation blank, LCS or inhouse standard fail acceptance criteria, redigest and reanalyze batch.

C. Should the matrix spike or sample duplicate analysis fail acceptance criteria, a non-conformance report must be generated or the sample QC must be reanalyzed.

XV. Batching Program for Phosphorus

A. Double click on Phoenix MDB (2K MDE) to get to main menu.

B. Click on QA/QC Batching and double click on Prep Batching.

C. Go to the Batch square and type in "PHOS-WM" or "PHOS-SM".

D. Go to New Batch and click, this brings up the last batch made.

E. Click again and this brings up a new list of samples to pick for each batch to be made.

F. Click on numbers under Batches to build for the number needed.

G. Click on Build Batch.

H. Finish making the batch by filling in QC sample, weight/volume, initials and finish date.

I. All samples MUST be batched. They cannot be added to the Sequence Program if they are not in a batch.

J. All batches must have Initial sample weight/volume entered by the analyst before the batch can be added to the Sequence Program.

K. Samples cannot be transferred if % Solid is still pending.

L. Samples cannot be transferred if the batch LCS fails.

M. Changing the QC Sample:

1. A batch cannot be loaded in the Sequence Program until it has been assigned a QC sample. However, a QC sample can be changed.
2. To change a QC sample, select the batch in Prep Batching and Clear the finish date.
3. Change the QC sample to the desired QC sample. The LCS and Blank will automatically change in the Sequence Program.
4. The original spike and dup will remain. Do not select them for transfer and the results will go nowhere.
5. The spike and dup for the new QC sample will have to be added manually to the end of the sequence.

N. Updating the Calibration:

1. When recalibrating the instrument, change the dates in the set-up to reflect the effective ending date of prior calibration.
2. Enter a new record. This can be done by copying an existing record and pasting it on a new line.
3. Update the appropriate date, Slope, y-intercept, LCS true value and source, spike true value, etc.

O. Selecting or Deselecting Samples for Transfer:
1. Before transferring samples, the Batch Blank and Batch LCS must be selected. This is necessary so when a sample is selected, the program knows which QC is associated with it.
2. If a Blank or LCS is deselected, all samples in the batch will be deselected.

P. Rerunning QC Samples:
1. QC can be re-analyzed by re-adding the samples and appropriate QC record to the end of the sequence.
2. Deselect the original run(s) and select the new one, and the corresponding samples.

XVI. Data Transfer Program for Phosphorus

A. Click on Phoenix MDB (2K MDE) to go to the main menu.
B. Click on Data Transfer.
C. Double Click on Phosphate Sequence and Data Transfer.
D. Select "P" on Run Type drop down box.
E. Click on New Sequence or Add Batch for however many to be done.
F. After batches are completed, add analysts initials to bottom and click on Transfer to Labworks.
G. Click on Present Log to print a copy and exit page.

XVII. References

A. Standard Methods for the Examination of Wastewater, 22nd ed., 2011. Methods used: 4500-P B2 for hydrolysis; 4500P B5 for digestion; 4500-P E for orthophosphate and color formation.
B. Phosphorus, All Forms, Environmental Express Hot Block Standard Procedure. Method used: Colorimetric, Ascorbic Acid, Single Reagent.
C. USEPA Method 365.3, Phosphorus, All Forms, 1978.

Appendix A- Phosphorus Glassware Cleaning Instructions

1) Make new 10% HCl solution at least once a week.
   a) Dump old solution in acid waste.
   b) Rinse bottles and caps thoroughly with deionized water.
      i) Bottles are usually in hood #8.
   c) Fill bottles to 900 mL line with deionized water.
   d) In a hood, fill bottles to 1000 mL line (the bump near the top), with concentrated HCl.
   e) Cap bottles and CAREFULLY invert several times to mix.

2) Handwash the 60 mL vessels (NOTE: Some vessels have a 50mL volumetric line for digestions, while others have a 25mL volumetric line for color developement. They are washed the same way!)
   a) Pour out the water that the vessel has been soaking in, while in the white floats.
   b) Fill with hot water, add a squirt of Phosphate free detergent and scrub with brush.
      i) Brush is the clean, white bristled brush hanging to the right of the sink.
      ii) The Phosphate free detergent is in a squeeze Nalgene bottle near brush.
      iii) Remove any sharpie marks on the outside of the vessel while scrubbing.
   c) Rinse washed vessels numerous times with DI water.
   d) Place the scrubbed / rinsed vessels upright in the plastic storage trays.
      i) Trays can usually be found piled up in the phosphorus area.
         (1) Blank trays are for "25 mL" vessels
         (2) Numbered trays are for "50 mL" vessels.
   e) In a hood, carefully fill each vessel to the brim with HOT 10% HCl solution, which was heated in Step #2.
      i) Use a hotglove borrowed from the ammonia setup if necessary; the acid solution should be hot enough to be slightly uncomfortable, but not boiling hot.
   f) Let the vessels soak in HCl solution for a few minutes
      i) The time necessary to pour another tray should be sufficient.
   g) Using the funnel that was stored with the bottles, pour the hot HCl solution back into its bottle. Cap it and store in hood #8 when finished.
   h) Take the tray of acid washed vessels to the sink for rinsing.
      i) Rinse three times with deionized water and pour out.
      ii) Fill vessels to the brim with deionized water
   i) Store clean deionized water filled tray of vessels either on the phosphorus countertop or in the shelves in the rear storage room.
      i) Cover vessels with clean paper towel to protect them.
   j) Dump DI water in vessels and rinse once more with DI before use.

Revision History Log for SOP #321 TP

Date:	Revision #:	Summary of Changes:	Submitted By:	Approved By:	Effective Date:
1/6/14	5	Simple & Complex LCS added, recording pH of sample, updated vessel cleaning procedure	Kathy Cressia	Eric Geyer	1/6/14
10/04/16	5.1	Section 1.0- added D, E, F, G (forms of phos), Section VII- added D, added EPA method to references, just referring to forms of Phos, added Appendix B- flow chart	Kathy Cressia	Eric Geyer	10/04/16
3/15/18	5.2	Doubled combined reagent recipe, updated method reference year for MUR	Kathy Cressia	Eric Geyer	3/15/18
7/12/22	5.3	Section V- Added preparation of simple and complex LCS. Section VII-B- Added procedure for soil analysis.	Linnea Skoglund	Eric Geyer	7/12/22

Expiration Date

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SOP No.: 324.2540D

Title: Total Suspended Solids (TSS) dried at 103°-105°C

Scope: This method covers the determination of suspended solids in drinking, surface, saline waters, and domestic and industrial wastes. The practical range of the determination is 5.0-2000mg/L. Samples containing more than 2000mg/L suspended solids require sample dilution prior to analysis.

I. Summary of Method

A. A well-mixed sample is filtered through a pre-weighed glass fiber filter. The filter is retained and dried to a constant weight at 104°C. The increase in filter weight represents the total suspended solids (TSS).
B. If total dissolved solids (TDS) is being determined on the sample, the filtrate may be retained for TDS analysis.

II. Interferences

A. Exclude large floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Because excessive residue on the filter may form a water-trapping crust, limit sample to that yielding no more than 200mg residue.
B. For samples with high TDS, thoroughly wash filter to insure no TDS will be measured as part of the TSS.

III. Sample Collection, Preservation and Storage

A. Samples for solids analysis are unpreserved and stored at 4°C prior to analysis.
B. Samples are analyzed as soon as possible, but not after a holding time of 7 days after sample collection.

IV. Equipment and Supplies

A. Glass fiber filters, Whatman 934-AH or equivalent.
B. Gooch crucibles of same size as filters, with adapter.
C. Filter flasks, 250ml or 500ml volume.
D. Drying oven, 104°C +/-1°C.
E. Desiccator. Change desiccant every month, or when desiccant changes color.
F. Graduated cylinder, 100mL.
G. Analytical balance, capable of weighing to 0.1mg.

V. Reagents and Standards

A. Laboratory deionized water.
B. Laboratory Control Sample; purchased. ERA Solids catalog #499 or equivalent.

VI. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.
B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.
C. Sample Duplicates (Dup)- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of the sample and duplicate indicate precision associated with laboratory procedures.

VII. Procedure

A. Preparation of gooch crucibles.
1. Clean and rinse well enough crucibles to complete a full batch of twenty samples, allowing one crucible for each sample, plus one for a LCS, one for a blank, and two crucibles for sample replicates. Be sure crucibles are marked for identification purposes.
2. Attach filter flasks to the filter set-ups. Place the rubber adapter to the top of the flask.
3. Insert a glass fiber filter disc into a clean gooch crucible, grid side down. Place the crucible to the adapter. With vacuum applied, wash the disc with 30mL DI water to insure a snug fit, and to rinse loose fibers from filter. Discard filtrate. Place crucibles in oven at 104°C for one hour.
4. Move crucibles to desiccator to cool for 1 hour. Handle crucibles using forceps. Oils from the skin can effect final results.

B. Batch Creation
1. Open Phoenix Laboratories Lims and click on QA/QC Batching,TSS/TDS/TS Batching.
2. Click on "New Batch" and use the pull-down menu to select TSS analysis. This will bring up all samples in the batching program that need to be run.
3. Create a batch of 20 samples or fewer by clicking on the box in the "Select" column.
4. Using the pull-down menus at the bottom of the window, choose a QC sample. If the batch contains more than 11 samples, choose a sample for the second dup. Click "OK"; this will bring up a TSS Batch Worksheet.
5. Using forceps to handle each gooch crucible, record the Dish ID # in the appropriate column. Then record the initial weight of each crucible in the"Tare

Weight" column of the spreadsheet electronically, using Wetlab Analytical #1A. (Please note: it is important to use forceps when handling the crucibles, as oils from skin can affect final results).

C. Preparation of samples.

1. Allow samples to come to room temperature before analysis.

D. Preparation of filter set-up.

1. Attach filter flasks to the filter set-ups. Place the rubber adapter to the top of the flask.
2. The flask will contain the sample filtrate. Mark it as waste unless TDS is to be performed in conjunction with TSS. Be sure to use clean, DI rinsed filter flasks for TDS determination.

E. Filtration of samples.

1. Place a pre-weighed gooch crucible on the adaptor, shake sample vigorously and rapidly measure appropriate sample volume into a graduated cylinder. Choose a sample volume to yield between 2.5 – 200mg of dried residue. If the volume filtered fails to meet the minimum yield, increase sample volume up to 1L.
2. Pour the sample into the filter set-up. Rinse the graduated cylinder with three successive 20mL portions of DI water, and pour washings into the filter set-up. Allow complete drainage between washings.
3. Continue suction for 3 minutes after filtration is complete.
4. If more than 10 minutes is needed to complete filtration, decrease sample volume.
5. If a representative sample aliquot is not possible by decanting, due to floating material, use a pipet submerged to the center of the sample container to extract a homogeneous representative sample aliquot. Exclude from analysis sand or other heavy materials that settle to the bottom of the sample container after vigorous shaking.
6. Place gooch crucibles with samples particulates trapped on the filter into the drying oven at 104°C. Reserve sample filtrate if TDS is to be determined.
7. Record on the TSS Batch worksheet: sample volume used, oven temperature, time and date samples were put into the oven.

F. Final Analysis of TSS.

1. After a minimum of one hour in the oven at 104°C, transfer the crucibles to a desiccator.
2. Cool in desiccator for a minimum of 1 hour and determine the first weight. Record weight electronically under the appropriate batch number.
3. Return crucibles to the 104C oven for at least an 1 hour.
4. Cool in desiccator for at least an 1 hour and determine the second weight. Record the weight electronically.
5. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% previous weight or less than 0.5mg, whichever is less.
6. Print out each completed batch number and file in the TSS logbook.

VIII. Calculations

A. The TSS value is calculated using the following equation:

$$TSS\ (mg/L) = \frac{(A - B) \times 1000}{SV}$$

Where: TSS = total suspended solids (mg/L)
A = average of final weights within constant weight criteria (g)
B = initial weight of gooch crucible (g)
SV = sample volume (L)

B. Calculating RPD:
The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$RPD, \% = \frac{(R1 - R2) \times 100}{(R1+R2)/2}$$

where: R1 = TSS value achieved for sample, mg/L
R2 = TSS value achieved for sample duplicate, mg/L

C. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the LCS sample, and then apply it to the following calculation:

$$\%\ Recovery, \% = \frac{(RL) \times 100}{(LTV)}$$

where: RL = achieved value for LCS sample, mg/L
LTV = true value of LCS, mg/L

IX. Quality Control

A. A reagent blank is analyzed with every batch of 20 or fewer samples. If the blank has a positive TSS value, the sample results are acceptable only if the blank is no more than 10% of the sample result. If the blank has a negative result of less than –5.0 mg/L, the sample results are acceptable only if the absolute value of the blank is no more than 10% of the sample result.

B. A Laboratory Control Standard (LCS) will be analyzed with every batch of 20 or fewer samples. The LCS must be recovered between 85-115%.

C. Sample duplicates are analyzed every 10 of fewer samples. The RPD must be ≤20%, else repeat sample and duplicate analysis to prove matrix effect.
D. Oven temperatures are recorded daily to insure stable oven temperatures. The drying oven must maintain temperature within 103°-105°C. Oven working thermometers are calibrated annually with NIST traceable thermometers.
E. The calibration of the analytical balance is checked daily using Class "S" weights: 50.0000g, 10.0000g, 1.0000g and 0.1000g. The balance is calibrated annually barring any problems throughout the year.

X. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.
B. Always wear safety glasses for eye protection as well as lab coats and gloves.
C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

XI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
B. Reagents and chemicals should be purchased and/or prepared in volumes consistant with laboratory use to minimize the volume of disposal.

XII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

XIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, limit of detection studies, precision and accuracy studies, proficiency test samples, blank analysis, laboratory control samples and sample duplicates.
B. See section IX Quality Control in this SOP for acceptable limits.

XIV. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the preparation blank or LCS fail the acceptance criteria given in Section IX, reanalyze batch.

B. Should the sample duplicate analysis fail acceptance criteria, reanalyze the sample and duplicate should sample volume permit. If sample volume is limited, replicate another sample in that batch.

XV. References

A. Standard Methods for the Examination of Waste and Wastewater, 23rd edition, 2015, Method No. 2540D, Total Suspended Solids Dried at 103°-105°C.

Revision History Log for SOP #324.TSS

Date:	Revision #:	Summary of Changes:	Submitted By:	Approved By:	Effective Date:
1/15/14	5	LCS vendor change, put drying time as "at least" 1 hr, calibration of oven thermometers, added the 0.1g class "s" wt to daily balance check	Kathy Cressia	Eric Geyer	1/15/14
3/22/18	5.1	MUR change of reference section	Kathy Cressia	Eric Geyer	3/22/18
8/22/19	5.2	Changed / added to Section VII.E.1 – to include minimum yield requirements	Kathy Cressia	Eric Geyer	8/22/19
1/10/22	5.3	MUR change of reference section	Kathy Cressia	Eric Geyer	1/10/22

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Effective Date: 07/26/22
Version Number: 3.4
Initiated By:
Approved By:

SOP Number: 336.353.2

Title: Total Nitrite as Nitrogen / Total Nitrate as Nitrogen

Scope: This method is applicable for the determination of concentrations of nitrites and nitrates in drinking, surface, and ground water, domestic and industrial waste, and solid samples. This method is used for wastewater samples originating from states that do not approve the IC for wastewater samples. This method is applicable for nitrite levels of 0.01 - 0.75 ppm and nitrate levels of 0.02 -2.5.0 ppm. Samples with nitrite levels in excess of 0.750 ppm and/or nitrate levels in excess of 2.50 ppm require sample dilution prior to analysis.

I. Summary of Method

A. Nitrate in a sample is reduced to nitrite by passage through a cadmium column in an alkaline environment. The resulting nitrite is combined with a sulfanilamide color reagent, which produces a strong pink color. The intensity of the pink color is proportional to the amount of nitrite in the sample.

B. To determine the amount of Nitrate in the sample it is necessary to subtract concentration of ambient nitrite from the concentration of transformed nitrite.
NO_3 = (NO_2 after Cd) – (NO_2 before Cd)

C. All samples that require a nitrate result require analysis of nitrite as well, regardless of whether or not it is requested by the client.

II. Sample Collection, Preservation and Storage

A. Samples are collected in clean plastic or glass containers.

B. Samples are not preserved and need to be analyzed within 48 hours from time of collection. If the Nitrite analysis is completed within the 48-hr hold time, the sample may be preserved with sulfuric acid and stored for up to 28 days at 4°C prior to completion of nitrate analysis.

C. Samples that are preserved with sulfuric acid cannot be used to test for nitrite. Furthermore, if there is no nitrite result to be subtracted form the "NO_2 after Cd" result, then no determination can be made as to how much of the "NO_2 after Cd" result was present as NO_2 initially. The best the lab can do to accommodate these clients is to report the combined result of nitrate and nitrite in a sample; that is, to report the "NO_2 after Cd" result or the "NO_2NO_3" result.

III. Interferences

A. Oxidizing agents such as Residual Chlorine may interfere by oxidizing the cadmium column. Remove residual chlorine by adding Sodium Thiosulfate ($Na_2S_2O_3$) solution.

B. EDTA is added to the buffer to reduce the negative interference of high concentrations of iron, copper, and other metals.

C. Samples that contain high concentrations of oil and grease can coat the surface of the cadmium, reducing its reducing capabilities. Extracting oils from the sample using an organic solvent prior to analysis can eliminate this interference.

D. As with all colorimetric analysis, turbidity or suspended matter can be an interference. Remove by filtering sample through 0.45um pore diameter membrane filter prior to analysis.

IV. Equipment and Supplies

A. Lachat QuikChem 8500 with both Nitrite and Nitrate Manifolds.

B. Cadmium column, Lachat Part #50237.

C. Refer to Lachat SOP #302 for consummables.

V. Reagents and Standards

A. Sodium Hydroxide, 6N. Borrowed from ammonia or phosphate method. Since we do not use a lot of this reagent, it is not worth having a sequestered reagent solely for the preparation of Ammonium Chloride Buffer for Nitrate analysis. (NOTE: When preparing 6N NaOH, decant some from the liter bottle into a separate receptacle. This will reduce the risk cross-contamination between analyses).

B. Ammonium Chloride Buffer. Into a 2-Liter volumetric flask, dissolve 170g Ammonium Chloride and 2.0g EDTA in about 1 liter DI water. Bring up to volume with DI water. Adjust the pH to 8.50+/-0.05 w/ 6N NaOH using a pH meter.
When adjusting pH of the buffer, use a separate receptacle to hold the buffer as the pH is taken. To reduce risk of contamination of the buffer from the pH probe, do not immerse the probe directly into the 2 liters of buffer.

C. Sulfanilamide Color Reagent. (NOTE: This reagent is good for both NO_2/NO_3 and NO_2.) Into a 1-Liter volumetric flask, dissolve 40g Sulfanilamide and 2.0g NED (N-(1-naphthyl)ethylenediamine dihydrochloride) in around 500mL DI water containing 100mL Phosphoric acid. Bring up to volume with DI water. Store in a dark bottle at 4°C. Prepare fresh monthly.

D. Nitrite Stock Solution, 1000ppm. RICCA Catalog # 5445-16 or equivalent.

E. Nitrite Standard Solution, 10ppm. Dilute 32.84mL Nitrite Stock Solution to 1 liter with DI water. Prepare fresh as needed, up to 3 months.

F. Nitrate Stock Solution, 1000ppm. RICCA Catalog # 5307-16 or equivalent.

G. Nitrate Standard Solution, 10ppm. Dilute 44.25mL Nitrate Stock Solution to 1 liter with DI water. Prepare fresh as needed, up to 6 months.

H. Nitrite LCS Stock Solution, 1000ppm, Environmental Express Cat # IC-N-M.

I. Nitrite Working LCS, 0.25ppm, 0.205mL of Nitrite Stock LCS into 250mL DI.

J. Nitrate LCS Stock Solution, 1000ppm, Environmental Express Cat # IC-NO-M.

K. Nitrate Working LCS, 1.00ppm, 1.106mL of Nitrate Stock LCS into 250mL DI.

L. **NOTE:** The Nitrite and Nitrate Working Standards in this SOP can be combined together along with the Chloride Working Standards of SOP 346 and the ortho-Phosphate Working Standards of SOP 355 to form a set of "4-point" Working Standards.

Nitrite Working Standards A-F. Prepare fresh as needed, at least monthly.

A. Dilute 25mL Nitrite Standard Solution to 500mL with DI water; t.v.= 0.50ppm
B. Dilute 17.5mL Nitrite Standard Solution to 500mL with DI water; t.v.=0.35ppm
C. Dilute 12.5mL Nitrite Standard Solution to 500mL with DI water; t.v.= 0.25ppm
D. Dilute 5.0mL Nitrite Standard Solution to 500mL with DI water; t.v.= 0.10ppm
E. Dilute 2.5mL Nitrite Standard Solution to 500mL with DI water; t.v.= 0.05ppm
F. Dilute 50mL of Nitrite Working Standard "D" to 500mL with DI water; t.v.= 0.01ppm

Nitrate Working Standards A-F. Prepare fresh as needed, at least monthly.

A. Dilute 75mL Nitrate Standard Solution to 500mL with DI water; t.v.= 1.50ppm
B. Dilute 50mL Nitrate Standard Solution to 500mL with DI water; t.v.= 1.00ppm
C. Dilute 25mL Nitrate Standard Solution to 500mL with DI water; t.v.= 0.50ppm
D. Dilute 5.0mL Nitrate Standard Solution to 500mL with DI water; t.v.= 0.10ppm
E. Dilute 2.5mL Nitrate Standard Solution to 500mL with DI water; t.v.= 0.05ppm
F. Dilute 50mL of Nitrate Working Standard "D" to 500mL with DI water; t.v.= 0.01ppm

M. Carrier is DI water.

VI. Procedure

A. Refer to SOP #302 on use of the Lachat QuickChem 8500 for general information on the operation of the instrument. This method includes information unique to the nitrite and nitrate chemistries.

B. Attach manifold for Nitrite chemistry.

C. Attach manifold for Nitrate chemistry. (NOTE: Be sure to keep the Cadmium column closed until buffer is running through the lines. Efficiency of the reducing capacity of the cadmium reduces as it is exposed to air. Once the reagents are flowing through the manifold to the waste line, it is safe to open the column by turning the dial next to the Cd column on the manifold).

D. At this time, make a visual assessment of the Cadmium column. Check for air bubbles, lines, gaps in the column or any change in the cadmium surface characteristics (Cd granules should appear dark gray). If air bubbles cannot be dislodged by ramping the pump speed and tapping on the column, then the column needs to be replaced with a new one. Keep at least two prepared columns on hand at any time. See the QC section for assessing the efficiency of the column.

E. Load background.

F. Create a worksheet for the samples to be analyzed, including all QC requirements. The two standards for the cadmium column efficiency check (see IV.E.) should be the first two samples on each run (The column efficiency needs to be >90% to pass). Check standards will be

included automatically after 10 samples. They must pass within 90-110% of true value, otherwise the system recognizes the error and stops automatically.

G. Start standards and samples.

H. If the correlation coefficient is at least 0.9975 and the RPD values are at 10% or less, the calibration passes. It may be necessary to remake standards.

I. After samples have been analyzed, any dilutions needed have been run, and all QC criteria have been met, print out calibration statistics, and staple them along with the chart records to the sample report. Highlight all reported results on the report sheet. Leave the run on the WetChem supervisor's desk for review.

J. Close the Cd column.

K. Run DI water through the manifolds for 10 minutes to wash out any chemicals that might dry, encrust the tubing and cause blockages the next time. Remove all the tubes from the DI water and dry out the tubes by allowing the pump to run for an additional 10 minutes.

VII. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.

B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.

C. Calibration standard- A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate instrument response with respect to analyte concentration.

D. Matrix Spike (MS)- An aliquot of environmental sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

VIII. Calculations

A. Calculating Nitrate:
It is necessary to subtract the result from Nitrite analysis (done separately) from the result off the Lachat (NO_2+NO_3) to get a value for Nitrate.

$NO_3 = (NO_2NO_3) - (NO_2)$

Where: NO_3 = final result for Nitrate as N, ppm
NO_2NO_3 = result from Lachat, ppm
NO_2 = result from Lachat, ppm

NOTE: Do not subtract negative NO2 values. Only positive NO2 values are subtracted.

B. Calculating RPD:
The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$\text{RPD, \%} = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

C. Calculating the sample spike recovery:
The sample spike is a test if the sample matrix is suitable for accurate testing. To calculate the % recovery, first calculate both the sample and the spiked sample. Then apply the two results to the following calculation:

$$\text{\% Recovery, \%} = \frac{(SR - R)}{STV} \times 100$$

where: SR = value of sample with added spike, mg/L
R = value of sample, mg/L
STV = true value of spike added to sample, mg/L

D. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the value of the LCS sample, and then apply it to the following calculation:

$$\text{\% Recovery, \%} = \frac{(RL)}{(LTV)} \times 100$$

where: RL = value for LCS sample, mg/L
LTV = true value of LCS, mg/L

IX. Quality Control

A. Prep Blank must be analyzed every batch of 20 or fewer samples. This is a DI water aliquot treated like a sample, undergoing all treatments the samples undergo. The prep blank must yield levels of nitrite and nitrate below the reporting level. The minimum detectable limit is 0.01mg/L for both nitrite and nitrate.

B. Laboratory Control Standards must be analyzed every batch of 20 or fewer samples. This standard comes from RICCA (or equivalent second source) and has a certified value. It must be recovered 90-110%. A failing LCS for a batch of samples requires re-analysis of the batch.

C. Continuing calibration checks must be analyzed every 10 samples, as is written into the software of the Lachat QuickChem 8000. They must pass within 90-110%. The calibration check for both nitrite and nitrate is the C standard from the calibration curves.

D. A Cadmium column efficiency check must be analyzed at the beginning of the run. Run a second source, 0.5 ppm Nitrate only standard through the column. Run a second source, 0.5 ppm Nitrite only standard through the column. The column efficiency is determined by this calculation: $\frac{\text{Nitrate peak Area}}{\text{Nitrite peak Area}} \times 100 = \%\ \text{Efficiency}$

The acceptable limits for this standard is +/-10%. If the % Efficiency result is outside of this range, the column must be repacked or replaced.

E. Sample replicates must be done every batch of 20 or fewer samples. They must have a RPD of no more than 20%.

F. Sample spikes must be done every batch of 10 or fewer samples. A known amount of nitrate is added to a sample to test the sample matrix. The spike need be recovered 90-110%, however, if recoveries fall outside of this range, and the LCS and Blank spike are acceptable, it is judged to be sample related and not system related. Report % recovery.

G. MDL studies are performed quarterly or when a different analyst is performing the analysis. Two replicates of a 0.05 mg/L standard are analyzed for both nitrite and nitrate.

H. A Limit of Detection (LOD) study must be analyzed annually. All sample processing steps of the analytical method shall be included in the determination of the LOD. The LOD study is achieved by analyzing a standard at no more than 2-3x the LOD. In many cases, a 1:1 dilution of the lowest calibration standard is prepared and analyzed. LOD recoveries must be 50 – 150%.

I. 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.

J. An initial demonstration of capability (IDOC) must be performed to prove the generation of acceptable data with regard to accuracy and precision. An initial demonstration must be performed by each analyst and consists of analyzing 4 LCS solutions, usually over a series of days.

K. Standards preparations are documented in the Standards Prep Logbook.

L. Reagent preparations are documented in the Nitrate/Nitrite Reagent Prep Logbook.

M. Lachat use and maintenance is documented in the Lachat Maintenance Logbook.

X. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.

B. Always wear safety glasses for eye protection as well as lab coats.
C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

XI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
B. Standards should be purchased in volumes consistant with laboratory use to minimize the volume of expired standards to be disposed.

XII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

XIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, semiannual proficiency tests, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates.
B. See section IX Quality Control in this SOP for acceptable limits.

XIV. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the calibration curve have a correlation coefficient of <0.9975, remake and reanalyze curve before processing samples.
B. Should the preparation blank, LCS or inhouse standard fail acceptance criteria, do not proceed. Find problem and reanalyze. All samples must be bracketed by passing Cal checks.
C. Should the matrix spike or sample duplicate analysis fail acceptance criteria, a non-conformance report must be generated or the sample QC must be reanalyzed.

XV. References

A. Nitrate by Automated Cadmium Reduction, Method 353.2, Methods for the Chemical Analysis of Water and Wastes, EPA 600 Series, Revision 2, 1993.
B. Nitrate Nitrogen by Automated Cadmium Reduction, Method 4500-NO3 F, Standard Methods for the Examination of Water and Wastewater, 22nd edition, 2000.
C. Nitrate/Nitrite Analysis, Method 10-107-04-1-C, Lachat Instruments QuikChem 8000, July 1995.
D. Nitrite Analysis, Method 10-107-05-1-O, Lachat Instruments QuikChem 8000, July 1995.

Revision History Log for SOP # 336

Date:	Revision #:	Summary of Changes:	Submitted By:	Approved By:	Effective Date:
2/12/15	3.1	Scope= new curve ranges, added new sections out of Summary, Sec. V.H adjusted A Std to reflect new range, added Sections VII, X – XIV, took Cd Column efficiency calc out of Sec. VIII, added D, H, I, J to Sec. IX, updated SM Reference in Sec. XV.	Kathy Cressia	Eric Geyer	2/12/15
5/10/17	3.2	Sec VIII.A- added "NOTE" to calculation, sec IX.D- updated Cd column efficiency check and added calculation, Sec IX.F- changed MS frequency to 10%, Sec XV.A- updated method revision and year	Kathy Cressia	Eric Geyer	5/10/17
6/9/17	3.3	Section IX.D- updated calculation based on area, section V.D, F, H-K- new sources of stock solution and second source	Eric Geyer	Kathy Cressia	6/9/17
7/26/22	3.4	Section V.C- Corrected amount of NED used. Section V.E and V.G- Updated amounts of stock solution used. Section V.L- Updated calibration standard concentrations. Section IX.G- Updated MDL procedure.	Linnea Skoglund	Eric Geyer	7/26/22

Expiration Date

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Effective Date: 01/12/25
Version No.: 2.2
Initiated By:
Approved By:

SOP No: 360.PCT

Title: PC Titrator for pH, Alkalinity, Conductivity & Turbidity

Scope and Applications:

pH: This method covers the electrometric determination of the pH of samples. Corrosivity is then determined as a function of the pH of a sample. The range of this method is from 0 to 14 pH units. A sample is deemed "corrosive" if its pH is less than 2.00 or greater than 12.50 pH units. Ideally, the pH is determined in the field by the sampler because the holding time is 'immediate'. Samples received in the lab should be analyzed as soon as possible, before the sample is submitted to the sample storage refrigerators by the sample receipt department. All pH samples analyzed in the laboratory are flagged as past holding time.

Turbidity: Turbidity is a measure of water's clarity and is important in producing products destined for human consumption. This method covers the determination of a sample's turbidity in the range of 0 to 40 NTU. Samples that have a turbidity of greater than 40 NTU require sample dilution prior to analysis. This method is suitable for any water that is free of debris and rapidly settling coarse sediment. Samples should be stored at 4°C prior to analysis and analyzed within 48 hours from the time of sampling.

Conductivity: This method is applicable to the measurement of conductivity in drinking, surface, and saline waters, domestic and industrial wastes. This method is suitable for samples with conductivity values of 5.0 to 10000*u*mhos/cm. Samples with conductivity values of greater than 10000*u*mhos/cm may be diluted prior to analysis. Resistance may be determined from the conductivity result, as follows: 1/C = R; where C = conductivity (*u*mhos/cm), and R = resistivity (Mohm/cm).

Alkalinity: This method covers the determination of alkalinity in drinking, surface, and saline waters, domestic and industrial wastes. This method is suitable for samples with alkalinity values between 5.0 mg/L to 2000 mg/L. Samples with an alkalinity greater than 2000 mg $CaCO_3$/L need to be run by-hand using a stronger titrant.

I. Summary of Methods:

A. This method covers the operation and maintenance of the PC Titrator auto-analyzer which measures for 4 analytes: pH (electrode), Alkalinity (titration), Conductivity (electrode) and Turbidity (nephelometric).

pH: The pH of the sample is determined electrometrically using a combination electrode. The pH meter is calibrated before each use using a series of standard solutions of known pH.

Turbidity: A turbidimeter is used to quantify the amount of light that is scattered as it is passed through a sample.

Conductivity: Conductivity is the numerical expression of the ability of an aqueous solution to carry an electric current. The conductivity is measured by use of a conductivity meter (wheatstone bridge).

Alkalinity: The Alkalinity of a sample represents the acid-neutralizing capacity of a sample. Strong acid is added to the sample until it reaches a designated pH. The amount of acid added is a function of the alkalinity of the sample.

II. Interferences:

pH:

A. Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gently wiping or detergent washing, followed by rinsing with DI water. An additional treatment with 1:10 HCl may be necessary to remove any remaining film.

B. Temperature effects the electrometric determination of pH. It is important to analyze standards and samples at the same temperature or use an automatic temperature compensation (ATC) probe if the temperatures are different.

Turbidity:

A. Dirty glassware and the presence of air bubbles are positive interferences, both of which can be avoided. Be sure all glassware is

free of scratches, smears from fingerprints, and stray dust. Discard any scratched or otherwise permanently marred piece of glassware.

B. True color, i.e., water color due to dissolved substances that absorb light, causes measured turbidities to be low. This effect is usually not significant in treated water.

Conductivity:

A. Because conductivity is a function of temperature, samples are analyzed at a standard 25°C. Remove samples from refrigerator and allow warming to room temperature before analysis.

Alkalinity:

A. Dissolved gases may be lost or gained during sample storage, and can add to or reduce the alkalinity of a sample. Minimize this interference by titrating promptly, by avoiding vigorous shaking, and by keeping the sample at a constant temperature.

III. Sample Collection, Preservation and Holding Times:

pH:

A. pH is a field parameter and should be analzyed immediately after sampling. Samples analyzed for pH in the laboratory must be flagged as analyzed past holding time.

B. Collect sample in a clean plastic or glass bottle with no preservative.

Turbidity:

A. Collect sample in a clean plastic or glass bottle with no preservative and stored at 4°C until time of analysis.

B. The holding time for Turbidity is 48 hours from time of collection.

Conductivity:

A. Collect sample in a clean plastic or glass bottle with no preservative and stored at 4°C until time of analysis.

B. The holding time for Conductivity is 28 days from time of collection.

Alkalinity:

A. Samples should be collected in a separate plastic 100mL container with no headspace. They must be unpreserved and stored at 4°C until time of analysis. Samples with Headspace should be documented as such on the sequence sheet.
B. Samples must be analyzed within 14 days of collection.

IV. Equipment and Supplies:

A. Man-Tech PC-Titration Analyzer with Autosampler; Cat. No. PC-1000-102.
B. 50mL Conical Vials; Environmental Express Cat. No. SC461 (or equivalent).

V. Reagents and Standards:

A. Primary Standard Buffer, 4.00 pH units; RICCA # IBF-040-L (or equivalent).
B. Primary Standard Buffer, 7.00 pH units; RICCA # IBF-070-L (or equivalent).
C. Primary Standard Buffer, 10.00 pH units; RICCA # IBF100-L (or equivalent).
D. 1412 µmhos/cm Potassium Chloride Conductivity Standard, Ricca Cat. No. 5890-1 (or equivalent).
E. NIST Traceable Conductivity Standard, 10.0*u*mhos/cm at 25°C. RICCA P/N 2236-16 (or equivalent).
F. NIST Traceable Conductivity Standard, 100*u*mhos/cm at 25°C. RICCA P/N 2237-16 (or equivalent).
G. NIST Traceable Conductivity Standard, 1000*u*mhos/cm at 25°C. RICCA P/N 2243-16 (or equivalent).
H. NIST Traceable Conductivity Standard, 10000*u*mhos/cm at 25°C. VWR Cat.#23226-625 (or equivalent).
I. NIST Traceable Conductivity LCS, 100*u*mhos/cm at 25°C. VWR Cat.#23226-589 (or equivalent second source).
J. 100 NTU Turbidity Standard; Man-Tech Cat. No. PC-1000-164 (or equivalent).
K. 0.02N H_2SO_4 Alkalinity Titrant: In a 2-Liter volumetric flask containing approximately 1500mL DI water, add 1.12mL concentrated H_2SO_4 and bring up to volume with DI water. **Carefully** invert to mix. To standardize the titrant:

1. Pipet 10.0 mL Sodium carbonate solution into a rinsed 125mL Erlenmeyer flask.
2. With a calibrated pH meter, titrate with 0.02N H2SO4 titrant to a pH of 4.5.
3. Record volume of titrant used.
4. Repeat procedure using only DI water (50 mL). One drop of titrant should be required to reach the endpoint on this blank DI water sample.
5. Calculate the normality of the titrant. If the result is not 0.02N remake the titrant.

L. 0.02N NaOH: In a 1-Liter volumetric flask containing approximately 500mL DI water, add 2.0mL 10N NaOH (VWR Cat. No. JT5674-2 or equivalent) and bring up to volume with DI water. **Carefully** invert to mix.

M. LCS Solution (pH, Conductivity and Alkalinity)- Ultra Minerals # QCI-710 or equivalent.

N. LCS Stock Solution (Turbidity)- Amco Clear Turbidity Standard 40 NTU #8017 or equivalent.

O. LCS Working Solution: 100mL LCS Stock Solution into 1L DI Water.

VI. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.

B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.

C. Calibration standard- A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate instrument response with respect to analyte concentration.

D. Sample Replicates (Rep)- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of the sample and duplicate indicate precision associated with laboratory procedures.

VII. Procedure:

A. Daily Maintenance

1. Prior to running calibrations and samples the instrument must go through a daily maintenance check to ensure accurate results.
2. The pH probe must be rinsed with deionized water, wiped with a kimwipe, and filled with pH fill solution.
3. The conductivity probe must be taken out of the holder, rinsed with deionized water, and gently wiped with a kimwipe on the outside only. NOTE: **DO NOT** wipe the black sensors on the inside of the probe as this will adversely affect the probes performance.
4. Rinse and wipe the metal turbidity sample tube. Check the plastic tubing that goes from the metal turbidity sample tube to the turbidimeter for anything that might affect the result. This tubing should be changed on a monthly basis or earlier if needed.
5. Fill the DI water reservoir at the back of the instrument to the "fill" line and also empty the two waste containers (check the pH of the waste, if it is neutral then it can be poured down the sink. If the waste is either acidic or alkaline then dispose of the waste in the appropriate satellite container.)
6. Fill the Alkalinity titrant bottle with 0.02N H_2SO_4 titrant.

B. Calibration

pH Calibration

1. The pH calibration is done daily. First, click the PC Titrator icon  on the desktop to open the software. Next, select "Run Titration" from the drop-down menu under the Titration tab (see Figure 4).
2. When the "Run Titration" screen opens, click on the "Add x Rows" button and type in the number of rows needed. For the pH calibration, normally 4 rows are added.
3. Double click on the "Schedule" box for Row1.
4. When the "Schedule Search Form" window opens select **pH only** from the "Available Selections" list and click "OK".
5. Repeat the last step for Rows 2, 4, & 5. Row 3 is similar except **pH calibration** is selected from the "Available Selections" list.
6. Next, click on the "Auto-Generate Order Number" button. The software will automatically assign an Order Number to the run, which is put in the "Order Number" box for row 1.
7. Click on & drag the order number until the entire column is full.
8. Type in a description of each sample in the "Sample Name" column. The first two rows are Blanks, the third row is the "pH

Calibration", the fourth row is a LCS, and the last row is a "pH 7.00" calibration check.

9. Under the Vial column, type in "1" for row 1, "2" for row 2, "3" for row 3, "6" for row 4 (the pH cal for line 3 needs 3 vials), "7" for the last row. The pH timetable should mimic that in Figure 7.
10. Next, pour 45mL of deionized water into a conical 50mL Vial for each of the two BLANKS. Place the 2 vials into the tray holes marked 1 & 2.
11. Pour 45mL of a pH 4.00 buffer into a vial and place vial into hole #3.
12. Pour 45mL of a pH 7.00 buffer into a vial and place vial into hole #4.
13. Pour 45mL of a pH 10.00 buffer into a vial and place vial into hole #5.
14. Pour 45mL of LCS into a vial and place vial into hole #6.
15. Pour 45mL of a pH 7.00 buffer into a vial and place vial into hole #7.
16. Once the vials are all in the tray click the green "Start" button (Figure 7.) to start the calibration.
17. Once the calibration is complete, the system will verbally notify you whether the calibration passed or failed.
18. Print out the passing calibration and include a copy with the data report.

Turbidity Calibration

The Turbidity calibration is done for any of the following: new standards, new tubing, new turbidity lamp, or calibration standards fail to meet QA/QC requirements.

1. First, click the PC Titrator icon  on the desktop to open the software. Next, select "Run Titration" from the drop-down menu under the Titration tab (see Figure 4).
2. When the "Run Titration" screen opens, click on the "Add x Rows" button and type in the number of rows needed. For the turbidity calibration, normally 5 rows are added.
3. Double click on the "Schedule" box for Row1.
4. When the "Schedule Search Form" window opens select TURBIDITY from the "Available Selections" list and click "OK".
5. Repeat the last step for Rows 2, 4-6. Row 3 is similar except Turbidity Calibration is selected from the "Available Selections" list.

6. Next, click on the "Auto-Generate Order Number" button. The software will automatically assign an Order Number to the run, which is put in the "Order Number" box for row 1.
7. Click on & drag the order number until the entire column is full.
8. Type in a description of each sample in the "Sample Name" column. The first two rows are Blanks, the third row is the "Turb Cal", the fourth row is a LCS, the fifth row is a "2.0 NTU Std" and the last row is a "Blank".
9. Under the Vial column, type in "1" for row 1, "2" for row 2, "3" for row 3, "**11**" for row 4 (the Turbidity cal for line 3 needs 8 vials), "12" for the fifth row & "13" for the last row. The turidity timetable should mimic that in Figure 8.
10. Next, pour 45mL of deionized water into a conical 50mL Vial for each of the two BLANKS. Place the 2 vials into the tray holes marked 1 & 2.
11. Pour 45mL of deionized water (0.02 NTU Std) into a vial and place into hole #3.
12. Pour 45mL of 0.20 NTU Standard into a vial and place vial into hole #4.
13. Pour 45mL of 0.50 NTU Standard into a vial and place vial into hole #5.
14. Pour 45mL of 1.00 NTU Standard into a vial and place vial into hole #6.
15. Pour 45mL of 2.00 NTU Standard into a vial and place vial into hole #7.
16. Pour 45mL of 5.00 NTU Standard into a vial and place vial into hole #8.
17. Pour 45mL of 10.0 NTU Standard into a vial and place vial into hole #9.
18. Pour 45mL of 50 NTU Standard into a vial and place vial into hole #10.
19. Pour 45mL of LCS into a vial and place vial into hole #11.
20. Pour 45mL of 2.0 NTU Std into a vial and place vial into hole #12.
21. Pour 45mL of deionized water (Blank) into a vial and place into hole #13.
22. Once the vials are all in the tray click the green "Start" button (Figure 8) to start the calibration.
23. The calibration is a point-to-point calibration and has no pass/fail criteria. However, should any of the calibration equations have a negative slope then the calibration must be rerun.

24. Print out the calibration and include a copy with every relevant data report.

Conductivity Calibration

The Conductivity calibration is done when QA/QC samples fail to meet acceptable criteria or when a new standard is opened.

1. First, pour a fresh aliquot of 1412 µmhos/cm conductivity standard into a 50mL conical vial.
2. Immerse the conductivity probe into the vial containing the 1412 standard until a stable reading is achieved.
3. Press the "CAL/CLR" button twice on the Mantech 4510 Conductivity Meter.
4. Check at least one other conductivity standard to ensure the calibration is valid.
5. If the calibration is not valid repeat steps 1-4.

C. Building a Sequence

1. To build a sequence for the PC Titrator open up the Phoenix LIMS program, select "QA/QC Batching" from the Main Menu, and "PCT Sequence File" from the right-hand list (see Figure 1).
2. The LIMS program will automatically list all pending non-soil samples from the WET3 & WET6 backlogs that require pH, turbidity, alkalinity, & conductivity (see Figure 2). The analyst has the choice of analyzing *just* the samples from WET3, *just* the samples from WET6, or the samples from *both* backlogs.
3. At this point any sample that is deemed "too dirty" to run on the PC Titrator can be unselected from the list and the necessary analysis can be completed using other approved methods.
4. To select a sample replicate simply click on a line that is designated "Rep-19" (19 is just an example as shown in Figure 2. The number will change to whatever vial number it is) and select a sample from the drop-down list. A replicate sample will be listed every tenth sample.
5. At this point click the "Build Sequence File" button at the bottom of the window. The file will be saved as the date (ie. 03-03-09A.txt) in the folder **P:/PCT**. When the new window opens and asks "Generate PCT Sequence File?" click "YES" and then "OK".

6. Before proceeding, ensure that the correct LCS lot numbers and true values are entered in the "LCS TV" tab (see Figure 3). These values are used to automatically calculate the percent recoveries during the data entry procedure.

D. Importing the Sequence

1. First, click the PC Titrator icon on the desktop to open the software. Next, select "Run Titration" from the drop-down menu under the Titration tab (see Figure 4).
2. Click on the "Load from Text File" button (see Figure 5), select the file you wish to import (ie. 03-03-09A.txt) and click "Open".
3. If a dilution is needed you must click on the Phoenix sample ID (ie. AR33245) and place a "space", dilution factor, & "x" after the sample ID (ie. AR33245 10x) so that the automatic data transfer program will calculate the correct result.
4. Once the sequence is ready to run, click the "Print Existing Timetable" button (see Figure 5). When the new window opens up (Figure 6) click the "Printer" option in the "Destination" box and then click the "Print" button. Press "Done" after the timetable prints out.

E. Loading the Sample Trays

1. Using the sequence timetable printout as a guide, pour the samples, blanks & QC samples into 50mL conical vials (up to the 45mL mark) and place the filled vials into the corresponding holes of the 122-position sample tray.

NOTE: Vial positions 121 & 122 are always reserved for turbidity cleaning solution & pH 4 buffer (to store probe) respectively.

2. If more than 120 vials are needed then the sequence will repeat starting again at vial position 1. The analyst must wait for the first set of duplicated vial numbers to finish being analyzed before replacing them with the second set.
3. Once the samples have been poured the instrument can be started simply by clicking the green "Start' button (see Figure 5).

F. Data Entry

Upon completing the samples, the instrument will automatically print out the data (Water Quality Report) at the defaulted printer.

Check the printout to ensure all QC parameters are met as defined in the QA/QC section of this SOP. If all the data passes the QA/QC requirements it can be entered using the Phoenix LIMS program:

1. First, double-click the "Copy PCT Data to Server" icon on the desktop of the Titrator computer. This will send the data to the server so it can be reviewed and entered.
2. From the LIMS Main Menu click the "Data Transfer" → "PCT Data Transfer" option (see Figure 9) to open up the data entry screen.
3. Select the file you are transferring. Generally, it is the very last file in the folder.
4. When the data file opens up the file will display the results with a checkmark in the "S" column for all pending analysis (unchecked boxes mean the sample is either already entered in Labworks or it is an unreportable QC sample). If a result is not needed, for any reason, uncheck the box.
5. Once all the data has been closely looked over & all the appropriate boxes have been checked, the analyst enters their initials in the space provided at the bottom of the screen and clicks the "Transfer Results to Labworks" button.
6. Click the "Print" button at the bottom left of the screen to print the results.
7. The Final Report will consist of the Run List, Sequence List, Calibrations, Raw Data (Water Analysis Report), & the Data Transfer Log. The completed report will then be put on the Wetlab Supervisor's desk for review.

VIII. Calculations

A. Multiply sample result by dilution factor where applicable.

B. Calculating RPD:
The RPD is the relative percent difference and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$\text{RPD, \%} = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

C. Calculating the LCS:

The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the LCS sample, and then apply it to the following calculation:

$$\% \text{ Recovery}, \% = \frac{(RL)}{(LTV)} \times 100$$

where: RL = achieved value for LCS sample, mg/L
LTV = true value of LCS, mg/L

IV. Quality Control

A. All reagents and standards are to be labeled with the following information: date prepared, date expires, preparer's initials, analyte, contents, and concentration of contents. Record preparation of all reagents in the reagent prep logbook.
B. The primary pH buffers and calibration standards are poured fresh at each calibration.
C. A sample prep blank of dilution water must be analyzed with each batch of twenty or fewer samples, as well as at the end of every run. Prep blanks must be determined to be BRL (below reporting level).
D. A bought standard (LCS) is run with each batch of twenty or fewer samples. The acceptable recovery of a LCS is 85-115%.
E. Sample replicates are analyzed every 10 of fewer samples. The RPD must be $\leq$20%, else repeat sample and duplicate analysis to prove matrix effect.

V. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these

compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.

B. Always wear safety glasses for eye protection as well as lab coats.

C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

VI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.

B. Standards should be purchased in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

VII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

VIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates.

B. See section IX Quality Control in this SOP for acceptable limits.

IX. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the preparation blank, LCS or in-house standard fail acceptance criteria, reanalyze batch.

B. Should the sample duplicate analysis fail acceptance criteria, a non-conformance report must be generated, or the sample QC must be reanalyzed.

X. References

A. Standard Methods for the Examination of Water and Wastewater, 22nd edition, Turbidity Method 2130B, Revised 2011.

B. Standard Methods for the Examination of Waste and Wastewater, 22nd edition, pH Method No. 4500-H^+ B, Revised 2011.

C. Standard Methods for the Examination of Waste and Wastewater, 22nd edition, Alkalinity Method No. 2320B, Revised 2011.

D. Standard Methods for the Examination of Water and Wastewater, 22nd edition, Conductivity Method 2510B, Revised 2011.

Revision History Log for SOP # 360

Date:	Revision #:	Summary of Changes:	Submitted By:	Approved By:	Effective Date:
3/7/18	2.1	Out of MDB, section V. A, B, C- new supplier and part numbers, V.O- new dilution for working solution, section VII.4- added metal to turbidity sample tube, section VII.B Calibration- Conductivity 1-5- new due to error in last SOP, section X- references updated per MUR	Kathy Cressia	Eric Geyer	3/7/18
1/12/25	2.2	Alkalinity scope- no dilutions, Section III. Alkalinity A. Headspace documentation added, Section V.K. 1-5 added standardization of titrant	Eric Geyer	Kathy Letourneau	1/12/25

Expiration Date

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Effective Date: 03/31/20
Version Number: 1.5
Initiated By: Kathleen Cressia
Approved By:

SOP No.: **506**

Title: Determination of Trace Elements by Inductive Coupled Argon Plasma (ICP) Spectroscopy

Scope: This procedure describes the determination of dissolved and total recoverable elements in ground water, drinking water, waste water, and air by ICP. This procedure is also applicable to total recoverable elements in sediment, sludges, biological tissue and solid waste samples. This procedure is the general ICP procedure, which covers the requirements of the SW-846 6010, EPA 200.5 and EPA 200.7 as approved in 40 CFR part 136 and 40 CFR part 141.

1.0 Summary

1.1 This procedure describes the simultaneous analyses of metals on the following elements (Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, P, K, Se, Ag, Au, Zr, Na, S, Sn, Sr, Ti, Tl, V, and Zn) by ICP. All samples are digested prior to analysis. For sample digestion information, refer to SOP #205, #219, #224, #231, #238 and #358.

1.2 When using EPA method 200.5 (Lead and Copper) all samples are digested and preconcentrated prior to analysis. Preconcentrating samples increases analytical sensitivity for meeting method detection limit (MDL) requirements. Therefore, when using this method, the need to measure sample turbidity prior the analysis is eliminated.

2.0 Sample Collection, Preservation and Storage

2.1 Samples can be collected in plastic, Teflon or glass. When using EPA method 200.5 it is recommended that only plastic or PTFE should be used to eliminate the possibility of contamination of boron or silica. They must be preserved with HNO_3 to a pH < 2. They must be stored at 4°C until the time of analysis.

2.2 Samples have a holding time of 6 months.

2.3 Digestions holding time is 180 days.

2.4 ICP analysis is performed on sample digests only.

3.0 Interferences

3.1 Spectral interferences are minimized by the optimization of background points and the use of inter-element correction factors.
3.2 Physical interferences are associated with viscous samples and can be minimized by diluting the sample.
3.3 Memory interferences result when analytes from the previous sample contribute to a signal in the new sample.
3.4 An internal standard measured to increase the reproducibility of measurements of high concentrations or help correcting for samples with varying viscosities.

4.0 Equipment and Supplies

4.1 100 mL Volumetric Flasks
4.2 100 mL Graduated Cylinders
4.3 250 mL Beakers
4.4 1000, 500, and 250 mL Plastic Storage Bottles
4.5 20.0 L Nalgene Carboy
4.6 10 and 50 mL Polystyrene Disposable Beakers
4.7 Pipettes and Pipette Tips
4.8 10.0 mL Oxford
4.9 1 mL Eppendorf
4.10 0.1 mL Eppendorf
4.11 Pump Tubing (Cole-Palmer and Glass Expansion)
4.12 Argon Gas (Liquid)

5.0 Instrumentation

5.1 SPECTRO Model BLUE CCD ICP-EOP, Laboratory computer and printer; and ESI SC4DX Autosampler.
5.2 SPECTRO Model ARCOS CCD ICP-EOP, Laboratory computer and printer; and ESI SC-4DX Autosampler.
5.3 SPECTRO ARCOS II FHX22 ICP-OES, Laboratory computer and printer; and Elemental Scientific FAST 4DX Autosampler
5.2 Sample induction system consists of these major components: Modified Lichte High Solids Nebulizer, cyclonic spray chamber and torch.
5.3 Fiber Optics use as optical transfer devices.
5.4 Elemental Scientific oneFAST sample introduction system

6.0 Reagents and Standards

6.1 Argon Gas
6.2 Deionized water, ASTM Type or equivalent

6.3 Concentrated Hydrochloric Acid, Trace Metals Grade.

6.4 Concentrated Nitric Acid, Trace Metals Grade.

6.5 2.5% Nitric Acid (HNO_3) and 1% Hydrochloric Acid (HCL) - used in standards preparations. Prepare fresh daily. Fill 1000 mL volumetric flask half-full with DI water, add 25 mL concentrated HNO_3 and 10 mL concentrated HCL, dilute to 1000 mL with Di water. Use this solution in the preparation of all standards and dilutions of all samples.

6.6 Standards – Metal Plasma Grade Standards, assorted vendors

6.7 Calibration Verification (ICV), Calibration Verification Sample (CVS), and Interference check sample (ICS) standards are currently supplied by Inorganic Ventures and Environmental Express.

GENERAL PRECAUTIONS:

- Avoid contamination of Stock Standards. Always pour out a small volume of standard stock solution into a new beaker before taking an aliquot.
- Never insert a pipet directly into the bottle.

7.0 Definitions

7.1 Calibration Verification Standard (CVS) – A purchased standard of a known concentration that is from a different source than the calibration standards. The CVS is used to determine laboratory performance.

7.2 Preparation Blank (Prep Blank) – An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents, or glassware.

7.3 Calibration Standard – A solution prepared from the dilution of stock standard solutions. The Calibration solutions are used to calibrate instrument response with respect to analyte concentration.

7.4 Matrix Spike (MS) – An aliquot of environmental sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

7.5 Laboratory Control Sample (LCS) or Blank Spike- the LCS is analyzed exactly like a sample and uses the same source and concentration as the MS but added to a clean (control) matrix (DI water). For soils, it is a purchased soil matrix standard.

7.6 Maximum contaminant level (MCL) – the maximum permissible level of a contaminant in water which is delivered to any user of a public water system.

7.7 Linear Range (LR) – the concentration range over which the instrument response to an analyte is linear.

7.7 Limit of Quantitation (LOQ) -- the minimum levels, concentrations, or quantities of a target analyte that can be reported with a specified degree of confidence.

8.0 Procedure

8.1 Preparation of Standards

8.1.1 Blank (2.5% HNO_3 and 1% HCL) – 25 mL of trace metal grade nitric acid and 10 mL trace metal grade hydrochloric acid diluted to 1000 mL DI water.

8.1.2 CLP 1 + 3 – 10 mL of Environmental Express CLP-CAL-1 and 10 mL of Environmental Express CLP-CAL-3 diluted to 1000 mL with 2.5% HNO_3 and 1% HCL.

8.1.3 ICP High CAL STD (CRDL_S) -- 20 mL of Inorganic Ventures PEL STD 1A Rev1 + 20 mL of Inorganic Ventures PEL STD 2 to 1L with 2.5% HNO_3 and 1% HCL.

8.1.4 ICP CAL CHK (ICV) -- 10 mL of Inorganic Ventures PEL STD 1A Rev1 + 10 mL of Inorganic Ventures PEL STD 2 to 1L with 2.5% HNO_3 and 1% HCL.

8.1.5 CRQL – 10 mL of 1:100 PEL STD CRDL-1 and 10 mL of 1:100 PEL STD CRDL-2 diluted to 1000 mL of 2.5% HNO_3 and 1% HCL.

8.1.6 CRDL -- 50 mL of 1:100 PEL STD CRDL-1 and 50 mL of 1:100 PEL STD CRDL-2 diluted to 1000 mL of 2.5% HNO_3 and 1% HCL.

8.1.7 CVS – Second source- 10 mL of Absolute Standard 200.7/6010/200.5 Custom Mix (50692) diluted to 1000 mL with 2.5% HNO_3 and 1% HCL.

8.1.8 ICSA – 10 ml of 2007ICS-4 diluted to 1000 mL 2.5% HNO_3 and 1% HCL.

8.1.9 ICSAB – 10 mL of 2007ICS-4 + 1 mL of CGSB1-1 + 1 mL 2007 ICS-1 + 1 mL 2007 ICS-3 diluted to 1000 mL with 2.5% HNO_3 and 1% HCL.

8.1.10 All Standards are prepared and transferred to Teflon storage bottles and labeled.

8.1.11 Interference Check Standards: Cr, Mn, Ti, Zn (10.0 ppm) are prepared with 1.0 mL of a 1000 ppm stock standard from Environmental Express and diluted to 100 mL with 2.5% HNO_3 and 1% HCL. A 1.0 ppm standard of As is prepared with 0.1 mL of 1000 ppm stock from Environmental Express and diluted to 100 mL with 2.5% HNO_3 and 1% HCL. Other interfering check standards are Ca 200.0 ppm, Al 50.0 ppm, Fe 200.0 ppm, and Na 500.0 ppm.

8.1.12 Spiked Sample Analysis: Inorganic Ventures QCP-QCS-1 & 2 - The spike is added before the digestion. Take 0.5 mL of each spiking solution and add to the sample. The final volume is 50 mLs. When performing a post-digestion spike, take 0.08 mL of each QCP-QCS-1 and QCP-QCS-2 and bring up to 8.0 grams of sample. For soil matrix post digestion spike take 0.16 mL of each QCP-QCS-1 and QCP-QCS-2 and dilute to 8.0 grams of sample.

8.2 Tuning and Calibration of the ICP

8.2.1 Torch Maintenance - Open the Torch box and visually inspect the glass, and RF load coils for cleanliness and any oxidation. Check all connections – Drain hose, nebulizer cap, Argon lines, and cooling water.

8.2.2 Peristaltic Pump - Install new pump tubing if the old one shows signs of flattening or stretching and connect to the nebulizer with capillary tubing. Pump DI water and adjust pressure on tension arms to obtain a smooth flow.

8.3 Start-Up

8.3.1 Turn the main switch on the unit to "ON". Switch on the computer allowing the operating system to boot up.

8.3.2 Open ESI Software.

8.3.3 Start the unit software "Smart Analyzer Vision" after the operating system has been completely booted. Allow they unit to stabilize for at least 60 minutes after switching it on. Also make sure that the operating temperature (15°C) has been reached

8.3.4 On the Smart Analyzer Vision software select the Analysis view. Flush the sample introduction system with argon for approximately 5 minutes by clicking the "flush" button. The following conditions should be set:

Coolant: 13.4 L/min
Auxiliary: 0.70 L/min – 1.0 L/min
Nebulizer: 0.9 L/min

8.3.5 To ignite the plasma click on the "plasma" button.

8.3.5.1 The sample introduction system is automatically flushed with argon again at this point. In the status line "Plasma is starting" should be displayed. It takes about 2 minutes for the plasma to ignite.

8.3.6 Start the peristaltic pump by clicking the "pump" button

8.3.6.1 Allow rinse water (5% HNO_3+ 5% HCl) mixture to run through the system for 30 minutes to allow the unit to heat up and stabilize the components.

8.4 Optimization

8.4.1 Make sure the optical system is "ICAlized". The system needs to be "ICALized":

- After a software message (wavelength drift).
- After switching on the unit and temperature stabilization.
- In the event of changes concerning the sample induction system (torch or nebulizer changed).
- Before setting up a new method.
- Before carrying out high-precision measurements.

8.4.2 To perform an "ICALization"

8.4.2.1 After the plasma has been ignited and the system flushed and rinsed select the function "ICALization" in the "System" menu. Follow the instructions displayed by the software.

8.5 Measuring the Samples:

8.5.1 Perform the calibration using:

8.5.1.1 Blank (2.5% HNO3 and 1% HCL), CRQL, CRDL, IPC 1:10, IPC, CLP 1 + 3, and ICSA.

8.5.1.2 After completing the calibration a regression sheet is printed. The correlation coefficient should be no less than 0.9975 for each element.

8.5.1.3 To control the quality of results measure:

- Calibration verification standard (IPC 1+2) ± 5% for ICV
- CVS (second source) ± 10% (± 5% 200.7 DW & WW)
- CRQL (Quantitation limit standard)
- CRDL (Detection limit standard)
- ICB (Initial Calibration blank)
- Interference check standard- ICSA ± 20%
- Interference check standard- ICSAB ± 20%
- CRDL_S- High standard check
- IPC 1+2 (CCV) ± 10%
- CCB

8.5.2 Fill the autosampler trays with samples.

8.5.2.1 Sequence Generator

8.5.2.1.1 In the Phoenix LIMS program open the QA/QC Batching, ICP Sequence. Once the sequence page is open select the instrument you are running and press "new", click yes for the prompt to build a new sequence.

8.5.2.1.1.1 At this point you can manually type in the sample number you are running and select the matrix.

8.5.2.1.1.2 You can add a whole batch by clicking "Add Batch". Type in the whole batch (ex. TMD-SM-XXXXXX). Click add batch to sequence.

8.5.2.1.1.3 Once all the samples/batches have been added to the sequence click on "build sequence" click ok. Go to the software and paste into the tray position.

8.5.2.2 Analyze prep blank, blank spike, sample duplicate, sample spike and samples. Analyze calibration verification standard and calibration blank every 10 samples to ensure the calibration is still consistent.

8.5.3 EPA 200.5 samples

8.5.3.1 When analyzing preconcentrated drinking water samples, this method can only be used to report analysis on samples that fall into the requirements listed below.

8.5.3.1.1 Operative matrix effects can occur from elevated dissolved solids therefore when calcium (Ca) concentrations are greater than 125 mg/L or the combined concentrations of calcium (Ca), magnesium (Mg) sodium (Na) and Silica (Si) are greater than 250 mg/L and the primary contaminant concentration exceeds 80% of the established maximum contaminant level (MCL) or action level. If a sample exceeds these criteria the sample will then be analyzed using 200.7 or 200.9 (sample run on AA).

8.5.3.1.2 When determining Lead by 200.5 the instrument must be able to analyze silica as well. When the levels of silica exceed 30 mg/L (when preconcentrated 2X) a suppressive effect on the lead has been observed. For samples containing silica above 30 mg/L and lead concentrations >10 ug/L, lead must be determined by

another approved method. These samples would then be run using EPA method 200.9, and run by AA.

8.5.3.2 When determining Lead and Copper by 200.5, the following additional quality considerations must be met:

8.5.3.2.1 Any routine samples where the Lead and Copper concentrations are determined to be ≥80% of the established MCL or action level must be reanalyzed by another approved method if the required matrix spike analysis does not verify the absence of a matrix interference. (Pb @ ≥0.012 ppm, and Cu @ ≥1.04 ppm)

8.5.3.2.2 Prior to analyzing Lead and Copper by 200.5, the calibration standards must be verified by the analysis of 3 LCS samples, and their determined mean concentrations must be within ±5% of true value. Although a second source is analyzed daily, this procedure must be performed on an annual basis and after the preparation of stock or calibration standards.

8.6 Switching off the Instrument

8.6.1 Flush the sample introduction system for approximately 10 minutes with the rinse solution. This is to eliminate the potential for crystallization within the sample introduction system.

8.6.2 Select the analysis view. Switch off the plasma by clicking the "Plasma" button.

8.6.3 Exit the software.

8.6.4 Shut down the computer.

8.6.5 Switch of the exhaust and the coolant water.

8.6.6 Release the pressure clamps on the peristaltic pump and release the pump tubing.

8.6.7 To switch off the unit completely turn the main switch to "Off".

9.0 Calculations

9.1 Calculation of Lead in Air

$$C\ (\mu g/m^3) = \frac{C_s\ V_s}{V}$$

where:

C_s = lead in sample (µg/mL)
V_s = sample volume (mL)
V = air volume sampled (m^3)

10.0 Maintenance

10.1 Daily Checks

10.1.1 Clean OPI. Using DI water and a Q-Tip clean the face of the OPI.
10.1.2 Change Torch.
10.1.3 Check Elbow. Make sure the elbow has no water or condensation in it. Change the elbow if any water droplets are present.
10.1.4 Change peristaltic pump tubing.
10.1.5 Check all tubing and feed hoses. Change anything that is kinked, flattened, or stretched.
10.1.6 Make sure you have enough rinse water in the carboy.
10.1.7 Check discharge container: if more than ¾ full empty and replace.
10.1.8 Change all QC and Calibration standards.
10.1.9 Check peaks on all elements you are calibrating. Au, Zr, and S need to be checked also.
10.1.10 Check Sc counts during calibration and check the spray chamber to verify nebulizer flow. A drastic drop in Sc count could be a partially clogged nebulizer. Clean or replace the nebulizer if you suspect it to be clogged.

10.2 Weekly Checks

10.2.1 Inspect torches. Remove all torches that appear to have deposits or residue in aerosol tube. Torches with excessively pitted ends of the tube should also be removed.
10.2.2 Clean torches by soaking them in Aqua Regia (mix 1 part concentrated nitric acid and 3 parts concentrated hydrochloric acid.) After allowing the torches to soak to remove residue thoroughly rinse all torches with DI water and allow to dry. Once dry, cover the ends of the torch with Parafilm.
10.2.3 Clean elbows by running a small brush with soap through it and rinsing with hot tap water followed by a DI water rinse. Dry the elbows and cover the ends with Parafilm.
10.2.4 The spray chamber needs to be cleaned and rinsed. They spray chamber does not need to be dried. High levels of sodium can be rinsed out faster with DI water than with the normal rinse operation.
10.2.5 Chiller water levels should be checked weekly to ensure proper OPI cooling.

10.3 Monthly Checks

10.3.1 Inspect window for spotting or debris. Sudden drops in low intensity lines should warrant this check. Sb, Se, Pb, Cd and As are pretty good indicators.

10.3.2 All introduction tubing should also be changed. Torch tubing should be checked and replaced if it becomes too easy to remove from the torch. Nebulizer tubing should also be changed if it's stretched from over pressurization.

10.3.3 Filter media should be cleaned or replaced.

11.0 Trouble Shooting and Corrective Action

10.1 Problem: Stable plasma won't start.
Action: Check system for leaks.

10.2 Problem: Generator cannot be started.
Action: Check power supply (fuses, circuit breaker).

10.3 Problem: ARGON lamp is lit.
Action: Increase argon admission pressure, or replace argon supply if empty.

10.4 Problem: WATER lamp is lit.
Action: Check for and remove blockages (dirt, lime buildup) to the system.

10.5 Problem: Melting of the torch tubes.
Action: Re-adjust torch, remove and clean blockages in the aerosol tube, search for and repair leaks, increase auxiliary gas flow rate, check that exhaust is turned on.

10.6 Problem: Plasma does not ignite.
Action: Re-adjust torch, flush the system with argon by pressing <+> and <-> key wrong argon quality (purity >99.996%).

10.7 Problem: Plasma trembles or pulsates.
Action: Clean and dry torch the aerosol tube, increase power slightly, clean nebulizer.

10.8 Problem: Nebulizer gas flow too low.
Action: Clean nebulizer.

10.9 Problem: Sparking-over at the coil.
Action: Dry coil with tissue paper, clean any dirt, adjust torch (must not touch coil).

10.10 Problem: CV fails for an element.
Action: The instrument may need to be re-calibrated.

10.11 Problem: ICSA or ICSAB fails for an element.
Action: Check background points for that element.
**** SEE SECTION 18: TABLE I FOR MORE TROUBLESHOOTING INFORMATION**

12.0 Quality Control

12.1 Instrument Detection Limits (IDLs)- IDLs are useful means to evaluate instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. IDLs, in ug/L, can be estimated as the mean of the blank results plus three times the standard deviation of 10 replicate analysis of the reagent blank solution. Use zero for the mean if the mean in negative. IDLs must be determined once on new equipment, and after any major instrument maintenance.

12.2 Initial Demonstration of Capabilities (IDOC)- IDOCs are obtained by generating data of acceptable precision and bias for target analytes in a clean matrix. IDOCs are analyzed by each analyst and repeated when significant changes are made to the instrumentation. Continuing Demonstrations of Capabilities (CDOCs) are analyzed and collected annually for each analyst. This information is kept in the analysts training file.

12.3 Linear Range (LR)- The linear range establishes the highest concentration that may be reported without diluting the sample. Following calibration, the laboratory may choose to analyze a standard at a higher concentration than the high standard in the calibration. The standard must recover within 10% of the true value, and if successful, establishes the linear range. The linear range standards must be run daily in order to report to that concentration. If a linear range standard is not analyzed, the highest standard in the calibration becomes the linear range. Annually, the high standard is analyzed after calibration, where the recovery should be within 5% of true value.

12.4 Method Detection Limit (MDL) studies are established for each element per the guidelines established in 40 CFR part 136 Appendix B.

12.5 Sample QC for preparation and Analysis (Batch QC)-

12.5.1 Prep Blanks (PB) or Method Blank- For each batch of samples digested and analyzed, a prep blank must be carried throughout the entire process

to aid in identifying when and/or if sample contamination is occurring. The prep blank is considered acceptable if it does not contain any target analytes at concentrations above the reporting level. Blanks my contain analyte concentrations greater than acceptance limits if the associated samples in the batch are unaffected (i.e. targets are not present in the samples or sample concentrations are >10x the blank concentration). If the prep blank is associated with affected samples, the analyst must order a 're-prep' on the entire batch. Prep Blanks are matrix matched.

12.5.2 Laboratory Control Sample (LCS) or Blank Spike- One LCS is digested in every batch of samples, and consists of a clean matrix (DI water) spiked with the same analytical spike and concentration as the matrix spike (MS). When the results of the MS analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the analysis is acceptable in a clean matrix. The LCS acceptance criterion is ± 15%, except for EPA method 200.5, which is ± 10%. In the case of soil matrices, the LCS consists of a purchased spiked soil control sample and the recovery criteria is 75-125%.

12.5.3 Matrix Spike (MS)- Assessing the effect of matrix should include the analysis of one matrix spike per batch of non-potable water or soil samples, or an MS every 10 samples for potable water analysis. The matrix spike evaluates both sample matrix affect and efficiency of sample preparation. For non-potable or soil samples, if recovery falls outside of ± 25%, the analyst must narrate. For drinking waters, the recovery must fall within 85 – 115%.

12.5.4 Sample Duplicates (Dup)- One field sample duplicate must be prepared and analyzed with every batch for precision information. The RPD between the sample and sample duplicate should not exceed 20%. Exceedences must be reanalyzed or narrated.

12.6 To evaluate the instrument calibration, the following are analyzed:

11.6.1 The calibration verification (ICV, CCV) standard is the mid-level standard which is analyzed after calibration and every 10 samples (acceptance criteria is ± 5% for Initial verification and ±10% for continuing verifications.)

11.6.2 The Calibration verification standard (CVS) is a second source standard that is analyzed prior to the samples to verify the validity of the calibration standards (acceptance criteria is ± 10% and ± 5% for drinking water and waste water by 200.7).

12.7 Lower level quantitation check standard (CRQL) is the lowest standard in the calibration curve, and 5x lower than the reporting level. It is analyzed at the beginning and end of each run, and every 8 hours.

12.8 Reporting level standard (CRDL) is analyzed at the beginning and end of each run, and every 8 hours. The acceptance criteria is ± 30%.

12.9 The spectral interference check standards (ICSA, ICSAB) are analyzed to verify the instrument background corrections and the interelement correction factors. These checks are analyzed at the beginning of each run, every 8 hours, and at the end of the run. The acceptance criteria is ± 20%.

12.10 Dilution Test- If the analyte concentration is within the linear range and sufficiently high, an analysis of a 1:5 dilution should agree within ± 20% or ± 10% for DW/WW by 200.7). A dilution sample is analyzed in every batch.

12.11 Post Digestion Spike- A post spike is analyzed every batch of samples. When performing a post-digestion spike, take 0.08 mL of each QCP-QCS-1 and QCP-QCS-2 and bring up to 8.0 mLs of sample. For soil matrix post digestion spike take 0.16 mL of each QCP-QCS-1 and QCP-QCS-2 and dilute to 8.0 mLs of sample. The acceptance criteria is ± 25% of the true value. Narrate if the post digestion spike fails criteria.

13.0 Safety

13.1 The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.

13.2 Always wear safety glasses for eye protection as well as a lab coat.

13.3 Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.

14.2 Standards should be purchased in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

15.0 Waste Management

15.1 It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hood and bench operations. Compliance with all sewage discharge permits and regulations is also required.

16.0 Method Performance

16.1 This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates.

16.2 See Section 11- Quality Control in this SOP for acceptance limits.

17.0 Corrective Action for Out-of-Control or Unacceptable Data

16.1 Should the calibration curve have a correlation coefficient of <0.9975, remake and reanalyze curve before processing samples.

16.2 Should the preparation blank, LCS, or in-house standards fail acceptance criteria, re-digest and re-analyze batch.

16.3 Should the matrix spike or sample duplicate analysis fail acceptance criteria, a non-conformance report must be generated or the sample QC must be reanalyzed. If a 200.5 (Lead and Copper) matrix spike fails criteria, the sample must be rerun by another approved method.

18.0 References

17.1 "Methods for Chemical Analysis of Water and Wastes", Environmental Protection Agency, Environmental Monitoring Systems Laboratory – Cincinnati (EMSL-CL), EPA-600/4-79-020, Revised March 1994 (Method 200.7 version 4.4).

17.2 "Determination of Trace Elements in Drinking Water by Axially Viewed Inductively Coupled Plasma- Atomic Emission Spectrometry", Environmental

Protection Agency – Cincinnati, EPA-600/R-06/115, October 2003 (Method 200.5 version 4.2).

17.3 "Test Methods for Evaluating Solid Waste (SW-846), Third Edition, EPA Office of Solid Waste, Final Update IV, (2/07), Method 6010C, "Inductively coupled plasma- atomic emission spectrometry".

17.4 "Test Methods for Evaluating Solid Waste (SW-846), EPA Office of Solid Waste, Final Update V, (7/14), Method 6010D, "Inductively coupled plasma- optical emission spectrometry".

17.5 SPECTRO Analytical Instruments Operator's Manual.

17.6 USEPA Method 29 - Determination of Metals Emissions from Stationary Sources, 8/2017

19.0 Tables

Table I: Troubleshooting

Fault	Cause	Remedy
Generator does not start	Power Supply	Check instrument power supply (fuses, main switch)
Error Message: Argon Pressure too low	Argon supply interrupted	
Error Message: Insufficient OPI cooling flow	Cooling agent supply interrupted.	• Check to ensure system (tubing etc) is not blocked (dirt, lime, deposits) • Check flow amount.
	Cooling agent supply pressure too low.	Increase inlet pressure (approximately 4 bar/60 psi)
Error Message: Unit door not closed.	Door not properly closed	Check closing mechanism

Error Message: Plasma exhaust error	Exhaust capacity too low	Check the unit filter for soiling or check the exhaust capacity.
Error Message: Current error on start	Error during start routine	Repeat start procedure

Plasma Torch melts	Torch incorrectly adjusted within the load coil.	Check whether the torch is positioned correctly.
	Aerosol tube blocked	Clean the torch.
	Leak in the argon connection to the torch.	Search for the leak with soapy solution (Snoop) and seal.
	Insufficient auxiliary gas flow setting.	Increase the auxiliary gas flow.
	Leak in the nebulizer system.	Search for leak with soapy solution (Snoop) and seal.
Plasma cannot be ignited	No Tesla discharge	Ignition cable not connected correctly
		Check the insulation for correct installation
	Torch not correctly centered within the load coil	Check the load coil setting
	Oxygen in sample intro-duction system	Flush the sample introduction system with argon
	Wrong argon quality	Argon with a quality of 4.6 or better is required (purity = 99.996%)

Plasma asymmetrical	Argon flush out of the OPI/SPI too high	Reduce the flow rate
	Plasma chamber extraction set too high	Reduce extraction
Plasma flickers or pulsates	Humidity or deposits in the aerosol tube of the torch.	Clean and dry the torch or replace it.
	Aerosol pulsates	• Clean the nebulizer • Replace the pump tube.
Plasma too bright	Power set too high	Decrease power
	Oxygen in sample intro-duction system.	Check for leaks and seal
Plasma extinguishes when nebulizer gas flow is switched on	Sample introduction tube not connected to the nebulizer.	Connect the tube and check fitting
	Oxygen in sample intro-duction system	Flush the system with argon before plasma ignition
	Leak in the sample intro-duction system	Find the leak and seal
No channel visible in the plasma	Nebulizer gas flow setting too low	Optimize the nebulizer gas flow
	Nebulizer blocked	Clean the nebulizer
	Leak in spray chamber outlet	Find the leak and seal
Error Message: Waste container level	Waste container is full	Remove the cover of container and properly dispose of the

indicator		content
Sparking-over at the load coil	Humidity	Turn off generator and dry the load coil with tissue paper (if humidity is visible)
	Dirt on the load coil	Switch off the generator and clean the load coil using a toothbrush.
Error Message: A new ICALization is required	Control peak drift detection	ICALize
Error Message: ICALization failed	Incorrect sample or incorrect flush time	Use the correct sample. Check the measurement parameters. Repeat the ICALization
	In the current method, no ICAL reference spectrum is defined	Select an ICAL reference spectrum for the method under method development
Error Message: ICAL reference does not fit to current transformation data.	A method with other ICAL basic parameters was loaded	ICALize the new method with the correct nebulizer type.
Error Message: Network Connection No communication between the PC and the unit.	IP address incorrect or used for a different purpose	Enter the correct IP address (online help). Only qualified IT staff should enter the address.

Revision History Log for SOP #506

Date:	Revision #:	Summary of Changes:	Submitted By:	Approved By:	Effective Date:
8/7/14	1	New SOP for Blue instrument, broken out from SOP#505	Laura Kinnin	Kathy Cressia	8/7/14
7/29/15	1.1	Sections 11.2.2 & 11.3.3- fixed 200.9 typo, Section 8.5.1.3- clarified ICV limits +/- 5% and CCV limits +/- 10%, Section 8.5.1.2- made CC match Section 16.1, which is >0.9975 and fixed formatting issues throughout SOP	Kathy Cressia	Phyllis Shiller	7/29/15
3/15/16	1.2	Added HCl throughout the entire SOP, CLP 1+ 3 changed volumes, CVS new source, deleted section 8.3.6.2	Laura Kinnin	Kathy Cressia	3/15/16
5/18/16	1.3	Combined SOP 505/506 together to have one ICP SOP. Added Arcos to Instrument list. Changed LCS second source to a CVS throughout SOP, and LCS now a blank spike. Section 8.5.1.1- put ICAL standards in order, Section 11.0- rewrote entire section using the terms we call QC in the batches and in the runs. Added information on where they come from and their criteria. Section 17.4- added 6010D method reference	Kathy Cressia	Phyllis Shiller	5/18/16
1/10/20	1.4	Added air to scope Added section 9 and 9.1 for Lead in air calculation. Added USEPA Method 29 to references	Kathy Cressia	Phyllis Shiller	1/10/20

3/31/20	**1.5**	**Added section 5.3 for new ICP Arcos 2 instrument**	**Kathy Cressia**	**Phyllis Shiller**	**3/31/20**

Chlorophyll A

References: **SM 10200 H,** Standard Methods for the Examination of Water and Wastewater, 18th Edition

1. Scope and Application

Matrices: Waters

Definitions: Refer to Alpha Analytical Quality Manual.

The concentration of photosynthetic pigments is used extensively to estimate phytoplankton biomass. All green plants contain chlorophyll *a*, which constitutes approximately 1 to 2% of the dry weight of planktonic algae. Other pigments that occur in phytoplankton include chlorophylls *b* and *c*, xanthophylls, phycobilins, and carotenes. The important chlorophyll degradation products found in the aquatic environment are the chlorophyllides, pheophorbides, and pheophytins. The presence or absence of the various photosynthetic pigments is used, among other features, to separate the major algal groups. This method describes the spectrophotometric method for determining chlorophyll *a* in phytoplankton.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by completing the record of training.

2. Summary of Method

Chlorophyll pigment is extracted from the plankton concentrate using aqueous acetone and the Optical Density (Optical Density (OD) = Absorbance) of the extract is determined with a spectrophotometer. The ease with which the chlorophylls are removed from the cells varies considerably with different algae. To achieve consistently the complete extraction of the pigments, the cells are disrupted with a tissue grinder. All work is conducted in subdued light to avoid degradation.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

The Reported Detection Limit is 2 mg/m^3.

4. Interferences

4.1 Turbidity: Turbidity is removed by filtration of the extract through a 1.0µm solvent-r resistant disposable filter.

4.2 Light Exposure: Light exposure to the sample will degrade the chlorophyll. Therefore collection and analysis are to be conducted in subdued lighting conditions.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

NOTE: When using the tissue grinder, be sure to hold the glass cuvette on the sides and not on the bottom. This is to ensure that the grinder will not injure the chemist, should the cuvette accidentally break.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in dark glass or dark plastic containers. Containers may be covered with aluminum foil to minimize degradation of the sample by light.

6.2 Sample Preservation

None.

6.3 Sample Shipping

No specific requirements.

6.4 Sample Handling

Samples are filtered as soon as possible after sample collection. Filters are stored in the dark, refrigerated at 4ºC for no more than 3 days.

7. Equipment and Supplies

7.1 Glass Cuvettes: 1 cm and 2.5 cm

7.2 Aluminum Foil

7.3 Tissue Grinder

7.4 Glass Fiber Filters: Gelman, P/N 61631, 47mm

7.5 Filtration Equipment: Vacuum pump; membrane filter funnel.

7.6 Forceps: Smooth-tipped, without corrugations on the inner sides of the tips.

7.7 Pipets: 1mL, glass

7.8 10mL Solvent-resistant syringe: with 1.0µm PTFE filter membrane.

7.9 Centrifuge

7.10 Centrifuge tubes: 15mL , graduated, screwcap

7.11 Genesys 5 Spectrophotometer, UV: with a narrow band-width (0.5 to 2.0nm)

7.12 Amber Glass Jars: 250mL, with covers

7.13 Filter discs: 1.0um pore size, solvent resistant

7.14 10mL syringe: Solvent resistant

7.15 Membrane Filter Funnels: 0.45 µm filter

7.16 Refrigerator: 4 °C

8. Reagents and Standards

8.1 Saturated Magnesium carbonate solution: Add 1g fine powdered $MgCO_3$ to 100mL DI. Undissolved material is not uncommon.

8.2 Acetone: Reagent grade BP 56 °C.

8.3 90% Aqueous Acetone/10% $MgCO_3$ working solution: 90 parts acetone (Section 8.2): 10 parts saturated $MgCO_3$ solution (Section 8.1). Store in a 250mL glass amber jar.

8.4 $MgCO_3$: Powder form, Lab grade (USP-FCC)

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank

The Blank consists of 10mL of 90% Aqueous Acetone/10% $MgCO_3$ working solution in a 15mL centrifuge tube covered with aluminum foil. It is steeped for at least 2 hours at 4°C alongside of the samples and is filtered through a 1.0µm solvent-resistant disposable filter.

The Spectrophotometer is zeroed at OD750 with the Blank.

9.2 Laboratory Control Sample (LCS)

Not Applicable

9.3 Initial Calibration Verification (ICV)

Not Applicable

9.4 Continuing Calibration Verification (CCV)

Not Applicable

9.5 Matrix Spike

Not Applicable

9.6 Laboratory Duplicate

A sample is analyzed in duplicate (if sample volume is available) once per batch of 20 samples or less

9.7 Method-specific Quality Control Samples

None.

9.8 Method Sequence

- Filter the sample onto a glass fiber filter.
- Wrap the filter in foil, secure in airtight bag, and place in 4 C refrigerator (if not immediately grinding).
- Grind the glass fiber filters in a tissue grinder with 90% Aqueous Acetone/10% $MgCO_3$ working solution.
- Steep the samples and Blank for 2 hours at 4°C.
- Clarify the sample extract and Blank by centrifuging and filtering.
- Zero the Spectrophotometer at 750, 664, 647, and 630 respectively, with Blank
- Determine OD's of the samples
- Perform calculations.

10. Procedure

10.1 Set-up

Perform all analysis in subdued light, with all containers covered in aluminum foil to avoid degradation of the chlorophyll.

10.1.1 Sample Filtration/Preparation

Concentrate the chlorophyll by filtering the whole volume of sample onto a glass-fiber filter as soon as possible after sample collection.

The sample container should be gently swirled before each portion poured to ensure the sample aliquots are homogeneous. If the sample has too much sedimentary material present, and the filtering process becomes sluggish, do not add further sample volume to the filtering unit. Make sure to note correct volume of sample filtered in the Micro logbook.

If the sample is to be analyzed immediately, record in the laboratory notebook the sample ID, date and time of filtration, sample volume filtered, and the chemist's initials. Also record the lot # of the glass-fiber filters and the filter funnels used. Proceed to Section 10.3.1.

Otherwise, if the sample is not to be analyzed at this time, the filter is carefully (to avoid piercing of the filter) placed onto a piece of aluminum foil and folded in half so the chlorophyll extract is folded onto itself. (This is to avoid the chlorophyll adhering to the aluminum foil.) The folded filter/foil is stored in a sealed plastic bag at 4°C until pigment extraction takes place (not to exceed 3 days). Note on the plastic bag the sample ID, date and time of filtration, sample volume filtered, and the initials of the chemist.

10.2 Initial Calibration

The spectrophotometer is zeroed at each wavelength with a Blank sample. The Blank sample is prepared as in Section 9.1.

10.3 Equipment Operation and Sample Processing

If the filter containing the chlorophyll has been stored in the refrigerator, transfer the following information into the laboratory notebook from the plastic bag in which the filter has been stored: the date and time of filtration, sample volume filtered, and the chemist's initials.

10.3.1 Pigment Extraction

Using forceps, carefully fold the glass-fiber filter containing the extract and place it in a 2.5cm glass cuvette that is covered with aluminum foil. Cover the filter with 5mL of 90% Aqueous Acetone/10% $MgCO_3$ working solution and place onto the tissue grinder. Grind at 500rpm for 1 minute. (Note: Whenever the 90% Aqueous Acetone/10% MgCO3 solution is used, the bottle it is contained within should be gently swirled first to ensure all undissolved material in the solution is uniformly dispersed.)

Transfer the slurry to a screwcap centrifuge tube that is covered with aluminum foil. Into the cuvette, rinse the grinder with a few mLs of 90% Aqueous Acetone/10% $MgCO_3$ working solution, and swirl to combine any leftover slurry. Add the rinse to the extraction slurry in the centrifuge tube. If there is still remaining slurry in the cuvette, use a 1mL glass pipette to transfer to the centrifuge tube. Adjust the total volume to a constant level

of 10mL with 90% Aqueous Acetone/10% $MgCO_3$ working solution. (Avoid excessive dilution of pigments.) Cover the centrifuge tube and swirl to ensure all of the slurry is mixed with the Aqueous Acetone.

If additional samples are to be ground, rinse the tissue grinder with Acetone (Section 8.2) and allow to dry before each sample.

Steep in darkness for at least 2 hours at 4°C, not to exceed 2 ½ hours. Record the times in the laboratory notebook.

Place the 15mL centrifuge tube that contains the sample into a 50mL centrifuge tube that has a KimWipe in the bottom. (The KimWipe is used to minimize the movement of the smaller centrifuge tube within the larger centrifuge tube.)

Clarify the extract by centrifuging in the closed centrifuge tube for 20 minutes at 2800rpm. Then filter the supernate through a 1.0µm solvent-resistant disposable filter. (Note: Make sure to not over-centrifuge, since acetone will break down integrity of centrifuge tube over time).

Decant the clarified extract into a clean, calibrated 15mL screwcap centrifuge tube covered with aluminum foil.

10.3.2 Spectrophotometric Determination of Chlorophyll *A* – Trichromatic Method

Transfer the Blank sample into a DI-rinsed 1cm glass cuvette. Also, transfer the clarified extract(s) into separate DI-rinsed 1cm glass cuvette(s).

Zero the Spectrophotometer with the Blank sample at 750nm. Read the Optical Density (OD) of the samples at 750nm. Record OD in the laboratory notebook.

Zero the Spectrophotometer with the Blank sample at 664nm. Read the Optical Density (OD) of the samples at 664nm. Record OD in the laboratory notebook. (The OD664 should be between 0.1 and 1.0, therefore prepare dilutions with 90% Aqueous Acetone/10% $MgCO_3$ working solutions as necessary to provide an OD within this range.)

Zero the Spectrophotometer with the Blank sample at 647nm. Read the Optical Density (OD) of the samples at 647nm. Record OD in the laboratory notebook.

Zero the Spectrophotometer with the Blank sample at 630nm. Read the Optical Density (OD) of the samples at 630nm. Record OD in the laboratory notebook.

10.4 Continuing Calibration

Not Applicable.

10.5 Preventive Maintenance

An instrument service company calibrates the Spectrophotometer-UV on an semi-annual basis. Certificates are kept on file.

11. Calculations

11.1 Calculations are automatically performed on an Excel Spreadsheet for the Chlorophyll A analysis. Input the following information into the Spreadsheet:

- Extract Volume (mL), as determined in the second paragraph of Section 10.3.1.
- Volume of Sample (L), as determined prior to filtration in Section 10.1.1
- OD 750
- OD 664
- OD 647
- OD 630

11.2 The actual calculation performed on the Spreadsheet is as follows:

The OD750 is a correction for turbidity. Therefore, subtract the 750nm OD value from the readings at the other wavelengths *before* using them in the equations below.

Using the *corrected* values, calculate Chlorophyll *a* in the extract as follows:

$$C_a \text{ (mg/L)} = (11.85 \times OD664 \times \text{dilution factor}) - (1.54 \times OD647) - (0.08 \times OD630)$$

After determining the concentration of pigment in the extract, calculate the amount of pigment per unit volume as follows:

$$\text{Chlorophyll } a, \text{ mg/m}^3 = \frac{C_a \times \text{extract volume, mL}}{\text{Volume of sample, L}}$$

- The *extract volume* is determined in the second paragraph of Section 10.3.1.
- The *volume of sample* is determined prior to filtration in Section 10.1.1.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedance and improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of blanks for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

Not applicable to this method.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1734 and 1739 for further information regarding IDC/DOC Generation.

Not applicable to this method.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 MDL/LOD/LOQ Generation

SOP/1734, 1739 IDC/DOC Generation

SOP/1728 Waste Management and Disposal SOP

16. Attachments

None.

Aquatic Analysts

Algae Analytical and Quality Assurance Procedures

January 15, 2021

Sample Handling

Sample Collection and Preservation

Phytoplankton are collected by filling bottles with natural water samples. Samples are collected at either discrete depths, or integrated through the photic zone of lakes. A volume of 125 mL is sufficient for most samples.

These samples are preserved with 1% Lugol's solution immediately after collection. Refrigeration is not necessary, and holding times are a year or more.

Sample Tracking

All samples received in the laboratory are immediately logged into a Sample Receipt Log. All samples are stored in a dedicated area until they are processed. After samples are processed and analyzed and data reports have been submitted to clients, samples are placed in storage for at least one year.

Sample Preparation

Permanent microscope slides are prepared from each sample by filtering an appropriate aliquot of the sample through a 0.45 micrometer membrane filter (APHA Standard Methods, 1992, 10200.D.2; McNabb, 1960). A section is cut out and placed on a glass slide with immersion oil added to make the filter transparent, followed by placing a cover slip on top, with nail polish applied to the periphery for permanency. A benefit to this method is that samples can be archived indefinitely; we have nearly 35,000 slides archived.

Microscopic Analyses

Algae Identifications

Aquatic Analysts has an extensive library of algae literature, including journal reprints, standard reference books, and internet reference sites. We also maintain files, notes, and photographs of algae we've encountered during the past 38 years of identifying algae. Most algae are identified by cross-referencing several taxonomic sources.

Enumeration

Algal units (defined as discrete particles - either cells, colonies, or filaments) are counted along a measured transect of the microscope slide with a Zeiss standard microscope (1000X, phase contrast). Only those algae that were believed to be alive at the time of collection (intact chloroplast) are counted. A minimum of 100 algal units are counted. (Standard Methods, 1992, 10200.F.2.c.).

Biovolume Estimates

Average biovolume estimates of each species are obtained from calculations of microscopic measurements of each alga. The number of cells per colony is recorded during sample analysis to arrive at biovolume per unit-alga. Average biovolumes for algae are stored in a computer, and measurements are verified for each sample analyzed.

Data Analyses and Reports

Sample Reports

Results of sample and data analyses are provided to the client in electronic format. Deliverables include individual sample reports, data summaries, database file, and combined species lists.

Individual sample reports include sample identification, a trophic state index, total sample density, total sample biovolume, and a list of algae species with their absolute and relative densities and biovolumes. All data are reported in Excel format.

Data summaries include sample identification, total density, total biovolume, the trophic state index, and the top 5 most common algae species (codes) and their relative densities. The summary format allows for easy calculations and graphs of algae sample data.

Database files include information for each species from each sample within a sample set. Information includes sample ID, species names and codes, densities and biovolumes, taxonomic group, and any notes on each sample.

Combined species lists of all species within related groups of samples allow greater sensitivity in comparing different lakes, sites, dates, or depth. Algae species are compiled according to their relative densities.

Trophic State Index

A Trophic State Index based upon phytoplankton biovolume has been developed from a data set of several hundred lakes located throughout the Pacific Northwest (Sweet, 1986, Report to EPA). The index was derived in a similar fashion as Carlson (1977) derived indices for Secchi depth, chlorophyll concentration, and total phosphorus concentration. The biovolume index ranges from 1 for ultraoligotrophic lakes to 100 for hypereutrophic lakes. Values agree well with Carlson's indices.

The index is defined as:

TSI (biovolume) = (Log-base 2 (B+1)) * 5

Where B is the phytoplankton biovolume in cubic micrometers per milliliter divided by 1000.

TSI values below 20 are generally considered to be ultraoligotrophic, values from 20-35 are oligotrophic, 35-50 mesotrophic, 50-65 eutrophic, and above 65 is hypereutrophic.

Quality Assurance

Microscope Calibration

Aquatic Analysts use a Zeiss Standard phase-contrast microscope primarily with a 1000X magnification for identification and enumeration of algal samples. The diameter of the field of view at 1000X magnification is 0.182 mm. The effective area of a filter is 201 millimeters square.

Algae are enumerated along a measured transect, measured accurately to 0.1 mm with a stage micrometer. The algal densities are calculated from the area observed (transect length times diameter of field of view), the effective filter area, and the volume of sample filtered.

The microscope was calibrated using a standard concentration of latex spheres provided by EPA (Cincinnati, OH). The concentration of these spheres was 12,075 per milliliter. Duplicate preparations of the standard spheres were analyzed; the average result was

11,700 spheres per milliliter (96.9 percent). The computer program used to calculate algae densities compensates for this 3.1% error.

Replicates

Replicate algae samples are analyzed at the client's request. We encourage blind replicates for approximately 10% of all samples collected. Replicates are assessed for algae abundance (relative mean difference of densities) and species composition (similarity indices, species lists).

Independent Analyses

Aquatic Analysts has participated in the analyses of split algae samples on several occasions, with general agreement between samples in terms of algae density and algae species compositions. On occasion, we also contract independent algae analysts for second opinions on some difficult to identify algae species.

Internal Data Verification

A custom computer program handles all calculations and data analyses. Final sample reports are compared with laboratory bench sheets before releasing data.

Data summaries, tables of similarity indices, abundance graphs, and combined species lists are searched for inconsistencies, outliers, and interrupted patterns that may indicate possible errors.

Archives

Aquatic Analysts maintains an herbarium of all microscope slides analyzed (over 35,000 to date). These may be reviewed if questions arise after data are reported. In addition, all computer data (sample tracking data, raw count data, final reported data, data analyses, narrative reports) are archived on CD's in permanent storage.