MARYLAND
DEPARTMENT OF
NATURAL RESOURCES

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David Goshorn, Deputy Secretary

Quality Assurance Project Plan

For the
Maryland Department of Natural Resources
Chesapeake Bay
Mainstem and Tributary Water Quality Monitoring Program- Chemical and Physical Properties Component

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Quality Assurance Project Plan for the
Maryland Department of Natural Resources
Chesapeake Bay Water Quality Monitoring Program -
Mainstem and Tributary Chemical and
Physical Properties Component

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PREFACE

This document is intended to describe in detail the activities conducted under the Chemical and Physical Properties Component of the Maryland Department of Natural Resources Chesapeake Bay Mainstem and Tributary Water Quality Monitoring Program. This is a coordinated program consisting of several components conducted in a similar manner for identical purposes in both the tidal tributaries and Mainstem of Maryland's Chesapeake Bay. This program is funded through the Maryland Department of Natural Resources and the U.S. Environmental Protection Agency. Guidance for this document can be found at https://www.epa.gov/quality/epa-qar-5-epa-requirements-quality-assurance-project-plans .

Specifically, this Quality Assurance Project Plan is composed of four standardized elements covering the project from planning, through implementation, to assessment.

A. Project Management
B. Data Generation and Acquisition
C. Assessment and Oversight
D. Data Validation and Usability

This Quality Assurance Project Plan is available on-line by using publication type 'Quality Assurance Project Plan' to search the Monitoring News and Reports page of the Maryland Department of Natural Resources (DNR) Eyes on the Bay website: http://eyesonthebay.dnr.maryland.gov

Version History

QAPP Version	Date Approved	Changes Made
1	**July 2023**	The QAPP was more closely aligned to EPA requirements.

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A: PROGRAM MANAGEMENT

A1. Title and Approval Sheet

Quality Assurance Project Plan for the
Maryland Department of Natural Resources
Chesapeake Bay Mainstem and Tributary Water Quality Monitoring Program -
Chemical and Physical Properties Component

Concurrence

Preparer/Author

Name: Thomas Parham, Principal Investigator Title: Director, Tidewater Ecosystem Assessment Division Organization: Maryland Department of Natural Resources	Signature: Date: 10/24/23

Management/Supervisor

Name: Richard A. Ortt, Jr., Title: Director, Resource Assessment Service Organization: Maryland Department of Natural Resources	Signature: Date: 10/24/2023

Quality Assurance Officer

Name: David Goshorn, Ph.D., Title: Quality Assurance Officer, Deputy Secretary: Maryland Department of Natural Resources	Signature: Date: 10/24/23

EPA Region 3

Name: Kaylyn S. Gootman Title: Chesapeake Bay Program Project Manager Organization: U.S. Environmental Protection Agency	Signature: Kaylyn S. Gootman Date: 10/30/23

Approval

EPA Region 3

Name: Durga Ghosh Title: R3 Approving Official Organization: CBP / USGS	Signature: Date: Durga Ghosh 10/30/2023

Note: This approval action represents EPA's determination that the document(s) under review comply with applicable requirements of the EPA Region 3 Quality Management Plan [https://www.epa.gov/sites/production/files/2020-06/documents/r3qmp-final-r3-signatures-2020.pdf] and other applicable requirements in EPA quality regulations and policies [https://www.epa.gov/quality]. This approval action does **not** represent EPA's verification of the accuracy or completeness of document(s) under review and is **not** intended to constitute EPA direction of work by contractors, grantees or subgrantees, or other non-EPA parties.

A2. Table of Contents

A3. Distribution List

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QAPP documents can be found online by selecting ‘Quality Assurance Project Plans’ from Publication Type at Eyes on the Bay: News and Reports

A3.1 Acronyms and Abbreviations

AA - Autoanalyzer
AP - Above pycnocline
APC - Analytical Problem Code
AgCl - Silver chloride
B - Bottom sample
BP - Below pycnocline OR barometric pressure
BOD - Biological Oxygen Demand
C - Carbon or Center
C4 - Chesapeake Center for Collaborative Computing
$CaCO_3$ - Calcium Carbonate
CBP - EPA's Chesapeake Bay Program
CBL - University of Maryland's Chesapeake Biological Laboratory
cm - centimeter
COMAR -Code of Maryland Regulations
CSSP - Coordinated Split Sample Program
CTV - Calculated Threshold Value
DI - De-ionized
DIWG - Data Integrity Workgroup
DL - Detection Limit
DNR - Maryland Department of Natural Resources
DO - Dissolved oxygen
DOC - Dissolved organic carbon
EPA - U.S. Environmental Protection Agency
E - East
g - Gram
H2O - Dihydrogen oxide (water)
HCl - Hydrochloric acid
H2S - Hydrogen sulfide
H2SO4 - Sulfuric Acid
ITAT - Integrated Trends Analysis Team
L – Liter
LDO - Luminescent Dissolved Oxygen
KCl- Potassium chloride
m - Meter
M- mid depth
MDE - Maryland Department of the Environment
MDH - Maryland Department of Health
MSA - Maryland State Archives
MDL – Minimum Detection Limit
MgCO3 - Magnesium carbonate
mg - Milligram
ml - Milliliter
mv - Millivolt
N - Nitrogen
NELAC - National Environmental Laboratories Accreditation Conference
NIST - National Institute of Standards and Technology
nm - Nanometer

no. - Number
NO2 - Nitrite
NO23 - Nitrate + nitrite
NO3 - Nitrate
NTU - Nephelometric Turbidity Units
NASL - Nutrient Analytical Services Laboratory
ODO - Optical Dissolved Oxygen
P - Phosphorus
PAR - Photosynthetic Active Radiation
PC - Particulate carbon
PIP - Particulate Inorganic Phosphorus
PN - Particulate nitrogen
PO4 - Phosphate
PP - Particulate phosphorus
ppt - Parts per thousand
ppm - Parts per million
PMTF -Procedure Modification Tracking Form
QAO -Quality Assurance Officer (unless otherwise noted, this refers to the DNR QAO)
QAPP - Quality Assurance Project Plan
QA/QC - Quality Assurance/Quality Control
QAT - Quality Assurance Tool
RAS - Resource Assessment Service
RPD - Relative Percent Difference
ROX - YSI 6150 Reliable Oxygen Sensor
R/V - Research vessel
S - Surface sample
SAS - SAS® software
SRS - USGS Standard Reference Samples Program
STAR - Scientific, Technical Assessment and Reporting
SIF – Silica
Si – Dissolved Silicate
SOP - Standard Operating Procedure
TDN - Total dissolved nitrogen
TDP - Total dissolved phosphorus
TPP - Total Particulate Phosphorus
TSS - Total suspended solids
TVS - Total Volatile Solids
UMCES - University of Maryland Center for Environmental Science
USGS - U.S. Geological Survey
µg - Microgram
µS - MicroSiemans
VSS - Volatile Suspended Solids
W - West
YSI® - Yellow Springs Instruments
ºC - degrees Celsius

A4. Project/Task Organization

This section lists the individuals and organizations responsible for the major aspects of the Maryland Department of Natural Resources Water Quality Monitoring Program.

Director: Richard A. Ortt, Jr., Director Resource Assessment Service, DNR. richard.ortt@maryland.gov
Responsibilities: The director is responsible for overseeing the administrative aspects of the program including fiscal management, coordination among other DNR managers and coordination with cooperating agencies and institutions.

Principal Investigator: Thomas Parham, Director and Principal Investigator, Tidewater Ecosystem Assessment, DNR. Tom.Parham@maryland.gov
Responsibilities: The director and principal investigator is responsible for overseeing the administrative aspects of the program including fiscal management, coordination among other DNR managers and coordination with cooperating agencies and institutions. This individual is also responsible for the technical design, implementation, and data analysis of the program.

Quality Assurance Officer: David Goshorn, Deputy Secretary/Quality Assurance Officer, DNR. david.goshorn@maryland.gov
Responsibilities: The Quality Assurance Officer is responsible for documenting and assuring the implementation of field, laboratory and data management procedures that comprise this study.

Field Sampling Operations and Quality Assurance: Kristen Heyer, Environmental Program Manager, Annapolis Field Office. Monitoring and Non-tidal Assessment, DNR. kristen.heyer@maryland.gov
Responsibilities: This individual is responsible for field office staff and the administration of the field sampling activities including sample collection, sample storage, and sample delivery to laboratories.

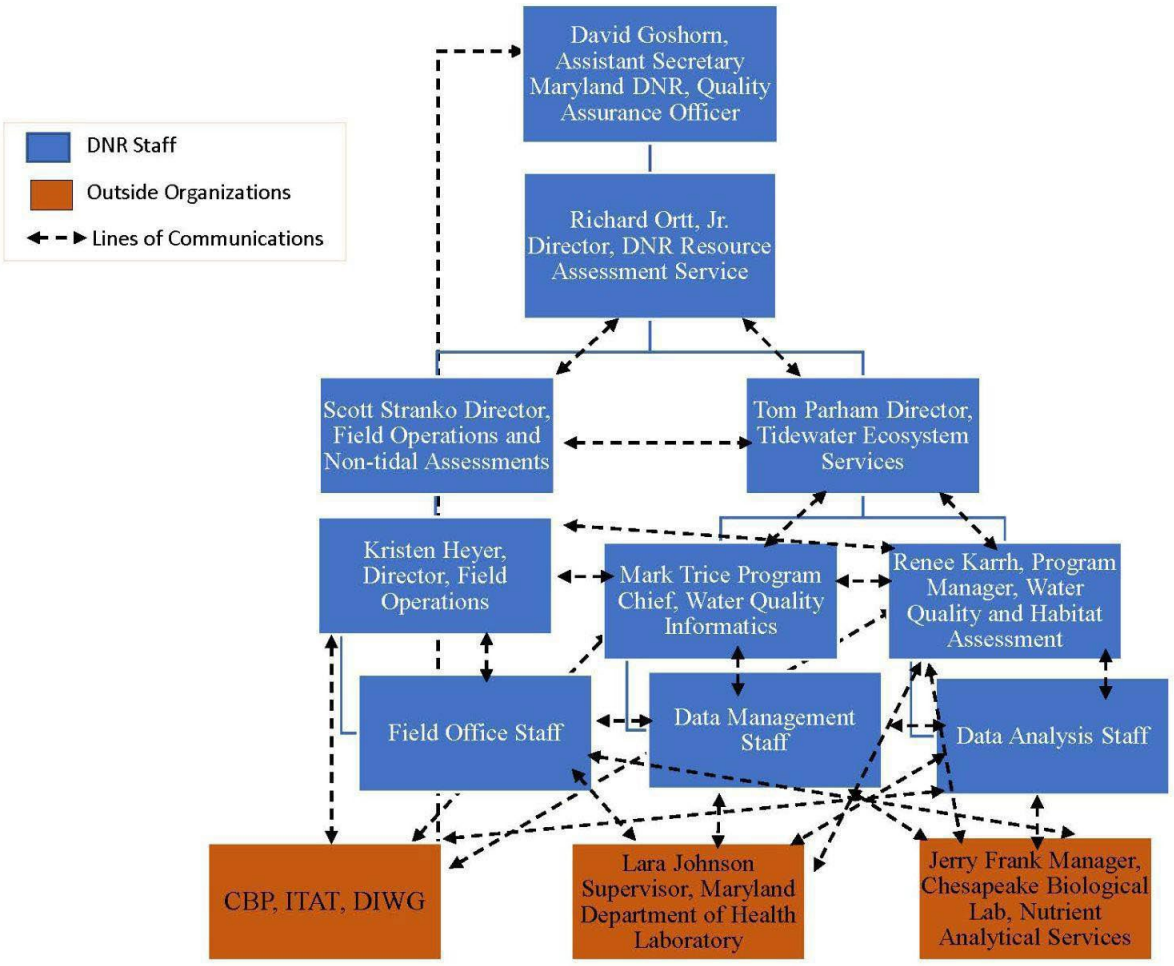
Laboratory Analyses/Water Column Chemistry: Lara Phillips, Laboratory Supervisor, MDH, Environmental Sciences Division lara.johnson@maryland.gov
Responsibilities: This person oversees the laboratory that completes some of the nutrient analysis and water chemistry for the project.

Laboratory Analyses/Water Column Chemistry: Jerry Frank, Manager Nutrient Analytical Services Chesapeake Biological Laboratory frank@umces.edu
Responsibilities: This person oversees the laboratory that completes some of the nutrient analysis and water chemistry for the project.

Data Management; Mark Trice, Program Chief, Water Quality Informatics, Tidewater Ecosystem Assessment, DNR mark.trice@maryland.gov
Responsibilities: This individual is responsible for overseeing the management of field and laboratory data collected under this program; managing historical field and laboratory data collected under this program; and maintaining existing data management software and oversight of data management staff.

Communications - Laboratory: Renee Karrh, Renee.Karrh@maryland.gov Tidewater Ecosystem Assessment, DNR Responsibilities: This individual is responsible for communications with Laboratory Supervisors and oversight of data analysis staff.

Figure 1. Organizational Chart for the Maryland Tidal Water Monitoring Program



A5. Problem Definition/Background/Objectives

At the completion of the U.S. Environmental Protection Agency's (EPA's) $27 million study of Chesapeake Bay, the Agency published a document entitled *Chesapeake Bay: A Framework for Action* (EPA 1983). This report strongly recommended a long-term water quality monitoring program to serve the Bay's management community by accurately describing the current state of the Bay Mainstem and tidal tributaries (baseline or 'status') and detecting long-term changes (trends) resulting from human activities. Management strategies at that time were hindered by the lack of precise information about the Bay and its response to increasing or decreasing pollution.

Managers, scientists, and statisticians recognized that to establish baseline conditions and then begin to identify trends would require a multi-year effort on the order of a decade or more. Long-term data were needed to overcome the natural year-to-year variability that can obscure changes due to human activities. As the EPA study drew to a close, scientists and managers convened in workshops to formulate plans on several topics, including water quality monitoring. The monitoring workshop recommendations for chemical and physical measurements were published in the appendices of *Chesapeake Bay: A Framework for Action*. The appendices described the chemical/physical monitoring plan in terms of station locations, parameters to be measured, and sampling frequency.

This Quality Assurance Project Plan (QAPP) describes Maryland's implementation of the coordinated Maryland, Virginia, and EPA Chesapeake Bay monitoring program as outlined in *Chesapeake Bay: A Framework for Action* (EPA 1983) and *Chesapeake Bay Program, Methods and Quality Assurance for Chesapeake Bay Water Quality Monitoring Programs* (CBP 2017). This part of Maryland's Chesapeake Bay Water Quality Monitoring Program is known as the "Chemical and Physical Properties Component" and covers monitoring in the Maryland portion of the Mainstem as well as the tidal tributaries.

The Maryland Department of Natural Resources (DNR) uses the data generated by means of the procedures in this QAPP to meet the four water quality monitoring objectives of the Chesapeake Bay Mainstem and Tributary Water Quality Monitoring Program:

1. Characterize the present state of the Bay Mainstem and its tributaries, including spatial and seasonal variation, using key water quality indicators.
2. Determine long-term trends or changes in key water quality indicators in relation to pollution control programs.
3. Track the progress of management strategies to reduce nutrient pollution.
4. Provide data for the Chesapeake Bay watershed and ecological models.

A6. Project Description

The CBP, under the Chesapeake 2014 agreement, is committed to reduce nutrient and sediment inputs into Chesapeake Bay. Nutrient and sediment allocations have been developed for tributary basins within the Bay watershed. This project is part of the cooperative effort of the CBP partners to provide comparable data to assess progress in meeting nutrient and sediment reduction goals to meet water quality criteria for the Chesapeake Bay.

The main outcomes of this monitoring program are to improve the measurement of nutrients and sediment concentrations for the calculation of loads discharged to the Chesapeake Bay watershed, improve the accuracy of the watershed model, help identify factors affecting nutrient and sediment loads and track changes in water quality over time and determine current conditions.

The scope of work for this monitoring program includes the measurement of chemical and physical parameters in the water column. Parameters such as nutrients, total suspended solids, chlorophyll *a*, dissolved oxygen and water clarity were selected to;

(1) provide information on eutrophication trends,
(2) calibrate Bay water quality models, and
(3) correlate living resources data to water quality data,
(4) inform management decisions.

Other parameters such as salinity and temperature are necessary to provide a more rigorous interpretation of these key water quality indicators. The same parameters are collected in the mainstem, large tributaries (Potomac and Patuxent Rivers), and minor tributaries except for 5-Day biochemical oxygen demand, dissolved organic carbon and silica.

- 5-Day biochemical oxygen demand, total alkalinity and turbidity samples will be collected at tidal Potomac River stations: MAT0016, MAT0078, PIS0033, RET2.1, RET2.2, RET2.4, TF2.1, TF2.2, TF2.3, TF2.4 and XFB1986.

- Dissolved organic carbon sample collection during Mainstem cruises was discontinued from 1996-2016. Beginning in May 2017, DOC sampling resumed at stations CB1.1, CB1.2, CB3.3C, CB4.3 and CB5.2. Mainstem DOC samples will be collected from March through September only.

- Silica (SIF) samples will be collected monthly, from the surface and above pycnocline layers, January through June 2023 at the plankton sampling stations (CB1.1, CB2.2, CB3.3C, CB4.3C, CB5.2, TF2.3, RET2.2, TF1.5, LE1.1, ET5.1 and WT 5.1). Silica samples will not be collected at any Mainstem or tributary stations July through December.

(A complete list of parameters measured, and detection limits is provided in Table 3.)

In 2019, Maryland Senate Bill 546, Nutrient Management – Monitoring and Enforcement, reinstated monitoring at nine stations on the Eastern Shore (TRQ0146, TRQ0088, CCM0069, XDJ9007, XCI4078, BXK0031, POK0087, XAK7810, MNK0146). The start of the sampling period for these sites was in January and February 2020.

The information gained from analyzing the entire suite of parameters allows managers to determine whether water quality goals established for living resources have been met and aids managers in establishing programs to control point and non-point sources of pollutants to the Bay.

Nutrient samples will be collected during the second Mainstem cruises in June and August each year. Nutrient samples will not be collected during the second Mainstem cruise in July each year (Table 1.).

Table 1. Chesapeake Bay Monitoring Sampling Schedule for Mainstem

The number of cruises per month is noted in each block. * Indicates that the second July cruise is readings only (no nutrients collected). Gray boxes indicate stations not sampled in that month. Note that for logistical reasons, the LE2.3 station (a Potomac tidal river station) is sampled on the same cruise as the Mainstem stations.

Station Name	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Total
CB1.1	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB2.1	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB2.2	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB3.1	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB3.2	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB3.3W	2*	2	1	1					1	1	1	2	11
CB3.3C	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB3.3E	2*	2	1	1					1	1	1	2	11
CB4.1W	2*	2	1	1					1	1	1	2	11
CB4.1C	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB4.1E	2*	2	1	1					1	1	1	2	11
CB4.2W	2*	2	1	1					1	1	1	2	11
CB4.2C	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB4.2E	2*	2	1	1					1	1	1	2	11
CB4.3W	2*	2	1	1					1	1	1	2	11
CB4.3C	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB4.3E	2*	2	1	1					1	1	1	2	11
CB4.4	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB5.1	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB5.2	2*	2	1	1	1	1	1	1	1	1	1	2	15
CB5.3	2*	2	1	1	1	1	1	1	1	1	1	2	15
LE2.3	2*	2	1	1	1	1	1	1	1	1	1	2	15

Figure 2. Map of the Maryland Department of Natural Resources Chesapeake Bay Mainstem and Bay Tributary Water Quality Monitoring Stations

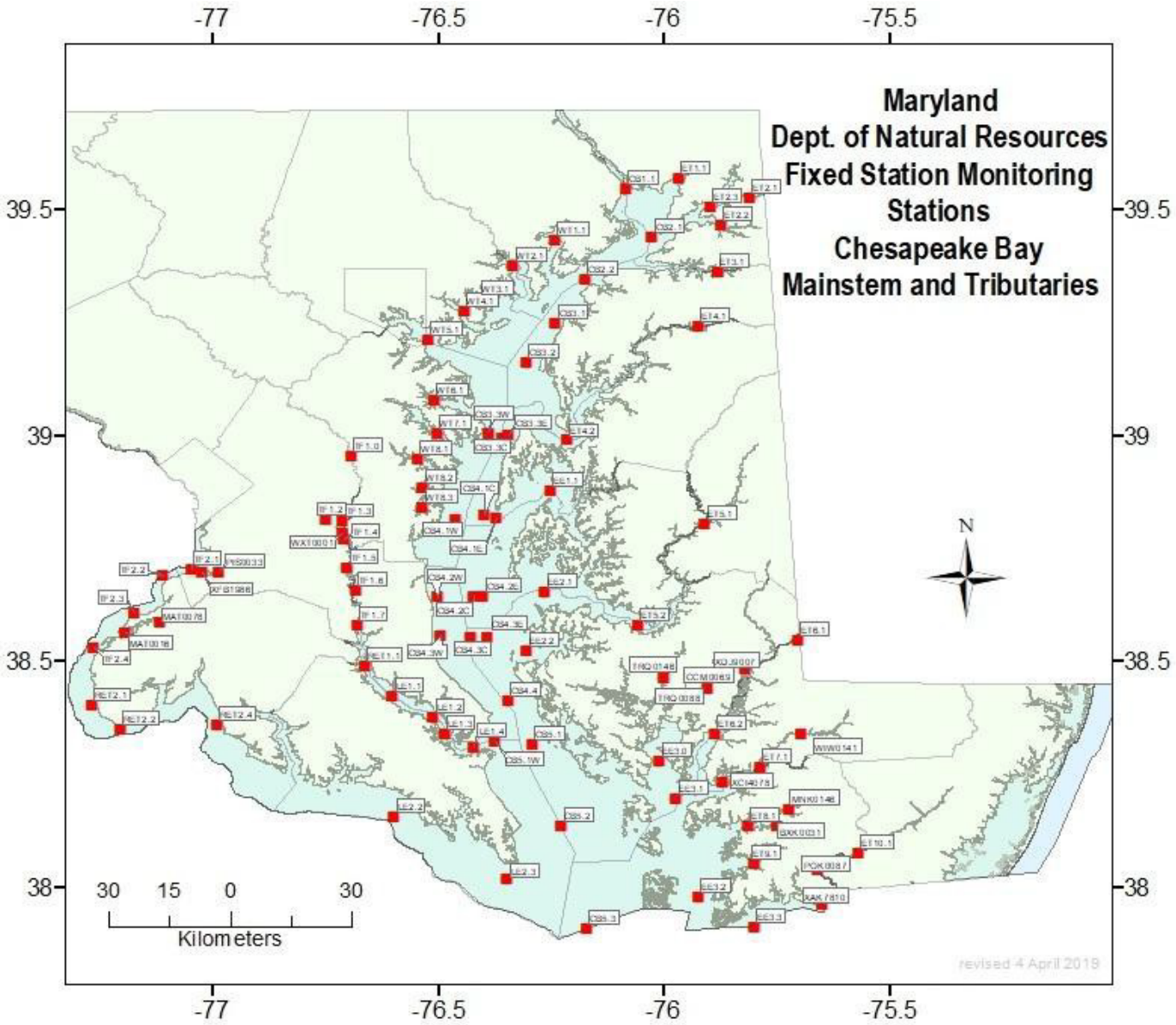


Table 2. Mainstem and Tributary sample locations and descriptions

Mainstem stations							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
CB1.1	-76.08481	39.54794	CBTF1	Mouth of Susquehanna River (700 yards from abandoned Light House on Hdg 040, 400 yards NNW of N 18 online with N 20). 5.7 m	PAR, VSS, Phytoplankton Mar - Nov whole water column composite Picoplankton July-Dec, DOC Mar-Nov	OEP XKH3147	15x2 14 sampling trips + 1 readings only
CB2.1	-76.02599	39.44149	CBTF1	SW of Turkey Point (1 nm from Turkey Pt Light on Hdg 240, 800 yards SE of RG A); 6.1m	PAR	CBI 927SS; OEP XJH6680	15x2 14 sampling trips + 1 readings only
CB2.2	-76.17579	39.34873	CB2OH	W of Still Pond (500 yards W of G 49, 1.75 nm S of Taylor Island Pt off Still Pond); 11.5m	PAR, VSS, Phytoplankton Mar- Nov whole water column composite live & fixed: July-Sept-whole water column composite picoplankton, DOC Mar-Sep	CBI 92OU, 921W, 922Y; OEP XJG0999	15x4 14 sampling trips + 1 readings only
CB3.1	-76.24050	39.24950	CB2OH	SE of Gunpowder Neck (2.1nm from south tip of Poole's Island Hdg 146, halfway between buoys 31 and 33); 11.2 m.	PAR	CBI 913R, 914S	15x4 14 sampling trips + 1 readings only
CB3.2	-76.30631	39.16369	CB3MH	NW of Swan Pt (400 yards NW of Tolchester Channel 13,1.9 nm from Swam Point on Hdg 328); 11.5 m	PAR	CBI 909; OEP XHG4953, XHG9915	15x4 14 sampling trips + 1 readings only
CB3.3C	-76.35967	38.99596	CB3MH	N of Bay Bridge (1.6 nm, from Sandy Point Light on Hdg 145, 0.4 nm NNE of bridge at edge of cable cross). 20.7 m.	PAR, VSS, Phytoplankton Mar - Nov- Above pycnocline composite-live and fixed. Picoplankton Jul- Sep-above pycnocline composite.	CBI 858C, 859B; OEP XFH1373, XGF9784;	15x4 14 sampling trips + 1 readings only

Mainstem stations							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
CB3.3E	-76.34517	39.00412	CB3MH	NE of Bay Bridge (1.9nm from Sandy Point Light on Hdg 260, 1 nm NNE of Bridge in East Channel); 8.2 m	PAR	CBI 859A; OEP XFH0293; EPA D3	11x2 Mar-Oct 10 sampling trips +1 readings only
CB3.3W	-76.38810	39.00462	CB3MH	NW of Bay Bridge (0.7 nm from Sandy Pt Light on Hdg 210, 0.7 nm SE Sandy Pt Water Tank); 9.1m.	PAR	CBI 859D; OEP XHF0366; EPA D1	11x2 Mar-Oct 10 sampling trips +1 readings only
CB4.1C	-76.39945	38.82593	CM4MH	SW of Kent Pt (0.5nm from Bloody Pt Light just West of line from Bloody Pt to G 83); 31.0 m	PAR	CBI 845G, 848E; OEP XFF9178; EPA '83DO	15x4 14 sampling trips + 1 readings only
CB4.1E	-76.37144	38.81809	CB4MH	S of Kent Pt (1.4 nm SE Bloody Pt Light, 300 yards SW buoy 1 for Eastern Bay); 23.7 m	PAR	CBI 851N; EPA '83DO; OEP XFF9178	11x4 Mar- Oct 10 sampling trips +1 readings only
CB4.1W	-76.46272	38.81498	CB4MH	SE of Horseshoe Pt (3.5nm from Bloody Pt. Light on Hdg 260, 1.6 nm E of Franklin Manor); 9.1 m	PAR	CBI 848G, H, I; OEP XFF1844, XFF8922	11x2 Mar-Oct 10 sampling trips +1 readings only
CB4.2C	-76.42127	38.64618	CB4MH	SW of Tilghman Island (2nm from Sharps Island Light on Hdg 290, 300 yards NE of CR buoy) 26.2 m.	PAR	EPA '83DO; OEP XEF8648	15x4, 14 sampling trips +1 readings only

Mainstem stations							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
CB4.2E	-76.40131	38.64499	CB4MH	SW of Tilghman Island (1.3nm from Sharps Island Light on Hdg 305, 0.9 nm E of CR buoy); 9.1 m	PAR	OEP XEF8859	11x2 Mar-Oct 10 sampling trips +1 readings only
CB4.2W	-76.50217	38.64354	CB4MH	NW of Plum Pt (6nm from Sharps Island Light on Hdg 280, 1.0 nm E of Camp Roosevelt); 9.1 m	PAR	OEP XEF8699; EPA '83DO	11x2 Mar-Oct 10 sampling trips +1 readings only
CB4.3C	-76.42794	38.55505	CB4MH	E of Dares Beach (0.5 nm W of R 78, 5.7 nm from Sharps Island Light, Hdg 220); 25.6 m.	PAR, VSS, Phytoplankton Mar-Nov, above pycnocline composite fixed and live. Picoplankton Jul- Sep-above pycnocline composite picoplankton, DOC Mar-Sep	OEP XEF3343	15x4 14 sampling trips + 1 readings only
CB4.3E	-76.39121	38.55624	CB4MH	Mouth of Choptank River (1.7 nm. East of R78, 5 nm. from Sharps Island Light on Hdg 195); 21.6 m	PAR	OEP XEF3465	11x4 Mar-Oct 10 sampling trips +1 readings only
CB4.3W	-76.49402	38.55728	CB4MH	E of Dares Beach (1nm. East of Dares Beach, 3nm. West of R78); 9.7 m	PAR	CBI 834H, J; OEP XEF3405	11x2 Mar-Oct 10 sampling trips +1 readings only

Mainstem stations							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
CB4.4	-76.34565	38.41457	CB4MH	NE of Cove Pt (2.4 nm from Cove Pt on Hdg 055); 28.6 m	PAR, Quarterly Split Sample Location	OEP XDF4693	15x4 14 sampling trips + 1 readings only
CB5.1	-76.29215	38.31870	CB5MH	E of Cedar Pt (1 nm. ENE of mid-channel buoy HI, 4nm. from Cedar Pt. on Hdg 070); 33.2 m	PAR	CBI 818N, 818P, 819N, 819O; OEP XCG9223	15x4 14 sampling trips + 1 readings only
CB5.1W	-76.37574	38.32522	CB5MH	Mid-channel on a transect between Cedar Pt and Cove Pt; 8.9m	PAR	OEP XCF9575	12x4; Sampled with Patuxent
CB5.2	-76.22787	38.13705	CB5MH	Mid Bay E of Pt No Point (3 nm. From Point No Point Light on Hdg 080); 29.0 m	PAR, VSS, Phytoplankton Mar-Nov above pycnocline composite-live & fixed. Picoplankton Jul- Sep-above pycnocline composite, DOC Mar-Sep	Benthos #58 (Versar); OEP XBG8262	15x4 14 sampling trips + 1 readings only
CB5.3	-76.17137	37.91011	CB5MH	NE of Smith Point (2nm. from Smith Point Light toward on Hdg 020, intersect MD/VA line and transect from Smith Pt to Holland bar Light); 25.3 m	PAR	USGS 37524807, 6094200; OEP XAG4699	15x4 14 sampling trips + 1 readings only

Patuxent Stations							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
TF1.0	-76.69411	38.95557	PAXTF	At bridge on US Rt. 50 (upstream side of bridge; USGS Gage No 59440); 3 m```		OEP PXT0603; USGS 01594440; EPA E	12x1
TF1.2	-76.75087	38.81430	WBRTF	Midstream of Western Branch at Water Street crossing in Upper Marlboro, MD; 3 m		OEP WXT0045	12x1
WXT0001	-76.71343	38.78539	WBRTF	Western Branch from pier at Mt Calvert House in Upper Marlboro, 0.1 miles above mouth; 1.0 m			12x1
TF1.3	-76.71227	38.81092	PAXTF	Mid-channel from MD Rt. 4 bridge near Wayson's Corner; 3.7 m		OEP PXT0494; EPA E5, 5	12x1
TF1.4	-76.70927	38.77302	PAXTF	West Shore from main pier at Jackson Landing; just below confluence with Western Branch; 3.0 m		OEP PXT0456; EPA E6A	12x1
TF1.5	-76.70146	38.71012	PAXTF	Mid-channel at Nottingham, 11.1m	PAR, VSS, Phytoplankton Mar- Nov surface live, DOC Mar-Sep	OEP PXT0402; EPA E8	12x4
TF1.6	-76.68382	38.65845	PAXOH	Mid-channel off the wharf at Lower Marlboro, 6 m.	PAR	OEP XED9490; EPA E9; J.H. 5945	12x3
TF1.7	-76.68101	38.58211	PAXOH	Mid-channel of transect heading of approx. 115 degrees from Jack's Creek; 3.1m	PAR, VSS	OEP XED4892; J.H. 5946	12x2

Patuxent Stations							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
RET1.1	-76.66429	38.49090	PAXMH	Mid channel, 0.5 km ENE of Long Point, 11.1 m	PAR	OEP XDE9401; EPA E14, 4, CB 1	12x4
LE1.1	-76.60176	38.42535	PAXMH	Mid-channel SSW of Jack Bay sandspit. NE of Sandgate; 12.5	PAR, VSS, Phytoplankton Mar-Nov above the pycnocline composite live and fixed sample. Picoplankton July- Sept above pycnocline composite DOC Mar-Sep	OEP XDE5339; EPA E15	12x4
LE1.2	-76.51132	38.37887	PAXMH	Mid-channel,1.6 km SW of Petersons Point. 17.8 m	PAR	OEP XDE2792	12x4
LE1.3	-76.48490	38.33980	PAXMH	Mid-channel 1200 m due N of Pt. Patience, ESE of Half Pone Point. 23.1 m	PAR, Mar-Nov Phytoplankton live collected from the surface	OEP XDF0407	12x4
LE1.4	-76.42151	38.31200	PAXMH	Mid-channel on a transect between Drum Pt. and Fishing Pt; 16.5m	PAR	OEP XCF8747	12x4

Potomac Stations							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
PIS0033	-76.98673	38.69842	PISTF	Piscataway Creek at Maryland Rt. 210 crossing; 1 m	Sampled in coordination with mainstem		12x1
XFB1986	-77.02317	38.69787	PISTF	Piscataway Creek off Ft. Washington Marina between DM4 and DM6, SW of dredged channel; 2m	Sampled in coordination with mainstem, Phytoplankton Mar- Nov live at surface		12x1
MAT0078	-77.11865	38.58852	MATTF	Mattawoman Creek at MD. Rt. 225 crossing; 1 m	Sampled in coordination with mainstem		12x1
MAT0016	-77.19345	38.56508	MATTF	Mattawoman Creek at green day beacon 5 off Sweden Pt; 2 m	Sampled in coordination with mainstem, Phytoplankton Jun-Aug live at surface	OEP XEA3687	12x1
TF2.1	-77.04876	38.70664	POTTF	At Fl buoy 77 off mouth of Piscataway Creek; 19 m	Sampled in coordination with mainstem, Phytoplankton Jun-Aug live at surface	OEP XFB2470;	12x3
TF2.2	-77.11111	38.69067	POTTF	Buoy 67 off mouth of Dogue Creek; 8 m	Sampled in coordination with mainstem, Phytoplankton Jun-Aug live at surface	OEP XFB1433; USGS 3841360 77054600	12x3
TF2.3	-77.17390	38.60820	POTTF	Buoy N54 mid-channel off Indian Head; 15 m	Sampled in coordination with mainstem, VSS, Phytoplankton Mar-Nov whole water column composite live & fixed, Picoplankton whole water composite, DOC Mar-Sep	OEP XEA6596	12x3
TF2.4	-77.26540	38.53010	POTTF	Buoy 44 between Possum Pt. And Moss Point; 9 m	Sampled in coordination with mainstem, Phytoplankton Jul- Aug-live surface	OEP, XEA1840; USGS	12x3

Potomac Stations							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
						06158710; EPA-Several	
RET2.1	-77.26910	38.40350	POTOH	Buoy 27 SW of Smith Point; 8 m	Sampled in coordination with mainstem	OEP XDA4238; EPA – Several	12x2
RET2.2	-77.20510	38.35250	POTOH	Buoy 19 mid-channel off Maryland Point; 11 m	Sampled in coordination with mainstem, VSS, Phytoplankton Mar-Nov-whole water column composite live & fixed. Picoplankton July-Sep whole water column composite.DOC Mar-Sep	OEP XDA1177; EPA - Several	12x3
RET2.4	-76.99063	38.36260	POTMH	Mid-channel at Morgantown bridge (US Rt. 301); 19 m	Sampled in coordination with mainstem, VSS, Phytoplankton Mar-Nov-whole water column composite live and fixed.	OEP XDC1706; USGS 01660800; EPA - Several	12x4
LE2.2	-76.59800	38.15760	POTMH	Potomac River off Ragged Point at Buoy 51B; 10 m	Sampled in coordination with mainstem, VSS, DOC Mar-Sep, Phytoplankton. Mar- Dec above pycnocline composite live, picoplankton above pycnocline composite sample fixed July - Sep	OEP XBE9541	12x4
LE2.3	-76.34770	38.02150	POTMH	Mouth of Potomac River (1.6 nm from Pt Lookout on Hdg 240, 0.5 nm NW of Whistle A); 19.8m	Sampled on mainstem cruise	OEP XBF0893	14x4

Tidal Tributaries							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
ET1.1	-75.96782	39.56976	NORTF	Northeast River at Day marker 12 off Hance Pt, mid-channel; 3 m	Phytoplankton June-Aug. live at surface	OEP XKI4220, XKI3717, XKI4523, XKI5025	12x2
ET2.1	-75.81135	39.52930	C&DOH	C&D Canal E of Rt. 213 Bridge at Chesapeake City; 13 m		OEP XKJ1810, XKJ1811	12x2
ET2.2	-75.87368	39.46704	BOHOH	Bohemia River off Hack Pt, 75 yards E-NE of day marker R 4, mid- channel; 3 m		OEP XJI8076, XJI7678; EPA U9	12x2
ET2.3	-75.89783	39.50873	ELKOH	Elk River SE of Old Cornfield Pt at G 21, mid-channel; 12		OEP XKI0661; EPA U10	12x2
ET3.1	-75.88203	39.36416	SASOH	Sassafras R from end of pier at Georgetown Yacht Basin, NW side of MD. Rt. 213 bridge; 5 m	Phytoplankton Mar-Nov, live at surface	OEP XJI1970; EPA U1	12x2
ET4.1	-75.92490	39.24370	CHSOH	Chester River at Rt. 290 bridge near Crumpton; 6 m		OEP CHE0367	12x2
ET4.2	-76.21510	38.99233	CHSMH	Lower Chester River South of Eastern Neck Island 200 yards SW of buoy FL G 9; 16m	Phytoplankton Mar-Nov, live at surface.	OEP XGG9572; CBI CHO9C	12x4
XGG8251	-76.14.840	38 58.267	CHSMH	Chester River at Kent Narrows			12x1
EE1.1	-76.25150	38.88000	EASMH	Eastern Bay between Tilghman Pt and Parsons Island, N of buoy R4; 13m	Phytoplankton Mar-Nov, live at surface	OEP XGG2649; CBI 851N	12x4

Tidal Tributaries							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
ET5.1	-75.90971	38.80645	CHOOH	Upper Choptank River 200 yards upriver from Ganey's Wharf, downstream of confluence with Tuckahoe Creek; 6 m	Phytoplankton Mar-Nov; at surface, live and fixed. Picoplankton Jul-Sept.	OEP CHO0429	12x2
ET5.2	-76.05870	38.58070	CHOMH2	Lower Choptank River, mid-river 50yards NNE of G l, W of Rt. 50 bridge at Cambridge; 11 m	Phytoplankton Mar-Nov- above pycnocline composite, live and fixed. Picoplankton Jul- Sep-above pycnocline composite fixed, DOC Mar-Sep	OEP XEH4766	12x4
EE2.1	-76.26430	38.65490	CHOMH1	Choptank embayment between Todd's Point and Nelson Pt; 8 m		OEP XEG9440, XEG9652	12x4
EE2.2	-76.30408	38.52609	LCHMH	Little Choptank River mid-channel West of Ragged Point, W of Buoy Fl g 3; 14 m		OEP XEG1617	12x2
EE3.0	-76.01033	38.28093	FSBMH	Fishing Bay at day marker 3, W of Roasting Ear Pt; 7 m	VSS, Phytoplankton Mar-Nov-live surface. Picoplankton Jul-Sept at surface	OEP XCH6994, XCH5991	12x2
TRQ0146	-76.00010	38.46566	FSBMH	Transquaking River at DeCoursey Bridge, 2.5m			12x1
CCM0069	-75.90480	38.44230	FSBMH	Chicamacomico River drawbridge & road crossing, 2.5m	Continuous monitoring 2000-2003		12x1
ET6.1	-75.70306	38.54833	NANTF	Upper Nanticoke River at old Rt. 313 bridge (fishing pier,1987) in Sharptown; 5 m	VSS, Phytoplankton Mar-Nov- live surface plankton	OEP NAN0302 1	12x2
ET6.2	-75.88834	38.34133	NANMH	Lower Nanticoke River mid-channel near Fl G 11; 3.5 m	VSS	Near OEP XDI0567	12x2

Tidal Tributaries							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
XDJ9007	-75.82098	38.48375	NANMH	Nanticoke River at Old Rt. 50 bridge in Vienna, 2m	DNA probe Pfiesteria 1998-2002		12x1
EE3.1	-75.97321	38.19685	TANMH	North Tangier Sound, NW of Haines Pt, 100 yards N of buoy R16; 13 m	Phytoplankton Mar – Nov, above pycnocline composite plankton-live and fixed; DOC Mar-Sep	OEP XCI1717	12x4
EE3.2	-75.92423	37.98139	TANMH	South Tangier Sound, mid-channel East of Smith Island, 500 yards NNW of buoy R8; 28 m	Phytoplankton Mar- Nov-live surface	OEP XAI8845, Near OEP XBI3003	12x4
WIW0141	-75.69569	38.34156	WICMH	Wicomico River at upper ferry crossing on Upper Ferry Road			12x1
ET7.1	-75.78793	38.26783	WICMH	Lower Wicomico River at Whitehaven, 150 yards downriver of Ferry Road, mid-channel; 7m	VSS, Phytoplankton Mar-Nov-live surface	OEP WIW0050	12x2
XCI4078	-75.86963	38.23379	WICMH	Wicomico River at Island Pt in channel at buoy FL14, 4.5m			12x1
ET8.1	-75.81411	38.13794	MANMH	Manokin River at upper extent of channel; approx. 100 yards NNE of buoy R 8, mid-channel; 6 m	VSS	OEP XBJ8215	12x2
BXK0031	-75.75156	38.13563	MANMH	Manokin River, Back Creek at Milliard Long Rd, 3m			12x1
MNK0146	-75.72235	38.17513	MANMH	Manokin River at an unnamed road off Stewart. Neck Rd, 4.5m			12x1

Tidal Tributaries							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
ET9.1	-75.80167	38.05500	BIGMH	Big Annemessex River, NW of Long Pt in channel S of day marker G5; 5m	VSS	OEP XBJ3312	12x2
ET10.1	-75.56630	38.08350	POCTF	Pocomoke River on Alt US Rt. 13 (Market St.) an old drawbridge in Pocomoke City, 5m	Striped bass spawning	OEP POK0170	12x2
POK0087	-75.65047	37.96396	POCOH	Pocomoke River off Rehoboth Rd in the Town of Rehoboth, 2m			12x1
XAK7810	-75.65047	37.96396	POCOH	Pocomoke River, mid mouth of the river, 3.5m	Phytoplankton (live)		12x1
EE3.3	-75.80148	37.91455	POCMH	Pocomoke Sound, near buoy WSA midway between Oyster shell Pt and Long Pt	Phytoplankton Mar- Nov-live at surface	Near OEP XAJ4719, Near VA EE3.1	12x2
WT1.1	-76.24205	39.43511	BSHOH	Bush River E of Gum Point, E of Fl G9 on power line support; 2 m		OEP XJG6254	12x2
WT2.1	-76.33465	39.37747	GUNOH	Gunpowder River, 200 yards E of Oliver Point at buoy G15; 2.5 m		OEP XJF2798	12x2
WT3.1	-76.40954	39.30538	MIDOH	Middle River East of Wilson Point at channel junction day marker WP; 3 m	Phytoplankton Mar- Nov-live at surface	OEP XIF5484; EPA M2	12x2
WT4.1	-76.44368	39.27755	BACOH	Back River, East of Stansbury Point, East of day marker R12; 2 m		OEP XIF6633, Near OEP XIF6732	12x2

Tidal Tributaries							
Station	**Longitude**	**Latitude**	**CBP Segment**	**Location/Depth**	**Sampling Coordination**	**Historical Station names**	**Annual Sample Freq. x No. Of Depths**
WT5.1	-76.52254	39.21309	PATMH	Patapsco River East of Hawkins Point at Buoy G3; 14 m	Phytoplankton Mar- Nov-above pycnocline composite-live & fixed. Jul- Sep-above pycnocline composite Picoplankton fixed, DOC Mar-Sep	OEP XIE2885	12x4
WT6.1	-76.51005	39.07851	MAGMH	Magothy River N of South Ferry Pt, mid-channel at buoy R12 and day marker G11; 5 m	Phytoplankton Mar- Nov-live surface;	OEP XHE4794	12x2
WT7.1	-76.50350	39.00764	SEVMH	Severn River, 200 yards upstream of Rt. 50/301 bridge and 150 yards off NE shore; 9 m	Phytoplankton Mar- Nov-live surface	OEP XHE0497	12x2
WT8.1	-76.54610	38.94960	SOUMH	South River South of Poplar Point at day marker R16; 9m	Phytoplankton Mar- Nov-live surface	OEP XGE6972	12x2
WT8.2	-76.53490	38.88696	RHDMH	Rhode River between Flat Island and Big Island; 3 m		OEP XGE3279	12x2
WT8.3	-76.53410	38.84250	WSTMH	West River just upstream of day marker R6; 4 m		OEP XGE0579	12x2

For logistical reasons, the Potomac component station LE2.3 is sampled with mainstem stations and Mainstem component station CB5.1W is sampled during Patuxent sampling.

For data analysis purposes, data users should take care at these two stations due to historical differences in laboratory methods used for different field sampling groups. Station LE2.3, while sampled as part of the Mainstem stations, is a Potomac station for data analyses and is included in CBP Segment POTMH_MD with other stations that were collected under tributary protocols. Station CB5.1W, while sampled as part of the Patuxent stations, is a Mainstem station for data analyses and is grouped in CBP Segment CB5MH_MD with other stations that were collected under Mainstem protocols. Data analysts need to take these differences into consideration when aggregating stations by CBP segment or by water body. Historical differences in laboratory methods used and analysis detection limits should be understood as they may impact the data analysis. This information is included in the CBP online database (CBP Water Quality Database (1984-present)) and more details are available in the online Data Users guide *2012 Guide to Using Chesapeake Bay Program Water Quality Monitoring Data*.

A7. Quality Objectives and Criteria

The tidal monitoring program is designed to provide laboratory and field data that will help the state characterize water quality throughout the Chesapeake Bay and tidal tributaries. Assessment of the quality of the data collected through the program can be expressed in terms of representativeness, completeness, comparability, accuracy, and precision.

Representativeness: Representativeness is the degree to which the sample data represents the actual conditions or concentrations present in the sampled population or area. Representativeness can be affected by experimental design, and sample collection and handling. The experimental design calls for monthly sampling on a pre-determined date, which is adequate for capturing long-term annual trends in concentration.

Comparability: Comparability refers to the confidence with which one data set can be compared with another. Comparability must be ensured so that the results for one station are of comparable quality to other stations. In addition, the data generated by the tidal monitoring program must also be of comparable quality to the data generated by other states and laboratories participating in the program. Comparability among data sets is assured using consistent field methods and protocols, participation in the CBP Data Integrity Workgroup and the use of field splits and blind audit samples.

Comparability of monitoring data is achieved because of quality assurance procedures at each phase of the data gathering and processing. It includes representative sampling and sample handling procedures, uniform laboratory methods and validation of laboratory data and procedures for reduction, validation and reporting of environmental data.

Completeness: Completeness is a measure of the amount of valid data obtained compared to the amount that was expected under normal conditions. Completeness is a condition to be achieved in order to meet the data requirements of the program. Factors that can affect completeness include problems encountered by the field crews such as adverse weather conditions or equipment failures and

laboratory-related issues such as sample preservation, exceeding holding times, and accidents. To ensure that data is of the quality required to support management decisions, Maryland's tidal monitoring program strives to provide monitoring data of known and consistent quality to the CBP by following the guidelines in the Methods and Quality Assurance for Chesapeake Bay Water Quality Monitoring Programs (EPA 2017). These guidelines recommend precision goals for field and lab measurements of <20 percent of the coefficient of variation; accuracy goals within 80 to 120 percent, and the completeness goals of 95 percent.

Accuracy: The accuracy (closeness to the true value) of the collected data is controlled and assured by the proper use, calibration, and maintenance of both field and laboratory equipment for the measurement of physical and chemical parameters. All instruments are identified by a unique number, used as an index for documentation of calibration, repair, and preventive maintenance. Where possible, standards used for calibration purposes are validated against a primary standard such as those available from the National Institute of Science and Technology (NIST). Daily quality control checks (including the running of blanks and standards) are used to control and assure laboratory accuracy.

Accuracy of laboratory results is also assessed through laboratory participation in the Chesapeake Bay Coordinated Split Sample Program (CSSP), the Blind Audit Program and the United States Geological Survey (USGS) Standard Reference Sample Program. More information on these programs is included in Section B5 and on the CBP webpage Quality Assurance/Split Sample and Blind Audit Programs.

Precision: Precision (repeatability) measures the closeness of values for a parameter within a data set. Quality control samples along with appropriate statistical techniques are used to ensure precision in the production of laboratory data. Precision of the chemical analytical methods is determined and documented from duplicate analyses.

MDH analyzes and provides results on the corresponding request forms for the field duplicates. MDH performs precision calculations for laboratory duplicates, but not for the field duplicates. Every tenth sample is analyzed in duplicate. The acceptable value for the relative percent difference (RPD) is +/- 10%. If the calculated RPD does not fall within the acceptable range, the corresponding analysis is repeated. Precision of the entire measurement system for laboratory-analyzed parameters, including field processing, storage, and chemical analysis, can be assessed from duplicate field samples. Based on previous analysis, there can be relatively large differences in measured values for certain water quality parameters.

At CBL, typically 10% of the total number of samples analyzed consist of laboratory duplicates and/or laboratory spikes. Certified parameters require laboratory duplicates to be analyzed every 20 samples within an analytical run, regardless of the total number of samples in that batch. The mean of the two values is reported as the concentration for that sample. If a difference of >10% is observed between replicates, then all the replicates for that analytical run are carefully reviewed. If only one of the duplicate pairs is in question, then only that sample is re-analyzed or qualified. If all show a similar trend, then instrumentation/reagent problems are suspected, and the analytical run is halted until such time as the problem is resolved. The spiked sample is analyzed, and its expected concentration calculated as the sum of the original concentration and the spike concentration, normalized for the constituent volumes. A comparison is made between the actual value and the expected value. These

concentrations (original, expected and actual) are recorded in a separate QA/QC data file. If a value of >120% or <80% (>110% or <90% for select parameters) is observed for percentage recovery of the spike, then all the spikes for that analytical run are carefully reviewed. If only one of the spikes is in question, then only that sample is re-analyzed. If all show poor recovery, then instrumentation/reagent problems are suspected, and the analytical run is halted until such time that the problem is resolved.

A8. Special Training/Certification

Maryland DNR field personnel are required to demonstrate proficiency in all aspects of sample collection. The CBP Quality Assurance Coordinator conducts periodic site visits to assure the continued proficiency of field personnel and adherence to the procedures specified in the Department's Standard Operating Procedures:

Training of personnel at MDH is conducted in the laboratory. Each new analyst is trained in the laboratory procedures they will be assigned to perform by an experienced analyst. Training is documented using the Division of Environmental Chemistry's training forms and signed by the Supervisor and the Division Chief.

Training of personnel at NASL occurs when the trainer and trainee perform analysis in tandem and in accordance with time periods specified in standard operating procedures for each analysis and instrument until satisfactory competency is achieved. On-site audits verify field and laboratory staff qualifications, experience and training programs.

A9. Documents and Records

Approved Quality Assurance Project Plans are valid for up to five (5) years and are reviewed annually and revised as needed. Revised QAPPs are submitted to the CBP Quality Assurance Officer for review and approval. The synopsis of change and versioning history is documented in the preface. Each version is numbered consecutively with the date of approval and a summation of changes made.

All of DNR's monitoring program QAPPs fall under the umbrella of the Maryland Department of Natural Resources Quality Management Plan. Documents and files needed for current tasks are maintained by the department units. Program Chiefs are responsible for ensuring that filing practices conform to the unit's records retention schedules.

The Project leader and/or Program Chief are responsible for identifying, preparing or reviewing, revising and maintaining current quality related documents and records including quality assurance project plans and standard operating procedures. Standard operating procedures may be referenced within quality assurance project plans as appropriate. The Project leader and/or Program Chief may delegate review and revising of quality related documents to lower-level quality assurance staff (such as field staff and laboratory staff) with final review and approval by the Project leader and/or Program Chief.

Records Retention

The Program Chief should ensure that out-of-date versions of quality related documents are properly archived for historical reference. The department is required to manage its records, including the establishment or revision of records retention schedules to ensure effective and efficient disposal of records not required by the department. The Maryland Department of General Services oversees the State Records Management Program.

The State Records Management Program ensures continual, efficient and secure records management consistent with State regulations (COMAR 14.18.02), and State law (Annotated Code of Maryland State Government Article 10, sections 608-611). Section 610 specifies that the head of each unit of government appoints a records officer from among the executive staff. A records officer serves as the liaison between the government unit and the State Archives and the Records Management Division. The records officer also develops and oversees the unit's records management program. The records officer for the DNR is:

Caroline Asher, Director, Audit and Management Review Maryland
Department of Natural Resources
580 Taylor Avenue C-3, Annapolis, MD 21401
Phone: (410) 260-8074,
Caroline.Asher@maryland.gov

The State of Maryland requires that each unit within a state agency submit a records retention plan for approval by the Maryland State Archives (MSA). The Chesapeake Bay Tidal Monitoring Program is under the direction of DNR's Resource Assessment Service (RAS). RAS' Records Retention Schedule 2813 is referenced by the MSA Agency Retention Schedules as Series 1468. Internal retention (vs archival) is documented by the Record Retention Cover Sheet (Figure 3) and is maintained within the unit itself.

Records Access

Chain of custody and confidentiality procedures (if applicable) are described in the standard operating procedures and/or the quality assurance project plans. Public access to documents and records of the department is controlled by Maryland's *Public Information Act* (State Government Articles 10-611 to 10-628). Information on the *Public Information Act* is available from the Maryland Attorney General's office (www.marylandattorneygeneral.gov). This Act allows the public a broad right of access to public records while protecting legitimate governmental interests and the privacy of rights of individual citizens. Documentation and data submitted to the department for transfer to EPA are public records subject to Maryland's P*ublic Information Act.*

Figure 3. Record Retention Cover Sheet

RECORDS INVENTORY AND RETENTION SCHEDULE COVER SHEET

Schedule Number (To be completed by DGS/Records Management Division)	**2813**

Agency Information

Department / Agency	Department of Natural Resources
Division / Unit	**Resource Assessment Service**
Mission Statement/Link to division/unit website	The Resource Assessment Service monitors and assesses waters throughout the state to provide essential information for restoration and protection programs.

Schedule Information

Supersedes Schedule(s)	
Amends Schedule(s)	

Preparer Information

Name of Preparer	Sharon Maenner Carrick
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Date	15 Mar 2021

Agency Approval

Name of Agency Director	Sharon Maenner Carrick
Agency Director Signature	Sharon Carrick
Date	15 Mar 2021

State Archivist Approval

State Archivist Signature	
Date	4/6/2023

DGS 550-14 (REV. 7/17)

END OF SECTION A

B: DATA GENERATION AND ACQUISITION ELEMENTS

B1. Sampling Process Design

B1.1 Location

A total of 22 Mainstem stations and 69 tributary stations are included in Maryland's Chemical and Physical Properties Component of the Chesapeake Bay Water Quality Monitoring Program (Figure 2 and Table 2). Station locations were selected to provide data that would satisfy the four objectives of the program stated above for the major tributaries and the Mainstem. The following describes the four sets of criteria used to determine the general location for stations:

Primary Selection Criteria. During the initial phases of the Bay Program, EPA developed a segmentation/characterization scheme of the Chesapeake Bay and its tributaries published in the appendices of Chesapeake Bay: A Profile of Environmental Change (EPA 1983). This scheme provided guidance for station selection by delimiting different regions (based on circulation, salinity, and geomorphology) such as tidal fresh, oligohaline, and mesohaline. Several primary goals were considered in selecting station locations. Selecting a suite of stations such that each segment would be characterized was the foremost goal. Another important criterion was the location of boundaries between segments (e.g., mouths of major tributaries and the upper boundary of the deep trough region). Boundary areas are important because of their influence on a particular region of the Bay or their relevance to problem areas. In large systems, i.e., the Potomac and Patuxent Rivers and the Mainstem, multiple stations were in each salinity zone due to the large size of these systems and their importance to management concerns. Many of the existing water quality monitoring stations in the Potomac River and Patuxent River were incorporated into the Baywide network as primary selection criteria because of the wealth of historical data at these stations (See Table 2 for historic station names).

Secondary Selection Criteria. Locations of documented water quality problems in certain areas served as secondary considerations in locating stations. For example, additional stations were included in the lateral dimension of the deep trough region of the Mainstem (designated as east (E), center (C) and west (W) stations, Table 2) to characterize the deep water anoxic/hypoxic conditions. Another example was the sitting of stations in some of the smaller tributary segments in areas that were profoundly impacted by point sources. Stations sited in these affected areas provide excellent opportunities to assess the effectiveness of control strategies targeted at reducing these major impacts.

Tertiary Selection Criteria. Another consideration in siting stations was their proximity to important living resource habitats and living resource monitoring sites. This criterion was accommodated only if the primary and secondary criteria above were also satisfied. These stations provide valuable data to correlate with living resources monitoring and thereby help to resolve the link between water quality and fluctuations in living resources.

Final Selection Criteria. The fourth and final consideration in locating stations was the historical record of water quality sampling. If a station already had a record of previous water quality data and it satisfied the three sets of criteria stated above, the station was adopted for this program to permit comparisons with historical databases. In selecting stations for the Patuxent and Potomac Rivers, this criterion was elevated to a primary criterion. Additional historical stations in the Patuxent and Potomac were adopted

into the CBP sampling program even if they did not fulfill all three sets of criteria above, because of the very long-term data sets associated with these stations. Table 2 includes the historic station names that correspond to the CBP stations.

Establishing Mid-Channel and Near-shore Stations. In both the Mainstem and tributaries, stations were selected in mid-channel locations to provide a characterization of the entire water column in that region and to capture the lowered oxygen levels in the deeper layers. The water column at mid-channel also provides a more stable environment than shallow locations, which are subject to ephemeral influences such as wind-driven resuspension of bottom sediments and periodic advection of deep-channel water masses; thus, mid-channel stations provide data with less short-term variability. Minimizing short-term variability is desirable to detect long-term trends. As mentioned above, in the Mainstem's deep trough region, lateral stations were established to track a particular concern. Two near-shore stations were located beside each of the four mid-channel stations. These near-shore stations were located at the 30-foot depth contour or at the boundary of adjacent embayments. Stations also were located at the boundary between the Mainstem and the two largest tributaries in Maryland—the Susquehanna and Potomac Rivers—to assess the water quality interactions occurring across these critical regions.

Updating the Segmentation Scheme. During 1997, a workgroup was established to re-evaluate the segmentation scheme using the data generated by the program from 1985-1996. DNR uses the current segmentation scheme established by the EPA CBP to classify stations and analyze data. Under the new segmentation scheme, three segments (CHOTF, NANOH and HNGMH) do not include long-term stations. The Chesapeake Bay Program, Analytical Segmentation Scheme, Revisions, Decisions and Rationales 1983-2003 and the Chesapeake Bay Program, Analytical Segmentation Scheme, Revisions, Decisions and Rationales, 1983-2003, 2005 Addendum provide detailed descriptions of the CBP's segmentation and its development.

Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll a for the Chesapeake Bay and Its Tidal Tributaries, 2008 Technical Support for Criteria Assessment Protocols Addendum summarizes previous segmentation work and documents recommended refinements of the segmentation scheme to address dissolved oxygen and water clarity assessment issues. More recently, the Technical Addendum Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll a for the Chesapeake Bay and Its Tidal Tributaries, 2017 Technical Addendum, provides previously undocumented features of the present procedures as well as refinements and clarifications to the previously published Chesapeake Bay water quality criteria assessment procedures (U.S. EPA 2004a, 2007a, 2007b, 2008, 2010).

Note that a total of eight addendum documents have been published by EPA since April 2003. Four addenda were published documenting detailed refinements to the criteria attainment and assessment procedures (U.S. EPA 2004a, 2007a, 2008, 2010) previously published in the original April 2003 Chesapeake Bay water quality criteria document (U.S. EPA 2003a). One addendum published Chesapeake Bay numerical chlorophyll a criterion (U.S. EPA 2007b). Three addenda addressed detailed issues involving further delineation of tidal water designated uses (U.S. EPA 2004b, 2005, 2010) initiating from the original October 2003 tidal water designated uses document (U.S. EPA 2003b).

Finally, one addendum documented the 92-segment Chesapeake Bay segmentation scheme (U.S. EPA 2008) after refinements to the CBP analytical segmentation schemes were documented (U.S. EPA 2005) building from the original U.S. EPA 2004 document (U.S. EPA 2004b). The 2017 addendum is the eighth addendum document developed through the Partnership and published by EPA.

B1.2 Frequency

Water column samples are collected once a month at most stations, for a total of twelve samplings per year. In the Chesapeake Mainstem, sampling will be conducted twice monthly in June, July and August, and once monthly during the remaining months, for a total of fifteen samplings per year. Sampling during the second bi-weekly July survey will consist of water-column profiles only. Eastern and western transect Mainstem station samples will not be collected from November through February, resulting in only eleven samplings a year. On the Potomac and Patuxent and smaller tributaries, twelve samplings will be conducted per year. This frequency of sampling permits assessments to be made on a seasonal basis, which is a time scale consistent with many of the natural intra-annual changes in water quality indicators.

Because of the relatively small sample sizes resulting from only two to four sampling events per season, it is more difficult to detect seasonal trends in data from stations sampled only once per month. Nevertheless, with a long-term program, sufficient data can be collected to determine seasonal patterns in most water quality parameters at each site with high statistical confidence.

This level of sampling frequency is judged to be the optimal allocation of effort given the limited level of resources. It provides for wide spatial coverage of almost every major tributary in Maryland as well as for information on the major systems that are the focus of major management strategies.

B1.3 Measured Parameters

The Chemical and Physical Properties Component of the Chesapeake Bay Water Quality Monitoring Program measures a broad suite of physical and chemical parameters that are indicative of the Bay's eutrophication problem. Several "natural" properties such as salinity and temperature in the water column provide important information for interpretation of water quality indicators and information on the impacts of climate change.

Some parameters, such as specific conductance, temperature, dissolved oxygen, and pH, are measured in situ using multi-parameter water quality instrumentation manufactured by Hydrolab® or Yellow Springs Instruments® (YSI). Salinity is calculated from conductivity and temperature. Photosynthetic Active Radiation (PAR) measurements are made in situ using a Li-Cor® quantum meter and probe. Secchi depth is measured using a weighted 20 cm diameter limnological Secchi disc with alternating white and black quadrants. The disc is attached to a graduated line.

B1.4 Field Measurements and Sampling

Sampling procedures have been formulated for each part of the Chesapeake Bay Mainstem and Tributary Water Quality Monitoring Program to take measurements that meet the program objectives in an efficient, cost-effective, and logistically practical manner.

A total of 22 Mainstem stations and 69 tributary stations are included in the Chemical and Physical Properties Component of the monitoring program (see Figure 2 and Table 2 above in Section A).

The sampling protocol includes grab samples and corresponding water column measurements at one or two measurements of the water column in well-mixed non-stratified regions and two additional measurements - one in the surface mixed layer, and one in the bottom mixed layer - where the estuary is stratified into the typical two-layered flow pattern.

Water column grab samples collected for subsequent analysis in the laboratory will be taken by submersible pump, bucket, Alpha or Kemmerer bottle. Details on filtration, containers, and storage techniques can also be found in Section B3 Sample Handling and Custody.

The water column is profiled for temperature, conductivity, dissolved oxygen, and pH using an *in-situ* probe that transmits data to a shipboard readout via cable. Profiling is conducted at a minimum resolution of 2-meter sampling intervals. In strata where there is appreciable change in conductivity or dissolved oxygen (i.e., at the pycnocline), 1-meter intervals are sampled. The protocols for determining profiling depths are detailed in Section B2 Water Column Sampling and Sample Procedures.

The number of depths sampled per station is listed in the last column of Table 2.

Tributary stations without stratification: One or two depths will be sampled at stations that do not normally exhibit vertical density stratification. For stations where samples are collected at a single depth, the grab will be collected from a depth of either 0.0 m or 0.5 m depending on the site. The depths of 0.5 meter below the surface and l.0 meter above bottom will be sampled at sites where grabs are made at only two depths.

Mainstem and minor tributaries with stratification: Four depths will be sampled at stations that are normally density stratified: 0.5 m below the surface, l.5 m above the upper limit of the pycnocline, l.5 m below the lower limit of the pycnocline, and l.0 m above the bottom. Grab sampling depths relative to the pycnocline will be determined according to the protocols described in Section B2. Above pycnocline depth and below pycnocline depth grab samples are collected at the following stations: CB2.2, CB3.1, CB3.2, CB3.3C, CB4.1C, CB4.1E, CB4.2C, CB4.3C, CB4.3E, CB4.4, CB5.2, CB5.3, EE1.1, EE2.1, EE3.1, EE3.2, ET4.2, ET5.2, LE2.2, LE2.3, RET2.4 and WT5.1.

Lower Patuxent stations: Four depth grab samples are collected at lower Patuxent sites where mid-water sampling is conducted at fixed depths to maintain consistency with historical-station sampling depths. In addition to surface and bottom water samples at the six Patuxent boat survey stations, upper mid-water samples are collected at 3.0 meters depth. At stations CB5.1W, RET1.1 and TF1.5, lower mid-water samples are collected at 6.0 meters. Lower mid-water samples are collected at 9 meters at stations LE1.1 and LE1.4. At stations LE1.2 and LE1.3 lower mid-water samples are collected at 12.0 meters.

Potomac stations: Grab samples on the Potomac boat survey are collected at three depths at five Potomac stations. In addition to surface and bottom water samples, to maintain consistency with historical-station sampling depths, mid-depth samples (M) are collected at 4.6 meters at stations RET2.2, TF2.4, TF2.3 and TF2.2. The station TF2.1 mid-depth sample is collected at 9.1 meters.

For the Mainstem stations only, when there is an odor of hydrogen sulfide present in the bottom sample or the below pycnocline sample, a Hach® Kit test for hydrogen sulfide presence on the bottom and/or below pycnocline sample(s) will be performed.

Water transparency will be measured by Secchi depth, determined in meters using a 20 cm standard Secchi disc lowered into the water column with a calibrated rope. Observations will be made on the shady side of the boat.

B1.5 Procedural Change Protocol

The CBP Quality Assurance Coordinator will be notified of the intent to make any substantial or long-term change to a procedure or method, either in the field or laboratory. These changes include items such as instrument type and sampling stations. The effects of any change in analytical instruments, reagents, calibration, digestion procedure, etc., will be quantified, documented and submitted to the CBP QA Coordinator prior to implementation. All modifications will be documented using the Chesapeake Bay Monitoring Program **Procedure Modification Tracking Form** (**PMTF**). The completed PMTF will be submitted to the DNR Quality Assurance Officer, CBP Quality Assurance Coordinator and CBP Water Quality Database Manager. Substantial changes will also require the update of this QAPP and will be documented in the Log of Significant Changes.

Minor changes in field or laboratory procedures, including detection limit changes, will be documented in the CBP metadata and data submission tables. Minor changes will not require the update of this QAPP.

Minor events and problems encountered during Chesapeake Bay Mainstem cruises will be reported in the CBP Monitoring Cruise Report (Section B10) and to the Program Manager to be included in all semi-annual reporting for the monitoring program grant. For all events, remarks relating to field work will be reported in the CBP WQ_Cruise and WQ_Event tables.

Modifications due to emergencies during a sampling cruise are authorized by the Chief Scientist with priorities for safety and completion of the cruise. The change should be documented within 30 days after the cruise, in either the PMTF or the Monitoring Cruise Report, depending on size or potential impact of the deviation on the data.

B1.6 Procedure Modification Tracking Form

Figure 2.1
CHESAPEAKE BAY MONITORING PROGRAM PROCEDURE MODIFICATION TRACKING FORM

PMTF # _____ **□ APPROVED □ DENIED**

This form is used to request approval for modifications and to document approved modifications made to Chesapeake Bay Program Office procedures or methods. It is not a substitute for timely contact with the CBPO Quality Assurance Officer or his/her designee, who may be reached at 1-800-968-7229. A detailed method description including the proposed modification must be attached to this form prior to submittal to CBPO.

DATE SUBMITTED		DATE APPROVED	
REQUESTOR NAME		ORGANIZATION	
NEWLY PROPOSED [ ] MODIFICATION	FIELD-APPROVED [ ] MODIFICATION	APPROVED BY: DATE:	
TYPE OF PROCEDURE / METHOD	SAMPLING [ ] FIELD MEASUREMENT [ ]	ANALYTICAL [ ] OTHER [ ] SPECIFY:	REPORTING [ ]
DURATION	PERMANENT [ ] TEMPORARY [ ]	EFFECTIVE DATE: START DATE: END DATE:	
PROCEDURE/METHOD DESCRIPTION			
MODIFICATION DESCRIPTION			
JUSTIFICATION FOR MODIFICATION			
ANALYTICAL PARAMETERS THAT MAY BE AFFECTED BY THIS CHANGE			
AFFECTED QA PLAN(S) (TITLE, REVISION, & DATE)			
AFFECTED CRUISE(S)			
PMTF COMPLETED BY	NAME:		DATE:

STATE APPROVAL: NAME _____ TITLE _____
SIGNATURE _____ DATE _____

CBPO APPROVAL: NAME _____ TITLE _____
SIGNATURE _____ DATE _____

METHODS AND QUALITY ASSURANCE FOR CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAMS, May 2017, CBP/TRS-319-17, Chapter 2, Figure 2.1
https://www.chesapeakebay.net/documents/CBPMethodsManualMay2017.pdf

B1.7 Log of Significant Changes

Procedural changes have been made over the years to address evolving water quality sampling program requirements, goals, budgetary changes, and recommendations of the Analytical Methods and Quality Assurance Work Group and other issues.

The Change Log is a chronological list of changes to the monitoring program. The list is composed of change implementation-dates and brief descriptive summaries of modified procedures (Table 4.).

Table 4. Log of significant changes for 117(e) grant years 2018-2022

Date Initiated	Procedural Changes
January 2018	None made
January 2019	None made
January 2020	Error code 14 was split into A and B codes where 14A = poor replication between pads, mean reported. Difference within 50%. Code 14B = poor replication between pads. Sample rejected because the difference is greater than 50%. Due to restrictions related to COVID-19, sampling was not conducted at main stem bay stations in March and April. Sampling was conducted through the first third of March for tributary stations. March tributary field data were completed and submitted to the CBP, but chlorophyll and laboratory samples were held beyond acceptable analysis times. April and May tributary sampling was not conducted. Main bay sampling resumed in May 2020, and tributary sampling resumed in June 2020.
April 2021	None made
April 2022	None made
September 2023	A Procedure Modification was approved to include a pre-wash of tubes and caps prior to the digestion and colorimetric analysis of total dissolved phosphorus.

Additionally, changes in measured parameter analytical detection limits are summarized in tabular form.

Table 3. Chesapeake Biological Laboratory Minimum Detection Limits

Red Boldface shows when DL changed

Chesapeake Biological Laboratory NASL

Parameter Minimum Detection Limits	1/1/17-12/31/17	1/1/18-12/31/18	1/1/19-12/31/19	1/1/20-12/31/20	1/1/21-12/31/21	1/1/22-12/31/22	1/1/23-12/31/23
CHLA	**0.62**	0.62	0.62	0.62	0.62	0.62	0.62
DOC	**0.16**	0.16	0.16	0.16	0.16	**0.21**	0.21
NH4	**0.002**	0.002	**0.013**	**0.009**	0.009	0.009	0.009
NO2	**0.0007**	0.0007	0.0007	0.0007	**0.0009**	0.0009	0.0009
NO23	**0.0007**	0.0007	0.0007	**0.0015**	0.0015	0.0015	**0.0009**
PC	**0.0633**	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633
PHEO	**0.74**	0.74	0.74	0.74	0.74	0.74	0.74
PN	**0.0105**	**0.0263**	0.0263	0.0263	0.0263	0.0263	0.0263
PO4	**0.0006**	0.0006	**0.0034**	0.0034	0.0034	0.0034	0.0034
PP	**0.0035**	**0.0021**	0.0021	**0.001**	0.001	0.001	0.001
SI	**0.0536**	**0.05**	0.05	0.05	0.05	0.05	0.05
TDN	**0.05**	0.05	0.05	0.05	0.05	0.05	0.05
TDP	**0.0015**	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015
TSS	**2.4**	2.4	2.4	2.4	2.4	2.4	2.4
VSS	**0.9**	0.9	0.9	0.9	0.9	0.9	0.9

B1.8 Section B. References

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B2. Sampling Methods

Maryland DNR Chesapeake Bay Mainstem and Tributary Water Quality Monitoring Program
Water Column Sampling and Sample Processing Procedures

B2.1 Depth Sampling Protocols

A. Hydrolab/YSI Depth Sampling Protocols (Mainstem and Tributary)

1. Take readings of temperature, specific conductance, salinity, dissolved oxygen, and pH at 0.5 m, 1.0 m, 2.0 m and 3.0 m. Thereafter, take readings at a minimum of 2.0 m intervals (subject to conditions specified in A.2. below) and at the bottom sample depth. Mainstem bottom sample depth is equal to the nearest whole meter that is at least one meter above the total depth. Tributary bottom sample depth is equal to the total depth minus one meter (not rounded).

2. If the change in DO exceeds 1.0 mg/l OR if the change in specific conductance equals or exceeds 1,000 micromhos/cm over any 2.0 m interval, take readings at the 1.0 m interval between these two readings. Take readings at 1.0 m intervals for total depths less than or equal to 10.0 m.

3. If the above pycnocline (AP) or below pycnocline (BP) sample depth has not been sampled for *in situ* parameters, obtain readings at this depth.

4. At a minimum, take readings at 0.5, 1.0, 2.0, 3.0 m, bottom, and every odd-numbered whole meter depth.

B. Grab Sampling Depth Protocols

1. At stations where two depths are sampled, take collections at:
   - 0.5 meter below the surface.
   - 1.0 meter above bottom (total depth) to nearest 1.0 m that is at least one full meter from the bottom (Mainstem).
   - 1.0 meter above bottom (tributaries).

   NOTES: If total station depth is ≤1.5 m, take a bottom sample at 0.5 m. Exercise caution when taking bottom samples; if disturbed bottom sediments appear to have been included in a sample, resample after sediment has settled or take sample slightly higher in the water column. If resampling occurs, note this on the field sheet.

2. **Pycnocline Exists**: At stations where 4 depths are sampled and a pycnocline exists (see Section C, below), take collections at:
   - 0.5 m below the surface.
   - 1.5 m above upper boundary of pycnocline.
   - 1.5 m below the lower boundary of pycnocline.
   - 1.0 m above bottom to nearest 1.0 m that is at least one full m from bottom (Mainstem).
   - 1.0 m above bottom (tributaries).

3. **No Discernable Pycnocline**: At stations where 4 depths are sampled and there is no discernable pycnocline (see Section C, below), take collections at:
   - 0.5 m below the surface.
   - at closest profile depth one third the distance from the surface to the bottom.
   - at closest profile depth two thirds the distance from the surface to the bottom.
   - 1.0 m above bottom (total depth) to nearest 1.0 m that is at least one full m from the bottom (Mainstem).
   - 1.0 m above bottom (tributary).

C. Pycnocline Determination (Only for Stations Sampled at four depths)

The pycnocline is a region in which the water density changes appreciably with increasing depth and thus forms a layer of much greater stability than is provided by overlying surface waters.

1. The pycnocline Calculated Threshold Value (CTV) is used to determine the boundaries of the pycnocline and to calculate the depths at which grab samples should be collected. The pycnocline Calculated Threshold Value (CTV) is derived using the equation below.

Where:

$$CTV = \frac{Cb - Cs}{Db - Ds} \times 2$$

C_b = bottom conductivity (micromhos/cm),

C_s = surface conductivity (micromhos/cm),

D_b = depth of bottom conductivity measurement (m),

D_s = depth of surface conductivity measurement (m),

CTV = calculated threshold value (micromhos/cm)

ex. bottom conductivity: 15800 micromhos/cm surface conductivity: 9500 micromhos/cm depth of bottom conductivity measurement: 14.6 m depth of surface conductivity measurement: 0.5 m

CTV = (15800 -9500) / (214.6-0.5) × 2 = 893.6 micromhos/cm

NOTE: micromhos/cm is equivalent to microSiemens/cm (µS/cm)

2. If the Calculated Threshold Value is greater than 500 micromhos/cm, a pycnocline exists with boundaries at the first and last depths where the change in conductivity is greater than the CTV. For example, continuing with the CTV value: 893.6 derived in the example calculation above, and evaluating conductivity readings moving up in the water column from the bottom (at 1-meter increments), the lower boundary of the pycnocline occurs at first depth where the change in conductivity from that measured at the preceding depth exceeds 893.6. Moving upward in the water column, the upper boundary of the pycnocline occurs at last depth where the change in conductivity from that measured at the preceding depth exceeds 893.6. Samples will be taken as described above in section B. 2.

   NOTE: In the rare cases when the sample is theoretically 'below the bottom' or 'above the surface', use the following procedures; if the below pycnocline (BP) sample is determined to be below the bottom sample, collect the BP sample at the bottom sample depth. If the above pycnocline (AP) sample is determined to be above the surface sample, collect the AP sample at 0.5 m.

3. Take samples as described in section B. 3. (No Discernable Pycnocline), above, if either of the following two conditions are true:
   - The CTV is less than 500 micromhos/cm.
   - The CTV is equal to or greater than 500 micromhos/cm BUT no depth interval exceeds that CTV.

NOTES: Upper and lower boundaries of the pycnocline may be the same point. If this is the case, collect the Above Pycnocline sample 1.5 m above the upper pycnocline limit and collect the Below Pycnocline sample 1.5 m below the lower pycnocline limit.

D. Hydrogen Sulfide (H_2S) Protocols

* H_2S was not sampled during the 2020-2021 sampling season due to staff shortage and COVID restrictions. H_2S sampling resumed in the 2022 sampling season.

1. For the Mainstem only, when there is an odor of hydrogen sulfide present in the bottom sample or the below pycnocline sample, perform a Hach Kit test for hydrogen sulfide presence on the bottom and/or below pycnocline sample(s).

2. Immediately upon collection of the sample that meets the requirements in D. 1. above, transfer a portion of sample from the sample bottle to the 25 ml Hach Test glass container (from the Hach Hydrogen Sulfide Test Kit, Model HS-6), for hydrogen sulfide determination.

3. Immediately perform a test for H_2S presence following instructions in Hach Hydrogen Sulfide Test Kit. Record results on the Cruise Report.

E. Secchi Depth

Secchi depth is a basic measurement of water transparency. The Secchi disk that is used is a 20 cm standard diameter disk that is divided into black and white quadrants. The Secchi line is marked off in 0.2-meter increments. Secchi is determined to the nearest 0.1 meter. The disc is lowered into the water until it disappears, and that depth is noted. The disk is then raised until it is barely visible. The Secchi depth is the point where the disc becomes visible. Secchi measurements are always done on the shady side of the pier/boat. Do not wear sunglasses while taking a Secchi reading.

F. Photosynthetic Active Radiation (PAR)

PAR readings (in µMoles/square meter/second) are taken in the field in order to calculate a light attenuation coefficient. Take PAR measurements with a LiCor quantum meter (Model LI-1400 Data Logger or Model LI-1500 Data Logger) with an attached underwater probe (Model LI-192SA). The probe is a flat, upwardly directed probe. Each underwater reading is paired with a reading from a flat, upwardly directed ambient light probe (model LI-190SA).

Begin a vertical profile of light penetration by taking an initial reading with the underwater sensor just below the surface of the water (0.1 m). Take subsequent measurements at either 0.25- m or 0.50-m intervals depending on the turbidity of the water column, (taking shallower measurements in more turbid water). Continue to take readings until a value less than ten percent (10 %) of the surface reading (0.1 m) is attained. Once the readings stabilize, allow at least five readings to flash on the display before recording the data reading for a specific depth. Record in the data logger the mean of the previous five readings that appear on the instrument display. Alternatively, the mean value may be recorded on the field datasheet. Underwater water and ambient readings must be recorded simultaneously. Be sure to collect additional profile readings if the ambient readings decreased significantly from the starting ambient reading.

The light measurements made for each profile are log-scale regressed against depth to determine the compensation depth, i.e., the depth of penetration of one percent (1 %) of the surface PAR. The compensation depth is used in computing the integrated carbon production for that water column. When light profiles are not available, the Secchi disk depth is used to calculate the compensation depth. Over the study period, 1984-1996, a regression has been made between the Secchi depth and the compensation depth for the same water column (for those stations where both Secchi data and LiCor data are taken). By using this regression, a compensation depth can be estimated from a Secchi depth.

Table 4. List of measured parameters and qualifiers for recording light attenuation.

FIELD	DESCRIPTION
SOURCE (PK, FK)	Code identifying agency or contractor that measured the data
PROJECT (PK, FK)	Agency monitoring project code
STATION (PK, FK)	CBP station name
SAMPLE_DATE (PK)	Date on which the PAR readings were taken
SAMPLE_TIME (PK)	Time at which the PAR readings were taken
DEPTH (PK)	Depth at which the PAR readings were taken (meters)
EPAR_S	PAR reading ($\mu M/m^2/s$) taken at the boat just before or during the measurement of PAR readings at depth
EPARU_Z	PAR reading ($\mu M/m^2/s$) taken at depth (up sensor)
UNITS	Units for PAR ($\mu M/m^2/s$)
METHOD	Method code identifying the field measurement procedure
COMMENTS	Comments related to the collection of PAR readings

B2.2 Sample Collection

A. Lower submersible pump to desired depth.

B. Allow the hose to flush completely before taking a sample (flush time is pump dependent).

C. Rinse a pre-marked sample container (plastic bottle) and cap three times with sample water.

D. Collect a sample, cap the bottle, and begin water sample processing and appropriate storage/preservation.

E. Any time a field duplicate is required (whenever indicated on the station lab data sheet), follow the procedures in the section "Split-sample collection method for field duplicates".

F. Enter all identifying information pertinent to samples collected on the lab and field sheets.

B2.3 Split Sample Collection Method for Field Duplicates

A. Samples for field duplicates are generated approximately one for every 20 samples collected.

B. Collect a sample as in section II-A and II-B above.

C. Rinse duplicate collection the container three times and fill with sample water.

NOTE: Collection container must be large enough to generate two complete samples. If more than one gallon of sample is needed for samples, fill a plastic bucket (2.5 to 5 gallon) with sample water and draw all samples from the bucket, taking care to maintain a homogeneous mixture as water is drawn from the duplicate container.

D. Begin water sample processing and appropriate storage/preservation.

E. Enter all identifying information pertinent to samples collected on lab and field sheets.

NOTE: Lab and field sheets must have a replicate number entered for each duplicate generated.

B3. Sample Handling and Custody

B3.1 Chlorophyll samples: filtration, processing and storage

A. For every depth sampled, clean bell and frit with deionized water (DI-water; stored in a high-density polyethylene container) generated at the Field Office. Set up bell and frit for filtering. Ensure that there is a trap in line between the manifold and the vacuum source.

B. Place a Whatman GF/F glass fiber filter pad (pore size = 0.7 μm) on the filter frit. When handling the pad, use clean forceps.

C. Mix the sample thoroughly by agitating the plastic sample container vigorously, then rinse the graduated cylinder three times with the sample.

D. Fill graduated cylinder with sample and filter desired volume through filtration unit. Keep the vacuum below 10 inches of Hg. Filter sufficient volume of sample (100 - 1500 ml) so that you have sufficient color on the filter pad. Do not filter the filter pad dry. In order to avoid cell damage, decrease the amount of vacuum as the final volume approaches the level of the filter and release the vacuum as the last of the water is pulled through the pad. Record the total volume filtered.

E. Add approximately 1 ml of $MgCO_3$ suspension (Laboratory grade from Fisher Scientific prepared in a 1.0 g $MgCO_3$ to 100 ml DI-water ratio) to the last 50 ml of sample in the filtration bell. This is equivalent to less than 1 mg of $MgCO_3$ per 15 ml extract.

NOTE: Filtrate for nutrient analysis should not be saved from this filtration.

F. Remove filter pad with forceps, fold filter in half with sample inside, and place in pre-marked foil square, and carefully fold square in thirds, horizontally and vertically, to seal filter inside. Be sure forceps do not touch sample residue on the filter pads, because the sample will adhere to the forceps.

G. Be sure that the foil square is marked with date, station, sample layer code, volume of sample filtered, sample number, and "CHLA".

H. Place sample FOIL into a pre-marked zip-lock plastic bag. Store the bag of chlorophyll samples in the Research Vessel freezer for Mainstem samples or an ice chest for tributary samples. If samples are stored on ice, place them in the freezer on return to the Field Office.

I. Record sample identifier, date, volume filtered (L), depth (m), layer, start time, end time, study code, submitter code, data category code, field scientist sign-off, and replicate number, if necessary, on chlorophyll volume sheet. This sheet is submitted to the laboratory with the samples.

NOTE: Filter pad with chlorophyll sample should be exposed to as little direct sunlight as possible. Store filter pad in foil as soon as possible.

NOTE: A lab replicate pad (different from the field replicate) is generated every 10 samples. Filter the exact same volume as the first pad. Place the second pad alongside the first pad into foil. The label on the foil will indicate "2 pads" to denote when to generate a replicate pad.

B3.2 Particulate fractions: filtration, processing, and storage.
(Particulate Phosphorus, Carbon, Nitrogen and Total Suspended Solids)

A. Processing and storage - PC, PN:

For each depth sampled, thoroughly clean all bells and frits with DI-water, set up filter apparatus, filters (two pre-combusted 25 mm GF/F filters, pore size = 0.7 μm), and bells for filtering. Filter 10-300 ml through each filter. Filter enough of the sample to leave noticeable color on the filter pad. Make sure the filter pad is filtered dry. Using forceps, fold each filter in half. Place both filters in a foil square labeled with date, PC/PN-CBL sample number, station, sample layer, and volume filtered. Fold as described in IV.F. and then place folded foil in a zip-lock bag and put in the freezer (large boats) or on ice (small boats).

B. Processing and storage - PP, TSS:

For each depth sampled, thoroughly clean all glassware with DI-water. Set up one flask, filter (one pre-weighed and numbered 47 mm GF/F filter placed with the pad number facing down), and bell for filtering. After rinsing a graduated cylinder three times with sample water, measure 50 - 300 ml of sample into the filter bell. Use the filtrate as an equipment rinse and discard. Note amount filtered through the filter. Then filter enough additional (another 50 -400 ml) to leave a noticeable color on the filter pad. Use this filtrate as required for filtered parameter analysis.

After collecting filtrate, make sure the filter is filtered dry. Then rinse the filter pad three times with 10 ml rinses of DI water, making sure the filter pad is filtered dry after each rinse. Using forceps, fold the filter in half. Make sure the pad number is clearly legible on one side only and not on the crease. Place filter in a foil square labeled with date, TSS/PP-CBL sample number, station, sample layer, and volume filtered. Fold as described in IV.F. Place foil squares in a

zip-lock bag and put in the freezer (large boats) or on ice in (small boats).

NOTE: A lab replicate pad (different from the field replicate) is generated every 10 samples. Filter the exact same volume as the first pad. Place the second pad alongside the first pad into foil. The label on the foil will indicate "2 pads" to denote when to generate a replicate pad.

Ten percent of the filters that CBL supplies for field filtering TSS must be pre- rinsed 3 times with deionized water, dried at 103-105 °C for 1 hour, then weighed, re- dried and reweighed until a constant weight is obtained.

C. Processing and storage - VSS:
VSS samples are collected from the surface and AP samples at predetermined stations. Thoroughly clean all glassware with DI-H_2O. Set up one flask, filter (1 pre-weighed, pre- combusted and numbered 47 mm GF/F filter), and bell for filtering. The number for the pad is written on the individual Petri dish that the pad came in. You must write this number on the foil square label and volume sheet. Also, when filtering is complete, place the piece of tape with the pad number from the Petri dish on the volume sheet. After rinsing a graduated cylinder three times with sample water, measure 50 - 300 ml of sample into the filter bell. Use the filtrate as an equipment rinse and discard. Note amount filtered through the filter. Then filter enough additional (another 50 -400 ml) to leave a noticeable color on the filter pad. You may use this filtrate as required for filtered parameter analysis.

After collecting filtrate, make sure the filter pad is filtered dry. Then rinse three times with 10 ml rinses of DI water and make sure the filter pad is filtered dry after each rinse. Using forceps, fold each filter in half. Place the filter in a foil square labeled with date, VSS-CBL sample number, pad number, station, sample layer, and volume filtered. Fold as described in IV.F. Place foil squares in the TSS/PP zip-lock bag and put in the freezer (large boats) or on ice in (small boats).

B3.3 Dissolved fractions: filtration, processing and storage
(NH_4, NO_2, NO_3, PO_4, Si, TDN, TDP, DOC)

A. This filtrate for the dissolved fractions always comes from particulate phosphorus/TSS filters described in section V. It is acceptable to use the filtrate from the VSS filtration if more volume is needed. Use GF/F filters, and pre-rinse the filter and flask with at least 50 ml of sample water. The sample must be collected prior to rinsing the pads with DI-water.

B. Processing and storage - NH_4, NO2 + NO3, NO_3, PO_4, Si:
Triple rinse, with filtrate, three like-numbered autoanalyzer (AA) vials and caps. Fill approximately 7/8 full, allowing for sample expansion upon freezing. Place the AA vials in a rack in the freezer. A fourth vial is collected for silica at a subset of stations. The silicate vial should be stored at 4 °C in the R/V refrigerator. On small boats, keep all samples iced in a cooler, and then freeze all but silica upon return to the Field Office. Place the silica samples in the refrigerator upon return to the Field Office.

NOTE: The number on all vials and test tubes is the CBL sample number. This should match

the number on TSS/PP and PC/PN foil pouches for each sample.

C. Processing and storage - TDN, TDP:
Triple rinse test tube, cap, and 10 ml graduated cylinder with filtrate. Be sure the number on the test tube corresponds to the number on the vials and sample number. Use a 10 ml graduated cylinder to measure EXACTLY 10.0 ml of filtrate. Shake any remaining rinse water out of the test tube. Pour into pre-rinsed test tube and cap sample, then freeze sample in test tube rack on large boats. On small boats, keep samples on ice in the cooler, then freeze upon return to the Field Office.

D. Processing and storage - DOC (collected at subset of Bay Tributary and Mainstem survey stations):
Triple rinse 60 ml container and cap with filtrate. Fill the 60 ml bottle to the shoulder with a filtrate and cap sample, then freeze in the DOC rack. On small boats, keep samples on ice, then freeze at the Field Office.

B3.4 Routine Maintenance of Filtration Units and Containers

For Mainstem cruises and after returning from the field

A. After each day's sampling on Mainstem cruises, filtration units, flasks, frits and graduated cylinders should be cleaned with a non-phosphorus liquid soap, rinsed with tap water three times, then rinsed with 10% HCl (prepared from concentrated HCl from Fisher Scientific diluted with DI-water), tap rinsed, and finally rinsed three times with DI-water. All open flasks, filtration units and graduated cylinders should then be covered to prevent contamination if filtering is not to begin immediately. The filtration unit used with the chlorophyll *a* filters should be washed with soap and rinsed with tap and DI-water and not be rinsed with 10 percent HCl.

B. Big boat units are cleaned at the end of each day's sampling. Small boat or land run units are rinsed with DI-water at end of each day's use and cleaned (with acid) weekly, or after processing 20 to 30 samples.

B3.5 Field Filtered and Source Water Blanks

A. Mainstem - One field filtered equipment blank will be collected each day. One unfiltered (source water) blank will be collected each day. The filtered equipment blank and source water blank will be collected and submitted at the same time.

B. Tributary- One field filtered equipment blank will be collected each month. One unfiltered (source water) blank will be collected each month. The filtered equipment blank and source water blank will be collected and submitted at the same time. The tributary field blanks will rotate through the sampling teams to ensure that all filtering equipment is being evaluated for contamination.

C. Both the Mainstem and Tributary blanks will be analyzed by CBL. If any of the blanks show results greater than the Minimum Detection Limit, DNR Field Office staff members will investigate the potential sources of contamination and will assess the significance of the contamination.

B4. Analytical Methods

B4.1 Laboratory Analysis

Measured parameters – including nitrogen, phosphorus, carbon and silicon species, total suspended solids, volatile suspended solids, and chlorophyll *a*, are determined in the laboratory by the University of Maryland Center for Environmental Science Chesapeake Biological Laboratory (CBL), Nutrient Analytical Services Laboratory. Turbidity, total alkalinity and five-day biological oxygen demand (only measured at a subset of Potomac stations) is determined in the laboratory by the Maryland Department of Health (MDH), Division of Environmental Sciences, Inorganics Analytical Laboratory. Table 5 lists the parameters measured, their detection limits, methods references, and holding times and conditions. See Appendix 1 for the list of NASL Standard Operating Procedures and analytical methods and weblinks at https://www.umces.edu/nasl/methods. See Appendix 2 for the MDH Inorganics Analytical Laboratory Standard Operating Procedures and analytical methods.

Laboratories Standard Operating Procedures (SOP) will be reviewed annually and revised when needed to reflect changes in procedures and instrumentation. When revisions are needed, the changes will be fully documented, the CBP Quality Assurance Coordinator will be notified, and an update of this QAPP will be submitted. All methods are written to comply with Methods and Quality Assurance for Chesapeake Bay Water Quality Monitoring Programs (2017) and National Environmental Laboratory Accreditation Conference (NELAC 2003) guidance and recommendations. Organization charts have been created. Documentation of procedures for logging-in and tracking samples, standards and reagents has been developed and are in place.

The CBL and MDH Laboratories shall retain all pertinent laboratory records for each sample for a period of five years as required by the CBP. The laboratories shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five-year custody period.

Table 5. Water Column Parameters, Detection Limits/Ranges, References and Holding Conditions

***IN SITU* MEASUREMENTS**				
Parameter (Units)	**Instrument**	**Detection Limit (or Range)**	**Method Reference**	**Holding Time and Condition**
Temperature (° C)	Hydrolab Series 5	-5 to +45ºC	Linear thermistor (HWQIUM-S4041, HWQIUM- S2)	Not applicable *in situ*
	Hydrolab Series 5	-5 to +50°C	Linear thermistor (HWQIUM-S3, HWQIUM-S4a, HWQIUM-S5)	
	YSI EXO	-5 to +50ºC	Thermistor of sintered metallic oxide (YSIUM- S6)	
	YSI EXO	-5 to +50°C	Thermistor	
Depth (m)	Hydrolab Series 5	0-100 m	Strain gauge pressure transducer, non-vented, stainless steel (HWQIUM-S3, HWQIUM-S4a, HWQIUM-S5)	
	YSI EXO	0-61 m	Differential strain gauge transducer, non-vented (YSIUM-S6)	
	YSI EXO	0 – 33 ft (S) 0 – 32 ft (M) 0 – 82 ft (D)	Stainless steel strain gauge	
Dissolved Oxygen (mg/L)	Hydrolab Series 5	0-20 mg/L	Standard Clark Au/Ag Polarographic Cell (HWQIUM-S4041, HWQIUM-S2, HWQIUM-S3, HWQIUM-S4a)	
	Hydrolab Series 5	0-50 mg/L	Standard Clark Au/Ag Polarographic Cell (HWQIUM-S5)	
	Hydrolab Series 5	0-20 mg/L	Optical Probe – Luminescent Dissolved Oxygen Probe (LDO) (HWQIUM-S5)	
	YSI EXO	0-50 mg/L	Optical Sensor – ROX Optical Dissolved Oxygen (YSIUM-S6)	
	YSI EXO	0-50 mg/L	Optical luminescence lifetime	

Parameter (Units)	Instrument	Detection Limit (or Range)	Method Reference	Holding Time and Condition
Specific Conductance	Hydrolab Series 5	0-200 mS/cm	Four nickel electrode cells with saltwater cell block (HWQIUM-S4041)	Not applicable *in situ*
	Hydrolab Series 5	0-150 mS/cm	Six nickel electrode cells with saltwater cell block (HWQIUM-S2)	
	Hydrolab Series 5	0-100 mS/cm	Six nickel electrode cells with saltwater cell block (HWQIUM-S3)	
	Hydrolab Series 5	0-100 mS/cm	0.25" x 1" oval bore with four graphite electrodes (HWQIUM-S4a, HWQIUM-S5)	
	YSI Series 6	0-100 mS/cm	Four electrode cells (YSIUM-S6)	
	YSI EXO	0-200 mS/cm	Four electrode nickel cells	
pH	Hydrolab Series 5	0-14 pH units	Paired bulb type Ag/AgCl glass *in situ* and rebuildable reference probes – reference probe in sleeve filled with saturated KCl/pH7 buffer and capped with replaceable porous Teflon™ junction (HWQIUM-S4041, HWQIUM-S2)	
	Hydrolab Series 5	0-14 pH units	Paired bulb type Ag/AgCl glass *in situ* probe and silver pellet reference probe – reference probe in sleeve filled with 4M KCl saturated with AgCl and capped with replaceable porous Teflon™ junction (HWQIUM-S3, HWQIUM-S4a, HWQIUM-S5)	
	YSI EXO	0-14 pH units	Combined glass bulb type electrode with Ag/AgCl reference electrode (YSIUM-S6)	
	YSI EXO	0-14 pH units	Glass combination electrode	
Secchi Depth (m)		0.1 - 7.0 m	20 cm diameter disk with alternating black and wh quadrants (Welch, 1948)	
Light Attenuation* (Photosynthetic Active Radiation) (two measurements: one from boat and one taken at depth with an up sensor)	Li-Cor Model LI1400	400–700 nm	Parsons (1977); Smith (1969), CBP F01	

* Light Attenuation is not measured by MD DNR on Tributary cruises except the Patuxent River. Light attenuation is measured on Mainstem cruises.

GRAB SAMPLES			
Parameter (Units)	**Laboratory Detection Limit**	**Method (Reference)**	**Holding Time and Condition**
Ammonium (mg/L)	0.009 mg N/L	Standard Methods 4500-NH3 G (2011)	Freezing-28 d
Biochemical Oxygen Demand (BOD)	NA	Standard Methods 5210 B (2005)	4ºC 48 hrs.
Chlorophyll *a* (μg/L)	0.62 μg/L	Standard Methods 10200H, (2005) Arar, 446.0 (EPA 1997)	Freezing-28 d
Dissolved Organic Carbon (mg/L as C)	0.16 mg/L	Sugimura and Suzuki (1988), EPA method 415.1 (EPA 1971)	Freezing-28 d
Dissolved Silicate (mg/L as Si)	0.05 mg/L	EPA method 366.6 (EPA 1997), Zhang 366.0 (EPA 1997).	4ºC - 28 d
Nitrite mg/L as N)	0.0009 mg/L	EPA method 353.2 (EPA 1993)	Freezing-28 d
Nitrite + Nitrate (mg/L as N)	0.0015 mg/L	EPA method 353.2 (EPA 1993) and enzymatic nitrate method. Instrumentation used: Aquakem 250 (enzyme reduction) and AutoAnalyzer II (cadmium reduction), ASTM D7781	Freezing-28 d
Orthophosphate (mg/L as P)	0.0034 mg/L	EPA method 365.1 (EPA 1993)	Freezing-28 d
Particulate Carbon (mg/L as C)	0.0633 mg/L	EPA method 440.0 (EPA 1997)	Freezing-28 d
Particulate Nitrogen (mg/L as N)	0.0263 mg/L	EPA method 440.0 (EPA 1997)	Freezing-28 d
Particulate Phosphorus (mg/L as P)	0.0010 mg/L	Aspila et al. 1976, EPA 365.1 (EPA 1993).	Freezing-28 d
Pheophytin *a* (μg/L)	0.74 μg/L	Standard Methods 10200H (2005) Arar 446.0 (EPA 1997)	Freezing-28 d
Total Alkalinity (mg/L as CaCO3)	0.75 mg/L	Standard Methods 2320 B (2005)	4ºC 14 d
Total Dissolved Nitrogen (mg/L as N)	0.05 mg/L	D'Elia et al. 1977; Valderrama 1981, Alkaline persulfate digestion. (Analysis by both by cadmium reduction and enzyme reduction post Alkaline persulfate digestion), EPA 353.2 (EPA 1993)	Freezing-28 d
Total Diss. Phosphorus (mg/L as P)	0.0015 mg/L	Valderrama 1981, Alkaline persulfate digestion, EPA 365.1 (EPA 1993)	Freezing-28 d
Total Suspended Solids (mg/L)	2.4 mg/L	Standard Method 2540 D (1998)	Freezing-28 d
Volatile Suspended Solids (mg/L)	0.9 mg/L	Standard Method 2540 E (1988)	Freezing-28 d
Turbidity (NTU)	0.1 NTU	EPA Method 180.1 (1993)	4ºC 48 hrs.

Table 5 References:

American Public Health Association (APHA), *Standard Methods for the Examination of Water and Wastewater, Method Number 10200H*, *Spectrophotometric Determination of Chlorophyll* 21st Edition, 2005.

American Public Health Association (APHA), *Standard Methods for the Examination of Water and Wastewater, 4500-NH3 D. Ammonia-Selective Electrode Method*, 20th Edition, 1998.

American Public Health Association (APHA), *Standard Methods for the Examination of Water and Wastewater, 4500-NH3 G. Automated Phenate Method*, 20th Edition, 1998.

American Public Health Association (APHA), Standard Methods for the Examination of Water and Wastewater, *pH Alkalinity by Titration*, 21st Edition, 2005.

American Public Health Association (APHA), Standard Methods for the Examination of Water and Wastewater, *Five Day Biological Oxygen Demand Test*, 21st Edition, 2005.

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Aspila, I., H. Agemian and A. S. Y. Chau. 1976. *A semi-automated method for the determination of inorganic, organic and total phosphate in sediments*. *Analyst* 101:187-197.

ASTM D7781-14, *Standard Test Method for Nitrite-Nitrate in Water by Nitrate Reductase,* ASTM International, West Conshohocken, PA, 2014, www.astm.org

D'Elia, C. F., P. A. Steudler and N. Corwin. 1977. *Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr*. 22:760-764.

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O'Dell, J.W. Method 350.1: *Determination of Ammonia Nitrogen by Semi-Automated Colorimetry*. Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH, Revision 2.0, 1993

O'Dell, J.W. Method 353.2: *Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry*. Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH, Revision 2.0, 1993

O'Dell, J.W. Method 365.1: *Determination of Phosphorus by Semi-Automated Colorimetry*. Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH, Revision 2.0, 1993

Parsons, T. R., Takahashi, M. and B. Hargrave. 1977. *Biological Oceanographic Processes*. Pergammon Press. Oxford. 332 p. (Pages 71-85).

B5. Quality Control

B5.1 Project Quality Assurance/Quality Control

The data collected as part of the Chemical and Physical Properties Component of the Chesapeake Bay Mainstem and Tributary Water Quality Monitoring Program are used in making management decisions regarding Chesapeake Bay water quality as described in the Section A6: Project Description. DNR will follow specific procedures to ensure that the design is properly implemented and that monitoring measurements are made and managed with sufficient accuracy, precision, and detection limits. General discussions of quality assurance and quality control aspects associated with coordinated split samples, a blind auditing program and USGS reference samples are provided in the subsections below.

The accuracy (closeness to the true value) of the collected data will be controlled and assured by the proper use, calibration, and maintenance of both field and laboratory equipment for the measurement of physical and chemical parameters. All instruments are identified by a unique number, used as an index for documentation of calibration, repair, and preventive maintenance. Where possible, standards used for calibration purposes will be validated against a primary standard such as those available from the National Institute of Standards and Technology (NIST).

B5.2 Field sampling QA/QC

Procedures to control and assure the accuracy of field measurements involve the calibration of field instruments, the verification of these calibrations, equipment maintenance, and collection of filter blanks. These procedures are detailed in Section B6: Field Instrument QA/QC and B7: Field Procedures QA/QC.

When field replicate control limits are exceeded, or when field blank values exceed lowest calibration standards, information about the issue is presented to the CBP Data Integrity Work Group (DIWG). The DIWG may suggest corrective actions to field and laboratory procedures.

B5.3 Laboratory analysis procedures

Precision (repeatability) of the chemical analytical methods will be determined and documented from duplicate analyses. Precision of the entire measurement system for laboratory-analyzed parameters, including field processing, storage, and chemical analysis, can be assessed from duplicate field samples. Duplicate field samples will be routinely collected approximately every 20 samples. The protocols for duplicate analyses in the laboratory are described in the Standard Operating Procedures in Appendices 1 and 2.

Daily quality control checks (using blanks, duplicates and spikes of certified standards) will be used to control and assure laboratory accuracy. See Appendix 1 weblinks for details on the frequency of running blanks and standards and for additional procedures for laboratory quality assurance and control. Accuracy is also assessed by an independent evaluation of laboratory proficiency which is required and accomplished by participation in analysis of split samples, blind audit samples and USGS reference samples.

B5.3.1 Chesapeake Bay Coordinated Split Sample Program (CSSP)

This interlaboratory testing program involves the distribution of identical surface water samples to participating state, federal and academic monitoring agencies. CSSP was established in June 1989 to establish a measure of comparability between sampling and analytical operations for water quality monitoring throughout the Chesapeake Bay and its tributaries. Samples are processed according to standard protocols and the results are evaluated quarterly to ensure comparable data is being produced. The protocols are available in the Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines Rev. 4 (EPA 2010) and its revisions.

Results are analyzed by appropriate statistical methods to determine if results differ significantly among labs. When a difference occurs, discussion begins regarding techniques and potential methods changes to resolve discrepancies and identify potential problems occurs via the Chesapeake Bay Data Integrity Workgroup. An example of the split sample custody log is provided in Section B10.

B5.3.2 Chesapeake Blind Audit Program

The CBP Blind Audit Program provides laboratory proficiency testing samples for dissolved and particulate nutrients and chlorophyll at the relatively low concentrations commonly found in estuarine systems. Prepared concentrates of dissolved and particulate substances, whose concentrations are unknown to the analysts, are distributed twice a year to multiple regional laboratories. NASL is the sole provider of the blind audit samples. The results provide a measure of laboratory accuracy as the samples are fully prepared prior to distribution and the errors associated with field filtering and subsampling are minimized.

The analytical results must fall within the 95% confidence interval for acceptance. If the results fall outside this range, corrective actions for each parameter and measurement are taken. Participants and final annual audit reports can be viewed at www.umces.edu/blind-audit-results-nasl . An example of the field sheet used to record sample number, time of collection and salinity when split sample water is collected can be found in Section B10.

B5.3.3 USGS Reference Samples

CBP laboratories also participate in the USGS Standard Reference Sample (SRS) Program to establish their accuracy and comparability to other laboratories at a national level. Samples are analyzed twice a year and results are submitted online through the SRS project website. USGS performs statistical analysis and releases them on the website by lab number. Bay Program staff downloads the data and graphs results from Chesapeake Bay laboratories for review at Data Integrity Workgroup meetings.

B5.3.4 On-site Audits

The EPA CBP Quality Assurance Officer will conduct periodic on-site audits of the laboratory and field programs. The DNR Quality Assurance personnel will communicate internally (amongst field, data management and data analysis staff) and confer with the laboratory Quality Assurance Officers to ensure that all aspects of the monitoring program are being conducted properly. These communications will address problems and opportunities in real-time rather than waiting for the annual review cycle.

B5.4 Data Quality Indicators

To ensure that data are of the quality required to support CBP management decisions, Maryland's Chesapeake Bay Mainstem and Tributary Water Quality Monitoring Program will strive to provide monitoring data of known and consistent quality to the CBP by following the guidelines outlined in Methods and Quality Assurance for Chesapeake Bay Water Quality Monitoring Programs (EPA 2017). These guidelines recommend precision goals for field and lab measurements of <20 percent of the coefficient of variation; accuracy goals within 80 to 120 percent, and the completeness goals of 95 percent.

Detection limit ranges are provided in Table 5 (Section B4). Field measurement minimum reporting limits are listed in Table 6.

Table 6. Minimum Reporting Limits for Field Measurements

PARAMETER	MINIMUM REPORTING LIMIT
Water Temperature	0.1 ºC
Depth	0.5 m
Dissolved Oxygen	0.0 mg/L
Conductance, Specific	Down to 1 micromhos/cm at low levels (accurate to 3 significant digits)
pH	0.1 pH units
Secchi Depth	0.1 m
Salinity	0.1 ppt
Light Attenuation (PAR)	0.05% at 100% light

B6. Instrument/Equipment Testing, Inspection and Maintenance Log

B6.1 Field Instrument Quality Assurance/Quality Control

Multiparameter Water Quality Instruments and Calibration

These procedures refer to Hydrolab Series 5 and Yellow Springs Instrument (YSI) Series 6 and EXO instruments. Detailed calibration procedures are performed as described in their respective operating manuals.

B6.1.1 Hydrolab Series 5 Instruments

Basic Notes:

- YSI instruments are equipped with optical dissolved oxygen sensors (Reliable Oxygen Sensor - ROX). YSI temperature, specific conductance, pH and depth sensors are different from their respective Hydrolab sensors but perform similarly.
- Both the Hydrolab and YSI optical dissolved oxygen sensors use similar luminescent technology to measure dissolved oxygen.
- Mainstem and Patuxent River cruises will exclusively use YSI instead of Hydrolab instruments. All other sampling activities will use Hydrolab or YSI instruments.

A. Set up a calibration logbook for each instrument with make, model, serial numbers and first-in-service date. Assign a letter for DNR use as required. Calibrations are best done in the field office instrument lab which is kept at a stable temperature of 20-25°C.

B. Calibrate instruments on Friday to use during the next week. If possible, calibrate the instrument within 24 hours of first field deployment. After one to four days of field deployment, post-calibrate instruments after last use to determine if calibration of any parameter drifted (see App V, Section I.C.1.c and d for procedure). If possible, post-calibrate the instrument within 24 hours after the last field deployment.

C. Calibrate specific conductance sensor with standards generated by the field office from dry KCl and deionized water with specific conductance equal to 0µS/cm. Standards are 147, 292, 718, 1413, 2767, 6668, 12900, 24820 and 58640 microSiemens/cm (µS/cm) (microSiemens/cm is equivalent to micromhos/cm at 25°C). Respective concentrations are 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 molar KCl. Calibrate specific conductance sensors of Series 5 instruments following a two-point linear protocol. Calibrate the zero point with the sensor dry and the slope with one of the above standards.

D. Calibrate pH sensor with premixed standards of pH 4.00, pH 7.00 and pH 10.00 purchased from Fisher Scientific. Standards are color coded (red for pH 4.00, yellow for pH 7.00 and blue for pH 10.00) and certified as accurate at 25°C (pH 4.00 ± 0.01, pH 7.00 ± 0.01, pH 10.00 ± 0.02) and used before their labeled expiration dates. Calibrate pH sensor with these standards

using a two-point linear protocol. First, calibrate the zero point with a pH 7.00 standard buffer. Then, calibrate slope with either pH 4.00 or 10.00 standard buffer. The slope buffer is selected so that pH measurements anticipated during field deployment are between the zero point and slope buffer values. The pH value of each buffer is adjusted for instrument temperature before calibration. A pH calibration value vs. temperature table (pH Calibration table) is supplied by the buffer manufacturer for each standard buffer. This value is the pH calibration point.

E. Calibrate the optical dissolved oxygen sensor (LDO) using a 1-point percent saturation protocol in the common standard of air saturated water. The volume of water must have a specific conductance less than 100 µS/cm. Determine the oxygen saturation calibration point in air-saturated water from theoretical DO saturation tables using the temperature from the instrument and local barometric pressure from a standard Fortner Mercury Barometer. A specific notation on the field data sheet shows that Hydrolab instruments are equipped with LDO sensors.

F. Temperature sensor is calibrated by the manufacturer and cannot be adjusted by the user.

G. Calibrate depth sensor by submerging it to a known depth at the field sampling station and calibrating to this known depth.

H. Record all calibration and post-calibration information (e.g., barometric pressure, calibration values and instrument readings), maintenance procedures and repairs in the instrument specific calibration logbook. An example of this log is included.

I. During calibration, post-calibration and field deployment, record in the calibration logbook any unusual circumstances that may affect instrument readings.

B6.1.2 YSI EXO1 and EXO2 Instruments

These procedures refer to Yellow Springs Instrument (YSI) EXO1 and EXO2 instruments. Detailed calibration procedures are performed as described in the operating manual.

Basic Notes:

- It is recommended to use a new clean sensor guard exclusively for calibration to minimize contamination of calibration standards.
- When filling a calibration cup with standards, fill to the first line when a full payload of sensors is installed and fill to the second line when fewer sensors are installed to ensure that sensors are fully immersed in calibration standard.
- Be sure to thoroughly rinse sensors with DI water between calibration standards to reduce contamination.
- Never accept a calibration that displays an error message.

A. Set up a calibration logbook for each instrument with make, model, serial numbers and first-in-service date. Assign a letter for DNR use as required. Calibrations are best done in the field office instrument lab which is kept at a stable temperature of 20-25°C.

B. Calibrate instruments on Friday for use during the next week. If possible, calibrate the instrument within 24 hours of first field deployment. After one to four days of field deployment, post- calibrate instruments after last use to determine if calibration of any parameter drifted (see App V, Section I.C.1.c and d for procedure). If possible, post-calibrate the instrument within 24 hours after the last field deployment.

C. Calibrate specific conductance sensor with standards generated by the field office from dry KCl and deionized water with specific conductance equal to 0 µS/cm. Standards are 147, 292, 718, 1413, 2767, 6668, 12900, 24820 and 58640 microSiemens/cm (µS/cm) (microSiemens/cm is equivalent to micromhos/cm at 25°C). Respective concentrations are 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 molar KCl. Calibrate specific conductance sensor following a two-point linear protocol with one of the above standards as the slope standard. The zero point is factory calibrated and cannot be adjusted by the user.

D. Calibrate pH sensor with premixed standards of pH 4.00, pH 7.00 and pH 10.00 purchased from Fisher Scientific. Standards are color coded (red for pH 4.00, yellow for pH 7.00 and blue for pH 10.00) and certified as accurate at 25°C (pH 4.00 ± 0.01, pH 7.00 ± 0.01, pH 10.00 ± 0.02) when used before their labeled expiration dates. Calibrate pH sensor with these standards using a two-point linear protocol. First, calibrate the zero point with a pH 7.00 standard buffer. Then, calibrate slope with either pH 4.00 or 10.00 standard buffer. The slope buffer is selected so that pH measurements anticipated during field deployment are between the zero point and slope buffer values. The pH value of each buffer is adjusted for instrument temperature before calibration. A pH calibration value vs. temperature table (pH Calibration table) is supplied by the buffer manufacturer for each standard buffer. This value is the pH calibration point.

E. Calibrate the optical dissolved oxygen sensor (ROX) using a 1-point percent saturation protocol in the common standard of air saturated water. The volume of water must have a specific conductance less than 100 µS/cm. Check and calibrate, if necessary, the YSI EXO Handheld Display Unit barometer to local barometric pressure in mmHg as measured from a standard Fortner Mercury Barometer. Determine the oxygen saturation calibration point in air-saturated water from theoretical DO saturation tables using the temperature from the instrument and local barometric pressure from a standard Fortner Mercury Barometer or display unit barometer. Note in the calibration if the display unit barometer was calibrated and reading used to calibrate the dissolved oxygen sensor. A specific notation on the field data sheet shows that YSI instruments are equipped with ROX sensors.

F. Temperature sensor is calibrated by the manufacturer and cannot be adjusted by the user.

G. Calibrate depth sensor by submerging to a known depth at the field sampling station and calibrating to this known depth.

H. Record all calibration and post-calibration information (e.g., barometric pressure, calibration values and instrument readings), maintenance procedures and repairs in the instrument specific calibration logbook. An example of this log is included.

I. During calibration, post-calibration and field deployment, record in the calibration logbook any unusual circumstances which may affect the instrument readings.

B6.1.3 Field Deployment and Verification of Instrument Performance

A. Before daily field deployment and, if possible, before deployment at each sample station, inspect sensors for damage. If damaged, do not use the instrument and deploy a second instrument. Teams carry two calibrated instruments in case one instrument fails or gives suspect measurements. Readings from the instrument in use are compared to those from the second instrument only when the field scientist recording measurements observes readings, (a) that are outside reasonably expected values, (b) that are variable or erratic, or (c) if the instrument displays an error message. If these instruments do not agree within QA/QC guidelines and the field scientist reasonably believes that the primary instrument is not working correctly, the second instrument is used. This is noted on the field sheet, cruise report, and instrument calibration log. The instrument supervisor is also informed. The suspect instrument should not be used until its performance is evaluated during post- calibration.

B. Before each day of a Mainstem Cruise both instruments receive a morning-of-use dissolved oxygen validation check. Set up the instruments for a dissolved oxygen calibration as appropriate for the type of sensor. Follow procedures for the dissolved oxygen validation check to adjust the calibration only if the reading is greater than ± 0.20 mg/L from the saturation calibration point. If the reading is greater than ± 0.50 mg/L, the instrument is not used for field measurements until evaluated by the instrument supervisor.

B6.1.4 Maintenance

A. Post Field Deployment Maintenance and Performance Verification

1. Daily: At the end of each day of use inspect all sensors for damage and record any damage in cruise report, monthly report, calibration log, and affected field data sheet(s). Then rinse sensors with de-ionized or tap water and install the storage cup filled with sufficient tap water so the pH and reference sensors are not submerged.

2. Weekly: At the end of each week, rinse the instrument (sonde and cable) and basket carrier with tap water. Wipe the display with a paper towel made wet with tap or deionized water. Rinse sensors with de-ionized or tap water and install the storage cup filled with sufficient tap water so the pH and reference sensors are not submerged.

3. Post-calibrate dissolved oxygen, pH and specific conductance for each instrument weekly on Friday after one to four days of field sampling. If possible, post-calibrate the instrument within 24 hours after last use. Before post- calibrating, inspect all sensors for damage and record any damage in the calibration log, cruise report, monthly reports, and affected field data sheets. If there is sensor damage, post-calibrate the instrument to evaluate sensor and instrument performance. Post-calibrate instrument only after sensors stabilize to room temperature (20-25°C). Post-calibrate instruments using the same

standards and procedures as were used during calibration except the calibration settings are not adjusted. For instruments with an optical DO sensor, visually inspect the luminescent material before post-calibration. If the DO sensor is damaged, describe the damage in the calibration log and post-calibrate the sensor as is. Damage to DO sensor is repaired before next calibration and field deployment. If during field deployment, instrument readings of pH and specific conductance fall outside the range of the zero and slope calibration standards, make additional post-calibration readings of appropriate pH and specific conductance standards so that field readings fall within the range from the zero calibration point to the additional post-calibration standard. All post-calibration standards and instrument readings are recorded in the calibration log.

4. If readings of a parameter during post-calibration are outside quality guidelines, note this in the calibration log and inform the field quality assurance supervisor. The supervisor will determine if the instrument is operating correctly and if associated field data is reliable.

Data Quality Guidelines During Post-calibration:

pH Sensor reads ±0.20 pH units of standard.

Dissolved Oxygen — Optical dissolved oxygen sensor reads ±0.50 mg/L. of calibration dissolved oxygen value

Specific Conductance

Standard µS/cm	Threshold ±5% of Standard µS/cm
147	8
292	15
718	36
1413	71
2767	139
6668	334
12900	645
24820	1241
58640	2932

Instrument parameter readings that are outside quality guidelines during post-calibration are flagged on field data sheets with the Analytical Problem Code (APC) value ‘F’. The description of APC ‘F’ is: “Field data instrument post calibration failed but data within theoretical limits, (e.g., post cal. failed but data kept)” see Section B10: Outline of Codes for Field and Laboratory Data.

All field data, including instrument data, are re-evaluated during quality assurance. If the analyst/biologist and Quality Assurance Officer determine that the data are not usable, values are flagged with the APC code 'V'. The definition for APC code 'V' is: "Sample results rejected due to quality control criteria".

B. Routine Sensor Maintenance and Performance Verification: sensor and overall instrument maintenance is conducted at approximately 8–12-week intervals based on instrument usage and performance.

Hydrolab Series 5 Instrument

a. Optical Dissolved Oxygen Sensor (LDO): Remove plastic LDO cap on end of sensor. Inspect cap for integrity of luminescent material, optical path for water, area under optical glass for condensation, and integrity of
o-ring seals. Water or condensation interferes with the optical path. If the cap will be reused, replace o-rings if damaged and reinstall cap on sensor.
Replace cap and o-rings if damaged. First, gently wipe the plastic cap exterior surface with cotton swab soaked with laboratory soap, then rinse cap with deionized water. Second, gently wipe the cap exterior surface with a new cotton swab soaked with Simple Green™, then rinse the cap with deionized water. Replace the cap once per year because luminescent material and zero dissolved oxygen performance degrade with age. Organic solvents, such as methanol and acetone, should never contact any part of this sensor.

b. Specific Conductance Sensor (graphite sensor): First, wipe all surfaces of the sensor with cotton swab soaked with laboratory soap, then rinse with deionized water. Second, wipe the sensor with a new cotton swab soaked with Simple Green™, then rinse with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor.

c. pH System (paired sensors - *in situ* and reference): *in situ* sensor is bulb type Ag/AgCl2 glass sensor. Reference sensor is a pellet of silver inside a sleeve capped with a porous Teflon™ junction and filled with electrolyte (4M KCl aqueous solution saturated with AgCl2). First, wipe the in-situ glass sensor with cotton swab soaked with laboratory soap, then rinse with de-ionized water. Second, wipe the glass sensor with a new cotton swab soaked with Simple Green™, then rinse with deionized water. Soak sensor in 0.1 N HCl for no more than 30 minutes, then rinse sensor with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor. Remove junction sleeve assembly from reference sensor. Remove and discard porous Teflon reference junction and associated o-ring from junction sleeve assembly. Inspect junction sleeve and silver pellet for integrity and replace if damaged. Do not clean the silver pellet. Remove and discard o-ring from reference sensor post. Lightly grease a new o-ring with silicone grease and install it on the reference sensor post. Install new junction and associated o-ring on sleeve. Firmly tighten junction on sleeve to compress o-ring seal but do not overtighten. Fill the sleeve

with fresh electrolyte, add two KCl pellets in the sleeve, and reinstall the sleeve on the reference sensor so that no air bubbles are inside the sleeve.

d. Depth Sensor (stainless steel differential strain gauge transducer): Inspect sensor port and remove any obstructions. No further maintenance is required.

e. Temperature Sensor (stainless steel thermistor): First, wipe with cotton swab soaked with laboratory soap, then rinse with deionized water.
Second, wipe with a new cotton swab soaked with Simple Green, then rinse with deionized water. Do not use any organic solvent, such as methanol or acetone, to clean this sensor.

YSI EXO1 and EXO2

f. Optical Dissolved Oxygen Sensor (ODO): Inspect membrane for integrity of luminescent material. *(Only remove the membrane if there are issues or suspected issues with readings. Remove membrane and inspect optical path for water, area under optical glass for condensation, and integrity of assembly o- ring seals. Water or condensation interferes with the optical path. If necessary, carefully clean optical glass with cotton swab moistened with deionized water. Gently remove any residual moisture from the optical glass with a dry cotton swab. Reinstall luminescent membrane assembly.)* Replace membrane assembly if damaged. First, gently wipe the membrane exterior surface with cotton swab soaked in laboratory soap, then rinse with deionized water. Second, gently wipe the membrane exterior surface with a new cotton swab soaked in Simple Green, then rinse with deionized water. Replace the membrane assembly once per year as luminescent material and zero dissolved oxygen performance degrade with age. Do not use any organic solvents, such as methanol or acetone, to clean this sensor.

g. Specific Conductance Sensor (four nickel electrode array): First, soak a small nylon bristle brush in laboratory soap and gently push back and forth multiple times through both channels. Rinse with deionized water. Second, soak a small nylon bristle brush in Simple Green™ and gently push back and forth multiple times through both channels. Rinse with deionized water.

h. pH System: EXO guarded pH System is a glass bulb type combination electrode consisting of a proton selective glass bulb reservoir filled with buffer at approximately pH 7 and an $Ag/AgCl_2$ reference electrode. First, inspect the glass bulb for cracks or breakage. Second, gently wipe the glass bulb with cotton swab soaked with laboratory soap, then rinse with deionized water. Third, gently wipe the glass bulb with a new cotton swab soaked with Simple Green™, then rinse with deionized water. If further cleaning is required, soak the glass bulb in 1 M HCl for 30 – 60 minutes, then rinse with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor. The pH sensor tip is user replaceable. Replace tip if sensor is out of range or broken. Record date and serial number of new sensor tip in calibration log.

i. Depth Sensor YSI EXO Sonde (differential strain gauge transducer): Ensure that access to four ports is clear of debris. Using a plastic syringe flush deionized water through one port and out the others. Repeat flush through each port.

j. Temperature Sensor YSI Model EXO (stainless steel thermistor): First, wipe sensor with cotton swab soaked with laboratory soap, then rinse with deionized water. Second, wipe the sensor with a new cotton swab soaked with Simple Green™, then rinse with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor.

2. Sensor Performance Verification: After routine sensor maintenance, the performance of Hydrolab and YSI instruments are verified as follows before assignment to field surveys. Instruments that do not satisfy these criteria are repaired in house or returned to the manufacturer for repair. Performance verification is documented in the calibration log for each instrument.

a. Temperature: Submerge sensor and traceable standard mercury thermometer in freshwater at room temperature (20° - 25°C). Sensor reading must be stable and within 0.20°C of the standard thermometer reading observed over a 2-minute interval.

b. Dissolved Oxygen: Calibrate optical sensor in the standard of air saturated water. Sensor reading before calibration must be stable (within 0.05 mg/L of reading) over a 2-minute interval. The sensor must calibrate to the saturation standard value and remain stable (within 0.05 mg/L of standard value) observed over a 2-minute interval.

c. pH: Calibrate system using the two-point linear protocol. Calibrate zero point with pH 7 standard buffer. Calibrate slope with pH 10 standard buffer. Check the response of the system to a pH 4 standard buffer but do not calibrate. The sensor should read stable pH values (within 0.01 pH units of reading) within 2- minutes or less of immersion in a standard buffer before and after calibration. Sensor readings of pH 4 standard buffer should be stable (within 0.01 pH units of reading) and within 0.20 units of standard value as determined from pH Calibration table.

During calibration, YSI pH sensors must have stable millivolt (mV) readings in standard buffers within the following ranges:

pH 7 buffer	-50 to +50 mV
pH 10 buffer	-230 to -130 mV
pH 4 buffer	+130 to +230 mV

If mV readings are not within these ranges, the pH sensor must be replaced.

d. Specific Conductance

Hydrolab Series 5 instruments calibrate in any of three autoranges (0 – 1500 µS/cm, 1500 – 15,000 µS/cm, and 15,000 – 150,000 µS/cm) using a two-point linear protocol. Sensor reading before calibration should be stable (within 1% of reading) over a 2-minute interval. Sensor reading after calibration should be stable and within 1% of standard over a 2-minute interval. Select a standard in another autorange and check linearity response. Sensor reading should be stable (within 1% of reading) and within 5% of standard value over a 2-minute interval.

YSI EXO instruments calibrate with a standard from one of the three Hydrolab autoranges above using a two-point linear protocol (see App V, Section I.A.3.c). Sensor reading before calibration should be stable (within 1% of reading) over a 2-minute interval. Sensor reading after calibration should be stable and within 1% of standard over a 2-minute interval. Select a standard in another Hydrolab autorange and check linearity response. Sensor reading should be stable (within 1% of reading) and within ±5% of standard value over a 2-minute interval.

e. Depth: Calibrate zero point in air. The sensor should calibrate and read stable values.

B6.1.5 Li-Cor Instrumentation Maintenance:

Photosynthetic Active Radiation (PAR) is measured using Li-Cor Bioscientific equipment. Each Li-Cor setup consists of an LI-1400 or LI-1500 display unit, an LI-190SA ambient light sensor, and an LI- 192SA underwater light sensor, an underwater leveling frame, and an underwater cable attached to a calibrated lowering-line.

The following factory-maintenance procedure ensures compliance with the manufacturer's required maintenance schedule. Each winter half of the ambient and underwater sensors are shipped to Li-Cor Bioscientific for re-calibration. The next year, the remaining ambient and underwater sensors are sent to the factory for re- calibration. Upon return from the factory, updated, sensor specific, correction values are entered into the displays before the equipment is deployed.

The LI-1400 and LI -1500 display units are battery powered. Batteries are to be replaced as needed.

Lowering lines are evaluated yearly to ensure depth markings are correctly located. Troubleshooting is performed as necessary before sending PAR measurement components to the factory for repair.

A Li-Cor equipment tracking maintenance log is used to document which instrumentation components are attached to specific display units. As well as provide a permanent record of all re-calibrations, battery replacements, lowering-line checks and equipment repairs.

B6.1.6 Secchi Disk

Each year the Secchi disk line is calibrated by comparing its 0.2m marks to a metal meter stick. Each mark is a small piece of colored flat synthetic webbing pulled through the line and sewn for security. Marks are moved if the webbing does not line up with the corresponding line on the meter stick.

B6.2 Field Audits

Annual audits of all field equipment logbooks, maintenance records and field procedures will be conducted by the field Quality Assurance Officer. This information will be reported to the DNR Quality Assurance Officer. (See Quality Assurance Project Plan, Section 8: Project Organization and Responsibility).

The following pages contain examples of calibration logs for Hydrolab Series 5, Hydrolab HL4, and YSI EXO instruments.

Note: The example Hydrolab Calibration log form and instructions are in use as of November 1, 2016. Revisions are planned. References to deprecated equipment and procedures will be removed and guidance for temperature thermistors will be added.

B6.3 Instrument Calibration Logs

The following pages are calibration logs and their documentation for Hydrolab Series 5, HL4, and YSI EXO instruments. These revisions have been used since July 2009.

B6.3.1 Hydrolab

INSTRUMENT CALIBRATION LOG DOCUMENTATION SERIES 4a/5 HYDROLAB

PAGE HEADER INFORMATION – row of information at top of page.

1. METER – record letter identifier, in upper case, for instrument on this log page.
2. PAGE NUMBER – record the next page number in sequence; pages numbered sequentially from first use of letter identifier.

LOG ENTRY – one column is one log entry.

HEADER INFORMATION

1. DATE – record date with month and day as two-digit fields each and year as a four-digit field. Separate fields with slash.
2. TIME – record time in military format (hours and minutes as two-digit fields each) when beginning work.
3. LOCATION – record place where work is performed as one of four choices (office, home, field, or motel); if not one of four choices, be as specific as possible.
4. CALIBRATION TYPE – record type of work performed as one of these choices:
    - CAL – calibration performed before field deployment; calibration adjusted if necessary.
    - POST CAL – post-calibration performed as calibration check after field deployment, no calibration adjustments.
    - CHECK – check calibration of specific parameter(s); calibration adjustments possible.
    - TEST – instrument performance test performed for maintenance or repair reasons.
5. PROJECT – record project(s) on which instrument intended to be used or was used.
6. CHECKED BY – record initials of person(s) performing work; initials are a three-character field. Separate multiple persons with slash.

DISSOLVED OXYGEN – CLARK POLAROGRAPHIC CELL

1. TEMPERATURE – record temperature in degrees centigrade as displayed on the instrument. Reading used to determine "CALIBRATION D. O." entry.
2. BAROMETRIC PRESSURE – record temperature corrected local barometric pressure in millimeters of mercury from a Fortin mercury barometer. Reading used to determine "CALIBRATION D. O." entry.
3. CALIBRATION D. O. – record dissolved oxygen concentration in milligrams per liter from calibration chart or calculation.
4. D. O. READING – record dissolved oxygen concentration in milligrams per liter as

displayed on the instrument before making calibration adjustments.

5. ADJUSTED – circle "yes" or "no" if calibration setting was changed or not changed, respectively.

DISSOLVED OXYGEN – OPTICAL SENSOR

1. TEMPERATURE – record temperature in degrees centigrade as displayed on the instrument. Reading used to determine "CALIBRATION D.O." entry.
2. BAROMETRIC PRESSURE – record temperature corrected local barometric pressure in millimeters of mercury from a Fortin mercury barometer. Reading used to determine "CALIBRATION D.O." entry.
3. CALIBRATION D.O. – record dissolved oxygen concentration as percent saturation and milligrams per liter from calibration chart or calculation.
4. D. O. READING – record dissolved oxygen concentration as percent saturation and milligrams per liter as displayed on the instrument before making calibration adjustments.
5. ADJUSTED – circle "yes" or "no" if calibration setting was changed or not changed, respectively.

SPECIFIC CONDUCTANCE

A. ZERO POINT – record "zero" reading from the instrument display before making calibration adjustments. Circle "yes" or "no" if the calibration setting was changed or not, respectively.

B. SLOPE

1. TEMPERATURE – record temperature in degrees centigrade as displayed on the instrument.
2. STANDARD – record specific conductance of standard in microSiemens per centimeter as written on the bottle of standard.
3. METER READS – record specific conductance of standard in microSiemens per centimeter as displayed on the instrument before making calibration adjustments.
4. ADJUSTED – circle "yes" or "no" if calibration setting was changed or not changed, respectively.

pH

A. pH 7 – ZERO POINT

1. TEMPERATURE – record temperature in degrees centigrade as displayed on the instrument.
2. CHART pH – record pH in pH units from calibration chart.
3. METER READS – record pH in pH units as displayed on the instrument before making calibration adjustments.
4. ADJUSTED – circle "yes" or "no" if calibration setting was changed or not changed, respectively.

pH 4/10 BUFFER – SLOPE

5. TEMPERATURE – record temperature in degrees centigrade as displayed on the instrument.
6. CHART pH – record pH in pH units from calibration chart.
7. METER READS – record pH in pH units as displayed on the instrument before making calibration adjustments.
8. ADJUSTED – circle "yes" or "no" if calibration setting was changed or not changed, respectively.

BATTERY

Record letter or number identity of battery connected to instrument (record internal battery as letter or number identity of display). Record voltage reading of this battery as displayed on the instrument. Separate each field with a slash.

QA/QC SIGN OFF

Scientist who verified completeness and accuracy of log entry records his/her initials.

COMMENTS

1. DATE – record date of entry with month and day as two-digit fields each and year as a four-digit field. Separate fields with slash.
2. COMMENTS – comments should be long enough to cover the subject but short enough to be interesting. Initials of the person making the entry should be at the end of comments.

NOTE: To facilitate matching comments with log entry, a circled number should appear both at the top of the appropriate log entry column and preceding the date in the comments section. This circled number should be unique and sequential to each log page.

HYDROLAB INSTRUMENT CALIBRATION LOG **SERIES 5 METER _____** **PAGE NO.**

(April 10, 2018, GLG)

DATE: MM/DD/YYYY						
TIME: HHMM (MILITARY TIME)						
LOCATION: OFFICE, HOME, FIELD, MOTEL						
CALIBRATION TYPE: CAL, POST CAL, CHECK, TEST						
PROJECT:						
CHECKED BY: INITIALS						

DISSOLVED OXYGEN – OPTICAL SENSOR (air saturated water – percent saturation protocol)

TEMPERTURE: °C						
LOCAL BAROMETRIC PRESSURE: mm Hg						
SPECIFIC CONDUCTANCE: µS/cm						
CALIBRATION D. O.: mg/L						
METER READS: mg/L						
ADJUSTED TO CALIBRATION D.O.	YES NO	YES NO	YES NO	YES NO	YES NO	YES NO

SPECIFIC CONDUCTANCE (µSiemens/cm)

ZERO POINT: READING | ADJUSTED TO ZERO		YES NO	YES NO	YES NO	YES NO	YES NO	YES NO
SLOPE	**TEMPERATURE:** °C						
	CALIBRATION STANDARD: µS/cm						
	METER READS: µS/cm						
	ADJUSTED TO CAL. STANDARD	YES NO	YES NO	YES NO	YES NO	YES NO	YES NO

pH

pH 7 STANDARD ZERO POINT	**TEMPERATURE:** °C						
	CALIBRATION pH: pH units						
	METER READS: pH units						
	ADJUSTED TO CAL pH	YES NO	YES NO	YES NO	YES NO	YES NO	YES NO
pH 4 / 10 STANDARD SLOPE	**TEMPERATURE:** °C						
	CALIBRATON pH: pH units						
	METER READS: pH units						
	ADJUSTED TO CAL pH	YES NO	YES NO	YES NO	YES NO	YES NO	YES NO

BATTERY: DISPLAY | VOLTS	|	|	|	|	|	|

QA/QC SIGN OFF: INITIALS						

#	DATE: MM/DD/YYYY	INITIALS	COMMENTS

B6.3.2 YSI

YSI INSTRUMENT CALIBRATION LOG DOCUMENTATION EXO

PAGE HEADER INFORMATION – row of information at top of page.

1. METER – record letter identifier, in upper case, for instrument on this log page.
2. PAGE NUMBER – record the next page number in sequence; pages numbered sequentially from first use of letter identifier.

LOG ENTRY – one column is one log entry.

HEADER INFORMATION

1. DATE – record date with month and day as two-digit fields each and year as a four-digit field. Separate fields with slash.
2. TIME – record time in military format (hours and minutes as two-digit fields each) when beginning work.
3. LOCATION – record place where work is performed as one of four choices (office, home, field, or motel); if not one of four choices, be as specific as possible.
4. CALIBRATION TYPE – record type of work performed as one of these choices:
    - CAL – calibration performed before field deployment; calibration adjusted if necessary.
    - POST CAL – post-calibration performed as calibration check after field deployment, no calibration adjustments.
    - CHECK – check calibration of specific parameter(s); calibration adjustments possible.
    - TEST – instrument performance test performed for maintenance or repair reasons.
5. PROJECT – record project(s) on which instrument intended to be used or was used.
6. CHECKED BY – record initials of person(s) performing work; initials are a three-character field. Separate multiple persons with slash.

DISSOLVED OXYGEN – OPTICAL SENSOR

1. TEMPERATURE – record temperature in degrees centigrade as displayed on the instrument. Reading used to determine “CALIBRATION D.O.” entry.
2. BAROMETRIC PRESSURE – record temperature corrected local barometric pressure in millimeters of mercury from a Fortin mercury barometer. Reading used to determine “CALIBRATION D.O.” entry.
3. CALIBRATION D.O. – record dissolved oxygen concentration as percent saturation and milligrams per liter from calibration chart or calculation.
4. D. O. READING – record dissolved oxygen concentration as percent saturation and milligrams per liter as displayed on the instrument before making calibration adjustments.
5. ADJUSTED – circle “yes” or “no” if calibration setting was changed or not changed, respectively.

SPECIFIC CONDUCTANCE

A. SLOPE

1. TEMPERATURE – record temperature in degrees centigrade as displayed on the instrument.
2. STANDARD – record specific conductance of standard in microSiemens per centimeter as written on the bottle of standard.
3. METER READS – record specific conductance of standard in microSiemens per centimeter as displayed on the instrument before making calibration adjustments.
4. ADJUSTED – circle "yes" or "no" if calibration setting was changed or not changed, respectively.

pH

A. pH 7 – ZERO POINT

1. TEMPERATURE – record temperature in degrees centigrade as displayed on the instrument.
2. CHART pH – record pH in pH units from calibration chart.
3. METER READS – record pH in pH units as displayed on the instrument before making calibration adjustments.
4. ADJUSTED – circle "yes" or "no" if calibration setting was changed or not changed, respectively.

B. pH 4/10 BUFFER – SLOPE

1. TEMPERATURE – record temperature in degrees centigrade as displayed on the instrument.
2. CHART pH – record pH in pH units from calibration chart.
3. METER READS – record pH in pH units as displayed on the instrument before making calibration adjustments.
4. ADJUSTED – circle "yes" or "no" if calibration setting was changed or not changed, respectively.

QA/QC SIGN OFF: Scientist who verified completeness and accuracy of log entry records his/her initials.

COMMENTS

1. DATE – record date of entry with month and day as two-digit fields each and year as a four-digit field. Separate fields with slash.
2. COMMENTS – comments should be long enough to cover the subject but short enough to be interesting. Initials of the person making the entry should be at the end of comments.

NOTE: To facilitate matching comments with log entry, a circled number should appear both at the top of the appropriate log entry column and preceding the date in the comments section. This circled number should be unique and sequential to each log page.

B7. Instrument/Equipment Calibration and Frequency

B7.1 Cleaning procedures

(A-D are performed by Chesapeake Biological Lab staff members)

a. Autoanalyzer (AA) cups and caps: Cups and caps are used only one time and then are discarded.

b. DOC tubes: Place tubes in 10 % HCl bath for approximately 24 hours; follow by rinsing tubes several times in deionized water.

c. DOC caps: Place caps in 10 % HCl bath for approximately 24 hours; follow by rinsing tubes several times in deionized water.

d. TDN/TDP tubes: new tubes are digested using potassium persulfate followed by multiple deionized water rinses. Tubes that are "in-the-cycle" are cleaned by emptying old contents, rinsing the tubes and caps with 3-4 tap water rinses followed by 6 rinses with deionized water.

B7.2 Review of procedures for field and lab sheets in the field

e. "Scientist signoff" duties

The field scientist is responsible for recording values on the field data sheets and on the lab sheets. This includes entering all Hydrolab/YSI *in situ* values, calculating the pycnocline, and ensuring that the field data sheet is complete. This individual is also responsible for transcribing necessary header information onto the lab sheets.

f. "Senior scientist" duties

The individual who enters their initials in the 'senior scientist' boxes is the scientist who is officially designated as overseeing the cruise.

B7.3 Cruise Data

g. The senior scientist, as field quality assurance officer on cruise, should ensure that:

h. Thermometers are placed in refrigerator and freezer to monitor daily temperatures (4 °C for refrigerator and -10 to -20 °C for freezer) and record data on cruise report. (The refrigerator is used January-June and August and November for the Split, to keep silicate samples cool). If the temperatures are too high; they should be set lower if possible and if not possible, the captain of the research vessel should be notified.

i. Check with the Captain of the research vessel to ensure that weather and location instruments used onboard the ship (e.g., Raytheon factory calibrated barometer, anemometer, or GPS) are functioning properly and, if not, record it in the Cruise Report.

j. Check to make sure all equipment necessary to accomplish sampling is on board and functioning before leaving dock.

k. Document and report back to the field Quality Assurance Officer any deviations from existing protocol or problems that have arisen during the cruise.

B7.4 Dissolved Oxygen Calibrations and Checks

Dissolved Oxygen calibration checks shall be done every morning for Mainstem Monitoring. Typically, the instruments used on Mainstem employ optical DO probes and are checked using the common standard of air-saturated water. After correcting for the barometric pressure and temperature, the oxygen content of air saturated water can be checked against standard D.O. tables.

B7.5 Spare Instrument

As discussed in Section B6 (Field Instrument Quality Assurance/Quality Control), teams carry two calibrated Hydrolab/YSI meters in case of failure. The meter in use is compared to the reserve meter any time (a) the field scientist recording measurements observes values outside the "typically expected range"; (b) the meter generates variable or erratic values; or,
(c) the meter in use displays an error message. If the meters do not agree within acceptable limits, the reserve meter is used. This is noted under the additional comments section.

B7.6 Deionized water

The deionized water at the Field Office is generated from tap water using a Thermo Scientific Barnstead DIamond TII RO/DI system with a GE SmartWater external pre-filter. The RO/ DI system is linked to a Thermo Scientific Barnstead DIamond TII 60L storage reservoir. The system uses a thin film composite reverse osmosis membrane with pretreatment to produce RO water. This water is then put through a two-stage deionization process combined with UV oxidation and a 0.2- micron final filter. The reagent grade water provided by this system exceeds ASTM Type II and NCCLS/CAP Type I standards. All manufacturer recommendations are followed regarding cartridge replacement and system sanitation (Refer to Thermo Scientific. 2007. Barnstead DIamond TII Type II Water System Operation Manual.and Barnstead DIamond TII Type II Storage Reservoir Operation Manual). The GE SmartWater pre-filter was placed in-line to improve the integrity of feedwater going into the Barnstead DIamond System. The pre-filter is changed at least every three
(3) months or more frequently during periods of heavy use. A log is kept at the front of the DI System Manual to document all changes and updates made to the system.

B7.7 Transfer of nutrient samples/sheets to laboratory

All samples are delivered to CBL at the end of the sampling week. The samples are placed in the freezer at the Field Office until delivery. The silicate samples that are collected at a subset of stations are stored in the Field Office refrigerator. The samples are packed with dewatered ice in a cooler. Do not place the silicates directly in the ice as this may cause them to freeze. The volume sheets for each sampling run are placed in a bin marked "CBL" on the side of the Field Office freezer at the end of the field day. The laboratory (volume) sheets must be collected from the bin and accompany all samples to CBL.

B8. Inspection/Acceptance of Supplies and Consumables

Individual SOPs itemize the apparatus, equipment, materials, and supplies required for various monitoring equipment. In general, supplies and consumables are procured directly from life sciences and scientific equipment sources such as Thermo Fisher Scientific or from the vendor manufacturing the equipment used by field staff. Parts lists, including recommended replacement schedules, are itemized in most manufacturers' operating manuals. DNR uses this information to determine the appropriate procurement schedule and volume of consumables required to support continuing operations. Supplies and consumables are tracked by the field staff; when replacements are needed, the field office manager is notified, who is then responsible for purchasing. Supplies are inventoried in the field office for later distribution. Received materials are inspected to ensure the proper part number was received as ordered. General inspection to identify any damaged products is also performed. Parts received are dated so that storage duration can easily be determined. A revolving inventory system (first in, first out) is used to ensure that storage times do not affect the material's integrity. If a manufacturer or EPA requirement indicates a specific expiration period for supplies, those supplies exceeding expiration dates are discarded if not used within the acceptable period.

B9. Non-direct Measurements

- National Weather Service data
- Geographic location data
- Manufacturers' equipment operational literature

B10. Data Management

Data collection for the Chemical and Physical Properties Component of the Chesapeake Bay Mainstem and Tributary Water Quality Monitoring Program will begin when measurements from field recording instruments are entered onto field data sheets. A field logbook will be used to document any problems encountered in the field that might affect the field parameters or samples brought back to the laboratory. The senior scientist, on board each cruise, will ensure that all measurements are taken properly. All data acquisition processes in the field and laboratory measurements will be recorded in the Cruise Report to ensure data quality. After field personnel complete data sheets for a given calendar month, they will scan or make photocopies of the sheets to keep in the Field Office and send the original field sheets to data management staff at the DNR Tawes Building. The Field Office will also generate a Cross Reference Sheet for each set of field sheets, which is sent to the DNR data management personnel along with the field data sheets. The Cross Reference Sheet allows data management personnel to know what field, nutrient, lab, and chlorophyll lab sheets to expect. During and following the pandemic, these assorted

documents are also shared on a network drive to allow easier and more timely access to data processing and data quality assurance staff.

B10.1 Field Sheets

B10.1.2 Documentation and Procedures for Field Sheet and Lab Volume Sheets

The following code words describe procedures DNR uses to fill out Field Data Sheets, and Lab Volume Sheets (nutrient, suspended solids and chlorophyll) used for the Chesapeake Bay Mainstem and tidal tributaries water quality monitoring programs. Examples of Field Data Sheets: A, B and Patuxent River are described herein. Lab volume sheet, raw and processed LiCor data are emailed to the Data Management staff by station and are then processed into a usable format.

Water quality data columns on field data sheets A and B are different from Patuxent Field Data Sheet water quality columns because of differences in how LiCor data are handled. LiCor data is logged onto Patuxent Field Data Sheets. LiCor data collected on Mainstem surveys are downloaded, stored, processed and submitted separately. Differences between Patuxent Field Sheets and Field Sheets A and B are noted below.

Field Sheet A:

The Field Sheets are sent along with a Cross Reference Sheet from the Field Office to the Data Management Unit at the DNR Tawes Building. The Field Office must provide the following information on the Field Sheet.

1. Sequence Number (boxes 3-9, upper right-hand corner)

The following convention has been used to designate the 7-digit sequence number for the Mainstem, where YY is last two digits of year, NNN is the cruise number (that year), and SS is the station order for that week's cruise:

MAINSTEM Convention YYNNNSS

For example, sequence number 8401204 is the 12th cruise in 1984 at station 4 for that week's cruise.

The following convention has been used to designate the 7-digit sequence number for the tributary sampling, where YY is last two digits of year, MM is month, T is for tributary, P is for Patuxent, M is for Potomac, C is for CORE, and XX is an arbitrary ordering number:

TRIB Convention	YYMMTXX
PXT Convention	YYMMPXX
POT Convention	YYMMMXX
CORE Convention	YYMMCXX

For example, 9603P05 is the fifth field sheet for a March Patuxent cruise in 1996.

2. Sampling Station Number (boxes 10-18)

Enter the appropriate Chesapeake Bay Program station location (e.g., WT5.1, ET5.2) beginning with the box numbered 10. Put only one character (including decimal points) per box.

3. Start Date (boxes 20-25)

Enter the start date beginning with year, then month and then day. Use two numbers each for year, month and day. For example, March 2, 2017, would be entered as 170302.

4. Start Time (boxes 27-30)

Enter the start time of the sampling effort at a station location in military time.

5. End Date (boxes 32-37)

If the end date for a particular station is the same as the start date, the end date boxes can be left blank.

6. End Time (boxes 39-42)

Enter the end time of the sampling collection effort at a station location in military time. The end time is the time at the end of *in situ* data collection (meter readings).

7. Number of Samples (boxes 44-45)

Enter the number of samples taken (including duplicates) at the station location. Routinely, there are two to five samples collected at stations for the Chesapeake Bay Monitoring program.

8. Submitter Code (boxes 47-48)

The submitter codes specify the collection group and the lab that will perform the analyses.

9. Data Category Code (boxes 50-51)

The data category codes specify the code for the type of sample being collected. For example, for the Chesapeake Bay Program Main Bay Sampling, the code is 'MB' - Chesapeake Bay Monitoring Sample-MD. Main Bay".

10. Total Depth (M) (boxes 53-55)

Enter the total depth at the station in meters to the nearest 0.1 m for tributary stations and to the nearest 0.5 m for Mainstem stations.

11. Study Code (boxes 57-58)

The study codes indicate the type of monitoring program. For example, '01' is the study code for the "Chesapeake Bay Monitoring Program - Main Bay".

12. Sample Method (line #2, box 10)

The sample method codes indicate the sample method used for the sampling effort. For example, '1' is the code for 'Grab Samples'.

Note: If no water samples are collected, the code is '7', (FIELD MEASUREMENTS ONLY).

13. Air Temperature degrees Celsius (line #2, boxes 11-14)

Air temperature is reported in degrees Celsius to the nearest 0.5 degrees. The value is recorded in boxes 12-14. Box 11 is used to indicate whether the temperature is above, below or exactly zero. If the temperature is above zero, write a plus (+) in box 11. If the temperature is below zero, write a minus (-) and leave box 11 blank if the temperature is 0 degrees. If the air temperature is a single digit (-/+ 4.0), a zero must be placed in box 12 of the field sheet for example: -04.0.

14. Tide State (line #2, box 18)

Tide state code 'E' specifies an ebb tide.

15. Weather Code Yesterday (line #2, boxes 20-21)

Enter the code for yesterday's weather in these boxes. Additional weather information can be included in the comments section if appropriate.

16. Weather Code Today (line #2, boxes 23-24)

Enter the code for current weather (while at station) in these boxes. Additional weather information can be included in the comments section if appropriate.

17. Percent Cloud Cover (line #2, boxes 25-27)

Enter the amount of cloud cover in these boxes. Percent Cloud Cover is reported as values from 000 to 100 percent. Numbers must be **right** justified, e.g., 5 (not 5).

18. Wind Direction (line #2, boxes 28-30) Record wind direction using the codes: N - Northerly direction S - Southerly direction E - Easterly direction W - Westerly direction.

Record wind direction in boxes 28-30 using up to three letters to designate the prevailing conditions. An example of wind direction would be 'north by northeast' and the codes in boxes 28-30 would be 'NNE'. If only one or two letters are needed to designate the conditions, use the boxes beginning with box #28 for the codes. Letters must be **left** justified, e.g., S W (**not** S W)

19. Wind Velocity (knots) (line #2, boxes 31-32, 33-34)
Record wind velocity in knots in boxes 31-32, 33-34. Record the minimum (or lower range) velocity in boxes 31-32; record the maximum (or upper range) velocity in boxes 33-34. For example, if the wind is

blowing from 7 to 10 knots, the minimum wind velocity is '07' and the maximum wind velocity is '10'. If only one number is needed to designate the wind velocity conditions, enter the identical numbers in both the boxes for minimum velocity as well as in the boxes for maximum velocity. Beaufort Wind Force Scale values may be used when recording wind velocity. 01-03, 04-06, 07-10, 11-16, 17-21, 22-27, and 28-33.

Num.	Wind speed				Mean wind speed (kt/km/h/mph)	Description	Wave height		Sea conditions	Land conditions
	kt	km/h	mph	m/s			m	ft		
0	0	0	0	0-0.2	0 / 0 / 0	Calm	0	0	Flat.	Calm. Smoke rises vertically.
1	1-3	1-6	1-3	0.3-1.5	2 / 4/ 2	Light air	0.1	0.33	Ripples without crests.	Wind motion visible in smoke.
2	**4-6**	7-11	4-7	1.6-3.3	5 / 9 / 6	Light breeze	0.2	0.66	Small wavelets. Crests of glassy appearance, not breaking	Wind felt on exposed skin. Leaves rustle.
3	**7-10**	12-19	8-12	3.4-5.4	9 /17 /11	Gentle breeze	0.6	2	Large wavelets. Crests begin to break; scattered whitecaps	Leaves and smaller twigs in constant motion.
4	**11-16**	20-29	13-18	5.5-7.9	13/24/ 15	Moderate breeze	1	3.3	Small waves.	Dust and loose paper raised. Small branches begin to move.
5	**17-21**	30-39	19-24	8.0-10.7	19/35/ 22	Fresh breeze	2	6.6	Moderate (1.2 m) longer waves. Some foam and spray.	Smaller trees sway.
6	**22-27**	40-50	25-31	10.8-13.8	24/44/27	Strong breeze	3	9.9	Large waves with foam crests and some spray.	Large branches in motion. Whistling heard in overhead wires. Umbrella use becomes difficult.
7	**28-33**	51-62	32-38	13.9-17.1	30/56/35	Near gale	4	13.1	Sea heaps up and foam begins to streak.	Whole trees in motion. Effort needed to walk against the wind.

20. Secchi (M) (line #2, boxes 35-38)

Record Secchi depth in meters to the nearest 0.1 meter.

21. Flow Value (line#2, boxes 39-46)

Note that flow is not recorded in regular scientific notation but is recorded as follows. Box #39 is the flow basis code, where:

1 = measured in cubic feet per second (CFS)
2 = estimated in cubic feet per second (CFS)
3 = measured in million gallons per second (MGS)
4 = estimated in million gallons per second (MGS)
5 = measured in gallons per day (GPD)
6 = estimated in gallons per day (GPD)

Boxes 40-44 are for the five-digit mantissa and box 45 is for the exponential value in base 10. These boxes are to be left blank aboard the boat or other stations where flow is not recorded.

For example, estimated flow 4.5cfs = 2.450001, where "2" indicates that the flow is estimated in cubic feet per second, "45000" indicates that the mantissa is 4.5000, and "1" indicates multiply the mantissa by 10^1.

The final box, #46, is for marking greater or less than (G or L).

Note: Flow value is not a required parameter and is seldom measured.

22. Senior Scientist (line #2, boxes 47-49)

The three initials of the senior scientist (the scientist in charge of the sampling effort for that day) are entered in these boxes. If the scientist has only 2 initials the letters are flush left with box 49 empty.

23. DO Method (line #3, box 50)

Method code values currently used are: ‘H’ for Hydrolab Clark Cell; ‘L’ for Hydrolab LDO; and ‘R’ for YSI ROX. A switch to YSI EXO began in 2020.

24. Equipment Set Unit # (line #3, boxes 51-52)

The numbers assigned to equipment packages are recorded in these boxes.

25. Probe Number (line #3, boxes 53-54)

Enter the Hydrolab or YSI probe number in these boxes. If using spares, enter the same equipment letter

in the probe number box and record spare number in comments boxes.

The text of the label over boxes 53-54 on the field sheets used on the Patuxent River project is "LiCor Number" instead of "Probe Number". (See Patuxent field sheet example at the end of this section).

26. Flow/Tide Unit Number (line #3, boxes 55-56)

Enter in boxes 55-56 the number of the meter used to measure the flow value. These boxes should be left blank if flow was not recorded for the station.

The text of the label over boxes 55-56 on the field sheets used on the Patuxent River project is "LiCor Method" instead of "Flow/Tide Unit Number". (See Patuxent field sheet example at the end of this section).

27. Wave Height (M) (line #3, boxes 57-59) Wave height is recorded in meters. Values used for wave heights are

0.00 m=flat calm 0.09 m= slight ripple 0.20 m= ripple-1 foot

0.40 m= 1-2 feet 1.00 m= 2-4 feet 1.5 m= 4-6 feet

28. Upper Pycnocline Limit (M) (line #3, boxes 60-62)

The calculated value for the upper pycnocline limit is recorded in meters and is entered in these boxes. If no pycnocline exists, leave these boxes blank.

29. Lower Pycnocline Limit (M) (line #3, boxes 63-65)
The calculated value for the lower pycnocline limit is recorded in meters and is entered in these boxes. If no pycnocline exists, leave these boxes blank.

30. Scientist Signoff (line #3, boxes 66-68)

A DATA SHEET WITH NO SCIENTIST SIGNOFF WILL NOT BE SENT TO THE DATA ENTRY SERVICE.

The scientist who checked over the field sheet for:

- the correct codes
- the correct date
- the correct start time and end time
- the correct sampling station number
- reasonable values for the parameters

Values for the parameters are entered on the sheet and properly enters his/her initials in these boxes. Ideally, the individual who initiates the signoff is a separate individual from the one who enters the values on the data sheet. This process of using two separate individuals whenever possible, one to enter

the values onto the sheet and one to check over the values that are entered, can help minimize transcription errors and correct aberrations in protocol. However, when a scientist works alone, the same scientist who enters the values checks the sheets before leaving the station.

31. Comments (beginning on line #3 - #5) Any comments that are necessary to fully describe the sampling effort should be entered in the Comment section. Use one box for each character, decimal point, or period.

32. Replicate Number (line #6, box 11).
Patuxent River Survey Replicate Number (line #6, box 10)

If the values for specific conductance, water temperature, DO, etc. are repeated for a single depth and are entered on the field sheet, indicate this by entering the replicate number (from 2 to 9) in these boxes. A blank in line #6, box 11 defaults to 1. A blank in Patuxent River line #6, box 10 defaults to 1.

33. Depth (M) (line #6, columns 13-15)
Patuxent River Survey Depth (M) (line #6, columns 11-14)

Enter the depth at which the suite of parameters is measured (in meters).

34. Water Temperature degrees C (line #6, columns 17-20)

The water temperature is recorded in degrees Celsius. The value is recorded in columns 18-20; column #17 is to indicate a minus (-) value. Leave this column blank if the temperature is greater than or equal to zero; write in a minus (-) sign if it is below zero.

Patuxent River Survey Water Temperature (line #6, columns 15-18).

On the Patuxent River Survey, the temperature value is recorded in columns 16-18; column #15 is used to indicate a minus (-) value. Leave this column blank if the temperature is greater than or equal to zero; write in a minus (-) sign if it is below zero.

35. Field pH (line #6, columns 22-25)
Patuxent River Survey Field pH (line #6, columns 19-22)

Enter values for field pH in these columns (round pH to the nearest tenth).

36. Value Corrected (line #6, column 27)
Patuxent River Survey Value Corrected (line #6, column 23)

Use one of the three codes for DO correction (usually “C”).

37. DO (mg/l) (line #6, columns 28-32)

Enter the DO value in columns 29-32. Column #28 is used to indicate greater than (G) or less than (L)

values. A less than (L) in column #28 indicates that the value for DO in columns 29-32 is less than the detection limit for the DO probe. The code "C" may be used in the column designated for G/L if no value is recorded due to probe/ instrument failure. The code "F" may be used in the column designated for G/L if the data appears normal, but the probe/ instrument failed post calibration check due to damage after sampling. The code "V" may be used in the column designated for G/L if the probe post is calibrated outside of QA guidelines. Enter Patuxent River Survey DO value in columns 25-28. Column #24 is used to indicate greater than (G) or less than (L) values. A less than (L) in column #24 indicates that the value for DO in columns 25-28 is less than the detection limit for the DO probe. The code "C" may be used in the column designated for G/L if no value is recorded due to probe/ instrument failure. The code "F" may be used in the column designated for G/L if the data appears normal, but the probe/ instrument failed post calibration check due to damage after sampling. The code "V" may be used in the column designated for G/L if the probe post is calibrated outside of QA guidelines.

38. Specific Conductance (microSiemens/cm) (line #6, columns 34-39)
Patuxent River Survey Specific Conductance (microSiemens/cm) (line #6, columns 29-34)

Enter the values for specific conductance in columns 35-39. Use column #34 to indicate greater than (G) or less than (L) values. The code "C" may be used in the column designated for G/L if no value is recorded due to probe/ instrument failure. The code "F" may be used in the column designated for G/L if the data appears normal, but the probe/ instrument failed post calibration check due to damage after sampling. The code "V" may be used in the column designated for G/L if the probe post is calibrated outside of QA guidelines.

Enter Patuxent River Survey values for specific conductance in columns 30-34. Use column #29 to indicate greater than (G) or less than (L) values. The code "C" may be used in the column designated for G/L if no value is recorded due to probe/ instrument failure. The code "F" may be used in the column designated for G/L if the data appears normal, but the probe/ instrument failed post calibration check due to damage after sampling. The code "V" may be used in the column designated for G/L if the probe post is calibrated outside of QA guidelines.

NOTE: Hydrolab reports microSiemens/cm.

39. Salinity (ppt) (line #6, columns 40-43) salinity values are rounded to the nearest tenth. Patuxent River Survey Salinity (ppt) (line #6, columns 35-38)

Enter a value for salinity in columns 40-43.
Enter a value for Patuxent River Survey salinity in columns 35-38.

40. Lab Login Section (line # 6, columns 49-63)
(See 40B below: Patuxent River Survey Layer Code and LiCor Section (line # 6, columns 39-49)

This section is used to record the number of replicate water samples which were collected, the depth at which the samples were collected, the layer from which the samples were collected, and the bottle numbers that the samples were assigned. (Note the designation AP and BP indicate above and below pycnocline only if a pycnocline actually was present. If no pycnocline they indicate below surface and

above bottom at 1/3, 2/3 depths.)

A. Replicate (line #6, column 49) If more than one sample is collected for analysis at an identical depth, indicate this by entering a 1, 2, 3, etc. to differentiate the replicates. Leaving this column blank results in a default to 1.

B. Sample Depth (M) (line #6, columns 50-52)

Record the depth in meters at which the samples were collected. Meter readings are required for this depth.

C. Layer Code (line #6, columns 53-54)

Indicate at which layer the samples were collected. Enter layer code (S=surface, B=bottom, AP=above pycnocline, BP=below pycnocline, M=mid water column). Left justify single-character codes (i.e., codes with only one letter).

D. Bottle Numbers (line #6, columns 55-63)

Enter the bottle numbers assigned to the samples. Up to nine alphanumeric characters can be used. If less than nine characters are used, left justify. These bottle numbers are the same as those indicated on lab sheets.

40B. Patuxent River Survey Layer Code and LiCor Section (line # 6, columns 39-49)

This section is used to record the layer from which the bottle samples were collected and Deck and Underwater LiCor readings.

A. Layer Code (line #6, columns 39 and 40)

Indicate at which layer the samples were collected. Enter layer code (S=surface, B=bottom, AP=above pycnocline, BP=below pycnocline). Left justify single-character codes (i.e., codes with only one letter).

B. LiCor Deck (micromols/m^2) (line #6, columns 41-44)

Record the LiCor deck value in micromols/m^2 at depths where readings were taken.

C. LiCor Underwater (micromols/m^2) (line #6, columns 41-44)

Record the LiCor underwater value in micromols/m^2 at depths where readings were taken.

NOTE: Bottle Numbers on Patuxent River Surveys are entered in an unnumbered column to the left of Patuxent River Survey Replicate Number (line #6, column 10).

41. Pycnocline Threshold Calculations

This section is used as a worksheet to calculate the pycnocline. The following symbols are used in the formula.

Δ = Delta (used to indicate change)

$\bar{X}$ = Mean

$\bar{X}\ \Delta\ M$ = indicates mean change (Delta) per meter

42. Date entered (entered by keypunch at bottom left of sheet)

Date returned from keypunching (entered by keypunch at bottom of sheet).

43. Page of (bottom right of sheet)

If only one sheet is generated at a station, leave this blank; the default value is 'page 1 of 1.' When two sheets are generated at one station, enter in this area 'page 1 of 2' for the first sheet generated, and 'page 2 of 2' for the second sheet generated. The second sheet generated at a sampling location is Field Sheet B, discussed next.

Field Sheet B:

Use Field Sheet B when two field sheets are generated at one sampling location.

1. Sequence Number

Use the same convention (described above) for sequence numbers for this field sheet. The second sheet generated at one location must have the identical sequence number as the first sheet. The two sheets should not be stapled together.

2. Top Half of Form

The top of this form only has lines for Sampling Station Number, Date, Start Time, and End Time (the boxes have been replaced with lines). Enter this information to alleviate the problem of mismatched or unidentifiable sheets.

3. Bottom Half of Form

The bottom half of this form is the same as the field sheet previously discussed. There is no need to enter information on the second sheet for the Lab Login or pycnocline calculation.

Lab Volume Sheet (also called filtering volume sheet, for nutrient, suspended solids and chlorophyll analyses)

When nutrients, suspended solids and chlorophyll samples are collected, a lab sheet is generated, and serves as a Sample Transfer Sheet. The lab sheet lists multiple stations that contain information for

several samples on one sheet. Information on the sheet includes the sample number, layer, depth, time, salinity, and volume sampled for each set of parameters (e.g., TSS/PP, PC/PN, CHLA). This sheet is filled out by field personnel and must accompany the samples to CBL. CBL produces electronic files which are uploaded into MD DNR Water Quality Data Management system.

1. Cruise Identification Number (Mainstem stations only)

Enter the cruise identification number in the space provided (year and cruise number, e.g., 97018 for 1997, Cruise Number 18).

2. Date

Enter the date in the space provided. It does not need to be in any specific format.

3. Scientist Signoff

The scientist must check the sheet for completeness and accuracy, and then initial in the signoff space.

4. Station, Sample Number, Layer

Enter the station, sample number, and layer code (S=surface, B=bottom, AP=above pycnocline, BP=below pycnocline, M=mid water column), if not preprinted.

5. Sampling Time (column 5)

Enter the sampling time in military time in column 5.

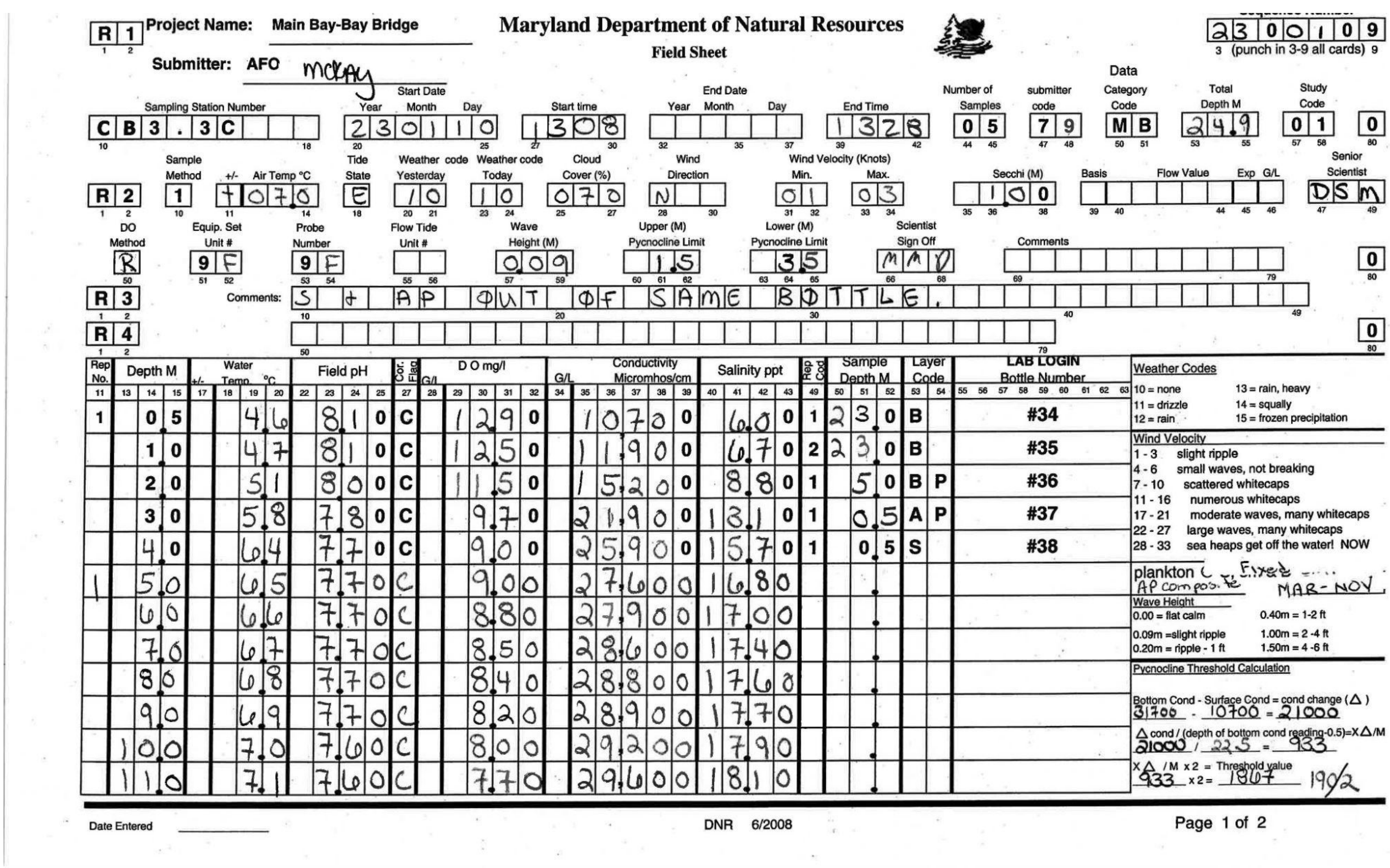
6. Salinity (column 6)

Enter the salinity in parts per thousand (ppt) in column 6.

7. Vol. (ml) (final 3 or 4 columns)

In the final 3 or 4 columns, enter the volume sampled for each set of sample parameters (e.g., TSS/PP, PC/PN, VSS, CHLA) in milliliters.

B10.1.3 Mainstem Field Sheet A



R 1 Project Name: Main Bay-Bay Bridge

Maryland Department of Natural Resources

Field Sheet

Sequence Number: 2 3 0 0 1 0 9 (punch in 3-9 all cards)

Submitter: AFO McKay

Sampling Station Number	Start Date (Year / Month / Day)	Start time	End Date (Year / Month / Day)	End Time	Number of Samples	submitter code	Data Category Code	Total Depth M	Study Code	
CB3.3C	23 / 01 / 10	1308		1328	05	79	MB	24.9	01	0

	Sample Method	+/-	Air Temp °C	Tide State	Weather code Yesterday	Weather code Today	Cloud Cover (%)	Wind Direction	Wind Velocity (Knots) Min.	Max.	Secchi (M)	Basis	Flow Value	Exp	G/L	Senior Scientist
R 2	1	+	07.0	E	10	10	070	N	01	03	1.00					DSM

DO Method	Equip. Set Unit #	Probe Number	Flow Tide Unit #	Wave Height (M)	Upper (M) Pycnocline Limit	Lower (M) Pycnocline Limit	Scientist Sign Off	Comments	
R	9F	9F		0.09	1.5	3.5	MMV		0

R 3 Comments: S + AP OUT OF SAME BOTTLE.

R 4 | 0

Rep No.	Depth M	+/-	Water Temp. °C	Field pH	Cor. Flag	G/L	D O mg/l	G/L	Conductivity Micromhos/cm	Salinity ppt	Rep Cod	Sample Depth M	Layer Code		LAB LOGIN Bottle Number
1	0.5		4.6	8.10	C		12.90		1070.0	6.00	1	23.0	B		#34
	1.0		4.7	8.10	C		12.50		1190.0	6.70	2	23.0	B		#35
	2.0		5.1	8.00	C		11.50		1520.0	8.80	1	5.0	B	P	#36
	3.0		5.8	7.80	C		9.70		2190.0	13.10	1	0.5	A	P	#37
	4.0		6.4	7.70	C		9.00		2590.0	15.70	1	0.5	S		#38
1	5.0		6.5	7.70	C		9.00		2760.0	16.80					
	6.0		6.6	7.70	C		8.80		2790.0	17.00					
	7.0		6.7	7.70	C		8.50		2860.0	17.40					
	8.0		6.8	7.70	C		8.40		2880.0	17.60					
	9.0		6.9	7.70	C		8.20		2890.0	17.70					
	10.0		7.0	7.60	C		8.00		2920.0	17.90					
	11.0		7.1	7.60	C		7.70		2960.0	18.10					

Weather Codes
10 = none; 11 = drizzle; 12 = rain; 13 = rain, heavy; 14 = squally; 15 = frozen precipitation

Wind Velocity
1 - 3 slight ripple
4 - 6 small waves, not breaking
7 - 10 scattered whitecaps
11 - 16 numerous whitecaps
17 - 21 moderate waves, many whitecaps
22 - 27 large waves, many whitecaps
28 - 33 sea heaps get off the water! NOW

plankton C + Fixed ... AP composite MAR-NOV.

Wave Height
0.00 = flat calm; 0.40m = 1-2 ft
0.09m = slight ripple; 1.00m = 2-4 ft
0.20m = ripple - 1 ft; 1.50m = 4-6 ft

Pycnocline Threshold Calculation
Bottom Cond - Surface Cond = cond change (Δ)
31700 - 10700 = 21000
Δ cond / (depth of bottom cond reading-0.5) = XΔ/M
21000 / 22.5 = 933
XΔ /M x 2 = Threshold value
933 x 2 = 1867 1902

Date Entered ______ DNR 6/2008 Page 1 of 2

Mainstem Field Sheet B

R 1 (1 2) Project Name: Main Bay: Bay Bridge

Submitter: AFO- McKay

Maryland Department of Natural Resources
Field Sheet

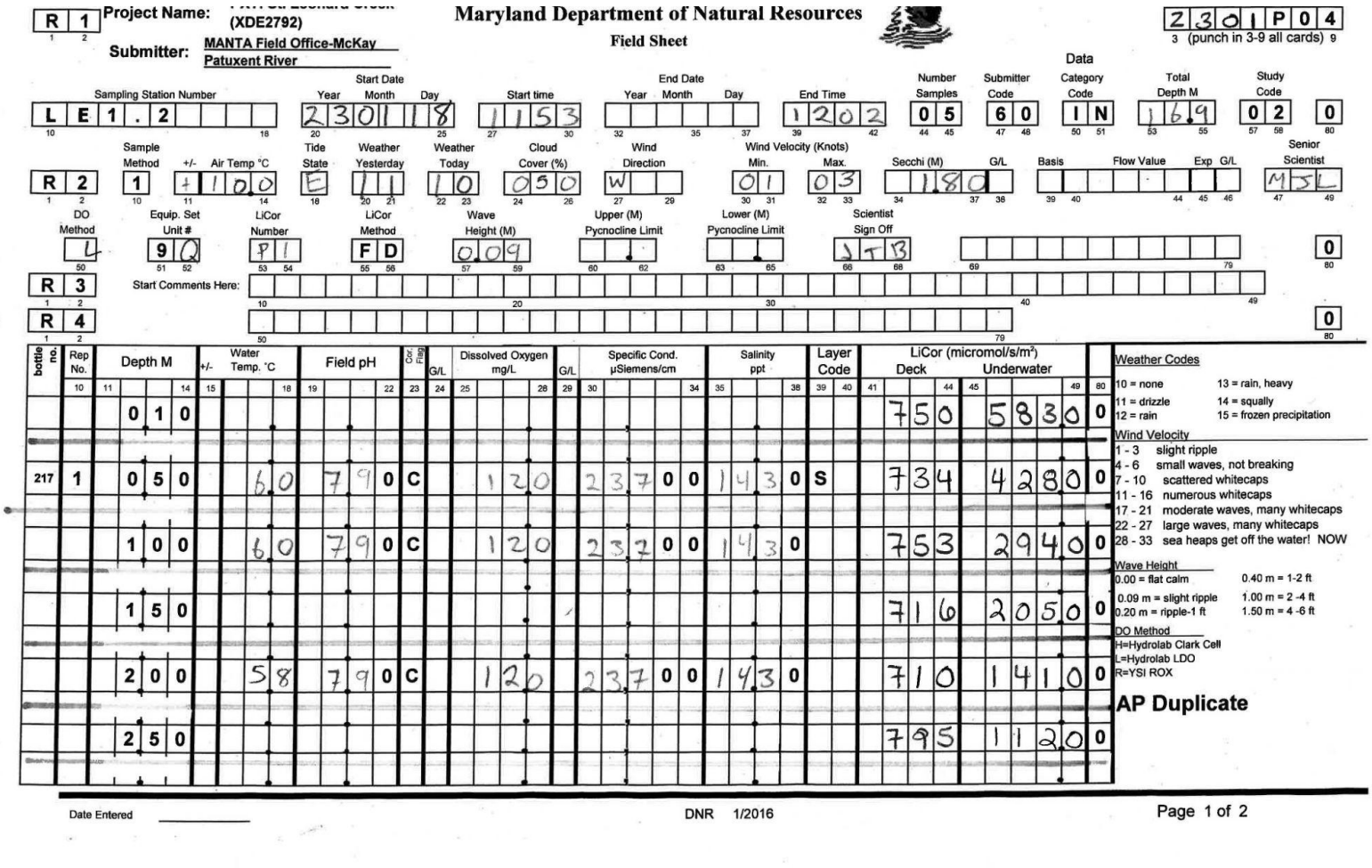
2 3 0 0 1 0 9 (3 punch in 3-9 all cards) 9

Sample Station Number: CB3.3C DATE: 1/10/23 Start Time: 1308 End Time: 1328

Rep No. (11)	Depth M (13-15)	+/- (17)	Water Temp °C (18-20)	Field pH (22-25)	Cor. Flag (27)	G/L (28)	D O mg/l (29-32)	G/L (34)	Conductivity Micromhos/cm (35-39)	Salinity ppt (40-43)	Rep Code (49)	Sample Depth M (50-52)	Layer Code (53-54)	LAB LOGIN Bottle Number (55-63)
	1.3		7.3	7.60	C		7.30		30,200	18.50				
	1.5		7.4	7.60	C		7.10		30,500	18.80				
	1.7		7.6	7.60	C		6.90		31,000	19.10				
	1.9		7.7	7.50	C		6.70		31,500	19.40				
	2.1		7.8	7.50	C		6.70		31,700	19.60				
1	2.3		7.8	7.50	C		6.80		31,700	19.60				

Date Entered _____ DNR 1/2005 Page 2 of 2

B10.1.4 Patuxent River Field Sheet A



R 1 Project Name: (XDE2792)
Submitter: MANTA Field Office-McKay Patuxent River

Maryland Department of Natural Resources
Field Sheet

2301P04 (punch in 3-9 all cards)

Sampling Station Number	Start Date Year	Month	Day	Start time	End Date Year	Month	Day	End Time	Number Samples	Submitter Code	Data Category Code	Total Depth M	Study Code
LE1.2	23	01	18	1153				1202	05	60	IN	16.9	02

R 2

Sample Method	+/-	Air Temp °C	Tide State	Weather Yesterday	Weather Today	Cloud Cover (%)	Wind Direction	Wind Velocity (Knots) Min.	Max.	Secchi (M)	G/L	Basis	Flow Value	Exp	G/L	Senior Scientist
1	+	10.0	E	1	10	050	W	01	03	1.8	G					MSL

DO Method	Equip. Set Unit #	LiCor Number	LiCor Method	Wave Height (M)	Upper (M) Pycnocline Limit	Lower (M) Pycnocline Limit	Scientist Sign Off
L	9Q	P1	FD	0.09			JTB

R 3 Start Comments Here:

R 4

bottle no.	Rep No.	Depth M	+/-	Water Temp. °C	Field pH	Cor. Flag	G/L	Dissolved Oxygen mg/L	G/L	Specific Cond. µSiemens/cm	Salinity ppt	Layer Code	LiCor (micromol/s/m²) Deck	Underwater	
		010											750	5830	0
217	1	050		6.0	7.90	C		1.20		23700	1430	S	734	4280	0
		100		6.0	7.90	C		1.20		23700	1430		753	2940	0
		150											716	2050	0
		200		5.8	7.90	C		1.20		23700	1430		710	1410	0
		250											795	1120	0

Weather Codes
10 = none; 11 = drizzle; 12 = rain; 13 = rain, heavy; 14 = squally; 15 = frozen precipitation

Wind Velocity
1 - 3 slight ripple
4 - 6 small waves, not breaking
7 - 10 scattered whitecaps
11 - 16 numerous whitecaps
17 - 21 moderate waves, many whitecaps
22 - 27 large waves, many whitecaps
28 - 33 sea heaps get off the water! NOW

Wave Height
0.00 = flat calm; 0.09 = slight ripple; 0.20 = ripple-1 ft; 0.40 m = 1-2 ft; 1.00 m = 2 -4 ft; 1.50 m = 4 -6 ft

DO Method
H=Hydrolab Clark Cell
L=Hydrolab LDO
R=YSI ROX

AP Duplicate

Date Entered _____ DNR 1/2016 Page 1 of 2

Patuxent River Field Sheet B

R 1 (1 2) Project Name: PXT: St. Leonard Creek (XDE2792)

Submitter: MANTA Field Office-McKay

Maryland Department of Natural Resources
Field Sheet

Sequence Number: 2 3 0 1 P 0 4 (3 punch in 3-9 all cards 9)

Station Number: LE 1.2 Date: 1118123 Start Time: 1153 End Time: 1202

Bottle Number	Rep No.	Depth M	+/-	Water Temp. °C	Field pH	Cor. Flag	G/L	Dissolved Oxygen mg/L	G/L	Specific Cond. µSiemens/cm	Salinity ppt	Layer Code	LiCor (micromol/s/m²) Deck	LiCor (micromol/s/m²) Underwater	
215	1	3 0 0		5 6	7 8 0	C		1 2 0		2 3 8 0 0	1 4 4 0	A P	7 9 9	7 6 6	0
		6 0 0		5 9	7 8 0	C		1 1 3		2 4 2 0 0	1 4 6 0				0
		9 0 0		5 9	7 8 0	C		1 1 2		2 4 3 0 0	1 4 7 0				0
214	1	1 2 0 0		5 9	7 8 0	C		1 1 1		2 4 3 0 0	1 4 7 0	B P			0
213	1	1 5 0 0		6 0	7 7 0	C		1 1 0		2 4 4 0 0	1 4 8 0	B			0
		1 6 0 0		6 0	7 7 0	C		1 1 0		2 4 4 0 0	1 4 8 0				0
216	2	3 0 0		5 6	7 8 0	C		1 2 0		2 3 8 0 0	1 4 4 0	A P	7 9 9	7 6 6	0
		3 5 0											8 3 7	5 9 9	0

Date Entered _____ DNR 1/2016 Page 2 of 2

B10.1.5 Filtering and Volume Sheet

CBL
CRUISE # 22015
DATE 12-5-22

RECEIVED DEC 09 2022 By

page 1 of 3
MAIN BAY-WINTER
DNR-MANTA

SCIENTIST SIGNOFF LJF

STATION	SAMPLE #	LAYER CODE	DEPTH (M)	TIME (MLTY)	SALINITY (ppt)	TSS/PP Vol (ml)	VSS Vol (ml)	PC/PN (ml)	Chloro (ml)
LE2.3	5	B	18	1018	19.9	250		100	250
	6	BP	13		19.9	450		100	250
	7	AP	7		19.5	500		100	350
	8	S	0.5		18.6	500		150	500
CB5.3	1	B	26	1112	21.5	500		200	500
	2	BP	17		21.4	500		200	500
	3	AP	9		20.5	500		↓	500
	4	S	0.5		20.4	500		↓	500
CB5.2 Jan & Feb Silicates 11,12,13	9	B	30	1215	21.3	250		100	250
	10	BP	21		20.6	500		100	250
	11	AP	11		19.8	500		200	500
Pad #	12	S	0.5		19.7	500	C-388 500	200	500
Pad #	13	S dup	0.5		19.7	500	C-389 500	200	500
CB5.1	14	B	34	1313	21.1	500		200	500
	15	BP	23		20.5	500		200	500
	16	AP	11		19.3	500		200	500
	17	S	0.5		18.9	500		200	500
CB4.4	18	B	31	1403	21.4	450		100	350
	19	BP	21		20.9	450		100	350
	20	AP	11		19.1	500		100	350
	21	S	0.5		18.7	500		200	500
DI Blank Silicates	81	processed		1320	0.0	500	500 C490	200	500
Nov, Jan, Feb Pad #	82	unprocessed			0.0	No unprocessed pads day 1, Only water.			

Totals silicate 5 TDN/TDP 23 :3; TSS/PP=22; PC/PN=22; CHLA=22

C 389 C 388 C 490

B10.1.6 Cruise Reports/Semi-Annual Progress Report Documentation and Procedures

The Cruise Report is filled out by Field Office personnel for each cruise and is provided to the Water Quality and Habitat Analysis Program Manager at DNR. Every six months, the Program Manager combines and summarizes the Cruise Reports, creating a Semi-Annual Progress Report to submit to the CBP.

The Cruise Report includes the following: cruise identification number, name of the water quality monitoring program, scheduled sampling date, name of the Field Office representative who submits the sheet, additional sampling activities, station names, sampling dates and times, filtration completion times, station departure time, the presence or absence of hydrogen sulfide odor and results of any Hach tests conducted, the research vessel name, the names of the captain, crew, and scientific party, the departure-from-dock time and location, the return-to-dock time and location,
weather conditions, air temperature, barometric pressure, estimated wind speed and direction, equipment conditions, morning dissolved oxygen check, sample status and additional comments.

Information filled out by Field Personnel:

Page 1

1. Cruise I.D. (top left of sheet) (Mainstem)

Enter the cruise identification number in the space provided at top left of sheet.

2. Page____of_____(top right of page)

When more than one sheet is generated and sent with samples, enter this information in the area provided, 'Page_____of_____'. If only one sheet is generated, indicate this by entering page 1 of 1.

3. Day # (top right of page, under page number) (Mainstem)

Provide the day number of the cruise (i.e., Day #1, Day #2, or Day #3)

4. Study Location (top of sheet)

If not preprinted, enter the name of the study location (e.g., Mainstem Cruise Report) at the top center of the sheet.

5. Scheduled Sampling Date

Enter the scheduled sampling date in the space provided.

6. Submitted by

Enter the name of the field scientist who originates the sheet.

7. Station Sampled (1st column of sheet)

The station sampled should be preprinted in the first column of the sheet. If not preprinted, enter the station name. (For example, if the samples were collected from station CB5.3, the station sampled would be "CB5.3").

8. Date

Enter the actual date sampled in the space provided.

9. Time

Enter the time the samples are taken.

10. FF (finished filtering) (Mainstem) Enter the time that filtering is finished.

11. LS (left station) (Mainstem)

Enter the time of leaving the station.

12. H_2S odor (Mainstem)

For both below pycnocline (BP) and bottom (B) layer samples:

> If H_2S odor is present (rotten egg smell), enter "+" and perform a Hach test for hydrogen sulfide. Record the Hach reading.

13. If no H_2S odor is present, enter "-".

14. Cruise I.D. (top left of sheet) (Mainstem)

Provide the cruise identification number in the space provided at top left of sheet.
Cruise ID numbers consist of last 2 digits of year, 0, and cruise # of the year. For example, the cruise ID for the third trip of 2008 would be 08003.

15. Date

Enter the actual sampling date in the space provided.

16. R/V Utilized

Enter the name of the research vessel in the space provided.

17. Captain, Crew and Scientific Party

Enter the names of the Captain, Mate, scientists and occasional collaborators or observers on board. Identify the agency/company that the scientists and observers represent (e.g., DNR, CBL, and Baltimore Sun).

18. Departure Time and Location

Enter the departure time and location.

19. Return time and location

Enter the return time and location.

20. Weather conditions

- Enter the air temperature in degrees Celsius for the morning (AM) and afternoon (PM).
- Enter the barometric pressure in inches of mercury for the morning (AM) and afternoon (PM).
- Enter the estimated wind speed in knots and the direction from which the wind is blowing for the morning (AM) and afternoon (PM).

21. Equipment conditions

Enter the refrigerator (FRIDGE) temperature in degrees Celsius. January–June, August and November only (no Silicate samples in July, August, Sept. October, December).
Enter the freezer temperature in degrees Celsius.

22. Morning Dissolved Oxygen (DO) Check (Mainstem)

23. Enter the meters checked, whether the meters were changed or not during the DO check and which meter is being used for the day. Meter readings are logged in Cruise Report when a sonde is changed during a survey.

24. Sample Status
Enter the status of the sample in cases when unusual events might affect a sample. For example, a refrigerator/freezer failure, or samples transported at odd times.

25. Additional Comments
Enter additional comments as needed.
Pages 3 and 5 are the same as Page 1 (for additional stations). Pages 4 and 6 are the same as Page 2 (for additional stations).

Maryland Department of Natural Resources
RAS/MANTA

Chesapeake Bay Mainstem
Progress Report / Cross Reference Sheet

Month/ Year: January 2023

Submitted by: Debbie McKay

Station	Day	Depth (M)	Sequence #	Sample #	Nutrients (CBL)	Chloro. (CBL)	Plankton Fixed composite	Comments
CB5.3 Smith Point	09	24.0	2300101	1			N/S	Could only sample Bottom at 24.0 meters due to rough seas. 0.5 and 1.0 meter are the same depth. Scattered showers overnight.
		12.0		2			N/S	
		3.0		3			N/S	
		0.5		4			N/S	
LE2.3 Point Lookout	09	18.0	2300102	5			N/S	Scattered showers overnight.
		14.0		6			N/S	
		0.5		7			N/S	
		0.5		8			N/S	
CB5.2 Point No Point	09	30.0	2300103	9			N/S	Bottom sample and readings at 30.0 meters. Touching Bottom at 31.0 meters. Scattered showers overnight.
		18.0		10				
		8.0		11				
		0.5/1		12				
		0.5/2		13				
CB5.1 Cedar Point	09	34.0	23001504	14			N/S	No pycnocline-1/3 and 2/3 sampling. Touching bottom at 35.0 meters.
		23.0		15			N/S	
		11.0		16			N/S	
		0.5		17			N/S	

Page 1 of 4

B10.2 Laboratory Sheets

B10.2.1 Documentation and Procedures for the Analytical Lab Sheet or File

Lab Volume sheets will be initiated in the field. The Lab Volume sheets will be used to record basic information about samples, such as station, date, depth, and volume filtered. The sheets will serve as sample transfer sheets, traveling with the samples to CBL's Nutrient Analytical Services Lab, or the MDH Inorganics Analytical Laboratory, for analysis. Both the sheets and the samples will be logged in at the respective labs.

Most of the nutrient analysis and all of the chlorophyll analysis for the Main bay and tidal tributary monitoring program will be completed by CBL. At CBL, data generated from nutrient and chemical analyses will be recorded directly to an Analytical Lab electronic file instead of a physical Analytical Lab sheet. CBL laboratory results are electronically shared with DNR on cloud drives with access limited to appropriate laboratory and DNR analytical personnel. CBL keeps active control charts. Each instrument has an operator dedicated to that instrument. The dedicated operator is responsible for keeping track of the slopes of the regression analysis for that instrument to determine if the analyses are "in control." The analyst will review the data and, if the data exceed their control limits, the entire run will be re-analyzed. Re-analysis can occur for any number of reasons, such as a poor r squared (R^2) on the standard curve, the wrong set of pump tubes (which would provide abnormally low peaks), or high blank values (in the case of DOC). See Appendix 1 for Chesapeake Biological Laboratory procedures and methods weblinks.

For a subset of Potomac stations, samples for three parameters (BOD, Turbidity and Total Alkalinity) will be sent to MDH for analysis. At MDH, data generated for these parameters will be recorded on paper Analytical Lab sheets, one for each date/station/layer. Paper Analytical Lab sheets are delivered by courier to DNR and then sent to a typesetting service for entry into an electronic file. MDH also scans lab sheets into PDF files and posts them to a shared cloud drive with access limited to appropriate laboratory and DNR analytical personnel. The original copies are kept on file at MDH and a copy of them is sent to Data Management staff.

MDH keeps active quality control sample charts to determine if the analyses are "in control." Each instrument has trained analysts dedicated to that method. The dedicated operator is responsible for meeting all Quality Control requirements including but not limited to determining the acceptability of the correlation coefficient of the calibration curve and acceptability of results for blanks, spikes, external quality control samples, etc. as specified on the Data Review Checklist included in each data packet. The analyst will review the data and repeat any analysis if the data does not meet control limits. See Appendix 2 for Inorganics Analytical Laboratory procedures and methods.

B10.2.2 Split Sample Program and Custody Log

Information about the Split Sample and Blind Sample Programs program is discussed in Section B5 and online. An example of the field sheet used to record sample number, time of collection and salinity when split sample water is collected follows. Volumes are filled in the next morning when samples are processed for the Laboratories.

MAIN BAY SPLIT SAMPLE CUSTODY LOG

BOTTLE NUMBERS: F1,F2,F3,F4,

LOCATION: CB4.4

COLLECTED FOR: South River Federation

COLLECTION DETAILS: DATE:_____ TIME:_____ DEPTH:_____m SALINITY:_____PPT

COMMENTS:(unusual conditions, problems, floating algae, rain, etc.)

SPLITTING DETAILS: COMPOSITE SUB SPLIT BY:
COMPOSITE CONTAINER sequential bottles
FILLED BY: submersible pump @ m into a 30 gallon Nalgene container

Splitting Sequence

Order # Agency	order # Agency	order # Agency	order # Agency
1---A1 VADCLS	8--- A2 VADCLS	15--- A3 VADCLS	22--- A4 VADCLS
2---B1 ODU	9--- B2 ODU	16--- B3 ODU	23--- B4 ODU
3---C1 CBL	10---C2 CBL	17--- C3 CBL	24--- C4 CBL
4---D1 VIMS	11---D2 VIMS	18--- D3 VIMS	25--- D4 VIMS
5---E1 HP	12-—E2 HP	19--- E3 HP	26-— E4 HP
6---F1 SRF	13---F2 SRF	20--- F3 SRF	27--- F4 SRF
7---G1 DNREC	14---G2 DNREC	21--- G3 DNREC	28--- G4 DNREC

TRANSFER SEQUENCE:	DATE	TIME	BY WHOM?	TEMP. OF SAMPLE (circle one)
Composite collected & split	_____	_____	DNR/_____	ambient
Subsample picked up	_____	_____	_____	0°C 4°C ambient
Subsamples delivered to lab	_____	_____	_____	0°C 4°C ambient

FIELD PROCESSING INFORMATION

BOTTLE #	FIELD PROCESSING DONE	DATE/TIME	BY WHOM?

NOTE: PLEASE SEND A COPY OF THIS COMPLETED FORM TO: Main Bay Split, Lenora Dennis, Maryland Dept of Natural Resources, TEA/C-2, 580 Taylor Avenue, Annapolis MD, 21401, (410) 260-8647.

Blue Plains Split Custody Log:

Collected for: MD/MDHMH+DSL
Bottle No.(s): A1, A2, A3, J1, J2, J3

POTOMAC COMPONENT SPLIT SAMPLE CUSTODY LOG

COLLECTION DETAILS: DATE: 12/11/2017 TIME: 1044 (EST) DEPTH: 0.1 (M)
WTEMP 4.9 PH 8.27 LOCATION: PMS10 CONDUCTIVITY: 397 (umhos)
DO 13.1
COMMENTS: (unusual conditions, problem, floating algae, high solids, etc.)

SPLITTING DETAILS:		SPLITTING SEQUENCE	BOTTLE LABELLED
COMPOSITE CONTAINER		bottle 1	~~MDHMH - A1~~
FILLED BY:		bottle 2	DCLS - B1
multiple grabs	X	bottle 3	CRL - C1
pump		bottle 4	FCDPW - D1
other		bottle 5	ODU - E1
		bottle 6	OL F1
		bottle 7	USGS H1
		bottle 8	SRBC I1
		bottle 9	~~DSL~~ J1
		bottle 10	~~MDHMH - A2~~
		bottle 11	DCLS - B2
		bottle 12	CRL - C2
		bottle 13	FCDPW - D2
		bottle 14	ODU - B2
		bottle 15	OL - F2
		bottle 16	USGS - H2
		bottle 17	SRBC - I2
		bottle 18	~~DSL - J2~~
		bottle 19	~~MDHMH - A3~~
		bottle 20	DCLS - B3
		bottle 21	CRL - C3
		bottle 22	FCDPW - D3
		bottle 23	ODU - E3
		bottle 24	OL - F3
		bottle 25	USGS- H3
		bottle 26	SRBC- I3
		bottle 27	~~DSL - J3~~

TRANSFER SEQUENCE:	Date	Time	By Whom	Temp. of Sample (circle one)
Composite collected	12/11/17	1140	LB EO GH	0°C 4°C ~~ambient~~
Composite split	12/11/17	1219	LB EO GH	0°C (4°C) ambient
Subsamples picked up	12/11/17	1253	KJN	0°C (4°C) ambient
Subsamples delivered to lab				0°C 4°C ambient

FIELD/PRE-LAB PROCESSING INFORMATION:

Bottle #	Field Processing Done on Sample	Date/Time	By Whom
MD-A1	All samples processed for	12/12/17 @0635	DSM
MD-A2	TSS/VSS, PIP/PP, CHLA, PC/PN,	12/12/17 @0710	DSM
MD-A3	TDNTDP, DOC, NO2NO3, TDPLSi	12/12/17 @0735	DSM

Note: Please send a copy of this completed form to:
CSC, 410 Severn Avenue, Suite 110, Annapolis, MD 21403
Tel. (410)267-5749 Revised 12/4/12

B10.3 Data Management Sheets

B10.3.1 Documentation and Procedures for Data Status

Incoming datasets are tracked by a data processor/programmer when received from field or laboratory staff. Data is reviewed for completeness and any issues with missing data are resolved. Any data that require keypunching, are organized by month, project, and data type (field/lab) and copies are sent to a keypunching service in quarterly batches. Keypunch files are received back in electronic formats suitable for ingestion into DNR's data processing programs.

When a dataset is processed, and quality assurance materials are generated (field and lab verification sheets, data plots, and potential error logs) an email is sent from the data processor to the data analyst with a subject line in the format: MONTH YEAR PROJECT QA Materials Attached (eg. Sept. 2022 TRIB QA Materials Attached) and the various files attached. QA files are also on a central cloud drive. When the analyst has completed review of the dataset, they reply to the original email with needed corrections. The processor makes the necessary corrections and recreates QA materials for the analyst to review and ensure the necessary changes were successful. This process continues until the internal QA process is completed.

Data is then transformed into the required Chesapeake Bay Program format, and electronically submitted via the CBP DUET system. DUET returns a QAT file with lists of fatal and non-fatal errors. The QAT is sent in a second email chain from the processor to the analyst for review. The data processor with guidance from the analyst will respond with corrections for any fatal errors in the DNR internal and CBP formatted datasets. Non-fatal errors, such as range checks and possible sample coding issues are also reviewed and updated if necessary. Data are resubmitted to DUET and new QATs are reviewed, until all corrections are made successfully. The data processor/supervisor then communicates with the CBP data manager that data is complete and can be reviewed and accepted upon the approval of the CBP data manager. If the CBP data manager finds issues that require attention, the DNR processor and analyst will complete those revisions and resubmit the dataset to CBP.

DNR also maintains a public facing web page that lists the status of current datasets, in a table form and narrative format. It is regularly updated as changes occur and is helpful for informing data management staff and data users and reduces data inquiries to DNR and CBP data managers.

https://eyesonthebay.dnr.maryland.gov/eyesonthebay/DataStatus.cfm

CONVENTIONS FOR NAMING THE DATA SET FOR KEYPUNCHING PURPOSES

An eight-character text string is used for this data set name. This section contains the naming conventions for data set names for all monitoring projects. Any new sampling monitoring and data collection projects must follow these conventions.

1. CHESAPEAKE BAY MAINSTEM MONITORING PROJECT Data Set Name: MMYYDDD
Description: The data set name contains the data sampling month, year, and data type only. The first three characters of the data set name (MMM) stand for the sampling month. The next two characters (YY) of the data set name are the last two digits of the sampling year. The last three characters of the data set name (DDD) stand for sample collection type. The following types are available for this project:

DATA TYPE	DATA DESCRIPTION
FLD	Field Data
LAB	Laboratory Data
CHL	Chlorophyll Data

Example of Mainstem Data Set Name: For field data sheets for January 1998 data, the data set name is 'JAN98FLD'.

2. MARYLAND TRIBUTARY MONITORING PROJECT Data Set Name: TMMMYYDD
Description: The data set name begins with the project initial 'T', followed by the data sampling month (MMM), year (YY), and data type (DD). The last two characters of the data set name (DD) stand for data type. The following types are available for this project:

DATA TYPE	DATA DESCRIPTION
FD	Field Data
LB	Laboratory Data
CH	Chlorophyll Data

Example of a Tributary Data Set Name: For field data sheets for January 1998 data, the data set name is 'TJAN98FD'.

3. MARYLAND PATUXENT RIVER INTENSIVE SURVEY (PART OF MARYLAND TRIBUTARY MONITORING PROJECT)

Data Set Name: PTMMMYYD

Description: The data set name begins with the project initials 'PT', followed by the data sampling month (MMM), year (YY), and data type (D). The last character of the data set name (D) stands for data type. The following types are available for this project:

DATA TYPE	DATA DESCRIPTION
F	Field Data
L	Laboratory Data

[Note: Chlorophyll data for the Patuxent is included in the tributary data set.]

B10.3.4 Data Entry Request Form Documentation and Procedures

When submitting a job for data entry service, a data entry request form must be completed with the information specified below.

RESOURCE ASSESSMENT ADMINISTRATION DATA ENTRY REQUEST FORM

1. AGENCY CONTROL NO: _____

The agency control number is used by the Data Processing Department (D.P.D.) to track keypunch jobs. The number is assigned by the Maryland Department of Natural Resources (MDDNR) Data Processing Programmer Trainee when preparing the request form.

2. D.P.D. CONTROL NO: _____

The D.P.D. control number field is optional and can be used by the Department of Data Processing for tracking.

3. APPLICATION REQUESTED ID (JOB ID) _____

The application Requested ID is an eight-character alphanumeric value followed by a water quality monitoring project data type description enclosed in parentheses.

Three different request IDs are used for Maryland Mainstem and tributary water quality monitoring field data sets: A34202CB (Main Bay field), A34200CB (Patuxent field) and A34205CB (Tributaries field).

4. Requested By: _____

The name of the MDDNR Data Processing Programmer Trainee is used to identify the person submitting the data entry request form to the Data Processing Department.

5. Date Sent: _____

Date sent is optional and may be used to document when the date the request form was sent to the Data Processing Department. The MDDNR Data Processing Programmer Trainee maintains a log of this information separately.

6. Date Originals Returned: _____

Date originals returned are optional and may be used to document the date the field sheet originals were returned to MDDNR. The MDDNR Data Processing Programmer Trainee maintains a log of this information separately.

7. Agency: _____

Agency is the agency submitting the data entry request to the Department of Data Processing. The abbreviation "DNR" for Department of Natural Resources is used in the agency field.

8. Telephone:_____

The telephone number is the voice contact number of the Data Processing Programmer Trainee who submitted the data entry request.

9. Email received: _____

The email received field is optional and may be used to indicate whether an electronic mail message was received by the Data Processing Programmer Trainee. The MDDNR Data Processing Programmer Trainee maintains this information in the form of email messages.

SPECIAL INSTRUCTIONS TO D.P.D.

Control Information

10. Deliver Documents To:

DNR, Tawes State Office Bldg., D-2, 580 Taylor Ave, Annapolis, MD 21401.

The DVD containing electronic files produced by the Data Processing Department, and the original field data sheets that were sent to the Data Processing Department with the data entry request should be delivered to DNR at the address specified above.

11. Dataset Name:

_____

Enter the name of the .ORG file. For example, for Patuxent November 2015 field data, use the description 'MAY07LAB.ORG'.

12. REMARKS:

_____

Comments may be entered in the remarks field.

Example of Data Entry Request form

Note: The Date Received stamp in the example was applied when the original field sheets were received by the Department of Data Processing.

RESOURCES ASSESMENT ADMINISTRATION
DATA ENTRY REQUEST FORM

AGENCY CONTROL NO: 0043 D.P.D. CONTROL NO:_____

APPLICATION REQUESTED ID (JOB ID)
A34200CB (Patuxent Field)

Requested By: Lenora Dennis Agency: DNR
Date Sent: _____ Telephone: 410-260-8647
Date Originals Returned: _____ Email Received: _____

SPECIAL INSTRUCTIONS TO. D.P.D

Control Information	Data Set Name
Deliver Documents To:	PTNOV15F.ORG
DNR	
Tawes State Office Bldg., D-2	
580 Taylor Ave.	
Annapolis, Md. 21401	

DATE RECEIVED DEC 10 2015

REMARKS

B10.3.5 Cross Reference Sheet Documentation and Procedures

The following documentation outlines the conventions for filling out the Cross Reference Sheet. (Note: Although the sheet has a subheading "Progress Report" or “Progress Report / Cross Reference Sheet”, it is generally known as the Cross Reference Sheet and should not be confused with the "Cruise Reports/Bi-annual Progress Report".)

The Cross Reference Sheet is sent along with Field Sheets from the Field Office to the DNR Tawes Building, so that the DNR data management staff knows what data to expect in the form of field sheets and lab data.

The Cross Reference Sheet includes the name of the program, the sampling month and year, and the name of the Field Office representative who originated the sheet. Columns with headings: Station, Day, Depth (m), Sequence #, Sample # list the samples and replicates that were collected. Columns with the headings: Nutrients (CBL), Chlorophyll (CBL), and Plankton are used to track whether DNR data management has received the analytical results. The Comments column is used to enter information explaining missing samples, stations, field abnormalities, or potential data problems.

The structure of the Mainstem and Potomac and minor tidal tributaries cross reference sheets are the same. Patuxent River cross reference sheets are slightly different. Examples of each cross-reference sheets follows:

Maryland Department of Natural Resources
RAS/MANTA
Chesapeake Bay Water Quality Monitoring

Potomac (CORE/COG)

Progress Report / Cross Reference Sheet

Month/ Year: January /2023 **Submitted by: James Bailey**

Station	Day	Depth (M)	Sample #	Sequence #	MDH (nutrients)	Chloro. (CBL)	Comments
ANA0082	4	0.0	C-39	2301M12			WATER VERY BROWN; BARGE, DEREDGE EQUIPMENT DOWNSTREAM.
RCM0111	4	0.0	C-36	2301M13			
POT1184	4	0.0	C-38	2301M14			
CJB0005	4	0.0	C-37	2301M15			
SEN0008	4	0.0	C-47	2301M16			SCATTERED SHOWERS YESTERDAY
POT1471	4	0.0	C-46	2301M17			SCATTERED SHOWERS YESTERDAY
POT1472	--	~~0.0~~	~~C-45~~	~~2301M18~~	--	--	STATION DISCONTINUED OCTOBER 2022.
MON0020	--	~~0.0~~	~~C-44~~	~~2301M19~~	--	--	STATION DISCONTINUED OCTOBER 2022.
POT1595	4	0.0	C-43	2301M20			SCATTERED SHOWERS YESTERDAY
POT1596	4	0.0	C-42	2301M21			SCATTERED SHOWERS YESTERDAY
PMS-10	--	~~0.1/1~~	~~A1~~	23XXM22			NO SPLIT THIS MONTH.
		~~0.1/2~~	~~A2~~				
		~~0.1/3~~	~~A3~~				

CORE MDH SAMPLES DELIVERED BY COURIER. **POT1472** DISCONTINUED OCTOBER 2022; WHITE'S FERRY IS CLOSED DOWN AND ACCESS TO VIRGINIA SHORELINE IS UNAVAILABLE. **MON0020** DISCONTINUED OCTOBER 2022; BRIDGE RESTORATION DELETED SHOULDERS AND SAMPLING ON BRIDGE IN TRAFFIC LANES IS UNSAFE. STATION CAN ONLY BE ACCESSED WITH EXTREME EFFORT WADING ACROSS THE RIVER BUT ONLY AT LOW FLOW STAGE AND IN ABSENCE OF ICE, AS HIGH STAGE CONDITIONS CREATE SERIOUS RISK OF FLOWING TREE DEBRIS, HYPOTHERMIA AND DROWNING.

Example Mainstem Cruise Report (page 1):

CRUISE I.D.	23001			Page	1	of	6
						Day	1

MARYLAND DEPARTMENT OF NATURAL RESOURCES
WATER QUALITY MONITORING DIVISION
MAINSTEM CRUISE REPORT- WINTER

Scheduled Sampling Date: January 09, 2023	Submitted by:	Debra McKay

Additional Sampling Activities: none

TABLE OF STATIONS SAMPLED

STATION #	DATE	TIME	COMMENTS
LE2.3 Point Lookout	1/9/23	0909	FF 0959 LS 0947 H_2S odor BP (-) B (-) Too rough for Licor.
CB5.3 Smith Point	1/9/23	1020	FF 1106 LS 1054 H_2S odor BP (-) B (-) Too rough for Licor.
CB5.2 Point No Point	1/9/23	1142	FF 1231 LS 1212 H_2S odor BP (-) B (-) Too rough for Licor.
CB5.1 Cedar Point	1/9/23	1249	FF 1335 LS 1322 H_2S odor BP (-) B (-)
CB4.4 Cove Point	1/9/23	1341	FF 1427 LS 1416 H_2S odor BP (-) B (-)

*FF: FINISHED FILTERING; LS: LEFT STATION; H_2S ODOR: (-) ABSENT, (+)

Mainstem Cruise Report (page 2):

CRUISE I.D.	23001				Page	4	of 6
DATE: 1/10/2023							Day 2
Vessel Utilized: RV Rachel Carson							
PERSONNEL:							
		DNR:					
Captain: Michael Hulme		Meter: Debbie McKay					
Mate: Rob Nilsen		TSS/PP: Maryn LeClair					
		Chla/PC/PN: Sara Miller					
		Hosing/paperwork: Michael Dhillon					

LOCATION & TIMES

Depart dock : 0755 Solomons Island, MD

Arrive dock: 1348 Sandy Point State Park, MD

WEATHER CONDITIONS

	AM	PM	Please give a general description of the day's weather
Air Temp (°C)	+2.0	+7.0	
Barometer (mm/hg)	764.2	762.8	
Wind Speed & Direction (knots)	NW 1-3	N 1-3	

EQUIPMENT CONDITIONS

	AM	PM	Problems?
Freezer temp (°C)	-25.0	0.0	
Fridge Temp (°C)	+4.0	+5.0	

MORNING DO CHECK

meter #	E (EXO)	changed?	no	Used F today
meter #	F (EXO)	changed?	no	

SAMPLE STATUS: BT 2 samples returned to office

ADDITIONAL COMMENTS:

Example Patuxent Cruise Report (page 1):

MARYLAND DEPARTMENT OF NATURAL RESOURCES
WATER QUALITY MONITORING DIVISION
PATUXENT CRUISE REPORT

Scheduled Sampling Date: 01/18/2023 Submitted by: Debbie McKay

Additional Sampling Activities: None

TABLE OF STATIONS SAMPLED

STATION	DATE	TIME	COMMENTS
CB5.1W	1/18/2023	1050	
LE1.4	1/18/2023	1110	
LE1.3	1/18/2023	1135	
LE1.2	1/18/2023	1153	
LE1.1	1/18/2023	0917	
RET1.1	1/18/2023	0947	
TF1.7	1/18/2023	1014	
TF1.6	1/18/2023	1040	
TF1.5	1/18/2023	1105	

Example Patuxent Cruise Report (page 2):

R/V UTILIZED					
PERSONNEL:					
CPT: CREW:			Guests:	DNR:	MD2538A: Jamie Strong Victoria Ilko R/V Seabiscuit: Andy Watts Taylor Wagner
LOCATION & TIMES					
DEPARTED DOCK:					0845 Solomons Boat ramp /0830 Benedict Boat Ramp
FUEL DOCK:					Arrival: Departure:
ARRIVED AT DOCK:					1130 Solomons Boat ramp/1320 Benedict Bridge ramp
WEATHER CONDITIONS:					
	AM		PM		General description (e.g. nice)
Air Temp.	+15.0/ +14.0	°C	+18.0/ +17.0	°C	Windy
Barometer	29.74/ n/a		29.74/ n/a		
Wind Speed & Direction	W11-16/ NW 17-21	kts	NW 07-10/ SW 17-21	kts	
SAMPLE STATUS:					
ADDITIONAL COMMENTS:	Stations were sampled on 4/17/23 due to staffing. Patuxent was sampled with 2 boat teams. MD2538A sampled CB5.1W-LE 1.2 and R/V Seabiscuit sampled LE 1.1 –TF 1.5. Both boats used about 30 gallons of fuel each.				

B10.3.6 Combined CBL and CBP codes

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
Laboratory accident, sample damaged during processing	1	no	A	Laboratory Accident
			AA	Field Accident
			B	Chemical Matrix Interference
			~~BB~~	("Torn filter pad". No longer a valid code. Use TP instead - see CBL code #19)
Insufficient sample - typically inadequate liquid volume or sediment mass required for requested analysis	2		D	Insufficient Sample
Analysis conducted by another laboratory	3			
Sample frozen when received (should have arrived un-frozen)	4	yes	X	Sample not preserved properly
Sample received thawed (should have arrived frozen)	5	yes	X	Sample not preserved properly
Sample not received; sample received in condition that prevents analysis	6	no	RR	No sample received by lab from field office
Lost results	7	no	A	Laboratory Accident

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
Sample contaminated	8	no	R	Sample Contaminated
Sample results rejected due to quality control criteria	9	no	V	Sample results rejected due to QC criteria (May appear as the incorrect and outdated CBL code W "Duplicate results for all parameters". All W codes should be changed to V.)
Sample not preserved properly	10	yes	X	Sample not preserved properly
Analyzed in duplicate, results below detection limit	11			
Instrument failure	12	no	C	Instrument Failure
			CC	Cannot Calculate Given Available Data
			F	Post-Calibration Failure Likely Due To Equipment Damage After Sampling; Data Appear Normal
Foil pouch very wet (salty) when received from field; mean reported	13			
Poor replication between pads, mean reported. Difference is within 50%.	14A[1]	yes	FF	Mean Reported Due To Poor Replication between Pads
Poor replication between pads. Sample rejected because the difference is greater than 50%	14B[1]	no	V	Sample results rejected due to QC criteria

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
Sample size not reported - either mass or volume	15	yes	DD	Sample Size Not Reported (Assumed)
Sample mislabeled	16	no	RR[2]	No sample received by lab from field office (Substitute for outdated CBP code LL.) Important: There is no CBP code for "Sample mislabeled". Without proper labeling, there is no way to be sure that the sample is correct. Delete any reported values and use code RR for "No sample received by lab".
Over 20% of sample adhered to pouch and outside of pad	17	yes[3]	MM	Over 20% of Sample Adhered To Pouch And Outside Of Pad Important: This code is used by the lab to identify a problematic sample. A reported value indicates that the analyst was confident in the laboratory result, and the value should be kept. A missing value indicates that the sample was so compromised that the analyst could not report a value.
Sample not collected	18	no	RR	No sample received by lab from field office
Torn filter pad	19	yes	TP	Torn filter pad (Substitute for outdated CBP code BB.)

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
Pad unfolded in foil pouch	20	yes	none	There is no CBP code for "Pad unfolded in pouch". Code 20 identifies a problematic sample, but a reported value indicates that the analyst was confident in the laboratory results.
Particulates found in filtered sample	21	yes	NN	Particulates Found in Filtered Sample
			I	Suspect Value Has Been Verified Correct
			IQ	Cannot Determine If Part Exceeds Whole Value and Whether or Not Difference Is Within Analytical Precision
			J	Incorrect Sample Fraction for Analysis
Assumed sample volume, usually based on COC (pouch vol used if different from COC) and only when verification with sampler is not possible	22	yes	JJ	Volume Filtered Not Recorded (Assumed) (Substitute for outdated code PP.)
			L	LiCor Calibration Off By >= 10% per Year. Use with Calculated KD Where Prob Of LU, LS, LB Exist In Raw
			LB	LiCor Calibration Off By >= 10% per Year for Both Air And Upward Facing Sensors

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
			LS	LiCor Calibration Off By >= 10% per Year for Air Sensor
			LU	LiCor Calibration Off By >= 10% per Year for Upward Facing Sensor
			NQ	Part Exceeds Whole Value and Difference Is Not Within Analytical Precision
			NV	Negative Calculated Value Is Valid Given Precision of Measured Water Quality Parameters; Actual Calculated Concentration Likely Is Low; Possibly Less than PQLS of Measured Water Quality Parameters
			P	Provisional Data
			Q	Analyte present, reported value is estimated; CONC is below the range for quantitation
			~~PP~~	("Assumed sample volume". No longer a valid code. Use JJ instead – see CBL code #22.)

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
Value exceeds a theoretical equivalent, but is within analytical precision	23	yes	QQ	Value exceeds a theoretical equivalent but is within analytical precision. (If any value in an inconsistent relationship is below the detection limit, do NOT assign the QQ error codes. Keep all the values and do NOT use error codes.) Important: If any value in an inconsistent relationship is below the detection limit, do NOT assign the QQ error codes. Keep all the values and do NOT use error codes.
Is greater than the acid persulfate total phosphorus by less than or equal to 0.01 MG P/L	24			
If NO2 > NO23 by </= 0.0019 MG N/L at STD. CAL of 9.0 for both, or </= 0.0030 MG N/L at a STD. CAL of 9.0 for NO2 and a STD CAL of 6.0 for NO23	27			
Dissolved organic carbon > total organic carbon, Total Dissolved Phosphorus > Total Phosphorus, Total Dissolved Nitrogen > Total Nitrogen	28	yes	QQ	Part Exceeds Whole Value Yet Difference Is Within Analytical Precision (If any value in an inconsistent relationship is below the detection limit, do NOT assign the QQ error codes. Keep all the values and do NOT use error codes.)

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
TVS > TSS, PIP > PP	29	yes	QQ	Part Exceeds Whole Value Yet Difference Is Within Analytical Precision (If any value in an inconsistent relationship is below the detection limit, do NOT assign the QQ error codes. Keep all the values and do NOT use error codes.)
Samples received more than 28 days from date of collection	30	yes	E	Sample Received After Holding Time
Samples received within 28 days of collection, but not within 7 days of collection, thus analysis within 28 days of collection not practical	31	yes	GG	Sample Analyzed After Holding Time
Samples not analyzed within 28 days of collection	32	yes	GG	Sample Analyzed After Holding Time
Original analysis performed within 28 days of collection, but reanalysis/reported results performed after 28 days of collection due to instrument failures, concentration range changes, QA/QC failures, or time constraints.	33	yes	GG	Sample Analyzed After Holding Time
BOD final readings not taken at the 5-day at +/- 3-hour threshold.	34	yes	GG	Sample Analyzed After Holding Time

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
			SS	Sample rejected due to high suspended sediment concentration
			U	Matrix problem resulting from the interrelationship between variables such as pH and ammonia
			UN	For DCDOH data, these values are issues or are nulls with no assigned problem codes. 8/27/2008
			~~W~~	("Duplicate results for all parameters". No longer a valid code. Use V instead – see CBL code #9).
			WW	High optical density (750 nm); actual value recorded
			N	None
Sample collection data (such as collection date and time) omitted by client. As a result, NASL is not responsible for method specified holding times.	35			
Sample diluted or standard calibration range changed to bring concentration/sample within linear range	36	yes	none	Code 36 relates to sample processing by the lab (dilution). CBL did not use code 36 until recently. In the past, samples that were diluted for lab analysis were not identified as such.

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
Value below method detection limit (MDL). Actual observed value reported.	U	yes	none	(Note: Qualifiers (< method detection limit) get assigned during data processing)
Value below method detection limit (MDL). Method detection limit reported.	L			
Value below method reporting limit (RL). Actual observed value reported.	BR	yes	none	

1) Following a lab audit, CBL started reporting samples with "poor replication between pads" using new codes to note how far off the values were. For CBP, this translates to either a FF code (Difference is within 50%) or a V code (Difference is greater than 50%)

2) There is no valid CBP code for "Sample mislabeled". Without proper labeling, there is no way to be sure that the sample is correct. Delete any reported values and use code RR for "No sample received by lab".

3) Code 17 is used by the lab to identify a problematic sample. A reported value indicates that the analyst was confident in the laboratory result, and the value should be kept. A missing value indicates that the sample was so compromised that the analyst could not report a value.

4) There is no CBP code for "Pad unfolded in pouch". Code 20 identifies a problematic sample, but a reported value indicates that the analyst was confident in the laboratory results.

5) Code 36 relates to sample processing by the lab (dilution). CBL did not use code 36 until recently. In the past, samples that were diluted for lab analysis were not identified as such.

END OF SECTION B

C: ASSESSMENT AND OVERSIGHT ELEMENTS

C1. Assessment and Response Actions

Field: If a station or specific sample cannot be collected, it is noted on the cross-reference sheet. Specific problems associated with field collection of a site are also noted on the field sheet. Conditions that may affect data results are included in the comments section of the field sheet so that they are available to each data analyst. If post calibration results are outside acceptable limits, the individual calibrating notifies the Field QA Officer who decides if data should be deleted or flagged. If split sample results suggest that there is a problem with the data, the issue is thoroughly discussed by laboratory and field representatives at the Data Integrity Workgroup and possible solutions are offered. The Field QA Officer regularly reviews Equipment Logbooks to ensure that all field staff are following QC procedures. Standard maintenance recommended by Hydrolab^{TM} is performed at six-week intervals. All serious Quality Control issues are reported directly to the Field Office Project Chief. Audits of the field staff are conducted as needed.

Laboratory: Instrument preventive maintenance, repairs, and analytical corrective actions are documented in laboratory notebooks or the Division's Analytical Corrective Action forms. Corrective actions are initiated by the laboratory analyst, with the input of the Lead Scientist of the Laboratory Section, if necessary. The Lead Scientist and the Supervisor review corrective actions. A copy of the completed form (Appendix C of the MD Department of Health SOPs) is submitted to the division QA officer, and the original is kept in the laboratory. The MDH Division of Environmental Sciences is audited approximately every three years by EPA Region 3 or CBP staff.

NASL has a policy and procedure for implementing corrective or preventive action when non- conforming work or departures from policies and procedures, or potential improvements have been identified. In these instances, a NASL Corrective/Preventive Action Form is employed. Identification of the root cause of the problem, as well as documentation of follow-up procedures is required. The Laboratory Manager will ensure the implementation and effectiveness of mandated corrective actions are verified by follow-up audits no more than 30 days after the written request for corrective action. The Laboratory Quality Assurance Officer arranges for an internal quality system review annually. The audit is carried out by NASL personnel who are independent (if possible) of the activity being audited. The review assesses the requirements of the quality assurance manual against laboratory operations, and laboratory operations against the laboratory's quality assurance manual and SOPs. The order of operations for the annual protocol review is:

1. Calculate MDLs
2. Perform Internal and Chemistry Audits (per NELAC requirements)
3. Review/revise SOPs
4. Review/revise Quality Manual

Data Management: The DNR database management group is the first line of defense for data correction. Maryland DNR data management personnel review all incoming data and compare the data to the cross-reference file. Data management personnel verify the submitted data and apply corrections to the physical datasheet if errors are identified. During the data-import process, a Data Processing Programmer makes all corrections to the data and key fields as they are imported into the WQ Database

System. The Data Processing Programmer assists where needed in constructing better tools to edit large quantities of data corrections if necessary. Documenting the correction is handled within the WQ Maintenance process. If the correction is fairly generic, edits to the changes are logged. Data or other information that has been entered incorrectly on field or lab sheets must be corrected by drawing a single line through the incorrect entry and initialing and dating the correction.

C2. Reports to Management

Reports to management are contained in the outline of deliverables in the project Scope of Work. Any changes to the QAPP or to the SOPs referenced herein will be documented and approval of the DNR Principal Investigator and Quality Assurance Officer will be obtained prior to implementation.

The key objectives of the Chesapeake Bay Mainstem and Tributary Water Quality Monitoring Program are to accurately describe the current state of the Bay Mainstem and tidal tributaries and to detect long-term trends. Trends are analyzed using techniques recommended by the CBP's Integrated Trends Analysis Team (ITAT) and are described in a separate QAPP:

> Maryland Department of Natural Resources (DNR). 2023. Maryland Department of Natural Resources Quality Assurance Project Plan for the Chesapeake Bay Tidal and Non-tidal Monitoring Programs Long-term Trends Analysis Methods, Version 1.

Beyond analysis of the Maryland monitoring data, DNR staff members participate in CBP monitoring activities to produce Bay-wide analyses and reports with cooperating state, federal and local agencies. This activity leads to a better Bay-wide understanding of water and habitat quality and addresses the linkage between water quality and living resources.

Beginning in 2011, water quality current conditions and trends analytical results became available via MD DNR's Eyes on the Bay web site that allows users to select parameters and metrics (https://eyesonthebay.dnr.maryland.gov/eyesonthebay/statustrends.cfm) . Methods for current conditions and trend calculations are also available on Eyes on the Bay (https://eyesonthebay.dnr.maryland.gov/eyesonthebay/status_trends_methods.cfm).

The monitoring data also are used extensively in mathematical modeling efforts to project the water quality response of Chesapeake Bay to various management alternatives. Bay models are regularly updated and refined.
(https://www.chesapeakebay.net/what/programs/modeling/phase-7-model-development).

END OF SECTION C

D: DATA REVIEW, VERIFICATION AND USABILITY

D1: Data Review, Verification and Validation

Is conducted at four levels by DNR data management personnel.

At the first level, DNR data management personnel will review cross reference sheets and field data sheets:
(1) comparing field sheets to cross reference sheets to ensure that all field sheets have been received.
(2) reviewing all field sheets to check that they are filled out completely and legibly, and (3) sending the sheets to a data entry service for keypunch. At the data entry service, the field sheet data values will be double entered to minimize errors at the keypunch stage. The entered field data will be sent back to DNR as electronic files for further processing.

At the second level, a Data Processing Programmer will process and integrate the field, lab and chlorophyll datasets, and generate reports and plots for data verification using the Water Quality Import v3 software. The WQ Import v3 software is a series of Microsoft Access databases with extensive VBA programming. The WQ Import v3 software is used to import data and cross reference files and to conduct data management activities, such as performing initial data checks, conducting major key field checks, performing parameter range checks (including measured and calculated parameters), conducting combination checks for specific parameters, generating error reports and verification plots, reformatting data, creating a database, and submitting data.

Third, electronic copies of data plots, verification lab/chlorophyll/field sheets, and error logs will be sent to a data analyst for verification and editing. The data analyst will ensure that measured or calculated information for all types of data is correct and that the codes associated with parameters are properly established. Possible errors will be identified and sent to the laboratory or field office for verification or verified by phone or email. Any necessary corrections will be conveyed on an edit form, which will be emailed to a programmer. The programmer will make changes to correct the electronic data set, re-run the verification programs, and update the verification reports and plots for the analyst to review that the appropriate updates were made. This procedure will be repeated until a clean data set is produced.

The fourth step will be for data management staff to ensure that the overall data verification processes are completed, all data errors are corrected, and that the finalized data sets are created and formatted to be consistent with historical data sets. The final data set combining the field, lab, and chlorophyll data is created as an “MDB file" after the completion of data verification processes. This final data set will be stored in the designated DNR data library subdirectory on a DNR cloud network drive for data user access. A formatted submission data set and associated data documentation will also be transferred to the CBP Data Center on a monthly basis. Submission of data to CBP returns a QAT file that lists fatal and non-fatal flaws (e.g., range checks, unexpected data, missing information, etc.). A copy of the QAT is sent to the data analyst, and together with a programmer, edits are made to the internal and CBP formatted databases until both are corrected, all fatal QAT flaws are addressed, and non-fatal flaws are assured to not be an issue.

D1.1 Data Verification Conducted on Water Quality Data

1. Individual Data Parameter Checks:

(a) Range check for numeric data parameters (reports error if data are outside the normal range for that parameter).

(b) Character validation checks for character data parameters (reports error if the character data are not appropriate for that parameter).

2. Parameter Combination Checks:

(a) Field Data:

- Sample layer depth check (checks to make sure layer depths are appropriate, e.g., reports error if surface layer depth is greater than 1.0 m, surface depth is greater than bottom depth, etc.).
- Upper and lower pycnocline check (reports error if pycnocline depths are outside expected range).
- Maximum and minimum wind parameter check (reports error if minimum wind exceeds maximum wind).

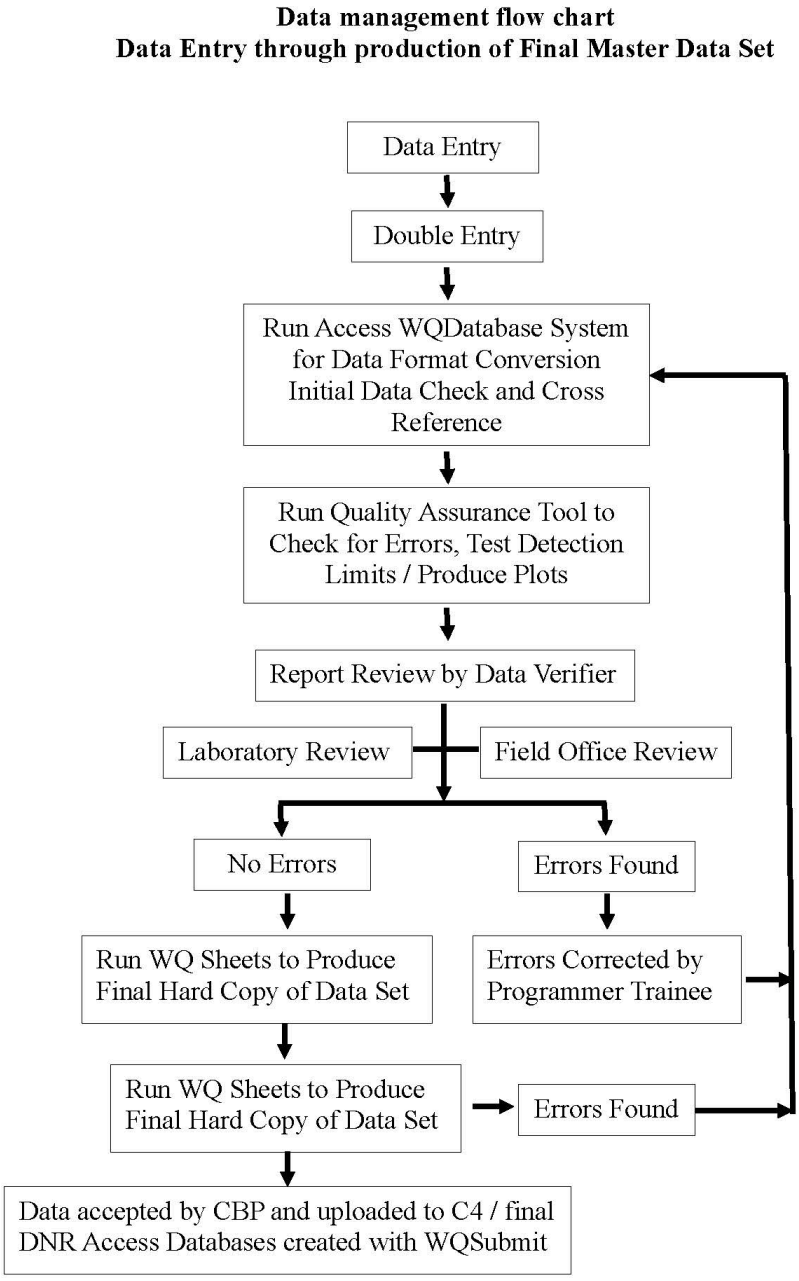
(b) Laboratory Data:

- APC code check for all laboratory related parameters (reports if APC code has been reported).
- G code (greater than or less than detection limit flag) checks for all laboratory related parameters (reports if lab has flagged values as greater or less than the detection limit).
- Parameter combination check for the following parameters:
  Reports an error when PO4 > TDP
  Reports an error when NO23 + NH4 > TDN
  Reports an error when NO2 > NO23

(c) Chlorophyll *a* data: APC code checks with light path, extraction volume, and/or optical density parameter (reports an error if values are outside expected range).

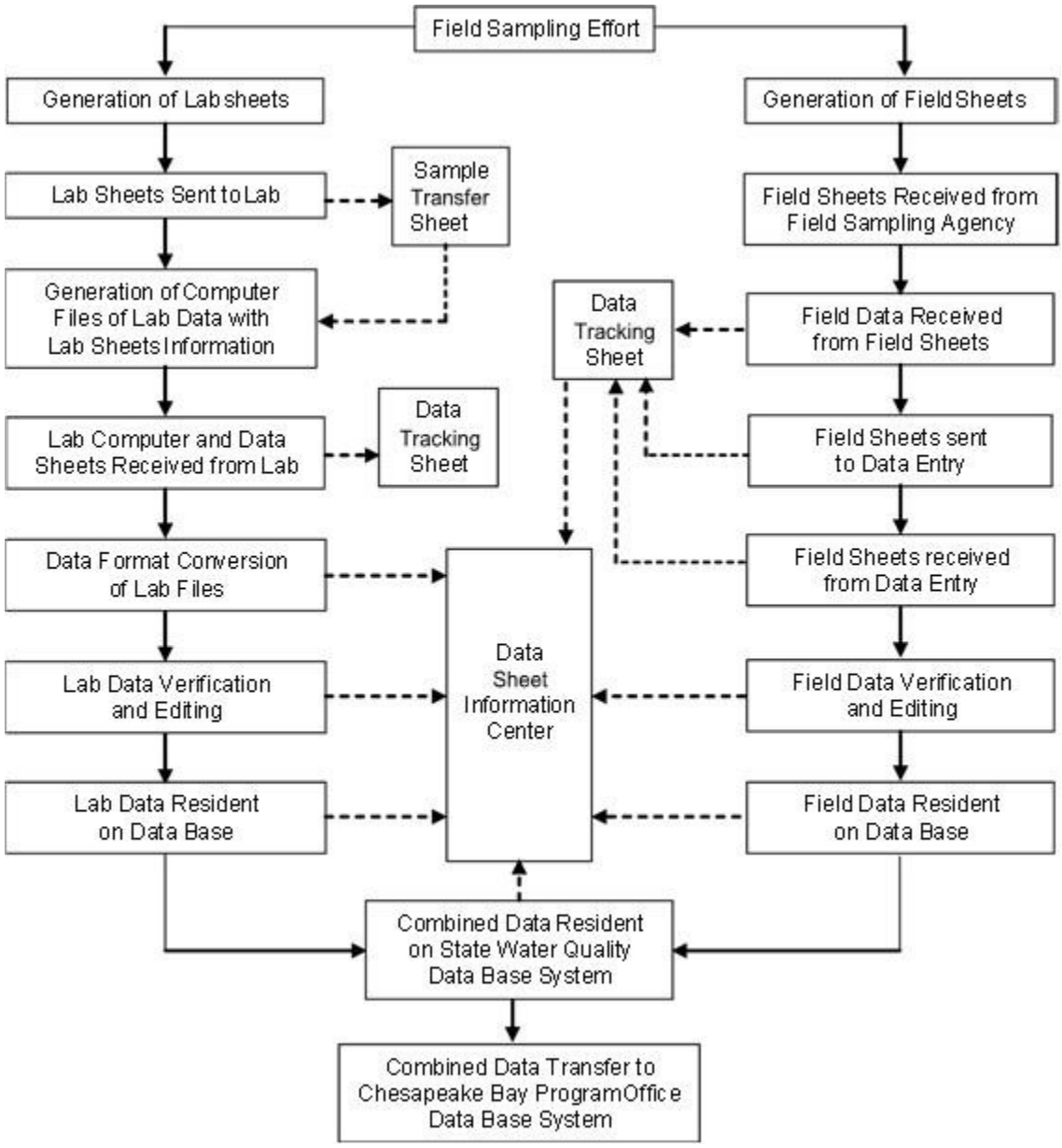
3. Verification Plots for Review: Sampling data and times with values for all chemical and physical parameters are plotted by station for review by data analysts. Analysts look for patterns and identify any outliers or unusual values to be checked for errors (Figure 4.). The Data Management flow chart tracks data entry through the production of the final master dataset (Figure 5.)

Figure 4. Data Management Flow Chart



This data tracking system has been designed and implemented to track the progress of data through the data management system. Data Status Forms will be assigned to all data files received (see Section B10 for example sheet and documentation). Data sheets and tracking sheets used in data management will be stored at the DNR Tawes Building for ten years or more. The data tracking system is diagrammed in Figure 5.

Figure 5. Data Tracking Flow Chart



Additionally, data from duplicate field samples will be reviewed by a data analyst. These procedures are described in Section B10, Data Management and C1, Assessments and Response Action.

The data management group validates key fields. The key fields ensure that the data are accurate and will not be lost or duplicated within the system. After the key fields are validated, the values are plotted to discover any anomalies. The scientists/project managers review the reports and determine if any additional edits are needed to data values. These edits are reported to the Data Processing Programmer who makes the changes.

D2. Verification Validation Methods, Reports, Plots and Edit Forms

The procedures for data collection and the forms used are described in Section B10. The generated Quality Assurance files are presented below.

D2.1 Typeset field sheet.

Maryland Department of Natural Resources

Field Sheet

Sequence Number 2201503

Station Name	Project Code
CB5.2	MAIN

Sample Date	Arrival Time	Departure Time	Sample Number	Measured Depth	Air Temperature	Tide Code	Weather Yesterday	Weather Today	Cloud Cover (%)	Wave Height
12/5/2022	12:15	12:37	5	31.7	9	F	10	10	95	0.2

Wind Direction	Wind Min. Velocity	Wind Max. Velocity	Equipment Set Unit No.	Probe Number	Photometer Unit Number	Pycnocline Lower	Pycnocline Upper	Secchi	G/L
SE	4	6	9E	9E				02.30	

Description :
CLOUDS R THIN; NO PYCNO; 1/3 2/3 SAMPLES

Parameter List:

Rep	Sample depth	Water Temp	PH	DO	SPCOND	Salinity	Calc. Salinity	Rep Code	Sample depth	Layer Code	INSDEC	INSUW	EPAR_S	EPARU_Z
1	0.5	10.7	7.9	9.9	31600	19.7	19.59	1	0.5	S				
2	0.5	10.7	7.9	9.9	31600	19.7	19.59	2	0.5	S				
1	1	10.7	7.9	9.9	31800	19.8	19.73	1	1	M				
1	2	10.7	7.9	9.8	31800	19.8	19.73	1	2	M				
1	3	10.7	7.9	9.7	31800	19.8	19.73	1	3	M				
1	5	10.7	7.9	9.5	31800	19.8	19.73	1	5	M				
1	7	10.7	7.9	9.5	31900	19.8	19.8	1	7	M				
1	9	10.7	7.9	9.5	31900	19.8	19.8	1	9	M				
1	11	10.7	7.9	9.5	31900	19.8	19.8	1	11	AP				
1	13	10.7	7.9	9.5	31900	19.8	19.8	1	13	M				
1	15	10.7	7.9	9.5	31900	19.9	19.8	1	15	M				
1	17	10.8	7.9	9.4	32100	20	19.94	1	17	M				
1	19	11.1	7.8	9.1	32600	20.3	20.29	1	19	M				
1	21	11.3	7.8	8.8	33100	20.6	20.64	1	21	BP				
1	23	11.4	7.8	8.7	33300	20.8	20.78	1	23	M				
1	25	11.5	7.8	8.6	33600	21.1	20.99	1	25	M				
1	27	11.6	7.8	8.5	33900	21.2	21.2	1	27	M				
1	29	11.6	7.8	8.5	33900	21.3	21.2	1	29	M				

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D2.2 Typeset chlorophyll *a* sheet.

Maryland Department of Natural Resources

Chlorophyll Sheet — **Chl Sequence No** 3-S07

Project Code MAIN **SampleDate:** 7/14/2022

Parameters:

Station Name	SEQ	Rep#	Layer Code	Sample Depth	EXVOL_ML	APC CODE	LIPAT_CM	SAMVOL_L	OD630B	OD645B	OD647B	OD663B	OD664B	OD665A	OD750A	OD750B	PHEO	CHLA
CB1.1	3-S07	1	S	0.5	10		5	0.25	0.023	0.031	0.035	0.113	0.114	0.075	0.005	0.005	002.136	008.330
CB1.1	3-S07	1	B	5	10		5	0.25	0.013	0.018	0.021	0.068	0.068	0.051	0.005	0.005	003.247	003.631
CB2.1	3-S07	1	S	0.5	10		5	0.25	0.021	0.027	0.031	0.105	0.106	0.078	0.007	0.007	004.635	005.981
CB2.1	3-S07	1	B	6	10		5	0.25	0.023	0.028	0.033	0.108	0.110	0.080	0.006	0.006	004.656	006.408
CB2.2	3-S07	2	S	0.5	10		5	0.25	0.020	0.027	0.031	0.104	0.105	0.076	0.005	0.005	004.422	006.194
CB2.2	3-S07	1	S	0.5	10		5	0.25	0.020	0.026	0.030	0.103	0.104	0.075	0.005	0.005	004.272	006.194
CB2.2	3-S07	1	AP	3	10		5	0.25	0.018	0.024	0.028	0.094	0.095	0.071	0.005	0.006	004.956	004.913

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D2.3 Typeset nutrient parameters sheet.

Maryland Department of Natural Resources

Lab Sheet

Station Name	Project	Sample Date	Arrival Time	Sample Depth	Layer Code	Replicate Number	Sample Number	Sequence Number
CB5.3	MAIN	7/12/2022	10:07	25	B	1	4	202207120001

Sample Description :
HAZY, OXFORD SAMPLE

LAB Description :

Parameters	Type	Method Code	APC Code	DL	Value	Visible	Enabled	Pseudo	Calculated
NH4	F	L01			0.133	☑	☑	☐	☐
NO2	F	L01			0.0101	☑	☑	☐	☐
NO23	F	L01			0.02	☑	☑	☐	☐
PC	N	L01			0.373	☑	☑	☐	☐
PN	N	L01			0.0715	☑	☑	☐	☐
PO4	F	L01			0.0193	☑	☑	☐	☐
PP	N	L01			0.0082	☑	☑	☐	☐
TDN	N	L01			0.44	☑	☑	☐	☐
TDP	N	L01			0.0253	☑	☑	☐	☐
TSS	N	L01			3.8	☑	☑	☐	☐

D2.4 Lab Quality Assurance Check

N CHECK DNR MAINSTEM DEC 2022

QUALITY CONTROL CHECK NITROGEN

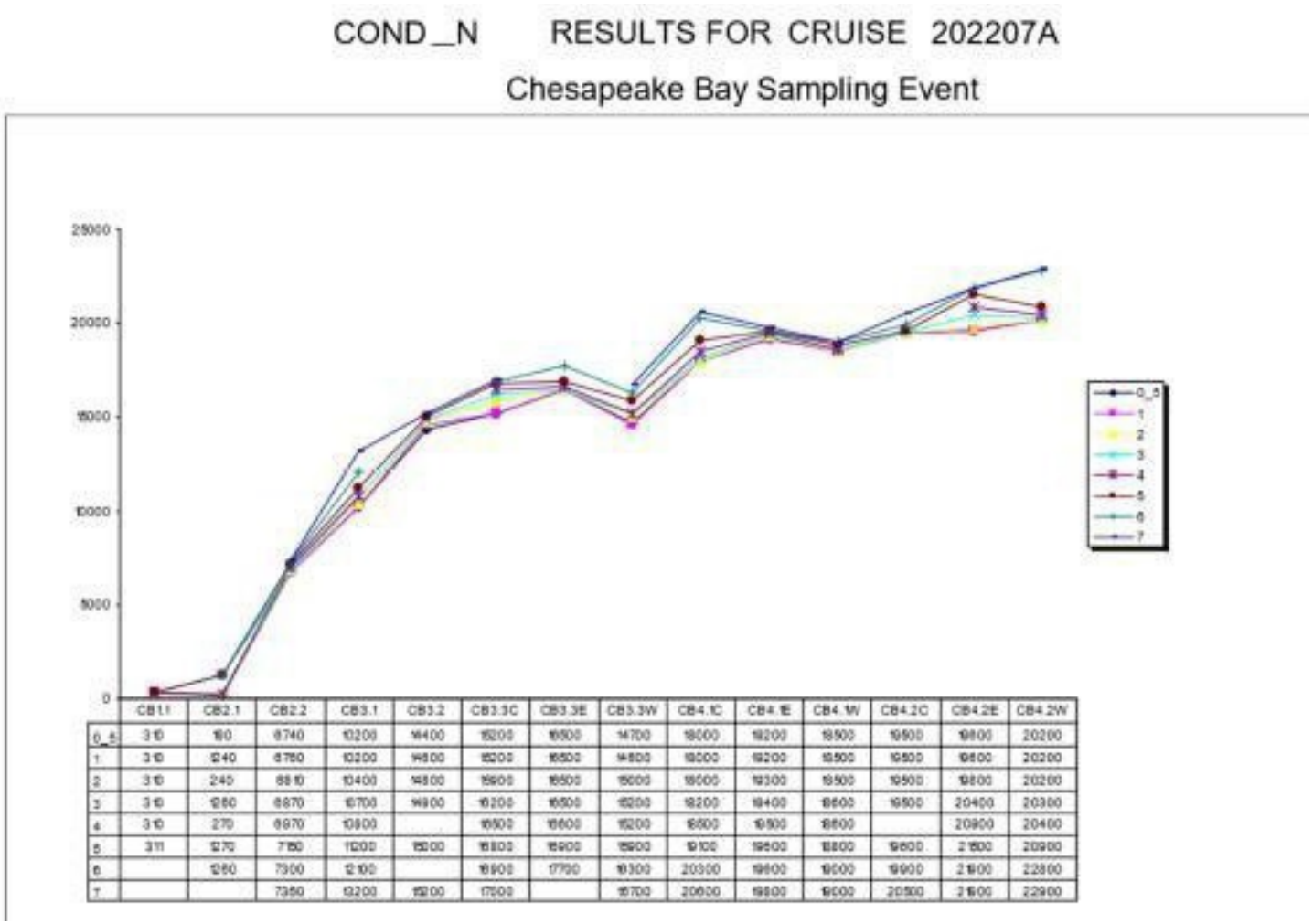
3 Sig Figs

No qualifiers
1 corrections
3/2/23
KB

✓ JM 3/8/23

SAMPLE #	NO23	NO2	DIFF	NH4	TDN	NH4+NO3	DIFF
1	0.0035	0.0009	0.0026	0.021	0.27	0.0245	0.2455
2	0.0034	0.0006	0.0028	0.019	0.26	0.0224	0.2376
3	0.0008	0.0005	0.0003	0.010	0.25	0.0108	0.2392
4	0.0011	0.0007	0.0004	0.009	0.26	0.0101	0.2499
5	0.0076	0.0012	0.0064	0.022	0.26	0.0296	0.2304
6	0.0072	0.0015	0.0057	0.022	0.27	0.0292	0.2408
7	0.0050	0.0012	0.0038	0.015	0.26	0.0200	0.2400
8	0.0010	0.0008	0.0002	0.009	0.26	0.0100	0.2500
9	0.0095	0.0020	0.0075	0.041	0.30	0.0505	0.2495
10	0.0063	0.0015	0.0048	0.028	0.27	0.0343	0.2357
11	0.0078	0.0017	0.0061	0.022	0.29	0.0298	0.2602
12	0.0085	0.0015	0.0070	0.021	0.29	0.0295	0.2605
13	0.0094	0.0017	0.0077	0.020	0.29	0.0294	0.2606
14	0.0152	0.0033	0.0119	0.100	0.41	0.1152	0.2948
15	0.0097	0.0023	0.0074	0.058	0.29	0.0677	0.2223
16	0.0155	0.0022	0.0133	0.038	0.33	0.0535	0.2765
17	0.0202	0.0029	0.0173	0.034	0.31	0.0542	0.2558
18	0.0154	0.0045	0.0109	0.119	0.37	0.1344	0.2356
19	0.0123	0.0032	0.0091	0.076	0.32	0.0883	0.2317
20	0.0191	0.0026	0.0165	0.042	0.32	0.0611	0.2589
21	0.0238	0.0026	0.0212	0.027	0.32	0.0508	0.2692
22	0.0289	0.0055	0.0234	0.110	0.40	0.1389	0.2611
23	0.0238	0.0036	0.0202	0.075	0.39	0.0988	0.2912
24	0.0264	0.0028	0.0236	0.023	0.30	0.0494	0.2506
25	0.0333	0.0030	0.0303	0.017	0.30	0.0503	0.2497
26	0.0258	0.0047	0.0211	0.091	0.41	0.1168	0.2932
27	0.0241	0.0038	0.0203	0.071	0.37	0.0951	0.2749
28	0.0482	0.0033	0.0449	0.031	0.37	0.0792	0.2908
29	0.0625	0.0035	0.0590	0.021	0.35	0.0835	0.2665
30	0.0301	0.0057	0.0244	0.121	0.45	0.1511	0.2989
31	0.0372	0.0054	0.0318	0.089	0.43	0.1262	0.3039
32	0.0510	0.0057	0.0453	0.074	0.39	0.1250	0.2650
33	0.1059	0.0057	0.1002	0.031	0.38	0.1369	0.2431
34	0.0519	0.0081	0.0438	0.098	0.43	0.1499	0.2801
35	0.0534	0.0081	0.0453	0.099	0.44	0.1524	0.2876
36	0.0813	0.0066	0.0747	0.069	0.41	0.1503	0.2597
37	0.2255	0.0054	0.2201	0.011	0.49	0.2365	0.2535
38	0.2199	0.0055	0.2144	0.015	0.51	0.2349	0.2751
39	0.1511	0.0090	0.1421	0.070	0.49	0.2211	0.2689
40	0.1600	0.0079	0.1521	0.066	0.50	0.2260	0.2740
41	0.2409	0.0061	0.2348	0.028	0.52	0.2689	0.2511
42	0.2666	0.0056	0.2610	0.024	0.53	0.2906	0.2394
43	0.1860	0.0072	0.1788	0.064	0.55	0.2500	0.3000

D2.5 Field Chart example

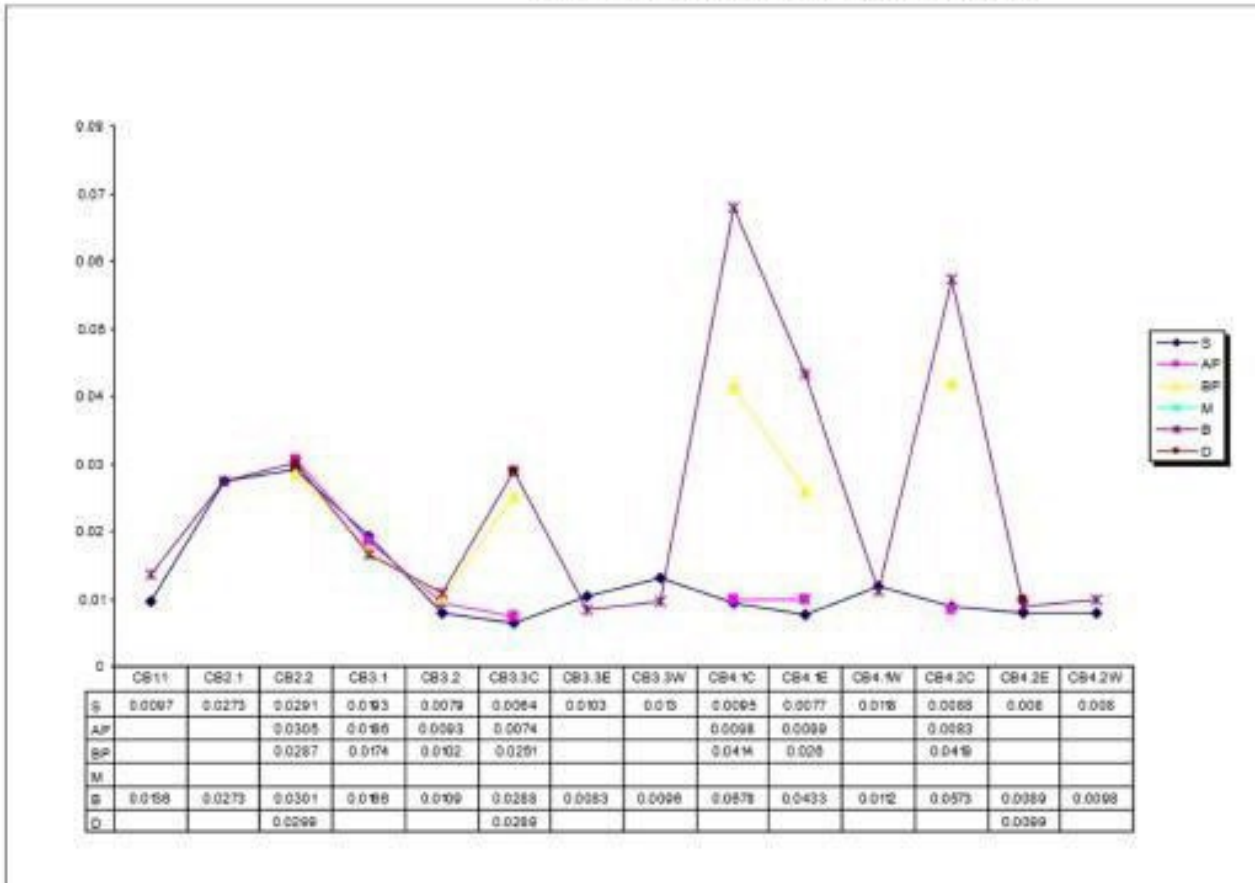


	CB1.1	CB2.1	CB2.2	CB3.1	CB3.2	CB3.3C	CB3.3E	CB3.3W	CB4.1C	CB4.1E	CB4.1W	CB4.2C	CB4.2E	CB4.2W
0_5	310	180	6740	10200	14400	15200	16500	14700	18000	18200	18500	19500	19800	20200
1	310	1240	6750	10200	14800	15200	16500	14800	18000	18200	18500	19500	19800	20200
2	310	240	6810	10400	14800	15900	16500	15000	18000	18300	18500	19500	19800	20200
3	310	1260	6870	10700	14900	16200	16500	15200	18200	18400	18600	19500	20400	20300
4	310	270	6970	10900		16500	16600	15200	18500	18500	18600		20900	20400
5	311	1270	7150	11200	15200	16800	16900	15900	19100	19500	18800	19600	21500	20900
6		1260	7300	12100		16900	17700	16300	20300	19600	19000	19900	21900	22800
7			7350	13200	15200	17500		16700	20600	19800	19000	20500	21600	22900

D2.5 Lab Results Chart example

TDP_N RESULTS FOR CRUISE 202207A

Chesapeake Bay Sampling Event



	CB1.1	CB2.1	CB2.2	CB3.1	CB3.2	CB3.3C	CB3.3E	CB3.3W	CB4.1C	CB4.1E	CB4.1W	CB4.2C	CB4.2E	CB4.2W
S	0.0097	0.0273	0.0291	0.0193	0.0079	0.0064	0.0103	0.015	0.0095	0.0077	0.016	0.0068	0.008	0.008
AP			0.0305	0.0186	0.0093	0.0074			0.0098	0.0099		0.0083		
BP			0.0287	0.0174	0.0102	0.0251			0.0414	0.026		0.0419		
M														
B	0.0158	0.0273	0.0301	0.0186	0.0109	0.0268	0.0083	0.0098	0.0678	0.0433	0.012	0.0573	0.0089	0.0098
D			0.0299			0.0269							0.0099	

D2.6 Data Verification example

Parameter Values falling outside of a reasonable range.

Column Check: Parameter Values are falling outside of a reasonable range

Field Seq No	StationName	Project Code	SampleDate	Depth	Layer	Rep. No	Parameter	Value	Lower DL	Upper DL
2201001	CB5.3	MAIN	8/8/2022	21	M	1	SALINITY	25.01	0	25
2201001	CB5.3	MAIN	8/8/2022	23	M	1	SALIN_FLD	25.2	0	25
2201001	CB5.3	MAIN	8/8/2022	23	M	1	SALINITY	25.23	0	25
2201001	CB5.3	MAIN	8/8/2022	25	B	1	SALIN_FLD	25.2	0	25
2201001	CB5.3	MAIN	8/8/2022	25	B	1	SALINITY	25.23	0	25
2201002	LE2.3	MAIN	8/8/2022	0.5	S	1	LOW_PYCNO	8.5	10	19
2201002	LE2.3	MAIN	8/8/2022	0.5	S	1	UPP_PYCNOC	6.5	8	17
2201003	CB5.2	MAIN	8/8/2022	0.5	S	1	LOW_PYCNO	22.5	10	19
2201005	CB4.4	MAIN	8/8/2022	0.5	S	1	AIR_TEMP	37	15	36
2201006	CB4.3E	MAIN	8/9/2022	0.5	S	1	LOW_PYCNO	20.5	10	19
2201006	CB4.3E	MAIN	8/9/2022	0.5	S	1	UPP_PYCNOC	19.5	8	17
2201019	CB3.1	MAIN	8/10/2022	0.5	S	1	LOW_PYCNO	6.5	10	19
2201019	CB3.1	MAIN	8/10/2022	0.5	S	1	UPP_PYCNOC	5.5	8	17
2201101	CB5.3	MAIN	8/22/2022	12	M	1	SALIN_FLD	25.3	0	25
2201101	CB5.3	MAIN	8/22/2022	12	M	1	SALINITY	25.23	0	25

D2.7 Data points flagged with Analytical Problem Codes

Column Check: ParameterAPCodes might not appropriate and need to verify

Lab Seq No	StationName	Project Code	SampleDate	Depth	Layer	Rep. #	Parameter	Type	Value	Problem
202208080003	CB5.3	MAIN	8/8/2022	8	AP	1	NO2	F	0.0232	QQ
202208080003	CB5.3	MAIN	8/8/2022	8	AP	1	NO23	F	0.0219	QQ
202208080004	CB5.3	MAIN	8/8/2022	0.5	S	1	NO2	F	0.0092	V
202208080004	CB5.3	MAIN	8/8/2022	0.5	S	1	NO23	F	0.0056	V
202208080010	CB5.2	MAIN	8/8/2022	24	BP	1	PC	N	0.319	FF
202208080010	CB5.2	MAIN	8/8/2022	24	BP	1	TSS	N	7.4	FF
202208080018	CB4.4	MAIN	8/8/2022	31	B	1	PC	N	0.312	FF
202208080020	CB4.4	MAIN	8/8/2022	8	AP	1	NO2	F	0.0017	QQ
202208080020	CB4.4	MAIN	8/8/2022	8	AP	1	NO23	F	0.0015	QQ
202208090027	CB4.3C	MAIN	8/9/2022	20	BP	1	NO2	F	0.001	QQ
202208090027	CB4.3C	MAIN	8/9/2022	20	BP	1	NO23	F	0.0015	QQ
202208090030	CB4.3W	MAIN	8/9/2022	9	B	1	PP	N	0.0247	V
202208090031	CB4.3W	MAIN	8/9/2022	0.5	S	1	NO2	F	0.0015	QQ
202208090031	CB4.3W	MAIN	8/9/2022	0.5	S	1	NO23	F	0.0015	QQ
202208090035	CB4.2C	MAIN	8/9/2022	19	BP	1	NO2	F	0.0016	QQ
202208090035	CB4.2C	MAIN	8/9/2022	19	BP	1	NO23	F	0.0015	QQ
202208090039	CB4.2E	MAIN	8/9/2022	9	B	2	NO2	F	0.004	QQ
202208090039	CB4.2E	MAIN	8/9/2022	9	B	2	NO23	F	0.0037	QQ
202208090040	CB4.2E	MAIN	8/9/2022	0.5	S	1	TSS	N		V
202208090044	CB4.1E	MAIN	8/9/2022	0.5	S	1	TSS	N		A
202208090046	CB4.1C	MAIN	8/9/2022	19	BP	1	PO4	F	0.0984	QQ
202208090046	CB4.1C	MAIN	8/9/2022	19	BP	1	TDP	N	0.0965	QQ
202208090050	CB4.1W	MAIN	8/9/2022	0.5	S	1	TSS	N	10.7	FF
202208100066	CB3.1	MAIN	8/10/2022	4	AP	1	TSS	N		A
202208100069	CB2.2	MAIN	8/10/2022	7	BP	1	PC	N	1.09	JJ
202208100069	CB2.2	MAIN	8/10/2022	7	BP	1	PN	N	0.201	JJ

D3 - Reconciliation with User Requirements

Numerous quality assurance checks of dataset compilation and the statistical analyses are performed to meet the goals of the Water Quality Monitoring Program:

1. Data is evaluated to ensure that the required number of months and years for each station are present in the analyzed dataset to meet the Acceptance Criteria.

2. Data passes through a series of checks to remove data that has specific Analytical Problem Codes (APC) which disqualify the data for analysis.

3. Data are graphically reviewed to ensure that all data for all years and all analyzed parameters is in the analysis dataset. If any data is not present, the analyst returns to the previous steps to determine what errors in the input database or the SAS program have prevented the data from being extracted or included, or to verify that the data does not exist.

4. All detection limits are verified in the intermediate datasets. This ensures that any measured value at or below the MDL at the time of sample collection for a given parameter is coded as below detection limit (Table 5). This also ensures that no data values that are greater than the MDL at the time of sample collection are incorrectly coded as less than the detection limit.

Further quality and completeness checks are performed once the trends results have been calculated:

1. Output files are reviewed to ensure the correct data has been analyzed and that the results are complete.

2. Results from the previous year's trends analysis are compared to the results of the current analysis to determine if any major changes occurred. If major changes occur, the analyst returns to the analysis datasets, program and output files to ensure that the results are correct.

3. Final verification of results is completed once the output files are submitted to the CBP analysts. Any irregularities or questions regarding the output files are communicated to the lead analyst/Program Chief and resolved as soon as the issue can be identified, and the remedy made.

The department's analysts prepare the output files but not any of the additional reporting the CBP makes to decision makers, such as Baywide maps of the results (combined with similar results from Virginia), or summary reporting. The department also submits an informal summary of the trends analysis project entitled 'Trends through year data methods and notes.docx' where year is the 4-digit end year of the trends analysis period as a documentation of the project activities.

The department's analysts participate in the Integrated Trends Analysis Team monthly meetings and offer expert advice on the limitations or considerations of the trends analysis itself and Maryland long- term data in general. The department's analysts are also available for any additional questions from the CBP analysts.

END OF SECTION D

APPENDIX 1 CBL NASL

University of Maryland, Chesapeake Bay Laboratory - *Nutrient Analytical Services Laboratory*

Laboratory Methods

Visit the website and click on any of the parameters to download the SOP.

Water Column Chemistry

- Ammonium Method
- Cadmium Nitrate Method
- Enzyme-Catalyzed Nitrate Method
- Nitrite Method
- Orthophosphate Method
- Silicate Method
- Total Dissolved Nitrogen and Total Nitrogen Enzyme-Catalyzed Method Total
- Dissolved Nitrogen and Total Nitrogen Cadmium Nitrate Method
- Total Dissolved Phosphorous and Total Phosphorous Discrete Photometric Analyzer Method
- Total Dissolved Phosphorous and Total Phosphorous Auto Analyzer II Method
- Total and Dissolved Organic Carbon Method

Particulates and Sediments

- Particulate Carbon and Nitrogen Method
- Particulate Phosphorous and Particulate Inorganic Phosphorous Method Particulate
- Biogenic Silica Method
- Total Suspended Solids and Total Volatile Solids Methods
- Chlorophyll Fluorometric Method
- Chlorophyll Spectrophotometric Method

Other Chemistries

- Hardness Method
- Inorganic Carbon and Alkalinity Method
- Biochemical Oxygen Demand (BOD) Method
- Dissolved Metals
- Ion Chromatography Anions Method
- Specific Conductance Method

Table 7. Nutrient Analytical Services Laboratory Methods

Water Column Chemistry	Method	Revised
Ammonium Method	*Standard Operating Procedure for Determination of Dissolved Inorganic Ammonium (NH4) in Fresh/Estuarine/Coastal Waters (References Standard Methods 4500-NH3 G-1997)*	1-May-2023
Cadmium Nitrate Method	*Standard Operating Procedure for Determination of Dissolved Inorganic Nitrate plus Nitrite (NO3+NO2) in Fresh/Estuarine/Coastal Waters Using Cadmium Reduction (References EPA 353.2)*	1-May-2023
Enzyme Catalyzed Nitrate Method	*Standard Operating Procedure for Determination of Dissolved Inorganic Nitrate plus Nitrite (NO3+NO2) in Fresh/Estuarine/Coastal Waters Using Enzyme Catalyzed Reduction (References EPA 353.2, Standard Methods #4500-N C, 4500-NO3 F)*	1-May-2023
Nitrite Method	*Standard Operating Procedure for Determination of Dissolved Inorganic Nitrite (NO2) in Fresh/Estuarine/Coastal Waters (References EPA 353.2)*	1-May-2023
Orthophosphate Method	*Standard Operating Procedure for Determination of Dissolved Inorganic Orthophosphate (PO4) in Fresh/Estuarine/Coastal Waters (References EPA 365.1)*	1-May-2023
Silicate Method	*Determination of Silicate from Fresh, Estuarine, and Coastal Waters Using the Molybdosilicate Method (Reference Method: Standard Methods #4500-SiO2 E-2011 or F-2011)*	1-May-2023
Total Dissolved Nitrogen Enzyme Catalyzed Nitrate Method	*Standard Operating Procedure for Determination of Total Dissolved Nitrogen (TDN) and Total Nitrogen (TN) in Fresh/Estuarine/Coastal Waters Using Alkaline Persulfate Digestion of Nitrogen to Nitrate and Measured Using Enzyme Catalyzed Reduction (References EPA 353.2, Standard Methods #4500-N C, 4500-NO3 F)*	1-May-2023
Total Dissolved Nitrogen Cadmium Nitrate Method	*Standard Operating Procedure for Determination of Total Dissolved Nitrogen (TDN) and Total Nitrogen (TN) in Fresh/Estuarine/Coastal Waters Using Alkaline Persulfate Digestion of Nitrogen to Nitrate and Measured Using Cadmium Reduction (References EPA 353.2, Standard Methods #4500-N C, 4500-NO3 F)*	1-May-2023
Total Dissolved Phosphorus Discrete Photometric Analyzer Method	*Standard Operating Procedure for Determination of Total Dissolved Phosphorus (TDP) and Total Phosphorus (TP) in Fresh/Estuarine/Coastal Waters Using Alkaline Persulfate Digestion of Phosphorus to Orthophosphate (PO4) with Colorimetric Analysis by Random Access Discrete Photometric Analyzer (References Standard Methods #4500-P.B.5, #4500 P.E, and EPA Method 365.1)*	1-May-2023

Water Column Chemistry	**Method**	**Revised**
Total Dissolved Phosphorus Auto Analyzer II System Method	*Standard Operating Procedure for Determination of Total Dissolved Phosphorus (TDP) and Total Phosphorus (TP) in Fresh/Estuarine/Coastal Waters Using Alkaline Persulfate Digestion of Phosphorus to Orthophosphate (PO4) (References Standard Methods #4500-P.B.5, #4500 P.E, and EPA Method 365.1)*	1-May-2023
Total and Dissolved Organic and Inorganic Carbon Method	*Standard Operating Procedure for Determination of Dissolved Organic Carbon/Non-Purgeable Organic Carbon (DOC/NPOC), and Total Organic Carbon (TOC) in Fresh/Estuarine/Coastal Waters using High Temperature Combustion and Infrared Detection. (References: SM5310B-2014)*	1-May-2023
Inorganic Carbon and Alkalinity Method	*Standard Operating Procedure for Determination of Aqueous Inorganic Carbon and calculated Carbonate Alkalinity in waters of Fresh/Estuarine/Coastal Waters. (References: ASTM D7573-09)*	1-May-2023
Particulates & Sediments		
Chlorophyll Spectrophotometric Method	*Standard Operating Procedure for Spectrophotometric Determination of Chlorophyll α in waters and sediments of Fresh/Estuarine/Coastal Areas. (References: SM10200H, EPA 446.0)*	1-May-2023
Particulate Carbon and Nitrogen Method	*Standard Operating Procedure for Determination of Carbon and Nitrogen in Particulates and Sediments of Fresh/Estuarine/Coastal Waters, Plant and Animal Tissue, and Soils Using Elemental Analysis. (Reference Method: EPA 440.0)*	1-May-2023
Particulate Phosphorus Method	*Determination of Total Particulate Phosphorus (TPP) and Particulate Inorganic Phosphorus (PIP) in Fresh/Estuarine/Coastal Waters (Reference Method: EPA 365.1, Rev. 2.0)*	1-May-2023
Total Suspended Solids and Total Volatile Solids Methods	*Determination of Total Suspended Solids (TSS) and Total Volatile Solids (TVS) in Waters of Fresh/Estuarine/Coastal Waters. (Reference Method: EPA Method 160.2 and Standard Methods 208 E.)*	1-May-2023

APPENDIX 2 MDH

Maryland Department of Health Inorganics Analytical Laboratory
Standard Operating Procedures and Methods

1. **Alkalinity**
2. **Biological Oxygen Demand (BOD)**
3. **Total Suspended Sediments**

MDH- Laboratories Administration
DIVISION OF ENVIRONMENTAL SCIENCES

SOP Title:	***Determination of Alkalinity by Titrimetry (Standard Method 2320 B)***
SOP No.:	CHEM-SOP-SM 2320 B
Revision:	4.4 Replaces: 4.3 Effective: 5/1/2022
Laboratory:	Inorganics Analytical Laboratory
POC:	Jacob Kilczewski jacob.kilczewski@maryland.gov

Laboratory Supervisor: Lara Phillips 4/25/2022

Signature Date

QA Officer: Molly Molloy 4/25/2022

Signature Date

Manager: Cynthia Stevenson 4/25/2022

Signature Date

Division Chief: 04/25/2022

Signature Date

Standard Method 2320 B
Sop No.: CHEM-SOP-SM 2320 B

REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	6/3/08	N/A	Taiyin Wei	6/2/08
1.0	12/09/09	Screen snapshots added to procedure, new Sample Run Log, tracking IDs for standards and reagents	Taiyin Wei	1/10
2.0	1/11	New SOP tracking number	Asoka Katumuluwa	1/11
3.0	4/12/12	Editorial and technical changes- Checklist update	S. Ameli J. Freeman-Scott	9/17/12
3.0	4/16/13	Reviewed The SOP	S. Ameli J. Freeman-Scott	6/16/13
4.0	10/31/14	Changed the format	A. Hamilton S. Ameli L. Phillips	12/01/14
4.1	6/1/15	Reviewed document, updated section 9.4	L. Phillips S. Ameli	7/1/15
4.1	5/2/16	Reviewed Document	L. Phillips S. Ameli	7/1/16
4.2	6/2/17	Reviewed Document and made organizational name changes	L. Phillips S. Ameli	7/1/17
4.3	6/4/18	Reviewed Document and updated section 13.5	L. Phillips S. Ameli	7/1/18
4.3	3/1/19	Reviewed Document	L. Phillips S. Ameli	3/4/19
4.4	4/22/20	Reviewed Document, updated run log	L. Phillips S. Ameli	5/1/20
4.4	4/9/21	Reviewed Document	L. Phillips C. Stevenson	5/1/21
4.4	4/22/21	Reviewed Document	J. Kilczewski L. Phillips	5/1/22

TABLE OF CONTENTS

Standard Operating Procedure
Determination of Alkalinity By Titrimetry
Standard Method 2320 B

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to drinking, surface, saline, domestic and industrial waters.

1.2 This method is suitable for all concentrations of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 mL. The sample must not be filtered, diluted, concentrated, or altered in any way.

1.3 Alkalinity is the acid-neutralizing or buffering capacity of a water body. The alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content; it is taken as an indication of the concentration of these constituents.

1.4 Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of water for irrigation.

2.0 SUMMARY OF METHOD

2.1 An unaltered sample is titrated to an electrometrically determined end-point of pH 4.5 using an automated system. The sample must not be filtered, diluted, concentrated, or altered in any way.

2.2 Alkalinity as $CaCO_3$ is determined from the volume required of a 0.02 N sulfuric acid (H_2SO_4) to titrate 50 mL of the sample. For samples with high alkalinities that require more than 50 mL of titrant, smaller sample volumes are used.

2.3 For samples of alkalinities less than 20 mg/L, the amount of the acid required to reduce the pH exactly 0.30 pH units below pH 4.5 is measured and an extrapolation technique is used to determine the equivalence point.

3.0 INTERFERENCES

Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Clean the electrode occasionally. Do not filter, dilute, concentrate, or alter sample.

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during reagent preparation and instrument operation.

4.2 The use of a fume hood, protective eyewear and clothing and proper gloves are recommended when handling acids.

4.3 Each employee is issued a *Laboratory Safety Manual* and a *Quality Assurance plan* and is responsible for adhering to the recommendations contained therein.

4.4 Each chemical should be regarded as a potential health hazard. A reference file of material safety data sheet (MSDS) is available in the lab.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Mantech PC Titration system, consisting of

5.1.1.1 PC-Titrator with Auto-Sampler

5.1.1.2 System Controller with monitor

5.1.1.3 Printer

5.1.1.4 Electrode - Sure-Flow Combination pH electrode, glass body, with BNC connector, Man-Tech # PCE-80-PH1200 or equivalent.

5.1.2 Analytical balance - Mettler Toledo AG204 or equivalent

5.2 Supplies

5.2.1 Glass beakers - 100 mL

5.2.2 Graduated cylinder - class A, 50 mL

5.2.3 Volumetric flasks - class A, 50 mL, 100 mL, 500 mL, and 1000 mL

5.2.4 Pipetters - 100 - 1000 µL, 500 - 5000 µL, and 1 - 10 mL

5.2.5 Carboy - 5 L, with spigot, Nalgene

5.2.6 Transfer pipettes - Samco, cat. # 231

5.2.7 pH Electrode filling solution - follow manufacturer's recommendations

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Deionized water

6.1.2 H_2SO_4, 0.02N - Fisher, cat. # SA 226-4

6.2 Standards

6.2.1 pH 4.0 buffer solution - Fisher, cat. # SB 101-500

6.2.2 pH 7.0 buffer solution - Fisher, cat. # SB 107-500

6.2.3 pH 10.0 buffer solution - Fisher, cat. # SB 115-500

6.2.4 Stock standard, 25,000 mg/L $CaCO_3$ (0.5N) - 10 mL/ 16 voluette ampoules, Hach, product # 14278-10

6.2.5 Intermediate standard, 5000 mg/L $CaCO_3$ - Pipet 5 mL of the stock standard (6.2.4) into a 25 mL volumetric flask. Bring to volume with deionized water. Prepare every two weeks.

6.2.6 Check standard, 50 mg/L $CaCO_3$ - Pipet 5 mL of intermediate standard (6.2.5) into a 500 mL volumetric flask. Bring to volume with deionized water. Prepare every two weeks.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in 1 liter polyethylene cubitainers and iced or refrigerated to 4 ºC. The holding time is 14 days.

7.2 The sample must not be filtered, diluted, concentrated or altered in any way.

8.0 QUALITY CONTROL

8.1 The acceptable range for the slope of the calibration curve is -65 mV to -53 mV. Calibration must be repeated if the slope falls outside this range.

8.2 A blank and a blank spike are analyzed at the beginning of the run. Blank concentration must be less than the reporting level of 1 ppm and the acceptable

value for the spike recovery is 90 - 110%. Blank, blank spike or sample spike not meeting the criteria is reanalyzed.

8.3 Every tenth sample is duplicated and spiked. The acceptable values for the relative percent difference (RPD) are ± 10 and for the spike recovery (SR) are 90 - 110%. If these do not fall within the accepted ranges, the corresponding analyses are repeated.

8.4 A check standard is run after every ten samples.

8.5 A QC sample is analyzed at the beginning and the end of each analytical run.

8.6 Data acceptance criteria are listed on the data review checklist. (Appendix A).

8.7 Laboratory participates in yearly ERA WatR Supply (WS) and WatR Pollution (WP) Proficiency Tests.

8.8 An initial demonstration of capability study is performed by each analyst performing the test.

9.0 PROCEDURE

9.1 Sample preparation

9.1.1 Prepare a list of samples to be analyzed on a Sample Run Log (Appendix B).

9.1.2 Pour approximately 60 mL of the pH 4, pH 7 and pH 10 buffers into each of the labeled 100 mL beakers.

9.1.3 Pour 50 mL portions of each well mixed sample, measured using a class "A" graduated cylinder, into labeled 100 mL beakers. Pour a duplicate of every tenth sample.

9.1.4 Spike blank and every tenth sample, or one sample per batch if analyzing less than 10 samples, by adding 1 mL of Intermediate standard solution (6.2.5) to 49 mL of deionized water and samples respectively.

9.2 Daily electrode preparation

9.2.1 Rinse the electrode with deionized water to remove crystal residue that may have formed on the surface during storage.

9.2.2 Check the electrolyte level in the reference cavity, which should be approximately ¼ inch below the fill-hole. If the electrolyte level is too

low, add filling solution (5.2.7) with a transfer pipet. Replace the cap, and rinse clean the electrode.

9.2.3 Remove fill-hole cover during calibration and measurement to ensure uniform flow of filling solution.

9.3 Weekly electrode maintenance

9.3.1 Disconnect the electrode from the unit. Empty the electrode with a transfer pipet. Rinse with deionized water and then fill up with filling solution. Connect the electrode.

9.3.2 Soak electrode in pH 4 buffer for a minimum of one hour.

9.3.2.1 Follow the steps in 9.4.1 to 9.4.3

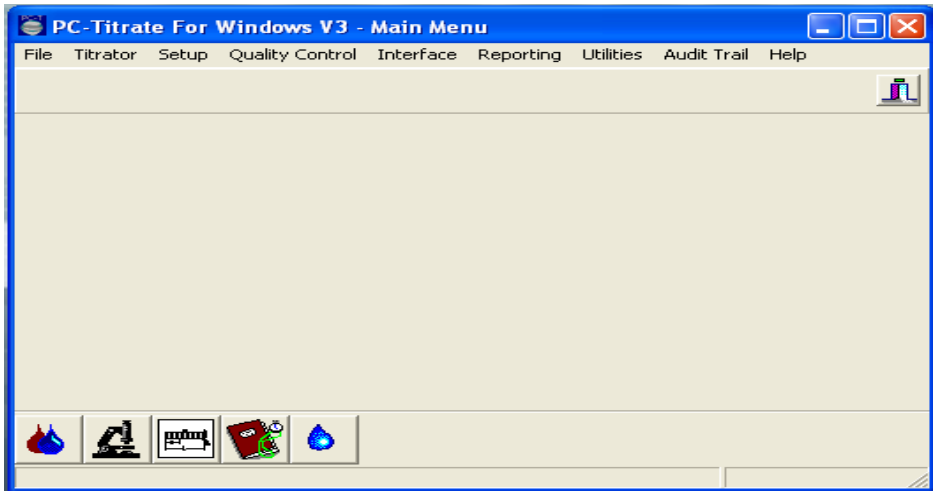
9.3.2.2 Place a beaker with pH 4 buffer in the # 1 position.

9.3.2.3 Select "Tubes" from "Zones", select "l" as the beaker number for "Tubes & the like". Click on "Go to this location XYZ" to send the probe to "l" position.

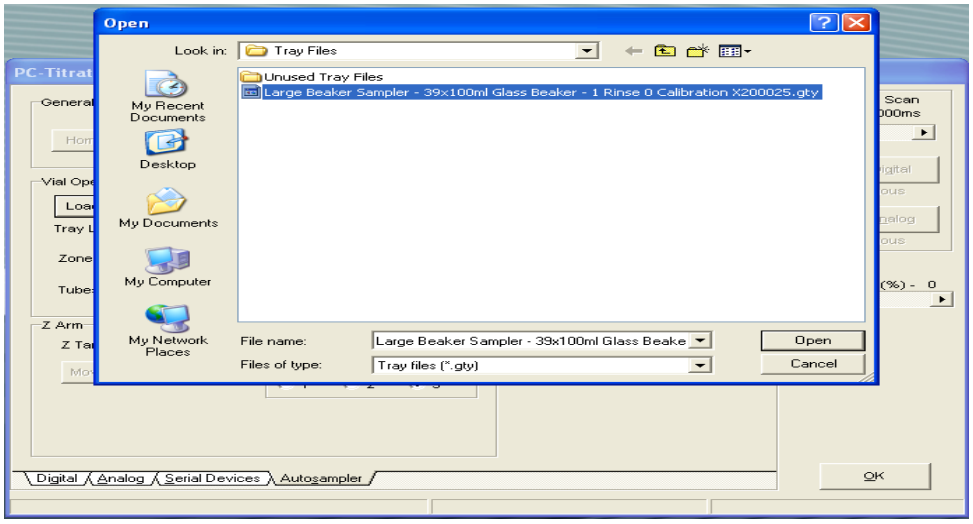
9.4 Instrument preparation

9.4.1 Check and fill the deionized water bottle and acid bottle.

9.4.2 Turn on the computer and the autosampler. Double click on "PC-Titrate V3".

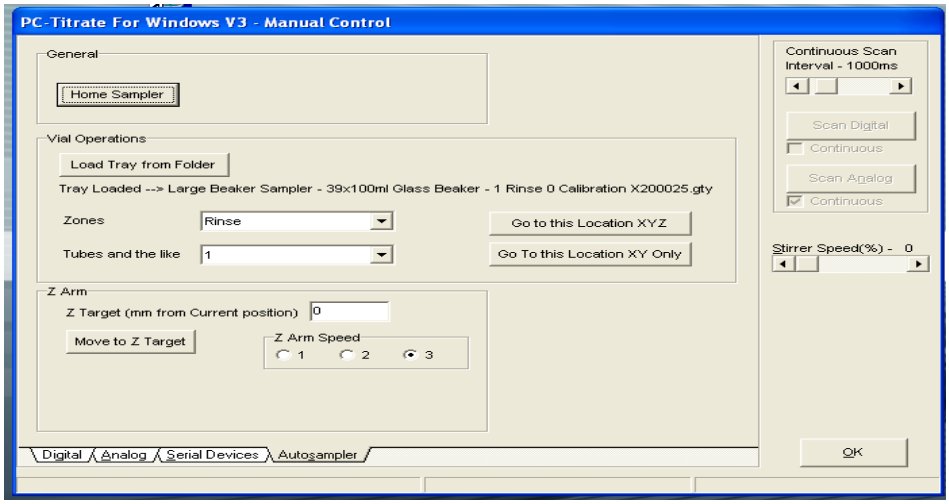


9.4.3 Click on "Titrator" and select "Manual control" from the pull-down list. Select "Autosampler", "Load tray from folder", Automax beaker, Open

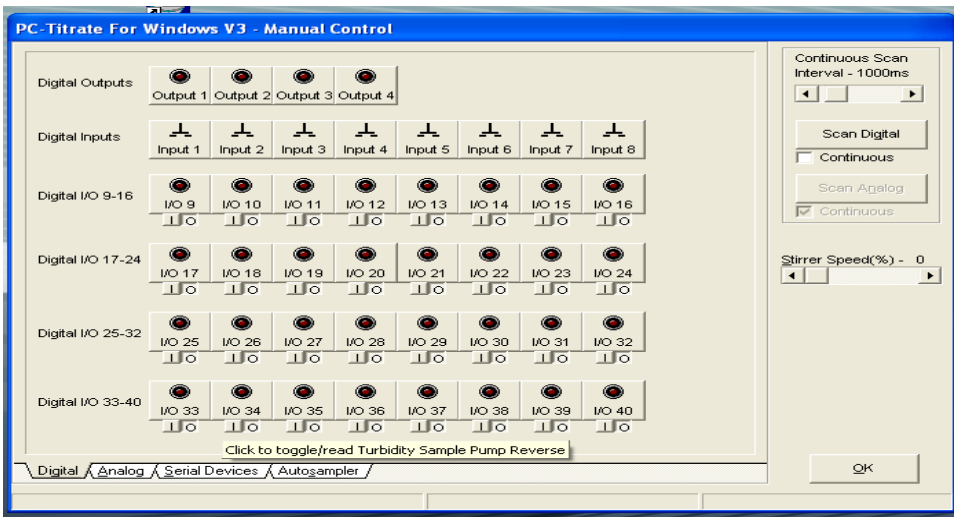


9.4.4 Click on "Home sampler" to send the probe to home position.

9.4.5 Select "Rinse" from "Zones" and "l" as the beaker number for "Tubes & the like". Click on "Go to this location XYZ" to send the probe to the rinse beaker.



9.4.6 Click on "Digit" tab and "Output 4" to rinse the probe and fill up the beaker. Click "Output 4" again to turn it off.



9.5 Buret preparation

9.5.1 Remove the titrant delivery line from the electrode block on the autosampler and place it into a waste beaker.

9.5.2 Check and fill the acid bottle.

9.5.3 Go to "Serial devices".

9.5.4 Click on the button labeled "Dispense l0%" to dispense the 0.02 N H_2SO_4 through the titrant delivery line. Repeat 2 more times or until no bubbles are observed in the flow.

9.5.5 Fill up the syringe by clicking on "Syringe full down".

9.5.6 Remove the dispenser tip from the waste beaker and return it to its position in the probe holder.

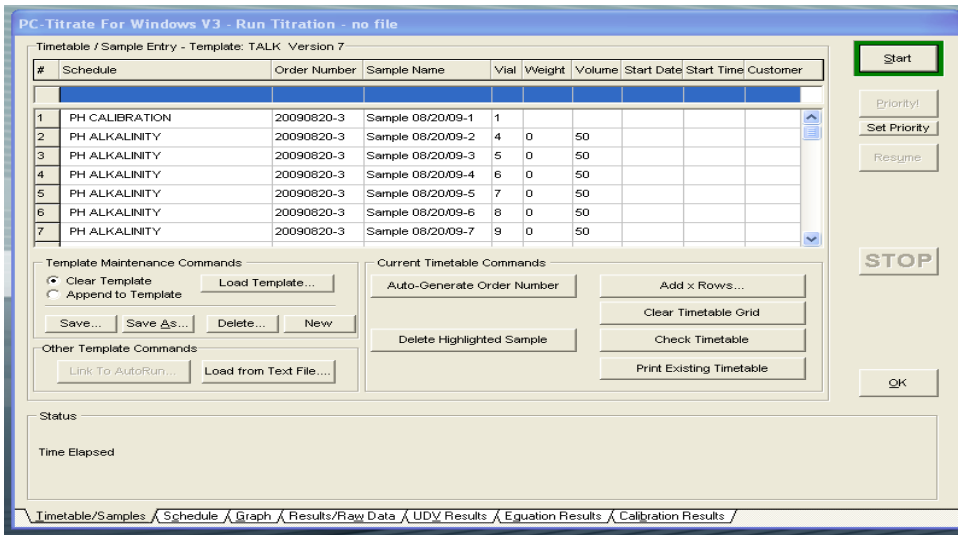
9.6 Daily electrode calibration and sample analysis

9.6.1 Place pH 4.0, 7.0 & 10.0 buffers into autosampler tray using position # 1, 2 & 3.

9.6.2 Click on the PC Titrate V3 tab.

9.6.3 Click on the book tab at the bottom labeled "pH cal 4-7-10" tab to call up the sample Table.

9.6.4 Place the samples after the calibration: The template will have "4-7-10" under sample name at the first row reserved for a schedule of "pH calibration" with a 1 in the vial number box. Enter sample names according to the sample run log (9.1.1) starting with the second row (vial #
4) a check standard, a blank, a blank spike, a QC, and samples to be analyzed. Enter a check standard, a blank, and a QC again at the end of the run. All other samples and checks are to be run with a "pH Alkalinity" schedule chosen.



#	Schedule	Order Number	Sample Name	Vial	Weight	Volume	Start Date	Start Time	Customer
1	PH CALIBRATION	20090820-3	Sample 08/20/09-1	1					
2	PH ALKALINITY	20090820-3	Sample 08/20/09-2	4	0	50			
3	PH ALKALINITY	20090820-3	Sample 08/20/09-3	5	0	50			
4	PH ALKALINITY	20090820-3	Sample 08/20/09-4	6	0	50			
5	PH ALKALINITY	20090820-3	Sample 08/20/09-5	7	0	50			
6	PH ALKALINITY	20090820-3	Sample 08/20/09-6	8	0	50			
7	PH ALKALINITY	20090820-3	Sample 08/20/09-7	9	0	50			

9.6.5 Highlight each excess line, and then click on "Delete Highlighted Sample" to remove all unused sample information.

9.6.6 Highlight a line and click on "Add x lines" to add additional lines. Left click on the mouse to relocate the lines.

9.6.7 Click "Check Timetable" to verify information entered are valid. Roll down the Table to make corrections if needed. Click "OK".

9.6.8 Load the samples according to the run list with the last sample followed by a beaker with the solution recommended by the probe's manufacturer.

9.6.9 Click on "Start".

9.6.10 To run a second tray using the same calibration: Double click on "pH Calibration" and replace it with "pH Alkalinity". Fill in sample names starting with the first row (vial #1). Make sure a set of the quality control samples: check standard, blank, and external QC is also being run at the beginning and at the end in the second tray.

9.6.11 Print the *Calibration Report* and a custom report of *Alkalinity Results* at the end of the run. Recall each titration curve by clicking on "Titrator", "Titration Replay", "Load", and then, selecting date and sample name. Click on "Select" to observe the titration curve. Click "OK" to return to the main menu.

9.6.12 Results can also be printed out by clicking on "Equation results" tab, "Print", and then "OK".

9.6.13 Go to "Manual control" and select "Autosampler" tab. Select "tubes" from "Zones" and "l" as the number for "Tubes & the like". Click on "Go to this location XYZ" to send the probe to the # l beaker with the solution recommended by the probe's manufacturer.

9.6.14 Shut down the computer and turn off the autosampler.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Alkalinities are calculated automatically by the PC-Titrate V.3 software based on 1 mL of 0.1N H_2SO_4 = 5.0 mg $CaCO_3$

10.1.1 Potentiometric titration to an end point of pH 4.5

$$\text{Alkalinity, mg } CaCO_3/L = \frac{\text{titrant dispensed, mL} \times 0.02N\ (H_2SO_4) \times 50{,}000}{\text{sample volume, mL}}$$

10.1.2 Potentiometric titration of low alkalinity

$$\text{Total Alkalinity, mg } CaCO_3/L = \frac{(2B - C) \times 0.02N\ (H_2SO_4) \times 50{,}000}{\text{sample volume, mL}}$$

where:

B = mL titrant to first recorded pH
C = total mL titrant to reach pH 0.3 unit lower

10.2 Calculate the percentage spike recovery of the laboratory fortified blanks and samples as follows:

$$\%SR = \frac{\text{spiked sample conc. - sample conc., ppm}}{\text{amount of spike added to sample, ppm}} \times 100$$

10.3 Calculate the relative percentage difference of the duplicated samples as follows:

$$RPD = \frac{\text{difference between the duplicates}}{\text{average of the duplicates.}} \times 100$$

11.0 DATA AND RECORDS MANAGEMENT

11.1 Instrument maintenance, instrument calibration, and quality control data are kept in binders and test results are kept in the file cabinet.

11.2 Normal turnaround time for samples submitted to this lab will be 2 to 10 days from receipt. Results are reported in writing on a sample analysis request form.

11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five-year custody period.

12.0 WASTE MANAGEMENT

12.1 Excess reagents, samples and method process waste are poured into the sink with running water.

12.2 Actual reagent preparation volumes are to reflect anticipated usage and reagent stability.

13.0 REFERENCES

13.1 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* Method Number 2320B, 21st Edition, 2005

13.2 Man-Tech Associates inc., *PC-Titrate Windows Software Manual,* version 3.0, November 2004.

13.3 U.S. Environmental Protection Agency, *Monitoring and Assessing Water Quality, 5.10 Total Alkalinity*, November 2006

13.4 Division of Environmental Chemistry, Maryland Department of Health, *Quality Assurance Plan,* SOP No. CHEM-SOP-QAP

13.5 Division of Environmental Chemistry and Division of Microbiology, Maryland Department of Health, *Quality Manual,* SOP No. QA-SOP-QM

APPENDIX **A**

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist - Alkalinity

Standard Methods 2320 B

Lab Numbers[1]: _____

Date Collected: _____ Date Analyzed: _____ Analyst: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	14 days @ 4°C		
Calibration Results	Slope = −65.00 to −53.00 mV		
External QC[2]	Beginning and end of each run		
	Within Acceptable range		
Reagent Blank	< Reporting level (1 mg/L)		
Blank Spike	1 per batch		
	Recovery = 90 - 110%		
Check Standard	After every 10th sample and at the end of the run		
	Concentration within 90 to 110% of the true value		
Duplicates/Replicates	Every 10th and the last sample or 1/batch, if less than 10 samples		
	RPD :S l0%		
Matrix Spike	Every 10th and the last sample or 1/batch, if less than 10 samples		
	Recovery = 90 - 110%		
Decimal Places Reported	0		
Changes/Notes	Clearly stated		

* Check (✓) if criteria are met.

_____
Analyst's Signature & Date

Reviewer's Signature & Date

_____
Supervisor's Signature & Date

[2]External QC
Identification =

True Value = _____ ppm
Range = _____ ppm

CONTROLLED DOCUMENT - Do Not Copy

DES-FORM-IAL-001 (07/17)

APPENDIX **B**

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Sample Run Log - Alkalinity

Standard Method 2320 B

Date:_____ Analyst: _____

Tray 1 Cup #	Sample ID	Dilution	Tray 1 Cup #	Sample ID	Dilution
1	pH 4		21		
2	pH 7		22		
3	pH 10		23		
4	Blank		24		
5	Ck Std		25		
6	QC		26		
7	Blank		27		
8	Blank -Spike		28		
9			29		
10			30		
11			31		
12			32		
13			33		
14			34		
15			35		
16			36		
17			37		
18			38		
19			39		
20					

Tray 2 Cup #	Sample ID	Dilution
1		
2		
3		
4		
5		
6		
7		
8		
9		

10		
11		
12		
13		
14		
15		
16		
17		
18		
19		
20		

Sample Name	Tracking ID
pH 4 Buffer	
pH 7 Buffer	
pH 10 Buffer	
H_2SO_4, 0.02N	

Lab #	Average	RPD	% Spk Rec

Sample Name	Prep Log ID
Intermediate Std, 5,000 ppm	
Ck Std, 50 ppm	
QC:	

DES-FORM-IAL-002 (05/20)
MDH- Laboratories Administration
DIVISION OF ENVIRONMENTAL SCIENCES

Title:	Determination of 5-Day Biochemical Oxygen Demand (Standard Method 5210 B)
SOP No.:	CHEM-SOP-SM 5210 B
Revision:	3.5 Replaces: 3.4 Effective: 5/1/22
Laboratory:	Inorganics Analytical Laboratory
POC:	Jacob Kilczewski jacob.kilczewski@maryland.gov

Laboratory Supervisor: Lara Phillips 4/25/2022

Signature Date

QA Officer: Molly Molloy 4/25/2022

Signature Date

Manager: Cynthia Stevenson 4/25/2022

Signature Date

Division Chief: 04/25/2022

Signature Date

CHEM-SOP-SM 5210 B
SOP N0.: CHEM-SOP-SM 5210

REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	6/4/08	N/A	Taiyin Wei	6/5/08
1.0	12/09	Tracking IDs for standards and reagents	Taiyin Wei	1/10
2.0	1/11	New SOP tracking number	Asoka Katumuluwa	1/11
3.0	2/12	New Procedure for new BOD analyzer	Cynthia Stevenson	12/12/12
3.1	10/31/14	Changed format	C. Stevenson S. Ameli	12/01/14
3.1	6/1/2015	Reviewed document	L. Phillips Y. Simms S. Ameli	7/1/15
3.1	5/31/2016	Reviewed document	L. Phillips Y. Simms S. Ameli	7/1/16
3.2	6/05/2017	Reviewed document and made organizational name changes, Updated 5.1.4, 9.3.2-9.3.3, 9.6.1, 9.11.1, 9.11.2.6 to 9.11.2.8 and Run Log	L. Phillips Y. Simms S. Ameli	7/1/17
3.3	6/4/18	Reviewed document added 9.10, updated section 13.7	L. Phillips Y. Simms S. Ameli	7/1/18
3.3	3/1/19	Reviewed document	L. Phillips Y. Simms S. Ameli	3/4/19
3.4	4/21/20	Reviewed document and updated contact information	Jacob Kilczewsk L. Phillips	5/1/20
3.4	4/9/21	Reviewed document	Jacob Kilczewsk L. Phillips	5/1/21
3.5	4/21/21	Reviewed document, updated 6.3.2, 6.5.7	J. Kilczewski L.Phillips	5/1/22

TABLE OF CONTENTS

Standard Operating Procedure

Determination of 5-Day Biochemical Oxygen Demand
Standard Method 5210 B

1.0 SCOPE AND APPLICATION

1.1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirement of wastewaters, effluents, polluted waters, and streams. The test has its widest application in measuring waste loadings to treatment plants and in evaluating the BOD-removal efficiency of such treatment systems. The application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water.

1.2 The BOD determination is an empirical test which measures the dissolved oxygen utilized during a specified incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous irons. It also may measure the amount of oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. The standard test conditions include dark incubation at 20 ºC for five days. The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be actually reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

2.0 SUMMARY OF METHOD

2.1 Appropriate dilutions of each sample and the quality control samples are incubated for 5 days (BOD) at 20 ºC in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

3.0 INTERFERENCES

3.1 Residual chlorine can interfere in this determination, and it is neutralized with Na_2SO_3, if present. Hach's USEPA-accepted DPD (N, N-diethyl-p-phenylenediamine) colorimetric method is used to detect any free chlorine in the sample.

3.2 The source water used for BOD sample dilution must be free of heavy metals, specifically copper, and toxic substances such as chlorine that can interfere with BOD measurements. Protect source water quality by using clean glassware, tubing, and bottles. Storage of prepared dilution water for more than 24 h after adding nutrients, minerals, and buffer is not recommended unless dilution water blanks consistently meet quality control limits.

3.3 Oxidation of reduced forms of nitrogen, mediated by micro-organisms, has been considered interference in the determination of BOD and can be prevented by an inhibitory chemical and reported results as carbonaceous biochemical oxygen demand (CBOD).

3.4 Exclude all light during the 5-day incubation period to prevent the possibility of photosynthetic production of dissolved oxygen (DO).

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during reagent preparation and instrument operation.

4.2 Each employee is issued a ***Laboratory Safety Manual*** and is responsible for adhering to the recommendations contained therein.

4.3 Use absorbent towels if material is spilled and wash residual into the drain.

4.4 Each chemical should be regarded as a potential health hazard. A reference file of the material safety data sheet (MSDS) is available in the lab.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 YSI Model 5100 dissolved oxygen meter

5.1.1.1 Dissolved oxygen (DO) probe

5.1.1.2 Membrane replacement kits for DO probe.

5.1.1.3 Mantech AutoMax 122 Autosampler with pumps

5.1.1.4 Computer and printer

5.1.2 Incubator, thermostatically controlled at 20 ± 1ºC

5.1.3 pH meter - Accumet pH meter 15, Fisher Scientific or equivalent

5.1.4 Magnetic stirrer or automatic stirrer

5.1.5 Buret - 50 mL

5.1.6 Drying oven - isotemp, gravity flow convection, 103 ºC to 105 ºC

5.1.7 Air compressor - 135 psi, Westward

5.2 Supplies

5.2.1 BOD bottles - 300 mL disposable bottles (cat. # D1001), botttle stoppers (cat. # D1025), and overcaps (cat. # D1050), Environmental Express

5.2.2 Carboy with spigot - 20 L capacity

5.2.3 Graduated Cylinders - 25, 50, 100, and 250 mL

5.2.4 Micropipetter - adjusTable volume ranges from 1.0 to 5.0 mL

5.2.5 Pipet tips - 5000 µL

5.2.7 Plastic beakers - polypropylene, 1000 mL,

5.2.8 Membrane kit for BOD probe - cat. # 5906, YSI

5.2.9 Filter Unit, 0.45 µm - Nalgene disposable sterilization filter unit, cat. # 09-740-25B, Fisher

5.2.10 Tubes - polypropylene with snap caps, sterile, 14 mL, cat. # 14-959B, Fisher

5.2.11 Glass pipettes - volumetric, class A, 5 mL

5.2.12 Flasks - volumetric, class A, 500 mL and 1000 mL

5.2.13 Glass rods

5.2.14 Stirring bars with stir plate or automatic stirrer

5.2.15 Weighing pans - aluminum, cat. #D57-144, Labsources, Inc.

6.0 REAGENTS

6.1 Dilution water

6.1.1 Aerate 19 liters (5 gallons) of deionized water in a 20 L carboy for a minimum of 30 minutes. The dissolved oxygen concentration of water used for BOD test must be at least 7.5 mg/L. Following aeration, leave the carboy to sit overnight or longer in a 20 oC incubator with the cap loosened to allow water to equilibrate.

6.1.2 Prepare dilution water one hour before use by emptying one premixed pillow of BOD Nutrient Buffer (Hach cat. # 14863-98) into aerated water (6.1.1) at 20 ºC. Mix well. Place in the incubator until ready to use.

6.2 Glucose-Glutamic acid (GGA) solution

6.2.1 Dry a few grams each of glucose or dextrose and glutamic acid in aluminum weigh pans for 1 hour at 103 ºC. Cool to room temperature in a desiccator.

6.2.2 Weigh out 0.15 g each of dextrose and glutamic acid and dissolve 800 mL of deionized water in a 1 L volumetric flask. Dilute to mark and mix well. Prepare fresh immediately before use.

6.2.3 Instead of preparing a fresh GGA solution each time, the solution prepared in 6.2.2 can be sterilized by filtering through a disposable sterilization filter unit, divided and stored in small volumes. If this procedure is followed, pour about 12 mL aliquots into each sterile 14 mL polystyrene tube, snap cap back on the tube, label, and store in the refrigerator. Prepare every two months.

6.2.4 Premade GGA is also commercially available. To prepare the standards, simply add the content of the 6 mL vial into each of the two BOD bottles marked for GGA.

6.3 Seeding material, prepare daily.

6.3.1 One bottle of wastewater from the Cox Creek Wastewater Treatment Plant is delivered to the laboratory every Tuesday. Store the wastewater in the incubator.

6.3.2 Shake the sample, let settle and then pour the supernatant into an Erlenmeyer flask about an hour before beginning the run to allow solids to settle to the bottom of the flask. The amount of supernatant to be added to each BOD bottle is between 1.0 mL to 3.0 mL depending on the color, odor and density of the wastewater.

6.4 Sample pH

6.4.1 Calibration buffers - pH 4.0, pH 7.0, and pH 10.0 - Fisher cat. # SB105,

6.4.2 Sulfuric acid (H_2SO_4), 1M - Slowly and while stirring, add 2.8 mL of conc. H_2SO_4 to 80 mL of deionized water. Dilute to 100 mL. Mix well, label and store for up to a year.

6.4.3 Sodium hydroxide (NaOH), 1N - Dissolve 4 g of NaOH in 80 mL of deionized water. Dilute to 100 mL. Mix well, label and store for up to a year.

6.5 Dichlorination

6.5.1 DPD free chlorine reagent power - cat. # 14070-99, Hach

6.5.2 Starch soluble for iodometry - cat. # 516-100, Fisher

6.5.3 Sodium sulfite solution (Na_2SO_3) - Dissolve 0.157 g of Na_2SO_3 in 100 mL of deionized water. This solution is not stable; prepare fresh daily.

6.5.4 Potassium iodide (KI) solution - Dissolve 10 g of KI in 100 mL deionized water. Mix well.

6.5.5 Acetic acid (CH_3COOH), 1:1 - Mix 20 mL deionized water with 20 mL glacial acetic acid.

6.5.6 Nitrification inhibitor - 2-chloro-6- (trichloro methyl) pyridine (TCMP), cat. # 2533, Hach

6.5.7 External Quality Control Sample - WatR Pollution Demand (ERA) or equivalent.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Keep samples at or below 4 ºC from the time of collection and analyze within 48 hours after collection.

8.0 QUALITY CONTROL

8.1 Dilution water quality check: The dilution water blank, prepared in 6.1, serves as a check on quality of unseeded dilution water and cleanliness of incubation bottles. The DO uptake in 5 days must not be more than 0.20 mg/L. If this value exceeds
0.20 mg/L, then evaluate the cause and make appropriate corrections.

8.2 Glucose-glutamic acid check: The glucose-glutamic acid check solution is the primary basis for establishing precision and accuracy and is the principal measure of seed quality and analytical technique. For the 300 mg/L mixed primary standard, the average 5 days BOD must fall within the range of 198 ± 30.5 mg/L. If the average value falls outside this range, evaluate the reason and take appropriate actions. Consistently high values can indicate the use of too much seed suspension, contaminated dilution water, or the occurrence of nitrification. Consistently low values can indicate poor seed quality, use of insufficient quantity of seed suspension, or the presence of toxic materials. If low values persist, prepare a new mixture of glucose and glutamic acid and check the sources of dilution water and the seed.

8.3 Minimum residual DO and minimum DO depletion*:* Only the dilutions resulting in a DO depletion of at least 2.0 mg/L and a residual DO of at least 1.0 mg/L after 5 days of incubation are considered to produce valid data.

8.4 Seed Control: The DO uptake attributable to the seed should be between 0.6 -1.0 mg/L. The volume of seed added should be adjusted to meet the required range of 198 ± 30.5 mg/L for glucose-glutamic acid check.

8.5 An external quality control sample with a known BOD value is analyzed each quarter.

8.6 The YSI dissolved oxygen meter is calibrated in air (water saturated), i.e. the probe is parked in a BOD bottle containing 1" of water.

8.7 Data acceptance criteria are listed in the data review checklist (Appendix A).

8.8 Laboratory participates in ERA WatR Pollution (WP) Proficiency Testing annually.

9.0 PROCEDURE

9.1 Sample preparation:

9.1.1 Prepare the sample run list for checking color, odor, pH and chlorine and for dilutions. (Appendix B)

9.2 Check samples for residual chlorine.

9.2.1 Using the Hach Swiftest dispenser, insert DPD free chlorine reagent powder into each test tube, add about 10 mL of sample and observe for any color change occurring within a few seconds. A pink color indicates presence of chlorine and therefore the samples(s) must be dechlorinated.

9.2.2 Determine the required volume of Na_2SO_3 needed to dechlorinate on a 50 mL portion of the pH adjusted sample. Add 0.5 mL of 1:1 acetic acid (6.5.5), 0.5 mL of KI solution (6.5.4) and a few drops of starch solution to sample. Using a 50 mL buret, titrate with Na_2SO_3 (6.5.3) solution to the starch-iodine (blue) end point. Record the volume used. Calculate and add the required volume of Na_2SO_3 solution to the pH adjusted portion of the sample (9.3.3).

9.3 Check sample pH.

9.3.1 Label 1 L polypropylene beakers with the sample numbers. Pour about 500 mL of samples into 1 L beakers. Pour 100 mL of sample if it has a strong sewage odor.

9.3.2 Calibrate the pH meter as stated in the meter directions. Standardize the pH meter using pH 4, 7 and 10 buffers. Record the slope and temperature in the logbook. Read each buffer after the calibration and record the results in the pH meter log.

9.3.3 Read the pH of each sample making sure they are stirred during the measurement. Adjust the pH of each sample to a final reading between 6.5 to 7.5. with 1N NaOH or 1M H_2SO_4. Record the final pH. Leave the pH meter on standby until the completion of the entire run for that day.

9.4 Sample dilution:

9.4.1 Bring samples to BOD room temperature (20 ºC) before making dilutions.

9.4.2 Check samples for color and odor.

9.4.3 Dilutions are prepared directly in BOD bottles. Transfer 200- and 100-mL aliquots of each prepared stream sample, 50, 25, 10 and 5 mL aliquots of each prepared sewage sample, and 10, 5, 1 and 0.5 mL aliquots of each prepared strong industrial wastes, as appropriate, into labeled BOD bottles using class A graduated cylinders and volumetric pipets. Rinse the cylinder between samples. Dilutions may need to be adjusted to reflect the qualities of the sample. Place the bottles in the correct order in the rack.

9.5 Nitrification inhibition:

9.5.1 If nitrification inhibition is desired add 3 mg of TCMP (6.5.6) to each 300 mL bottle before capping.

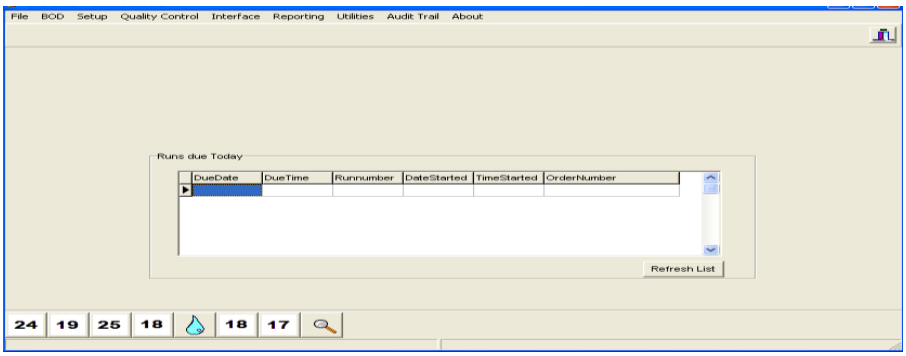
9.5.2 Note the use of nitrification inhibition in the reporting results.

9.6 Prepare autosampler using the "PC-BOD" software:

9.6.1 Push the bottle containing 1" of water up to the probe to create a seal. Warm up YSI 5100 for at least 30 minutes. Calibrate the probe. Ensure that it is set in **REMOTE** mode.

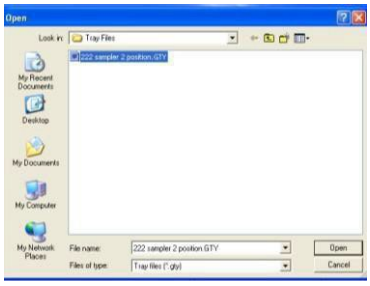
9.6.2 On the computer desktop locate the software icon.

Double click on the icon and the software will open to the main screen. If the icon is not present, open the software by clicking on the desktop 'Start' menu, followed by 'All Programs' and select 'PC-BOD'.



9.6.3 Under **BOD** select **MANUAL.**

9.6.3.1 Click on the '**Load Tray from Folder**' button. The window shown at right will appear.

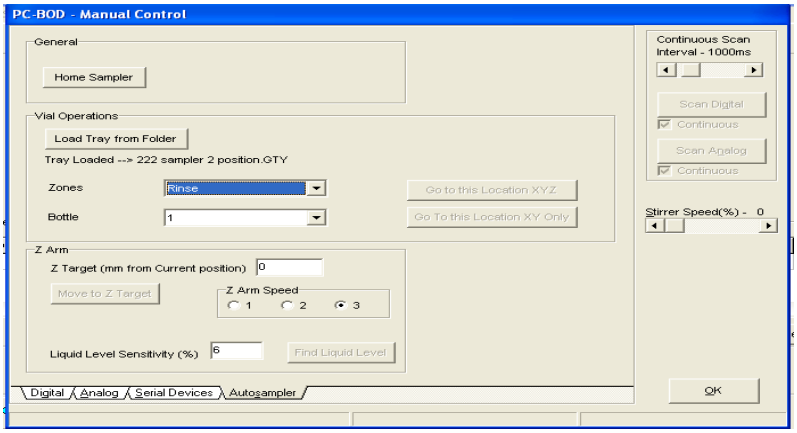


9.6.3.2 Click on the tray file named *271 sampler.* and then click on the '**Open**' button.

9.6.3.3 The **'Home Sampler**' button will become active and the 'zones' and 'bottle' windows will be filled in.

9.6.3.4 Click on the '**Home Sampler**' button. The sampler will move to the home position and the buttons to the right of **'zones**' & **'bottles'** will become active. If the sampler is already in the home position, it will appear that nothing is happening but within a few seconds the two buttons will become active. Remove the rack and place a waste beaker in bottle position 3.

9.6.3.5 To move the autosampler to a specific location first select the following zone: -Bottle: allows DO probe to go into a



bottle

9.6.3.6 Select the bottle location to move to by using the drop-down menu. For example, selecting 'Bottle' and '3' will allow the DO probe to go to the 3rd bottle position.

9.6.3.7 To move the autosampler to the specified location click on **'Go to this location XV only'** to move above the bottle position.

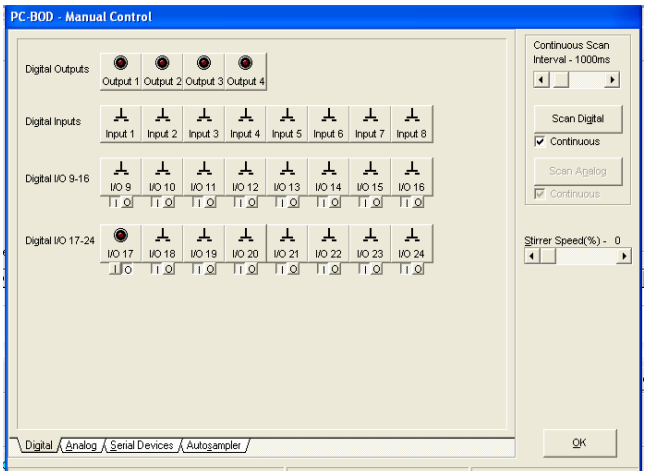
9.6.3.8 To move the autosampler only in the Z direction (up and down), enter the number of millimeters to move in the box next to '**Z Target (mm from current position)**'. Use a '-' sign before the number of millimeters to indicate moving in a downward

direction. Click '**Move to Z Target**' to move the sampler. For example, entering -43 will move the Z arm down 43mm.

9.6.3.9 Move the autosampler to bottle location **3** and lower it into a waste collection beaker by moving the autosampler down the Z axis by three **-43mm** increments.

9.6.4.0 Prime the pumps with the seed, nutrient water and rinse water.
9.6.4.1 Open '**Digital**' Tab: This tab allows the pumps and stirrer to be turned on or off. Click on the button listed below to turn the device on or off.

Output 1 - dilution pump
Output 2 - seed pump
Output 3 - inhibitor pump
Output 4 - DO probe stirrer
Output 17 - rinse pump



9.6.4.2 Turn on the seed pump,(**Output2**), ensuring that all the rinse water left in the line has been emptied into the waste beaker and the seed is being drawn completely through the line. Turn it off when the seed is dripping into the waste beaker.

9.6.4.3 Turn on the dilution pump, (**Output 1**), ensuring that all the rinse water left in the line has been emptied into the waste beaker and the nutrient water is being drawn through the line. Turn it off.

9.6.4.4 Return the Autosampler to the home position.

1. Open the **Autosampler** tab.
2. Click on '**home sampler**'
3. Click '**OK**'.

9.7 If there are no excessive delays in executing steps 9.6.3 to 9.6.4.4 continue to 9.8 to start the run. An example of a delay would be if dilution water is too high and needs to be degassed or the instrument malfunctions and needs to be restarted. In the case of significant delays, it is best to recalibrate the probe after the problems are resolved and running conditions are favorable and then proceed to section 9.8

9.8 Setting up a run manually.

9.8.1 From the run screen (**BOD/Run BOD**), click on the '**Edit**' followed by the '**Add X Rows**' button. Enter the number of rows that need to be added to the one already on the grid to give one row per bottle in the run. Click '**OK**' and the rows will be added.

9.8.2 Build the batch starting with one stabilizing water blank, two duplicated water blanks, three seeds at 10, 15 and 20 mL, two duplicated mixtures of 5 mL of G/G with 2-3 mL of seeds followed by 2 to 5 different dilutions of each sample plus 2- 3 mL of seeds. See appendix C for an example run and enter as shown.

9.8.3 Fill in the columns on the template. To remove extra lines, click the '**Delete Highlighted Sample**' button. Do not leave blank lines in the template.

9.8.4 Click '**Done Edit**' and the batch will be set up.

9.8.5 Click the '**Auto-Generate Order Number'** button. Enter operator's initials in the box in the upper left corner of the screen.

9.8.6 Load marked bottles into the autosampler racks.

9.8.7 Place the rack containing the first samples onto the autosampler.

9.8.8 Press the '**Start**' button to begin calibration and sample analysis. When prompted enter the rack number currently on the autosampler and press '**OK**'.

9.8.9 Following the screen prompts with regard to calibrating the autosampler and recording the results in the book.

9.8.10 Continue following the screen prompts to allow the auto dilutor to seed, dilute and take an initial D.O. reading of all the samples in the rack. If there are multiple racks the program will prompt for insertion of them at the correct time.

9.9 When a sample is supersaturated.

9.9.1 Stop, delete initial DO readings higher than 9.2.

9.9.2 Shake the diluted, seeded sample in the designated container to remove excess DO

9.9.3 Restart the run and the autosampler will begin with the first sample without a reading.

9.10 Using the manual BOD probe

9.10.1 In the case of instrumental error or malfunction that cannot be resolved, the sample can be run manually using the stand-alone BOD probe. Calibrate probe as in 9.12.1 then press the mode button to place in read mode.

9.10.2 Add the required amount of seed and dilution water to the sample. Turn on the timer and stirrer for 30s. Then hit the read button on the meter and record the DO reading. Follow this step for each sample.

9.11 Incubation: After all the samples in a rack have been diluted, seeded and had an initial DO reading taken, remove the rack from the autosampler. Place a stopper and cap on each bottle before incubating the sealed bottles for 5 days in the 20ºC incubation room with the lights turned off.

9.12 Read final DO:

9.12.1 Turn on the YSI 1500, push the bottle up to seal it to the probe and allow the meter to warm up for 30 minutes. On the DO meter, press **Calibrate** and then press **Autocal**. Note the readings in the logbook. Press the '**Mode**' button then choose '**Remote**' from among the options.

9.12.2 Loading an Existing Run in the computer.

9.12.2.1 Open the '**PC BOD'** program.

9.12.2.2 On the main screen click on '**BOD**' and then select '**Run BOD**'

9.12.2.3 Choose the '**Load Existing Runs**' tab. On this screen there are 4 buttons which indicate runs in various stages of completion. Choose '**Finals Due Today'** and highlight the row containing the appropriate run.

9.12.2.4 Click on '**Load Selected**' Enter the operator's initials in upper right window.

9.12.2.5 Place the rack with the samples to be run onto the autosampler.

9.12.2.6 Check instrument tubing is free from pinching and that rack is seated properly.

9.12.2.7 Make sure all caps are removed from BOD bottles.

9.12.2.8 To begin the run, click on the '**Start**' button and enter the number of the rack currently on the autosampler when prompted.

9.13 Regular maintenance of BOD probe

9.13.1 Prepare the oxygen probe electrolyte by filling the bottle included with

the kit to neck with deionized water. Shake well until crystals are dissolved.

9.13.2 Remove the old membrane cap assembly from the probe. Wipe clean the metal tip of the probe.

9.13.3 Take a new membrane cap assembly and fill in with the fresh electrolyte solution and then screw the cap assembly onto the probe.

9.13.4 Always park the probe in a BOD bottle containing one inch of D.I. water when not in use.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All the calculations are performed automatically by BOD Analyst software using the following equations:

10.1.1 Amount of dissolved oxygen consumed during the incubation period:

O_2 Depletion (mg/L) = Initial DO - Final DO

10.1.2 Seed factor used for correcting the BOD test for oxygen depletion resulting from the presence of seed:

$$\text{Factor (mg/L)} = \frac{O_2 \text{ Depl in seed control Vol seed in seed control}}{\text{Vol seed in seed control}} \times \text{Vol seed in sample}$$

10.1.3 BOD of the samples:

$$\text{BOD (mg/L)} = \frac{O_2 \text{ Depl in sample} - \text{Seed Factor}}{\text{Sample Volume, ml}} \times \text{Bottle Volume, mL}$$

10.2 If more than one sample dilution meets the acceptance criteria, report the average calculated by the software program.

10.3 If the O_2 depletion is less than 2 mg/L with 200 mL portion (maximum sample volume) of the sample, report the result from this dilution.

10.4 If all the sample dilutions produce a final DO of less than 1.0 mg/L, report the result from the highest dilution with a > sign.

11.0 DATA AND RECORDS MANAGEMENT

11.1 All Quality Control data are kept in a binder labeled as "Quarterly QC for BOD".

11.2 Normal turnaround time for BOD samples submitted to this lab is 7 to 10 days from receipt with a sample holding time of 2 days. Results are reported in writing on a sample analysis request form.

11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five-year custody period.

12.0 WASTE MANAGEMENT

12.1 It is the laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume and bench operation.

12.2 Samples and standards are poured down the drain while a large amount of water is running.

13.0 REFERENCES

13.1 United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Waste*, Method Number 405.1, August 1993.

13.2 American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 21st Edition, Method 5210 B, 2005.

13.3 YSI BOD ANALYST Operations Manual, 1999.

13.4 YSI 5905/5010 BOD Probe Instruction Manual, 1999.

13.5 PC-BOD Operator's Manual - Man Tech 2009

13.6 Division of Environmental Chemistry, Maryland Department of Health and Mental Hygiene, *Quality Assurance Plan,* SOP No. CHEM-SOP-QAP

13.7 Division of Environmental Chemistry and Division of Microbiology, Maryland Department of Health and Mental Hygiene, *Quality Manual,* SOP No. QA-SOP-QM

APPENDIX A

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist - BOD
Standard Method 5210 B

Lab Numbers[1]: _____

Date Collected: _____ Date Analyzed: _____ Analyst: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	48 hours @ 4 ºC		
Chlorine	Neutralized if present		
pH	Between 6.5 to 7.5; adjusted if out of range		
Initial DO	< 9.20 mg/L at 20 ºC		
Incubation Period	5 days		
DO uptake of dilution water	< 0.20 mg/L		
DO uptake of seeded dilution water (seed factor)	0.60 to 1.00 mg/L		
BOD for Glucose/Glutamic Acid (G/GA) solution	198 ± 30.5 mg/L		
Sample dilutions	Meet the requirements: Final DO 2' 1.00 mg/L and DO depletion 2' 2.00 mg/L		
	Decide on the value to be reported if requirements are not met.		
External QC[2] Analyzed quarterly	Last date analyzed		
	Within acceptable range		
Decimal Places Reported	1		
Reported Values	2' 2 mg/L; concentrations below this value reported with < sign for Chesapeake Bay samples as < 2 mg/L for all other samples.		
Changes/Notes	Clearly stated		

[1]Include beginning and ending numbers, account for gaps by bracketing.

Analyst's Signature & Date

Reviewer's Signature & Date

Supervisor's Signature & Date

[2]QC Sample: _____ True Value = _

Tracking ID: _____

Range = _____

Acceptable

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Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Sample Run Log -BOD
Standard Method 5210 B

Date: _____

Collection Date:

_____

Analyst: _____

Lab #	Sample Type	Dilution	Color	Odor	Cl	Chl. Neutr	pH	pH Adj. to
1.								
2.								
3.								
4.								
5.								
6.								
7.								
8.								
9.								
10.								
11.								
12.								
13.								
14.								
15.								
16.								
17.								
18.								
19.								
20.								
21.								
22.								
23.								
24.								
25.								
26.								

Sample Name	Tracking ID
pH 4 Buffer	
pH 7 Buffer	

pH 10 Buffer	
Seeds	

Sample Name	Prep Log ID
H_2SO_4, 1M	
NaOH, 1N	
Dilution water	
G/GA	

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Division of Environmental Chemistry
INORGANICS ANALYTICAL LABORATORY

EXAMPLE OF BATCH

Bottle#	Sample name	Sample Volume (mL)	Seed Volume(mL)
1	Calib		
2	Blank		
3	Blank		
4	Blank		
5	Seed		10
6	Seed		15
7	Seed		20
8	BOD GGA	5	3
9	BOD GGA	5	3
10	WW 1111	100	3
11	WW 1111	200	3
12	WW E12001111001	50	3
13	WW E12001111001	100	3
14	WW E12001111001	200	3
15			

APPENDIX D

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Troubleshooting

PROBLEM	CAUSE	SOLUTION
Autosampler jam.	Tangled lines.	Straighten the lines. Exit the Run. Home the Sampler. Reload the Run.
D.O. readings inconsistent/ unexpected.	Probe membrane is no longer intact.	Change membrane.
Initial Blank readings too high.	Dilution water supersaturated.	Degas carboy with Helium gas for 30 seconds.
Initial Sample readings too high.	Sample is supersaturated.	Stop the Run. Pour diluted sample into a shaker and shake for 30 seconds. Return to the BOD bottle and replace it in the rack. Delete the D.O. reading in EDIT mode. Restart the run.

SOP Title:	Determination of Turbidity by Nephelometry (EPA Method 180.1)
SOP No.:	CHEM-SOP-EPA 180.1
Revision:	3.5 Replaces: 3.4 Effective: 5/1/22
Laboratory:	Inorganics Analytical Laboratory
Author / POC:	Jeffrey Fernandez Jeffrey.Fernandez @maryland.gov

Laboratory Supervisor: Lara Phillips 4/25/2022

Signature Date

QA Officer: Molly Molloy 4/25/2022

Signature Date

Manager: Cynthia Stevenson 4/25/2022

Signature Date

Division Chief: 04/25/2022

Signature Date

CONTROLLED DOCUMENT - Do Not Copy

Revision	Date	Changes	Made By	Effective Date
0.0	6/3/08	N/A	Taiyin Wei	6/2/08
1.0	12/09	Tracking IDs for standards and reagents	Taiyin Wei	1/10
2.0	1/11	New SOP tracking number	Asoka Katumuluwa	1/10
2.0	6/13	Reviewed SOP	S. Ameli	6/13
3.0	10/20/14	Changed format	L. Phillips/J. Fernandez S. Ameli	12/1/14
3.0	6/1/15	Reviewed	L. Phillips S. Ameli	7/1/15
3.1	5/3/16	Reviewed and updated formatting and checklist	L. Phillips S. Ameli	7/1/16
3.2	5/2/17	Reviewed and updated formatting and checklist	L. Phillips/J. Fernandez S. Ameli	7/1/17
3.3	6/4/18	Reviewed SOP, updated section 8.6 and 13.6	L. Phillips/J. Fernandez S. Ameli	7/1/18
3.3	3/1/19	Reviewed SOP	L. Phillips/J. Fernandez S. Ameli	3/4/19
3.4	4/21/20	Reviewed SOP and edited for clarity.	L. Phillips J. Fernandez	5/1/20
3.4	4/9/201	Reviewed SOP	L. Phillips J. Fernandez	5/1/21
3.5	4/21/22	Reviewed SOP, update 5.2, 6.2 and sample run log	L. Phillips J. Fernandez	5/1/22

TABLE OF CONTENTS

Standard Operating Procedures
Determination of Turbidity by Nephelometry
EPA Method 180.1

1.0 SCOPE AND APPLICATION

1.1 Turbidity is a principal physical characteristic of water and is an expression of the optical property that causes light to be scattered and absorbed by suspended matter or impurities that interfere with the clarity of the water.

1.2 Determination of turbidity is a common component of water quality assessments. This method is applicable to drinking, ground, waste and saline waters.

1.3 The applicable range of Hach 2100AN Turbidimeters is 0 to 4000 nephelometric turbidity units (NTU). Drinking water samples with turbidity values greater than 40 NTU are diluted and re-analyzed.

2.0 SUMMARY OF METHOD

2.1 This method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of light scattered, the higher the turbidity.

2.2 Readings in NTUs are made using a nephelometer. Detectors of the nephelometer are in place to measure the 90° scattered light, the forward scattered light, the back scattered light and the light transmitted through the sample. The laboratory measures the value in the "Ratio On" mode, in which the instrument's microprocessor uses a mathematical calculation to ratio signals from each detector. The benefits of applying "ratio" on measurements include better linearity, calibration stability, wide measurement range, and the ability to measure turbidity in the presence of color.

3.0 INTERFERENCES

3.1 Etched, scratched, or dirty sample vials or dust contamination within the sample cell compartment and optical compartment scatter light and give inaccurate readings.

3.2 Samples containing air bubbles, coarse debris, or floating sediments can cause erroneous readings.

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during inversion of sample and reading of sample result. Use absorbent towels if material is spilled and wash residual into the drain.

4.2 Each employee is issued a ***Laboratory Safety Manual*** and is responsible for adhering to the recommendations contained therein.

4.3 Use absorbent towels if material is spilled and wash residual into the drain.

4.4 A binder of MSDS is available.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Hach Model 2100AN Laboratory Turbidimeter or equivalent- consisting of a nephelometer with a tungsten-filament lamp for illuminating the sample and detectors to measure scattered light.

5.1.2 Computer

5.1.3 Printer

5.2 Supplies

5.2.1 Sample cells - 30 mL capacity, item # 20849-00, Hach Co.

5.2.2 Pipettes - plastic, graduated and glass, class A, various sizes as needed.

5.2.3 Flasks - Volumetric, class A, 50 mL, 100 mL and 200 mL

5.2.4 Cylinder - plastic, graduated, various volumes as needed.

5.2.5 Gloves - Powder-free, nitrile, item #FF-700, Micro Flex.

5.2.6 Kimwipes - 14.7 x 16.6", item #34721, Kimberly-Clark.

5.2.7 Carboy - 2 $^{1}_{2}$gal, with spigot, item # 23210020, Nalgene.

5.2.8 Container - Plastic, for liquid waste, 1- or 2-liter size.

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Deionized water.

6.1.2 Hydrochloric acid, 6N - Fisher Scientific #LC15370-Z.

6.2 Standards

6.2.1 AMCO CLEAR Calibration Kit, for Hach 2100N/AN: 0, 20, 200, 1000, and 4000 NTU - Item # 85525, GFA Chemical or equivalent calibration kit. Use freshly poured portions for calibrating the turbidimeter and discard the used standards prior to each new calibration. Rinse with DI water and new standard before pouring fresh standards.

6.2.2 AMCO CLEAR Sealed Standards: 0.5, 1.0, 2.0, 5.0, 20, 50, 100, and 200 NTU - Item # 86180, 86443, 86534, 86492, 86122, 85385, 86124, and 86123 respectively, GFA Chemicals or equivalent standards. Read these standards at the beginning of each analytical run.

6.2.3 Quality Control Sample - ERA WatR Supply Turbidity or equivalent QC sample. Follow the manufacturer's directions.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in liter polyethylene cubitainers and refrigerated or iced to 4 ^{o}C until analysis to minimize microbiological decomposition of solids.

7.2 The holding time is 48 hours when preserved at 4 ^{o}C.

8.0 QUALITY CONTROL

8.1 Instrument Calibration

8.1.1 Primary standards (6.2.1) with concentrations ranging from 0 to 4000 NTU are used to calibrate the turbidimeter every two months.

8.1.2 Sealed secondary standards (6.2.2) with concentrations ranging from 0.5 to 200 NTU are analyzed before each day's run of samples. The instrument check is considered valid when each measured NTU value is within 90 - 110% of its true value. If the values do not fall within the acceptable range the instrument has to be recalibrated using the primary standards (6.2.1) or new standards should be ordered.

8.1.3 AMCO Clear standards are guaranteed to maintain the certified value for 1 year from ship date.

8.2 A mid-range check standard is analyzed after every ten samples and at the end of each run. If a check standard fails, the samples between the last satisfactory check standard and the unsatisfactory standard are re-analyzed.

8.3 Every tenth sample is analyzed in duplicate. The accepted value for the relative percent difference (RPD) is ± 10 %. If the reading does not fall within the accepted ranges, the corresponding analysis is repeated.

8.4 Deionized water is run at the beginning, after every ten samples, and at the end of the run. The accepted value for the blank is less than 0.07 NTU. Routine maintenance includes periodically clean sample cells. Also see Section 9.5.3.

8.5 A quality control sample is analyzed quarterly. Results are kept in a binder next to the instrument.

8.6 The U.S. EPA MDL40 procedures CFR Part 136, Appendix B) including the EPA *Definition and Procedure for the Determination of the Method Detection Limit*, Revision (2016); EPA *Methods Update Rule* (Final rule - August 28, 2017); EPA *Method Detection Limit - Frequent Questions*; and EPA Part 136 *Method Update Rule Revisions to Appendix B - MDL Procedure as Applied to Drinking Water* (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.

8.7 Data acceptance criteria are listed on the data review checklist (Appendix A).

9.0 PROCEDURE

9.1 Sample Cell Preparation

9.1.1 Clean the sample cells meticulously, both inside and out, and the caps.

9.1.2 Wash the sample cells with soap and rinse with deionized water.

9.1.3 After rinsing, immediately soak the sample cells in a 6N hydrochloric acid solution for a minimum of one hour.

9.1.4 After soaking, immediately rinse the sample cells with deionized water. Rinse a minimum of 15 times.

9.1.5 Immediately after rinsing the sample cells, cap the cells to prevent contamination from the air, and to prevent the inner cell walls from drying out.

9.1.6 Sample cells that are nicked or scratched must be replaced.

9.2 Index New Sample Cells

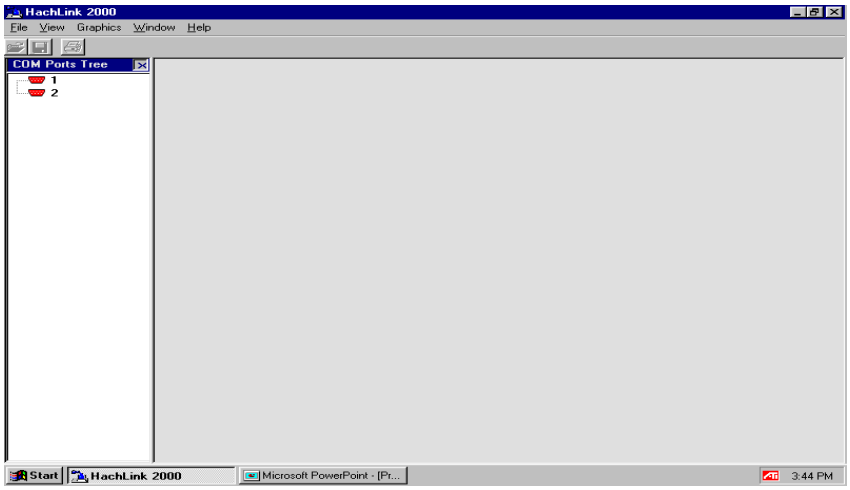
9.2.1 Fill clean sample cells with deionized water to the fill ring mark. Let samples stand for 30 seconds to allow bubbles to rise.

9.2.2 Measure the turbidity at several points of rotation, or as many points as needed, starting with placing the sample cell into the holder with the diamond mark at 6 o'clock position. Mark the orientation where the turbidity reading is the lowest. Use this orientation to perform all sample measurements.

9.2.3 Use the same indexed sample cell, if possible, to measure all the samples.

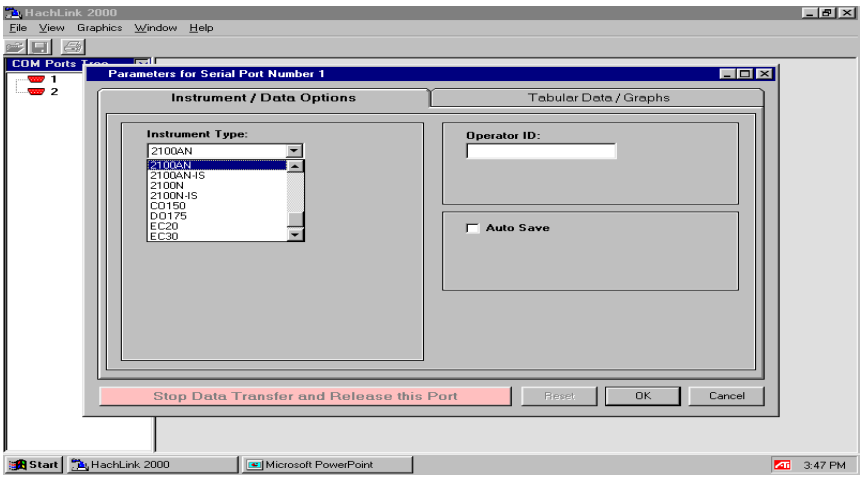
9.3 Instrument Start-up

9.3.1 Leave the turbidimeter on 24 hours a day if the instrument is used daily. Make sure "Ratio", "Sample" and "Signal Average" keys are in "ON" mode displayed by a green light. Maintain "Range" key in "Auto" mode. Select "NTU" from the "Units/Exit" key. Turn on the computer. Insert the disk marked as "Turbidity Data". Click on "Hachlink" on the desktop.

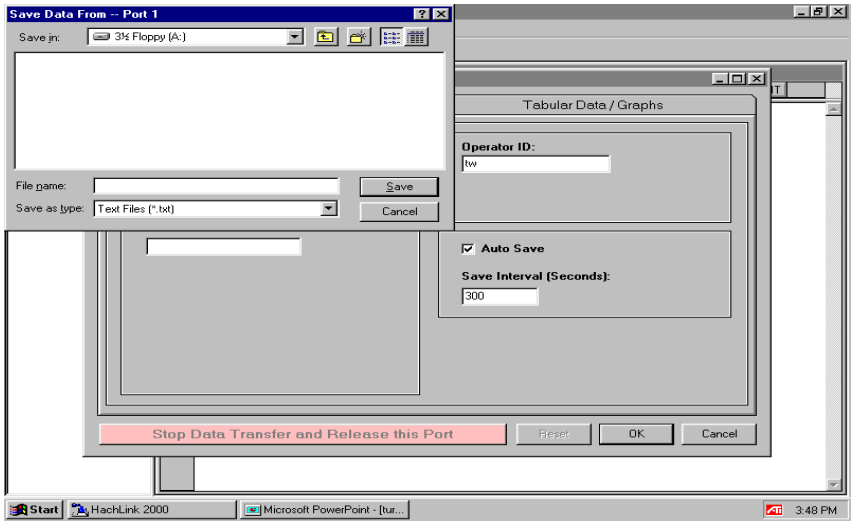


9.3.3 Select "COM Port 1" as the port type by clicking on "1".

9.3.4 Select "2100AN" from the pull-down menu of instrument types.

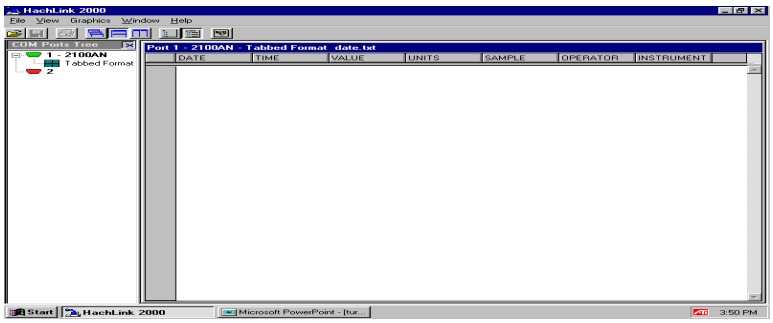


9.3.5 Enter operator I.D. and select "Auto Save".



9.4 Instrument Calibration

9.4.1 Select "Free Format" for calibration. Enter Date (Cal MM-DD-YY) as file name and click on "Save".



9.4.2 Press "Cal Zero". When 00 flashes in green the display; proceed. Do not shake or mix standards.

9.4.3 Place the "0" NTU standard into the cell holder, align the mark, then close the cell cover.

9.4.4 Press "Enter". The instrument display counts down from 60 to 0, and then makes a measurement.

9.4.5 The instrument automatically increments to the next standard, 01, as shown on screen in green display. Repeat steps 9.4.3 and 9.4.4 with the rest of the standards: 200, 1000 and 4000 NTU (When the instrument asks for 7500 NTU, press "Cal" to end it.)

9.4.6 Press "Cal Zero" again to store calibration information into memory. Press "Print". The instrument returns to the sample measurement mode.

9.4.7 Press "Cal" key to review Calibration Data. Use "L'" key to scroll through the standards. Press the "Print" key to print all of the calibration data in effect. Press the "Units Exit" key to return to the operating mode.

9.4.8 Read sealed secondary standards.

9.4.8.1 Follow step 9.3. Select "Tabled Format" for sample reading. Enter date as file name. Start with the deionized water as the blank. Thoroughly clean the outside of the sample cell and place it in the sample compartment. Close the sample holder cover.

9.4.8.2 Press "Enter", then press "Print" to save the reading.

9.4.8.3 Thoroughly clean each of the standard vials. Repeat steps 9.3.8.1 and 9.3.8.2 for all the standards: 0.5, 1.0, 2.0, 5.0, 20.0, 50.0, 100, and 200 NTU.

9.4.8.4 Press "Print". Keep the printouts in the binder marked "Instrument calibration data".

9.4.9 Check and fill the carboy with deionized water for rinsing the sample cell when performing sample measurements.

9.5 Sample Analysis

9.5.1 Prepare the list of samples for turbidity on the sample run log sheet (Appendix B) starting with blank, the daily check standards of 0.5, 1.0, 2.0, 5.0, 20, 50, 100, and 200 NTU, the deionized water, then enter each sample

number. Measure one replicate, one check standard and one blank for every ten samples. Read check standards again at the end of the run.

9.5.2 Follow step 9.3. Select "Tabled Format" for sample reading. Enter date as file name.

9.5.3 Fill the clean and dry glass cell with deionized water. Wipe dry, then insert the cell. If the reading is greater than 0.07 NTU, the cell should be cleaned with detergent and the process repeated. Press "Enter" to clear all previous data, and then press "Print" to transmit data to the computer and printer.

9.5.4 Place the 0.5 NTU sealed standard in the sample compartment. Close the cover. Press "Enter" and then press "Print".

9.5.5 Repeat for the rest of the standards.

9.5.6 Allow samples to reach room temperature to prevent fogging of the cell. Thoroughly mix the sample by gentle inversion. Do not shake. Quickly remove the cap and pour approximately 20 ml of sample into the cell for rinse. Immediately fill the cell with sample to volume line, wipe dry and insert into the turbidimeter. Align the index mark (9.2) on the cell with the raised mark on the spill ring around the cell holder opening. Be sure the cell has been pushed down completely and is held in place by the spring clip. Close the cover.

9.5.7 Wait for 30 seconds. Check the turbidity reading of the sample from the digital display. Press "Enter", then press "Print" to save the first Stable reading at approximately 15 seconds. If the turbidity reading fluctuates, take the cell out, invert to mix well and measure again. Observe the results in the display for accuracy.

9.5.8 Read the rest of the samples according to the run log sheet following step 9.5.6 and 9.5.7. Rinse the cell with deionized water, then rinse with some of the sample before each sample measurement.

9.5.9 For drinking water samples with turbidity exceeding 40 NTU, dilute the sample with turbidity-free water until turbidity falls below 40 NTU.

9.5.10 After reading all samples, double click the blank area outside the Table to go to "Microsoft Excel" Table. Enter all sample identifications according to the run log sheet into the sample column. Print out the results.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Calculate and report the average for the duplicated samples.

10.2 Multiply sample reading by the dilution factor to obtain the final result for diluted samples.

10.3 Calculate the relative percent difference for the duplicated samples as follows:

$$RPD = \frac{\text{differencebetweenthe duplicates}}{\text{average of the duplicates}} \times 100$$

10.3 All results are reported to one decimal place. The reporting level (RL) is 0.5 NTU. All sample concentrations below this value are recorded as less than 0.5 NTU (< 0.5 NTU).

11.0 DATA AND RECORDS MANAGEMENT

11.1 Normal turnaround time for samples submitted to this lab will be 2 to 10 days from receipt. Results are reported in writing on a sample analysis request form.

11.2 Instrument maintenance, instrument calibration, and quality control data are kept in binders and test results are kept in the file cabinet.

11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five-year custody period.

12.0 WASTE MANAGEMENT

12.1 It is the laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume and bench operation.

12.2 Samples and standards are poured down the drain while a large amount of water is running.

13.0 REFERENCES

13.1 United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes,* Method 180.1 Revision 2.0, August 1993.

13.2 Hach Company, *Model 2100AN Laboratory Turbidimeter Instruction Manual,* 1993.

13.3 Hach Company Technical Information Series - Booklet No. 11, *Turbidity Science,* 1998.

13.4 The American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* Method, 21thEdition, 2005.

13.5 Division of Environmental Chemistry, Maryland Department of Health and Mental Hygiene, *Quality Assurance Plan,* SOP No. CHEM-SOP-QAP

13.6 Division of Environmental Chemistry and Division of Microbiology, Maryland Department of Health and Mental Hygiene, *Quality Manual,* SOP No. QA-SOP-QM.

. 13.7 EPA *'Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. Dec 2016.*

APPENDIX A

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist - Turbidity

EPA Method 180.1

Lab Numbers:_____

Date Collected: _____ Date Analyzed:_____ Analyst: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	48 hours @ 4 ºC		
Instrument Calibration[2] (0 - 4000 NTU)	Every two months		
Daily Calibration Checks[3] (0 - 200 NTU)	Within 90 to 110% of true values		
Blank	< 0.07 NTU		
Check Standards	After every 10th sample and at the end of the run		
	Concentrations within 90 to 110% of the true values		
Duplicates/Replicates	Every 10th and the last sample or 1/batch of drinking water samples and 1/batch of wastewater samples, if less than 10 samples of each kind		
	RPD :: 10 %		
External QC[4] Every two months	Within acceptable range		
	Last date analyzed:		
Decimal places reported	1		
Reporting Level	0.5 NTU; concentrations below this value reported as < 0.5 NTU		
Measured Values	Within range of 0 to 40.0 NTU for drinking water and 0 to 4000 NTU for others		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

* Check (✓) if criteria are met.

_____ _____

Analyst's Signature & Date Reviewer's Signature & Date

Supervisor's Signature & Date

[1]Include beginning and ending numbers; account for gaps by bracketing.

[2]Sample Name: AMCO CLEARCalibration kit Tracking ID: _____

[3]Sample Name: AMCO CLEAR Standards Tracking ID: _____

Tracking ID:

[4]QC Sample:_____True Value = ____ _____

_____ Acceptable

Range =

APPENDIX B

Division of Environmental Sciences

INORGANICS ANALYTICAL LABORATORY

Sample Run Log - Turbidity

EPA Method 180.1

Analyst: _____

Sample #	Sample ID	Dilution	Conc. NTU
1	0.0 NTU		
2	0.5 NTU		
3	1.0 NTU		
4	2.0 NTU		
5	5.0 NTU		
6	10.0 NTU		
7	20.0 NTU		
8	50.0 NTU		
9	100 NTU		
10	200 NTU		
11	DI Water		
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			

Sample #	Sample ID	Dilution	Conc. NTU
31			
32			
33			
34			
35			
36			
37			

38			
39			
40			
41			
42			
43			
44			
45			
46			
47			
48			
49			
50			
51			
52			
53			
54			
55			
56			
57			
58			
59			
60			

Lab #	Average	RPD

QC Name	Prep Log ID

CONTROLLED DOCUMENT - Do Not Copy
DES-FORM-IAL-092 (05/22)

MDH - Laboratories Administration
DIVISION OF ENVIRONMENTAL SCIENCES

SOP Title:	Determination of Total Organic Carbon (Standard Method 5310 B)
SOP No.:	CHEM-SOP-SM 5310B
Revision:	4.2 Replaces: 4.1 Effective: 7/15/23
Laboratory:	Inorganics Analytical Laboratory
Author / POC:	Reza Hajarian Reza.hajarian@maryland.gov

Laboratory Supervisor:	Lara Phillips Signature	7/10/2023 Date
QA Officer:	Mohamed Habeeb Signature	07/11/23 Date
Manager:	Cynthia Stevenson Signature	7/12/2023 Date
Division Chief:	 Signature	07/12/2023 Date

STANDARD METHOD 5310 B
SOP No.: CHEM-SOP-SM5310B

REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	12/09	N/A	Taiyin Wei	1/10
1.0	8/11	New procedure section, new SOP tracking number	Reza Hajarian	8/11
2.0	9/12	Technical and editorial changes throughout the document	Reza Hajarian	9/12
3.0	11/14	Reviewed SOP-document control, editorial and technical changes	Reza Hajarian Lara Phillips Shahla Ameli	12/1/14
3.0	6/1/2015	Reviewed document and made changes to section 6.2	Reza Hajarian Lara Phillips Shahla Ameli	7/1/15
3.1	5/5/2016	Reviewed document and made formatting changes	Lara Phillips Reza Hajarian Shahla Ameli	7/1/16
3.2	6/1/17	Reviewed document, Organizational name changes, added 6.1.3, update 6.2.5, 8.2, 9.1.2 and checklist	Lara Phillips S. Ameli	7/1/17
4.0	6/4/18	Reviewed document, Updated sections 8.10,13.5, 13.6	Lara Phillips S. Ameli	7/1/18
4.0	3/1/19	Reviewed document	Lara Phillips S. Ameli	3/4/19
4.1	4/21/20	Reviewed document, edited for clarity.	Lara Phillips Reza Hajarian	5/1/20
4.1	4/9/21	Reviewed document	Lara Phillips C. Stevenson	5/1/21
4.2	5/27/22	Reviewed document, updated appendices, 6.2, 7.0	Lara Phillips Reza Hajarian	5/31/22
4.2	6/28/23	Reviewed document	L.Phillips, R.Hajarian	7/15/23

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STANDARD OPERATING PROCEDURES

DETERMINATION OF TOTAL ORGANIC CARBON

Standard Method 5310 B

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to drinking, surface and saline waters, domestic and industrial wastes and provides a speedy and convenient way of determining the degree of organic contamination.

1.2 The fraction of total organic carbon (TOC) that passes through a 0.45 µm pore diameter filter is defined as dissolved organic carbon (DOC).

1.3 The method is applicable to measurement of organic carbon above 0.5 mg/L

2.0 SUMMARY OF METHOD

Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion at 680 ºC. The carbon dioxide formed is purged from the sample, dried, and transferred with a carrier gas to a non-dispersive infrared gas analyzer (NDIR). The amount of carbon dioxide is directly proportional to the concentration of carbonaceous material in the sample.

3.0 INTERFERENCES

3.1 Carbonate and bicarbonate carbons represent interference under the terms of this test and must be removed or accounted for in the final calculation.

3.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a micro-liter type syringe. The opening of the syringe limits the maximum size of particles which may be included in the following measurements

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during reagent preparation and instrument operation. Use of gloves and eye protection is recommended when preparing solutions.

4.2 Each employee is issued a ***Laboratory Safety Manual*** and is responsible for adhering to the recommendations contained therein.

4.3 Each chemical should be regarded as a potential health hazard. A reference file of safety data sheets (SDS) is available in lab.

4.4 Gloves, lab coat, and protective eyewear must be used when removing the cover from the furnace and replacing the combustion tube.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Shimadzu TOC - V_{CPH} or TOC-$L_{CSH/CSN}$ Analyzer

5.1.2 Shimadzu ASI-V or ASI-L Autosampler

5.1.3 Computer

5.1.4 Printer

5.2 Supplies

5.2.1 Glass vials – 40 mL

5.2.2 Air – Compressed, ultra-zero, UN1002, GTS

5.2.3 Flasks – Volumetric, 200 mL, 1000 mL

5.2.4 Pipettes – Volumetric, 5 mL, 10 mL, 20 mL, 100 mL

5.2.5 Platinum Catalyst –Shimadzu Corp.

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Deionized water free from analyte of interest is used to prepare all the reagents and the standards to reduce the carbon concentration of the blank.

6.1.2 2N Hydrochloric Acid – Dilute 166 mL of concentrated Hydrochloric Acid to 1 liter with deionized water.

6.1.3 25% Phosphoric Acid-Diltute 250 mL Phosphoric Acid to 1000 mL with deionized water.

6.2 Standards

Sparge Check Solution, (TOC/TIC Standard) - To prepare this standard manually follow steps 6.2.1, 6.2.2 and 6.2.3 or purchase equivalent custom made standard.

6.2.1 Inorganic Carbon Stock Solution – Dissolve 4.41 g anhydrous Sodium Carbonate Na2CO3 in DI water then add 3.50 g Anhydrous Sodium Bicarbonate, NAHCO3. Dilute into a one liter volumetric flask and mix thoroughly. Prepare monthly and store in the refrigerator.

6.2.2 Organic Carbon Stock Solution – Dissolve 2.12 g Potassium Hydrogen Phthalate (KHP) in to a 1000 mL flask. Bring up to volume with DI water and mix well. Prepare monthly and store in the refrigerator.

6.2.3 TOC/TIC Standard – Add 100 mL DI water to a 500 mL volumetric flask. Add 5 mL of 6.2.1 and 5 mL of 6.2.2 to the flask. Mix well and bring up to volume. Prepare monthly and store in the refrigerator.

6.2.4 Potassium Hydrogen Phthalate (KHP) stock standard solution, 1000 ppm – Weigh and Stir to dissolve 2.125 g of KHP in about 800 mL of deionized water in a 1 L volumetric flask. Fill to the mark with deionized water. Mix thoroughly. Transfer to a reagent bottle, label, and store at 4ºC. Prepare monthly.

6.2.5 KHP working standard, 10 ppm, 20 ppm – Dilute 10 mL and 20 mL of KHP 1000 ppm stock solution to 1 liter in volumetric flasks respectively and mix thoroughly. Transfer to reagent bottles, label, and store at 4 ºC. Prepare weekly.

6.2.6 KHP working standards – Add 10.0 mL and 100 mL of the 10 ppm stock standard into two 200 mL volumetric flasks respectively. Dilute to mark with water and mix well. This makes working standards of 0.5 mg/L(MDL-ref) and 5.0, mg/L (check standard) respectively.

6.2.7 Calibration Standards- By using a vial filled with blank (0 ppm) and a vial of 20 ppm of KHP in the beginning of the tray (see Pg. 6), the instrument automatically prepares the standards of 0.5 ppm, 1ppm, 5ppm, and 10ppm of KHP that will be used for generating the calibration curve.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Refrigeration at 4º C prior to analysis is required to minimize microbiological decomposition of solids. The holding time is 48 hours for unacidified samples or 28 days if sample is acidified to pH<2 with HCl at the time of collection. Unacidified, filtered samples may also be stored at -20º C for 28 days.

8.0 QUALITY CONTROL

8.1 Reagent grade water is run as the blank control.

8.2 Replicates and spike are performed on every tenth sample with a minimum of one replicate and spike per run. Duplicated determinations should agree within 10% of their average.

8.3 Spike the sample by adding 100 µL of 1000 ppm stock solution into 20 mL of the sample. The acceptable spike recovery should be within 10% of the concentration added.

8.4 Quality control (QC) samples including check standard, spiked blank, and an external QC (An ERA QC with known expiration date, range and concentration is analyzed at the beginning and at the end of each run). Recoveries of check std, QC and blank spikes should be within 10% of its true value.

8.5 Instrument sparge check solution, TIC/TOC, is analyzed at the beginning of each run. A reading of 10 ppm of TOC indicates the sample had been properly acidified and inorganic carbon had been successively removed.

8.6 All the standards and samples are analyzed at least three times from each tube. The concentrations reported for the samples are the mean of the triplicates, calculated by the computer program.

8.7 Every tenth sample is duplicated (analyzed from two different tubes) and spiked. The accepted value for the relative percent difference (RPD) or spike recovery is ± 10 %.

8.8 Data acceptance criteria are listed on the Data Review Checklist (Appendix A).

8.9 The laboratory annually participates in ERA water supply (WS) and water pollution (WP) proficiency studies

8.10 The U.S. EPA MDL40 procedures CFR Part 136, Appendix B) including the EPA *Definition and Procedure for the Determination of the Method Detection Limit*, Revision (2016); EPA *Methods Update Rule* (Final rule - August 28, 2017); EPA *Method Detection Limit - Frequent Questions*; and EPA Part 136 *Method Update Rule Revisions to Appendix B – MDL Procedure as Applied to Drinking Water* (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and

revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.

9.0 PROCEDURE

9.1 Analysis Flow

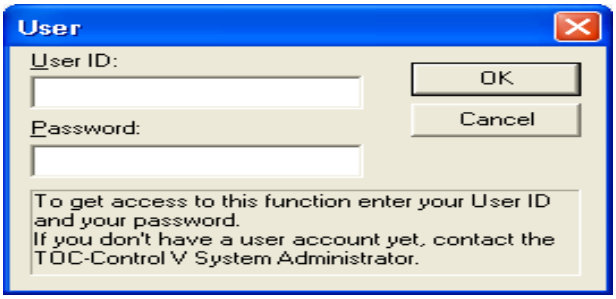
9.1.1 Checking the Dilution Water, Drain Vessel Water, and Humidifier water levels- Verify that water volumes are sufficient for analysis. If necessary, replenish water in all bottles.

9.1.2 Switch on TOC-V_{cph} or TOC-$L_{CSH/CSN}$ Analyzer.

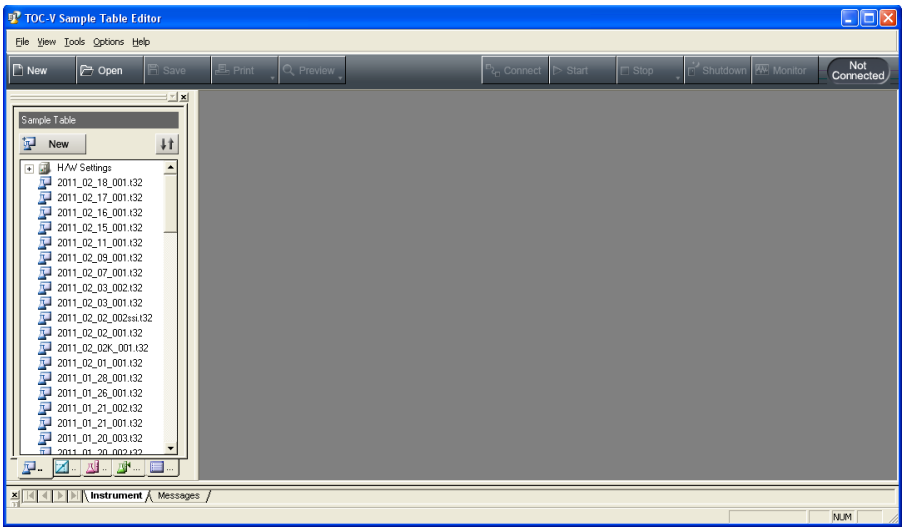
9.1.3 Turn on the computer.

9.1.4 Double click on TOC Sample Table Editor icon on the Monitor.

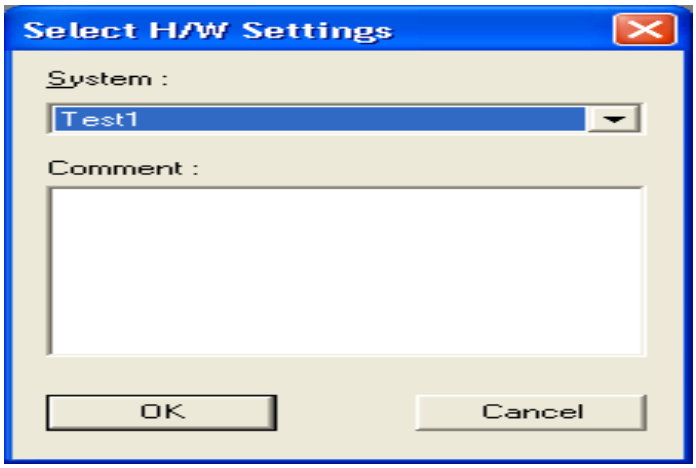
9.1.5 The "User" window is displayed.



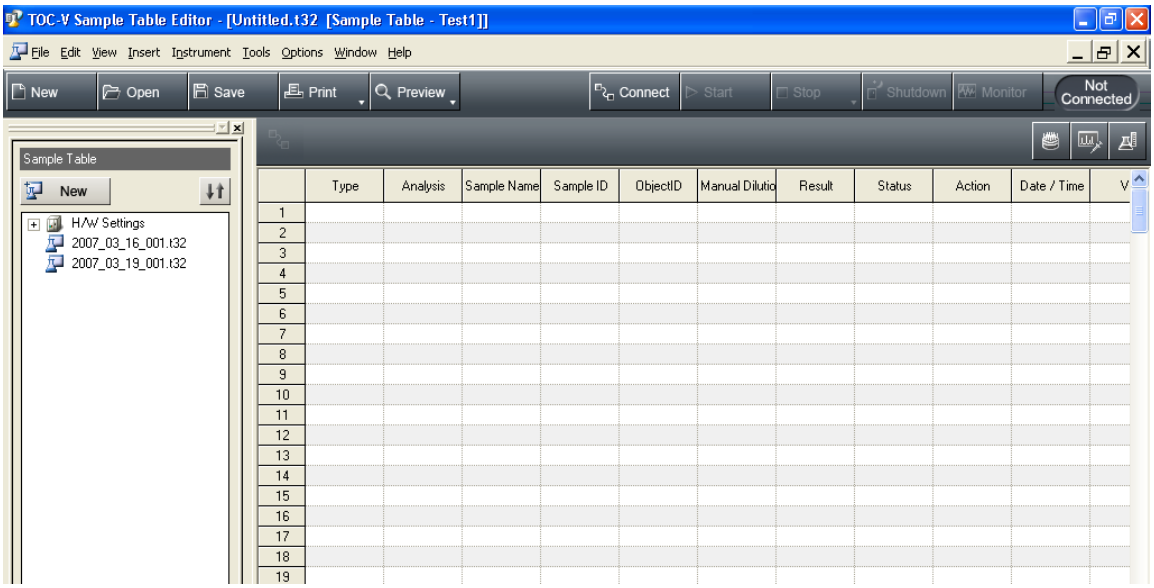
9.1.6 Click OK on the User. A TOC Sample Table Editor is opened.



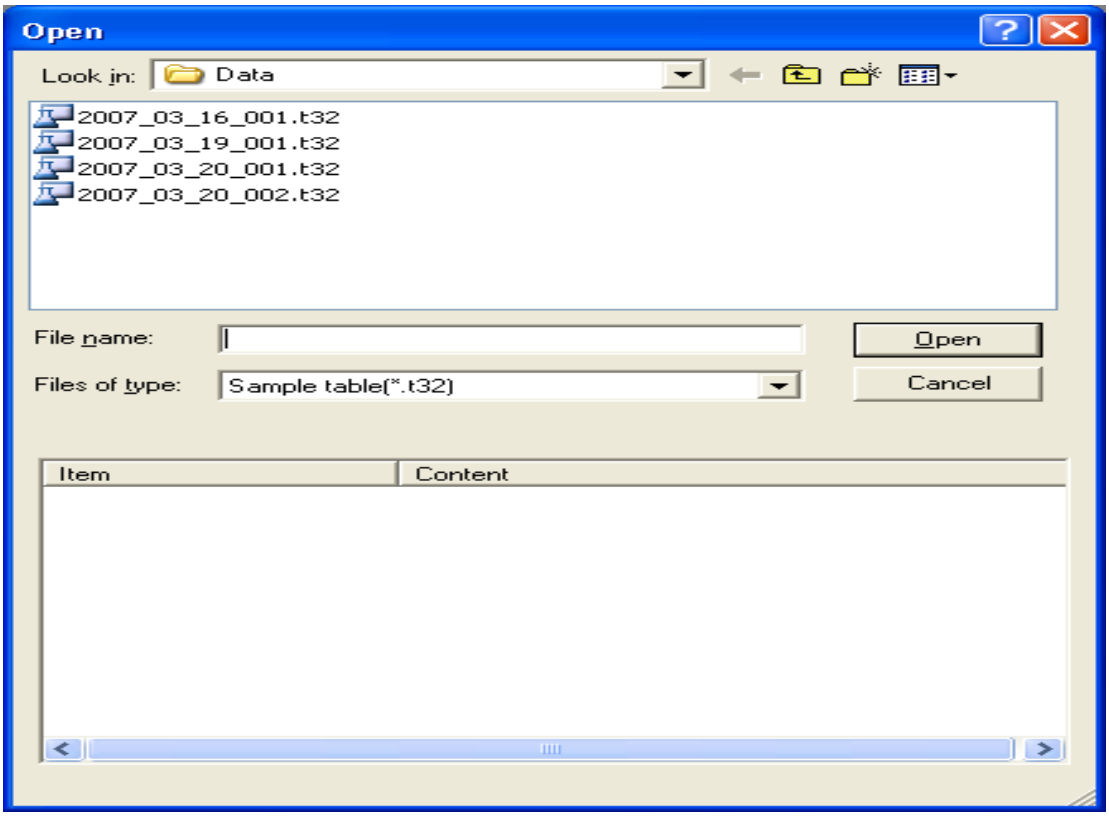
9.1.7 Click “New” on Sample Table Editor, The”Select H/W Settings” window is displayed



9.1.8 Click OK, an Untitled.t32 [sample table-TOC] is opened in the Sample Table Editor.

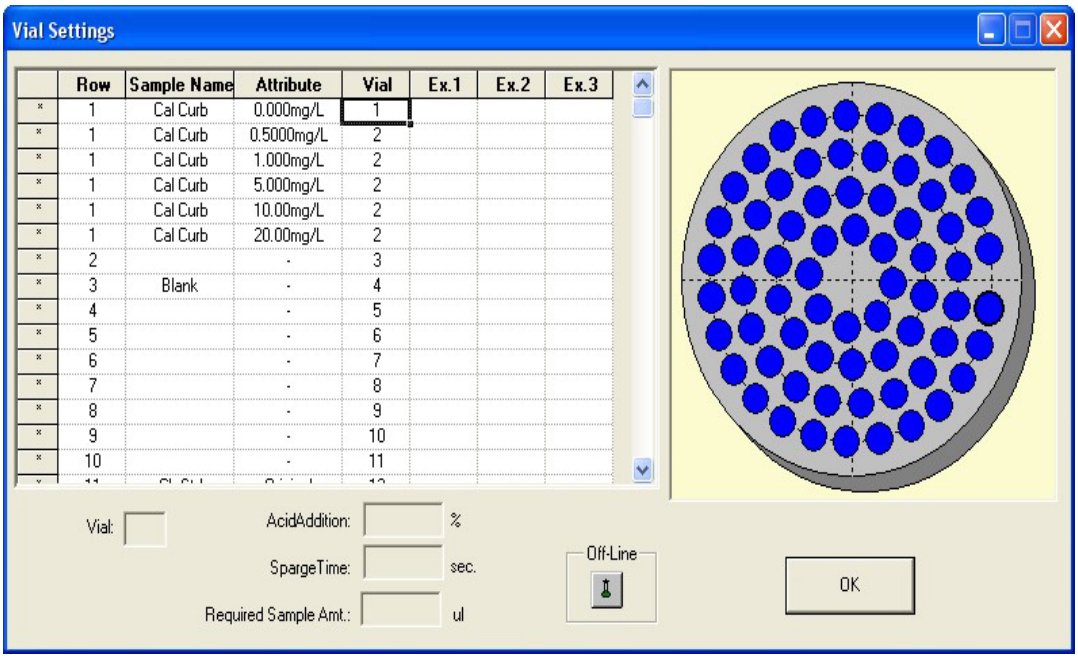


9.1.7 On TOC Sample Table Editor, select File, Import Schedule File in the menu Bar. The Open dialog is displayed.



9.1.8 Select the schedule file, and click Open. The schedule content is inserted into the sample table. It demonstrates calibration curve standards, quality control, check standard, blanks, etc.

9.1.9 To enter the vial numbers; enter a number in the sample ID column cell of sample table, click on the lower right part of the cell, and drag downward to enter a series of sample vial numbers all at once. Click on the first row of sample table, click Auto Sample icon, the Vial Setting dialog box is displayed. Select the cell where the last calibration standard is displayed and position the cursor precisely over the lower right corner of the selected cell until "+" is displayed. Click and drag. After all the samples viewed in vial setting, the vial numbers of the vials to be sampled in the ASI-V must be associated with the samples. Click OK in the lower left of "vial Settings."



9.2 Sample Loading

9.2.1 Place the blank vial in positions1 and the Calibration Standard 20ppm in position 2 of the turntable corresponding to the position specified in the ASI condition; i.e. vial 1-2. When automatic injection of acid is specified for NPOC measurement, the bottle containing 2N HCl must be placed next to analyzer.

9.2.2 Make a sample run list that starts with the 2 calibration check standards; a blank, the TIC/TOC check, and a QC, followed by sample names with

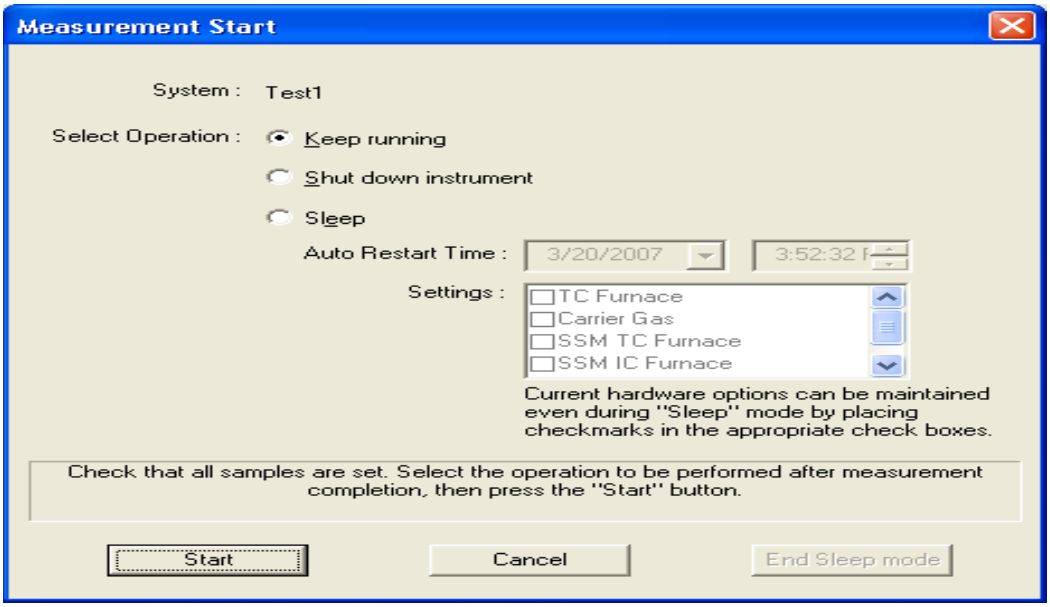
replicates and spikes for every ten samples. A blank, and a check standard are analyzed after every 10 samples. A blank, a check standard and a QC should also be included at the end of each run.

9.2.3 Load sample vials starting with position #1 on the turntable sequence as assigned in the sample worksheet.

9.2.4 The Sample Table must be connected to the connection instrument before analysis can be conducted. Click "Connect" either on the menu bar or click "Instrument-connect." The icon of the connected instrument and the "Ready" indicator in the Sample Table tab of the file viewer illuminate.

9.2.5 Check that the temperature is reaching 680 ºC and humidifier temperature is 1 ºC. Check the base line at range setting x1 and x50 for position, fluctuation, and noise

9.2.6 Starting the Instrument- Analysis can be started either by clicking "Start" of the menu bar or selecting "Instrument-Start Measurement". After clicking "Start", the "Measurement Start" window is displayed. Select the processing that will take place after analysis is complete. Finally, click the start icon at left corner of the Measurement Start window. Analysis starts. When measurement is complete, the results are displayed in the sample table, and analysis ends.



10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Standard curve of 0.0 ppm to 12.0 ppm is established daily and is used directly without shifting to origin assuming the TOC content in water used in preparing standard solution is small enough, with respect to the standard solution concentration, to ignore.

10.2 Calculate % of spike recovery of the laboratory fortified samples as follows

$$\%\,SR = \frac{\text{spiked sample conc. ppm - sample conc., ppm}}{\text{amount of spike added to sample, ppm}} \text{ x } 100$$

10.3 Calculate the % of relative percent difference for the duplicated samples as follows:

$$RPD = \frac{\text{difference of the duplicates}}{\text{average of the duplicates}} \text{ x } 100$$

11.0 DATA AND RECORDS MANAGEMENT

11.1 Instrument maintenance, instrument calibration, and quality control data are kept in binders and test results are kept in the file cabinet.

11.2 Normal turnaround time for samples submitted to this lab will be 2 to 10 days from receipt. Results are reported in writing on a sample analysis request form or through StarLims for drinking water samples.

11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five years custody period.

12.0 WASTE MANAGEMENT

12.1 Samples and standards are poured down the drain while flushing with large amount of cold water.

12.2 Actual reagent preparation volumes are to be reflected anticipated usage and reagent stability.

13.0 REFERENCES

13.1 United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Waste,* Methods 415, August 1993

13.2 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 21st Edition, 2005

13.3 Shimadzu Corporation, *Instrument Manual for Total Organic Carbon Analyzer Model TOC-5000*

13.4 Division of Environmental Sciences, Maryland Department of Health, *Quality Assurance Plan,* SOP No. CHEM-SOP-QAP

13.5 Division of Environmental Sciences, Maryland Department of Health, *Quality Manual,* SOP No. QA-SOP-QM

13.6 EPA *'Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. Dec 2016.*

APPENDIX **A**

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist – TOC/DOC

Standard Method 5310 B

Lab Numbers[1]:_____

Date Collected: _____ Date Analyzed: _____ Analyst: _____

Procedure	**Acceptance Criteria**	**Status***	**Comments**
Holding Time	48 hours @ 4 ºC 28 days @ – 20 ºC for filtered samples; 28 days @ 4 ºC for samples acidified to pH < 2 with HCl		
Calibration Curve	Corr. Coeff. ≥ 0.9950		
Sparge Check (TIC & TOC)	TOC = 9 – 11 ppm		
Reagent Blank	< Reporting level (0.50 mg/L)		
Matrix Spike	Every 10th and the last sample or 1/batch, if less than 10 samples		
	Recovery = 90 – 110%		
External QC	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the run		
	Concentration within 90 to 110% of the true value		
Duplicates/Replicates	Every 10th and the last sample or 1/batch, if less than 10 samples		
	RPD ≤ 10%		
Decimal Places Reported	2		
Measured Values	Within calibration range (0.50 to 20.00 ppm)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

* Check (√) if criteria are met. [1]Include beginning and ending numbers, account for gaps by bracketing.

_____ _____
Analyst's Signature & Date Reviewer's Signature & Date

_____
Supervisor's Signature & Date

Sparge Check: TIC & TOC Tracking ID: _____

QC Sample: _____ Tracking ID: _____

True Value = _____ Acceptable Range = _____

DES-FORM-IAL-081 (07/17)

APPENDIX **B**

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Sample Run Log –TOC/DOC-L

Standard Method 5310 B

Date: _____ Analyst: _____

Vial	Sample ID	Dil	Conc. (ppm)	Vial	Lab #	Dil	Conc. (ppm)	Vial	Sample ID	Dil	Conc. (ppm)
1	0 ppm		Cal. Std	27				53			
2	10 ppm		Cal. Std	28				54			
3	20 ppm		Cal. Std	29				55			
4	Blank			30				56			
5	Ex QC			31				57			
6	BLK QC			32				58			
7	TOC/TIC			33				59			
8	Blank			34				60			
9	BLK/SPK			35				61			
10	Blank			36				62			
11	MDL-Ref			37				63			
12	Blank			38				64			
13	CkStd 5ppm			39				65			
14	Blank			40				66			
15				41				67			
16				42				68			
17				43				69			
18				44				70			
19				45				71			
20				46				72			
21				47				73			
22				48				74			
23				49				75			
24				50				76			
25				51				77			
26				52				78			

Sample Name	Prep Log ID
KHP Stock Std 1000 ppm	
KHP Std 20 ppm	
KHP Std 10 ppm	
KHP Std 5 ppm	
KHP Std 0.5 ppm	
QC:	

Lab #	Average	%RPD	% Spk Rec

DES-FORM-IAL-111 (05/22)

APPENDIX **C**

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Sample Run Log –TOC/DOC-V

Standard Method 5310 B

Date: _____ Analyst: _____

Vial	Sample ID	Dil	Conc. (ppm)	Vial	Lab #	Dil	Conc. (ppm)	Vial	Sample ID	Dil	Conc. (ppm)
1	0 ppm		Cal. Std	27				53			
2	20 ppm		Cal. Std	28				54			
3	Blank			29				55			
4	BLK QC			30				56			
5	EX QC			31				57			
6	TOC/TIC			32				58			
7	Blank			33				59			
8	BLK/SPK			34				60			
9	Blank			35				61			
10	MDL-ref			36				62			
11	Blank			37				63			
12	CkStd 5ppm			38				64			
13	Blank			39				65			
14				40				66			
15				41				67			
16				42				68			
17				43				69			
18				44				70			
19				45				71			
20				46				72			
21				47				73			
22				48				74			
23				49				75			
24				50				76			
25				51				77			
26				52				78			

Sample Name	Prep Log ID
KHP Stock Std 1000 ppm	
KHP Std 20 ppm	
KHP Std 10 ppm	
KHP Std 5 ppm	
KHP Std 0.5 ppm	
QC:	

Lab #	Average	%RPD	% Spk Rec

MDH- Laboratories Administration
DIVISION OF ENVIRONMENTAL SCIENCES

SOP Title:	Determination of Orthophosphate- Low Level Flow Injection Colorimetric Analysis (EPA Method 365.1)
SOP No.:	CHEM-SOP-EPA 365.1
Revision:	4.2 Replaces: 4.1 Effective: 7/15/2023
Laboratory:	Inorganics Analytical Laboratory
Author / POC:	Jacob Kilczewski Jacob.kilczewski@maryland.gov

Laboratory Supervisor:	Lara Phillips Signature	7/11/2023 Date
QA Officer:	Mohamed Habeeb Signature	07/11/23 Date
Manager:	Cynthia Stevenson Signature	7/12/2023 Date
Division Chief:	 Signature	07/12/2023 Date

REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	6/3/2008	N/A	S. Ameli	6/2/2008
1.0	12/2009	Screen snapshots added to procedure, new Sample Run Log, tracking IDs for standards and reagents	S. Ameli	01/2010
2.0	08/2011	New SOP tracking number, technical and editorial changes	S. Ameli	8/18/2011
2.1	12/12/2012	Technical and editorial changes	C. Vares S. Ameli	12/12/2012
2.1	07/2013	Reviewed SOP	C. Stevenson S. Ameli	12/12/2012
3.0	11/19/2014	Formatting and document control changes	C. Stevenson R. Carpenter S. Ameli	12/01/2014
3.0	6/1/2015	Reviewed SOP	C. Stevenson	7/1/2015
3.1	5/5/2016	Reviewed and changes to 9.3.8	C. Vares S. Ameli C. Stevenson	7/1/2016
3.2	6/1/2017	Reviewed and made organizational name changes	C. Vares S. Ameli C. Stevenson	7/1/2017
4.0	6/13/2018	Reference new MDL requirements, 8.6	C. Vares S. Ameli C. Stevenson	7/1/2018
4.0	2/22/2019	Reference new MDL requirements, 8.6	C. Vares S. Ameli C. Stevenson	3/4/2019
4.1	4/17/2020	Reviewed and edited for clarity	I. Ji C. Stevenson	5/1/2020
4.2	3/19/2021	Reviewed SOP, Technical changes in section 10.1	I. Ji	5/1/2021
4.2	5/31/22	Reviewed SOP	I. Ji	5/31/2022
4.3	7/11/2023	Reviewed SOP, updated contact info, updated 9.1.2 and references	J.Kilczewski/L.Phillips	7/15/2023

TABLE OF CONTENTS

Standard Operating Procedure

Low Level Orthophosphate (Flow Injection Colorimetric Analysis)

EPA Method 365.1

1.0 SCOPE AND APPLICATION

1.1 This method determines orthophosphate (PO_4^{3-}) in drinking, ground, surface, domestic waters and industrial waste.

1.2 The applicable range of this method is 0.004 to 0.250 mg P/L.

2.0 SUMMARY OF METHOD

The orthophosphate ion (PO_4^{3-}) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex which is further reduced by ascorbic acid to form a blue complex, which absorbs light at 880 nm. The absorbance is directly proportional to the concentration of orthophosphate present in the sample.

3.0 INTERFERENCES

3.1 Silica forms a pale blue complex, which also absorbs at 880 nm. This interference is insignificant on the silica concentration of 1 mg SiO_2/L. If the silicate concentration is higher than 1 ppm, the sample result will not be reliable within the calibration range of the method.

3.2 Concentrations of ferric iron (Fe^{3+}) greater than 50 mg/L will cause a negative error due to precipitation of and subsequent loss of orthophosphate.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that can bias analyte response especially in low level detection of OP. To eliminate this problem wash glassware with 1:1 HCl and rinse with DI water.

4.0 HEALTH AND SAFETY

4.1 Accepted laboratory safety practices should be followed during reagent preparation and instrument operation. The use of a fume hood, protective eyewear, lab coat and proper gloves is required when preparing reagents.

4.2 The following chemical has the potential to be highly toxic or hazardous.

4.2.1 Sulfuric Acid

4.3 A reference file of Safety Data Sheets (SDS) is available to all personnel involved in the chemical analysis.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat Quick Chem FIA 8500 series.

5.1.1.1 XYZ Auto sampler ASX-520 series with sample, standard and dilution racks

5.1.1.2 Manifold or reaction unit

5.1.1.3 Multichannel Reagent Pump RP-100 series

5.1.1.4 Colorimetric Detector

5.1.1.4.1 Flowcell, 10 mm, 80uL, glass flow cell

5.1.1.4.2 880 nm interference filter

5.1.1.5 Computer, monitor, printer and The Flow Solution software.

5.2 Supplies

5.2.1 13x100 mm test tubes, Fisher # 14-961-27

5.2.2 16x125 mm test tubes, Fisher # 14-961-30

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Stock Ammonium Molybdate Solution- In a 1 L volumetric flask, dissolve 40.0 g ammonium molybdate tetrahydrate [$(NH_4)6Mo7O_{24}.4H_2O$] in approximately 800 ml DI water. Dilute to the mark and let stir for 4 hours. Store in a plastic container and refrigerate. May be stored up to two months when kept refrigerated.

6.1.2 Stock Antimony Potassium Tartrate Solution- In a 1 L volumetric flask, dissolve **3.22 g antimony potassium tartrate Trihydrate $K(SbO)C_4H_4O_6.3H_2O$)** or dissolve **3.0 g antimony potassium tartrate hemihydrate $K(SbO)C_4H_4O_6.1/2H_2O$),** in approximately 800 ml DI water. Dilute to the mark and let stir for few minutes. Store in a dark bottle and refrigerate. This stock may be used up to two months when kept refrigerated.

6.1.3 Molybdate color Reagent. 1 L– Add carefully, while mixing, 35 ml sulfuric acid to about 500 ml DI water. When the temperature is cool add 72.0 mL Stock Antimony potassium Tartrate and 213 mL Stock Ammonium Molybdate Solution. Dilute to the mark and mix well by inverting. Store in dark bottle. Degas with helium for 1 minute. Prepare fresh weekly. A prepared reagent can also be purchased from HACH Company, catalog number 52002.

6.1.4 Ascorbic Acid Reducing Solution, 0.33 M– In a 1 L volumetric flask, dissolve 60.0 g granular ascorbic acid in about 700 ml DI water. Bring to volume and invert to mix. Add 1.0 g dodecyl sulfate (CH_3 $(CH_2)_{11}OSO$ 3Na). Use degassed water to prepare this reagent. Prepare fresh weekly. Discard if the solution becomes yellow.

6.1.5 Sodium Hydroxide – EDTA Rinse - Dissolve 65 g sodium hydroxide (NaOH) and 6 g tetrasodium Ethylenediamine tetraacetic acid (Na4EDTA) in 1.0L DI water. Used for cleaning OP manifold lines.

6.1.6 Carrier – Use DI water for carrier degassed for one minute. Container for carrier should be acid washed with 6M HCl before each use.

6.2 Standards

6.2.1 Orthophosphate Stock Standard (1000 mg P/L) - This standard is pre-made and purchased from RICCA CHEMICALS (cat. no. 5839.1-16). If this stock standard is not available, prepare by dissolving 4.396 g of primary standard grade anhydrous potassium phosphate monobasic (KH2PO4) that has been dried in the oven for one hour at 105 º C in about 500 ml of DI water. Bring up to 1000 mL mark with DI water and store at 4º C. Prepare this standard monthly.

6.2.2 Intermediate Standard (50 mg P/L) - Pipette 5 ml of standard 6.2.1 into a 100 ml volumetric flask. Bring up to mark with DI water. Store at 4º C. Make weekly.

6.2.3 Spiking Solution (50 mg P/L) - This is the same as the intermediate standard, which is used to spike the samples. Pipette 30 µL of the spiking solution (standard 6.2.2) into 10 mL of DI water or 10 mL of sample, in order to make the blank spike and sample spike. The concentration value for spiking solution is 0.15 mg/L.

6.2.4 Working Standards - The working standards are prepared according to the following table every 48 hours:

Orthophosphate ppm	Combined Intermediate Std	Final Volume
0.000	DI water	100 ml
0.004	2.67 ml of std 0.150 ppm	100 ml
0.010	20 mL of std 0.050 ppm	100 ml
0.050	100 µL	100 ml
0.100	200 µL	100 ml
0.150	600 µL	200 ml
0.200	400 µL	100 ml
0.250	500 µL	100 ml

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in clean plastic or glass bottles.

7.2 Never use acid preservation for samples to be analyzed for LL/HL OP.

7.3 Samples to be analyzed for Orthophosphate only are cooled to 4ºC and analyzed within 48 hours. For short-term preservation freeze at –20ºC for not more than 28 days.

8.0 QUALITY CONTROL

8.1 An initial Demonstration of Performance (IDP) to establish the instrument's capability is required prior to its use in analyzing client's samples. The linearity of calibration range (LCR) and the ability to quantify the Quality Control Samples correctly are used to assess the performance.

8.2 A demonstration of capability study is performed by each analyst performing the test by analyzing four replicates of an external quality control sample during one or two analytical runs.

8.3 Immediately following daily calibration, a mid-range check standard and a calibration blank is analyzed, also after every ten samples (or more frequently, if required) and at the end of run. If a check standard fails, the samples between the last satisfactory check standard and the unsatisfactory standard are re-analyzed.

8.4 Every tenth sample is duplicated (analyzed from two different tubes) and spiked. The accepted value for the relative Percent Difference (RPD) or spike recovery is

± 10 %. If these do not fall within the accepted ranges, the corresponding analyses are repeated.

8.5 A known QC sample for Orthophosphate is run in the beginning and at the end of each run.

8.6 The U.S. EPA MDL procedures (40 CFR Part 136, Appendix B) including the EPA *Definition and Procedure for the Determination of the Method Detection Limit*, Revision 2 (2016); EPA *Methods Update Rule* (Final rule - August 28, 2017); EPA *Method Detection Limit - Frequent Questions*; and EPA Part 136 *Method Update Rule Revisions to Appendix B – MDL Procedure as Applied to Drinking Water* (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.

8.7 All the standards are run in duplicates: that is, two analyses from each tube. A linear calibration is performed daily before the sample run.

9.0 PROCEDURE

9.1 Sample preparation

9.1.1 Prepare a list of samples to be analyzed.

9.1.2 Spike every tenth sample by adding 30 uL of 50 ppm P/L (Intermediate Standard) into 10 mL DI water or 10 mL of sample.

9.1.3 Filter the turbid samples by inserting the Sera Filter inside a 16 X 125 mm test tubes containing the sample. Press the filter down and pour the filtered sample collected in the top into a 13 x 100 mm test tube for analysis.

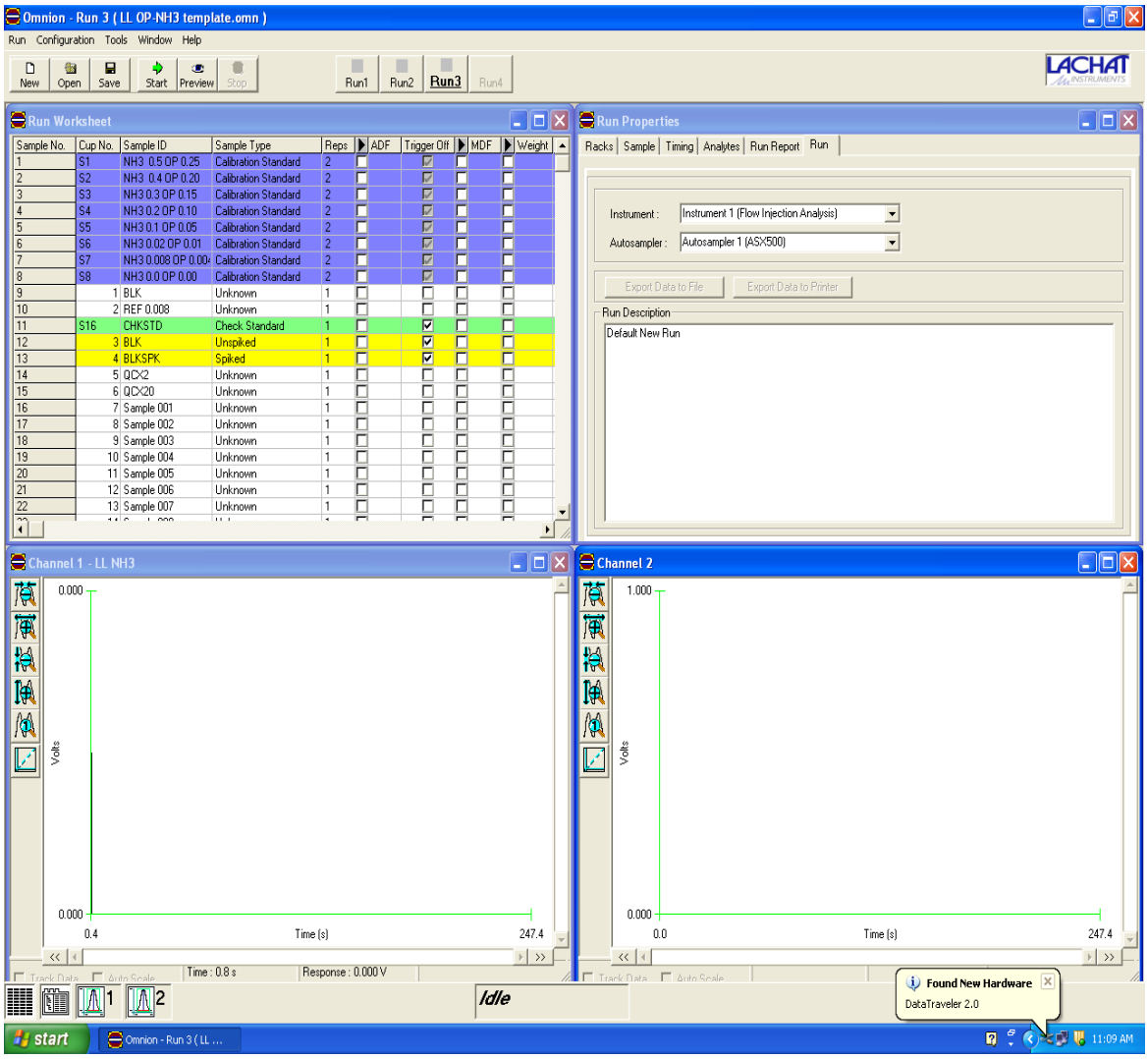
9.1.2 To prevent bubble formation, degas all most reagents, except those specified by the method (6.1.4) Ascorbic Acid Reducing Solution , with helium for 1 minute.

9.2 Instrument set-up and sample analysis

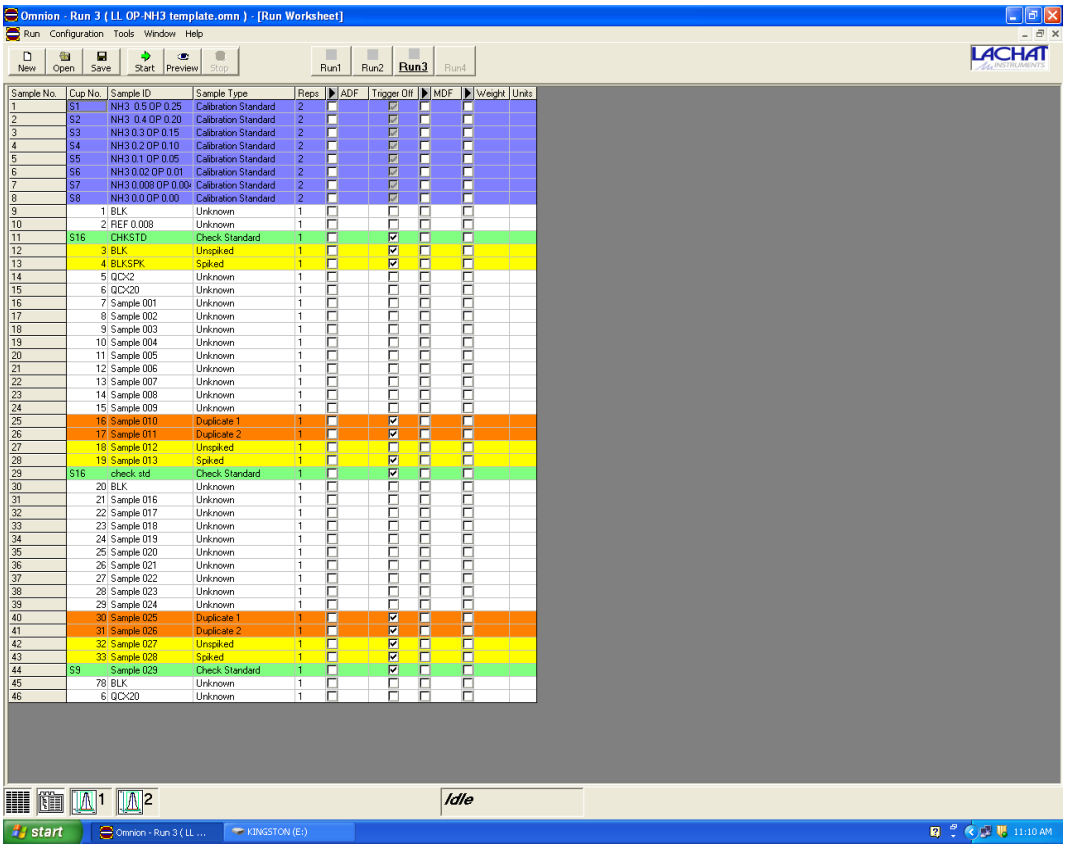
9.2.1 Set up manifold as in the diagram.

9.2.2 Turn on the Lachat instrument, computer, monitor, and printer.

9.2.3 Double click on **"LL OP/NH3"** to open the template, which consists of four windows. Samples are analyzed consecutively for orthophosphate and ammonia on the same system.



9.2.4 Maximize the **"Run Worksheet"** window at the top left hand corner of the screen by clicking on the middle square on that screen to open the worksheet template. Enter sample identifications in the sample ID column, making sure that all duplicates and spikes are entered in the appropriate locations of the worksheet. Identifications of the quality control samples analyzed at the beginning of the run and the locations of the duplicates and the spiked have been saved on the template. Press **"Enter"** key after each entry in order to save all entries.

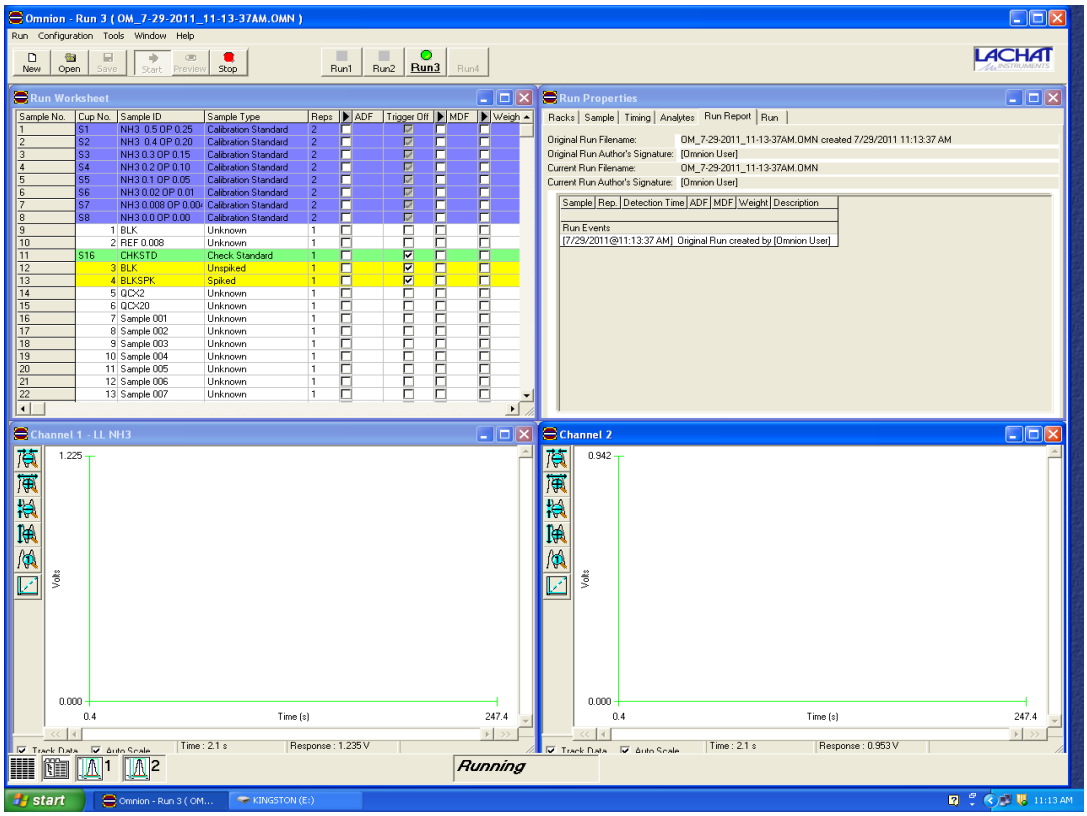


9.2.5 Print a copy of this worksheet by first double clicking on **"Run"** icon and then selecting **"Export Worksheet Data"**.

9.2.6 Click on **"Window"** tab and then, click on **"Tile"** to return to the screen with three windows.

9.2.7 Place standards in standard vials in the standard rack in order of decreasing concentration in positions S1 to S8 (position S8 is DI water-0.00 mg/L). Place the check standard vial in position 16 (S16) of the standard rack. Pour samples and quality control samples into 13 x 100 mm test tubes and place them in the sample racks according to the worksheet prepared in 9.2.4.

9.2.8 Pump deionized water through all reagent lines and check for leaks and smooth flow. Switch to reagents in the following order: 1. Ascorbic Acid, 2. Color Reagent. Continue pumping for about 10 minutes. Click on **"Preview"** tab to monitor the baseline.



9.2.9 Once a stable baseline is achieved, click on **"Stop"** tab to stop monitoring the baseline. Click on **"Start"** tab to begin the analysis.

9.2.10 If the calibration passes, instrument will continue to analyze the samples. If it fails, take appropriate corrective actions and recalibrate before proceeding to analyze samples.

9.2.11 Manual dilution will be performed to reanalyze samples with concentration exceeding the calibrated range.

9.2.12 After the run is complete, remove first the Color Reagent line and then the Ascorbic Reagent line placing them in DI water and rinsing for about 15 minutes. If necessary, rinse the OP reagent lines with the NaOH – EDTA rinse solution (6.1.5) for about 5 minutes followed by DI water for 10 – 15 minutes. Pump the tubes dry, release the pump tubing, and turn off the pump.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All the calculations are performed by the Omnion 3.0 software system. It uses a calibration graph of peak area versus concentration to calculate the phosphorus concentrations in the samples. All standards are analyzed in duplicate, and these points are used to generate the calibration curve. A duplicate peak may be excluded from the calibration if it is determined to be faulty (i.e. corrupted, damaged, misshapen) Samples with phosphorus concentrations greater than 0.250 ppm are manually diluted and reanalyzed.

10.2 Calculate the percentage spike recovery of the laboratory fortified samples as follows:

$$\% \text{ SR} = \frac{(\text{spiked sample conc.} - \text{sample conc.}), \text{ppm}}{\text{amount of spike added to sample, ppm}} \text{ x } 100$$

10.3 Calculate the relative percentage difference for the duplicated samples as follows:

$$\% \text{ RPD} = \frac{\text{difference between the duplicates}}{\text{average of the duplicates}} \text{ x } 100$$

11.0 DATA AND RECORDS MANAGEMENT

11.1 Completed data packages are scanned and stored electronically before being placed in the appropriate binders in the lab.

11.2 Report only those results that fall between the lowest and the highest Calibration standards. Samples exceeding the highest standard are manually diluted and reanalyzed.

11.3 Sample results for OP are reported in mg P/L. Report results to three decimal places. Report results below the lowest calibration standard as <0.004. For the Chesapeake Bay Program, only report all calculated results with the "L" sign for concentrations less than that of the lowest Standard.

12.0 WASTE MANAGEMENT

12.1 It is laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land buy minimizing and controlling all releases from fume and bench operation.

12.2 Samples and standards are poured down the drain while large amount of water is running. For more information consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society's

Department of Government Regulations and Science Policy, 1155 Street N. W., Washington D. C. 20036, (202) 872-4477.

13.0 REFERENCES

13.1 EPA Method 365.1, *Methods for the Determination of Inorganic Substances in Environmental Samples*, August 1993.

13.2 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 21st Edition, Method 4500- P E, 2005.

13.3 *Lachat Instruments QuickChem Method 10 – 115 – 01 – 1 – M,* Determination of Orthophosphate by Flow Injection Analysis.

13.4 Lachat Instruments, *Operating Manual for the Quikchem Automated Ion Analyzer*.

13.5 Division of Environmental Sciences, Maryland Department of Health, *Quality Assurance Plan*, SOP No. Chem-SOP-QAP.

13.6 Division of Environmental Sciences, Maryland Department of Health, *Quality Manual,* SOP No. QA-SOP-QM.

13.7 EPA Definition *and Procedure for the Determination of the Method Detection Limit, Revision 2* December 2016

APPENDIX A

Division of Environmental Sciences

INORGANICS ANALYTICAL LABORATORY

Data Review Checklist LL Orthophosphate

EPA Method 365.1

LabNumbers[1]:_____

Date Collected: _____ Date Analyzed: _____Analyst: _____

Procedure	Acceptance Criteria	Status (✓)	Comments
Holding Time	48 hours @ 4ºC/ 28 days @ –20ºC		
Calibration Curve	Corr. Coefficient. ≥ 0.9950		
Reagent Blank	< Reporting level (0.004 ppm)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10 samples		
	Recovery = 90–110%		
External QC	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the run		
	Concentration = 90–110% of the true value		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RPD ≤ 10%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.004–0.250 ppm)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

[1]Include beginning and ending numbers, account for gaps by bracketing.

_____ _____

Analyst's Signature & Date Reviewer's Signature & Date

_____

Supervisor's Signature & Date

Reagents	ID
Color Reagent	
Ascorbic Acid	

External QC

Identification = _____

True Value = _____ ppm

Range = _____ ppm

APPENDIX B

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist LL Orthophosphate/ LL Ammonia

EPA Method 365.1/ EPA Method 350.1

Lab Numbers: [1] _____

_____ Analyst: _____

Dates Collected: _____ Date Analyzed: _____

Procedure	**Acceptance Criteria**	**Status(✓)**	**Comments**
Holding Time	48 hours @ 4ºC; 28 days @ –20ºC		
Calibration Curve	Corr. Coeff. $\geq$ 0.9950		
Reagent Blank	< Reporting Level (0.004 ppm for OP; 0.008 ppm for NH_3)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10		
	Recovery = 90–110%		
External QC	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the		
	Concentration = 90–110% of the true value		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10		
	RPD ≤ 10%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.004–0.250 ppm for OP; 0.008–0.500 ppm for NH_3)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

[1]Include beginning and ending numbers, account for gaps by bracketing.

_____ _____
Analyst's Signature & Date Reviewer's Signature & Date

_____
Supervisor's Signature and Date

NH_3 Reagents	ID	OP Reagents	ID
Sodium Phenolate		Color Reagent	
Sodium Nitroprusside		Ascorbic Acid	
Sodium Hypochlorite			
EDTA Buffer			

External QC

Identification = _____

True Value = NH_3 _____ /OP _____ ppm

NH_3 Range = _____ ppm

OP Range = _____ ppm

MDH- Laboratories Administration
DIVISION OF ENVIRONMENTAL SCIENCES

Title: Determination of Nitrate/Nitrite and Nitrite (Low Level) Flow Injection Colorimetric Analysis *(EPA Method 353.2)*

SOP No.: CHEM-SOP - EPA METHOD 353.2

Revision: 4.3 Replaces: 4.2 Effective: 7/15/2023

Laboratory: Inorganics Analytical Laboratory

POC: Jewel Freeman-Scott
jewel.freeman-scott@maryland.gov

Laboratory Supervisor:	Lara Phillips Signature	7/10/2023 Date
QA Officer:	Mohamed Habeeb Signature	07/11/23 Date
Manager:	Cynthia Stevenson Signature	7/12/2023 Date
Division Chief:	 Signature	07/12/2023 Date

REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	6/3/2008	N/A	S.Ameli	6/2/2008
1.0	12/2009	Screen snapshots added to procedure, new Sample Run Log, tracking IDs for standards and reagents	S.Ameli	01/2010
2.0	08/2011	New SOP tracking number, editorial and technical changes	S.Ameli	8/18/2011
2.1	12/10/2012	Check list correction, addition to section 9.0	S.Ameli	12/10/2012
2.2	07/2013	Reviewed SOP	C. Stevenson S.Ameli	12/10/2013
3.0	10/2014	New SOP tracking number, editorial changes	C. Stevenson R. Carpenter S.Ameli	12/10/2014
3.0	6/1/2015	Reviewed SOP	C. Stevenson R. Carpenter S.Ameli	7/1/2015
3.1	5/5/2016	Reviewed SOP, formatting changes	C. Stevenson R. Carpenter S.Ameli	7/1/2016
3.2	6/1/2017	Reviewed and made organizational name changes	C. Stevenson S. Ameli R. Carpenter	7/1/2017
4.0	6/13/2018	Reference new MDL requirements, 8.7	C. Stevenson S. Ameli R. Carpenter	7/1/2018
4.0	2/22/2019	Reviewed SOP	S. Ameli R. Carpenter	3/4/2019
4.1	4/17/2020	Reviewed and edited for clarity.	J Freeman-Scott C. Stevenson	5/1/2020
4.2	3/19/2021	Reviewed SOP, Technical changes in section 10.1	J Freeman-Scott I. Ji	5/1/2021
4.3	4/29/2022	Reviewed SOP, Correction in 6.1.2 and 8.5	J Freeman-Scott I. Ji	5/31/2022
4.3	6/28/23	Reviewed SOP	L. Phillips	7/15/2023

TABLE OF CONTENTS

STANDARD OPERATING PROCEDURES

Nitrate/Nitrite and Nitrite (Low Level) Flow Injection Colorimetric Analysis

EPA Method 353.2

1.0 SCOPE AND APPLICATION

1.1 This method determines nitrite, or nitrate/nitrate in drinking, ground, surface, domestic waters and industrial waste.

1.2 The range of this method is from 0.020 mg/L to 4.00 mg/L for nitrate-nitrite and 0.002 mg/L to 0.400 mg/L for nitrite.

1.3 Nitrate is found only in small amounts in domestic wastewater, but in the effluent of nitrifying biological treatments nitrate may be found in concentrations up to 30 mg/L.

2.0 SUMMARY OF METHOD

Nitrate is reduced quantitatively to nitrite by passage through a copperized cadmium column. The reduced nitrate plus original nitrite is further determined by coupling with N-(naphthyl) ethylenediamine dihydrochloride. The dye produced has magenta color and is read at 520 nm, and is directly proportional to the concentration of analyte. Determination of nitrite takes place through the same procedure as Nitrate-Nitrite without a cadmium column.

3.0 INTERFERENCES

3.1 Interference from iron, copper or other metals is eliminated by addition of EDTA to the ammonium chloride buffer.

3.2 Suspended matter in the column will restrict sample flow. Remove suspended solids by filtration.

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

4.0 HEALTH AND SAFETY

4.1 Accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Use of lab coats, fume hoods, gloves and eye protection are required.

4.2 The following chemicals have the potential to be highly toxic or hazardous.

4.2.1 Cadmium

4.2.2 Phosphoric acid

4.2.3 Hydrochloric acid

4.2.4 Sodium Hydroxide

4.3 A reference file of Safety Data Sheets (SDS) is available to all personnel involved in the chemical analysis.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat QuickChem 8500 Automated Ion Analyzer, which includes the following:

5.1.1.1 Automatic sampler

5.1.1.2 Multi-channel proportioning pump

5.1.1.3 Injection module with a 12.5 cm x 0.5 mm ID sample loop

5.1.1.4 Manifold

5.1.1.5 Colorimetric detector

5.1.1.5.1 Flow cell, 10 mm path length

5.1.1.5.2 Interference filter, 520 nm

5.1.1.6 Computer with Omnion 3.0 Data system and printer

5.1.2 Analytical balance capable of weighing to the nearest 0.0001 g

5.1.3 Top loading balance for weighing chemicals for reagents

5.2 Supplies

5.2.1 Class A volumetric flasks, 50 - 1,000 mL

5.2.2 Class A volumetric pipettes, 1 - 10 mL

5.2.3 Automatic pipetters, 100 µL - 10 mL

5.2.4 Beakers, disposable, polypropylene, 50 mL (Fisher 01-291-10)

5.2.5 Test tubes, glass, 13 x 100 mm and 16 x 125 mm

5.2.6 Reagent storage bottles, plastic or glass

5.2.7 Cadmium Reduction Column (Lachat Part No. 50237A)

5.2.8 Ultra High Purity Helium gas for degassing

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Ammonium Chloride buffer, pH 8.5, 2 L - Dissolve 170 g of NH_4Cl and 2.0 g of disodium ETDA ($Na_2EDTA_2H_2O$) in about 1600 mL DI water in a 2 L beaker. Mix using a stir bar. Adjust the pH to 8.5 with 15 N sodium hydroxide solution and bring up to volume. Use filter paper to remove all the small particles from the reagent and refrigerate. Prepare monthly.

6.1.2 Sulfanilamide color Reagent, 1 L - Add carefully, while mixing, 100 mL 85% phosphoric acid (H_3PO_4) to 700 mL DI water in a 1 L volumetric flask. Add 40 g sulfanilamide and 1g N-1-naphthyl ethylenediamine dihydrochloride (NED) and stir to dissolve. Bring up to 1 L with DI water. Filter, store in amber bottle and refrigerate. This solution is stable for one month.

6.1.3 15 N Sodium Hydroxide - Add 150 g NaOH very slowly to 180 mL DI water in a 250 mL volumetric flask. (Caution: the solution will get very hot.) Mix until dissolved. Cool and store in a *plastic* bottle.

6.1.4 Carrier is degassed deionized water.

6.2 Standards

6.2.1 Nitrate Stock Standard (1000 mg/L of nitrate nitrogen) - Purchased from approved commercial supplier with expiration date. If this standard is not available, then weigh 0.7218 g of dried potassium nitrate KNO_3 (1000 mg/ L of nitrate nitrogen) in 100 mL volumetric flask. Prepare monthly.

6.2.2 Nitrite Stock Standard (1000 mg/L of nitrite nitrogen) - Purchased from approved commercial supplier with expiration date. If this standard is not available, then weigh 0.6072 g of dried potassium nitrite KNO_2 (1000 mg/L of nitrite nitrogen) in 100 mL volumetric flask. Prepare weekly.

6.2.3 Combined Intermediate Standard, 90 mg/L nitrate nitrogen and 10 mg/L nitrite nitrogen - Pipette 9 mL of standard 6.2.1 and 1 mL of standard 6.2.2 into about 70 mL DI water in a 100 mL volumetric flask. Bring up to

volume with DI water, mix, and store at 4 ºC. Use this standard as spiking solution. Prepare weekly.

6.2.4 Nitrate Cadmium check, 0.5 ppm - Dilute 100 µL of reagent 6.2.1 to 200 mL with DI water in a 200 mL volumetric flask. Prepare weekly.

6.2.5 Nitrite Cadmium check, 0.5 ppm - Dilute 100 µL of reagent 6.2.2 to 200 mL with DI water in a 200 mL volumetric flask. Prepare weekly.

6.2.6 Working Standards - The working standards are prepared by diluting the combined intermediate standard 6.2.3 in 100 mL volumetric flasks using the following table. Working standards are good for 48 hours.

Std Concentration NO3+NO2, ppm	Std Concentration NO2, ppm	Combined Intermediate Std
4.000	0.400	4 mL
2.000	0.200	2 mL
1.000	0.100	1 mL
0.500	0.050	500 µL
0.200	0.020	200 µL
0.080	0.008	80 uL
0.020	0.002	10 mL of 0.200/0.020 ppm
0.000	0.000	DI H_2O

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in plastic bottles or cubitainers, and are preserved by cooling to 4 º C. These samples are never acidified and their pH is usually between 5 and 9.

7.2 Samples are analyzed within 48 hours after collection. If they cannot be analyzed within this time period, they should be frozen at -20 ºC on the first day they arrive to lab. The holding time for frozen samples is 28 days.

8.0 QUALITY CONTROL

8.1 An initial Demonstration of Performance (IDP) to establish the instrument's capability is required prior to its use in analyzing client's samples. The linearity of calibration range (LCR) and the ability to quantify correctly Quality Control Samples are used to assess performance.

8.2 All the standards are run in duplicates: that is, two analyses from each tube. A linear calibration is performed daily before the sample run.

8.3 A mid-range check standard and a calibration blank is analyzed following daily calibration, after every ten samples (or more frequently, if required) and at the end of the sample run. If a check standard fails, the samples between the last satisfactory check standard and the unsatisfactory standard are re-analyzed.

8.4 Every tenth sample is duplicated (analyzed from two different tubes) and spiked. The accepted value for the relative percentage relative difference (RPD) and spike recovery is ± 10 %. Prepare sample spikes by adding 50 µL of standard 6.2.3 to 10 mL of samples. If these do not fall within the accepted ranges, the corresponding analyses are repeated.

8.5 An external quality control is analyzed at the beginning and at the end of each analytical run. External QC should be prepared monthly.

8.6 A deionized water blank is run in the beginning and after every tenth sample. Results for blanks should be < 0.002 for NO_2 and < 0.02 for NO_3+NO_2 mg N/L.

8.7 The U.S. EPA MDL procedures (40 CFR Part 136, Appendix B) including the EPA *Definition and Procedure for the Determination of the Method Detection Limit*, Revision 2 (2016); EPA *Methods Update Rule* (Final rule - August 28, 2017); EPA *Method Detection Limit - Frequent Questions*; and EPA Part 136 *Method Update Rule Revisions to Appendix B – MDL Procedure as Applied to Drinking Water* (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.

8.8 A demonstration of capability study is performed by each analyst performing the test by analyzing four replicates of an external quality control sample during one or two analytical runs.

9.0 PROCEDURE

9.1 Sample preparation

9.1.1 Prepare a list of samples to be analyzed and pour samples into labeled tubes (16 mm x 125 mm test tubes).

9.1.2 Spike the blank and every tenth sample by adding 50 µL of combined standard 6.2.3 to 10 mL of sample or DI water.

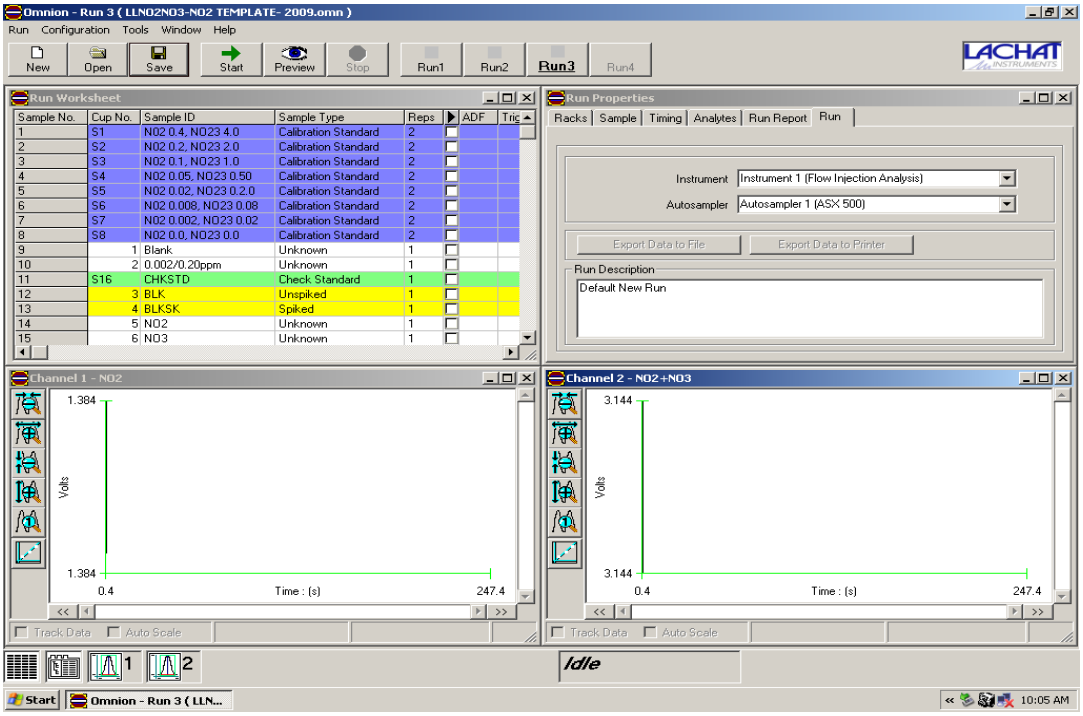
9.1.3 To prevent bubble formation, degas all reagents with helium for one minute.

9.2 Instrument calibration and sample analysis

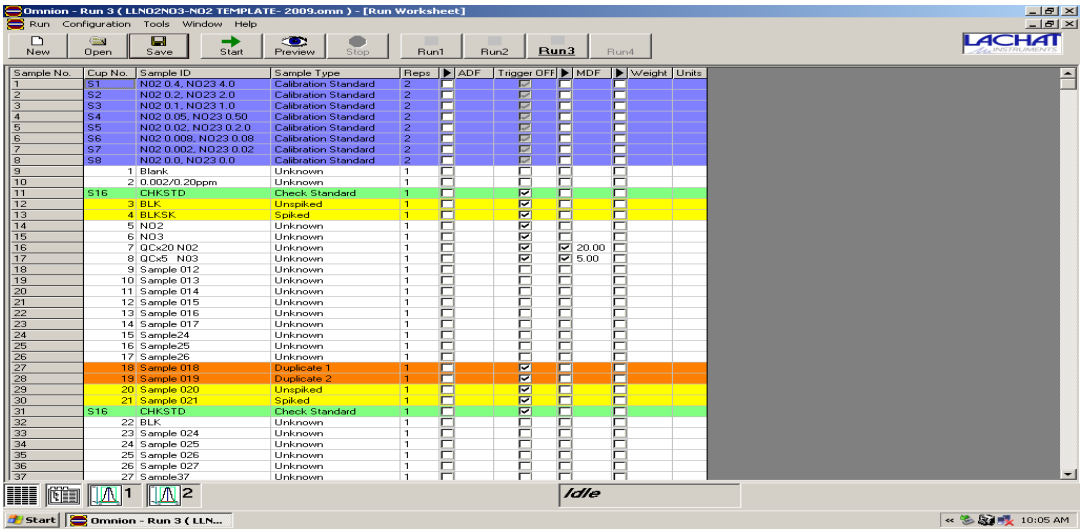
9.2.1 Set up manifold as in the method's manifold diagram.

9.2.2 Turn on the Lachat instrument, computer, monitor, and the printer.

9.2.3 Double click on Omnion and open the **"LL NO_3+NO_2/ NO_2"** folder to find the template, which consists of four windows.



9.2.4 Maximize the **"Run Worksheet"** window at the top left hand corner of the screen by clicking on the middle square on that screen.



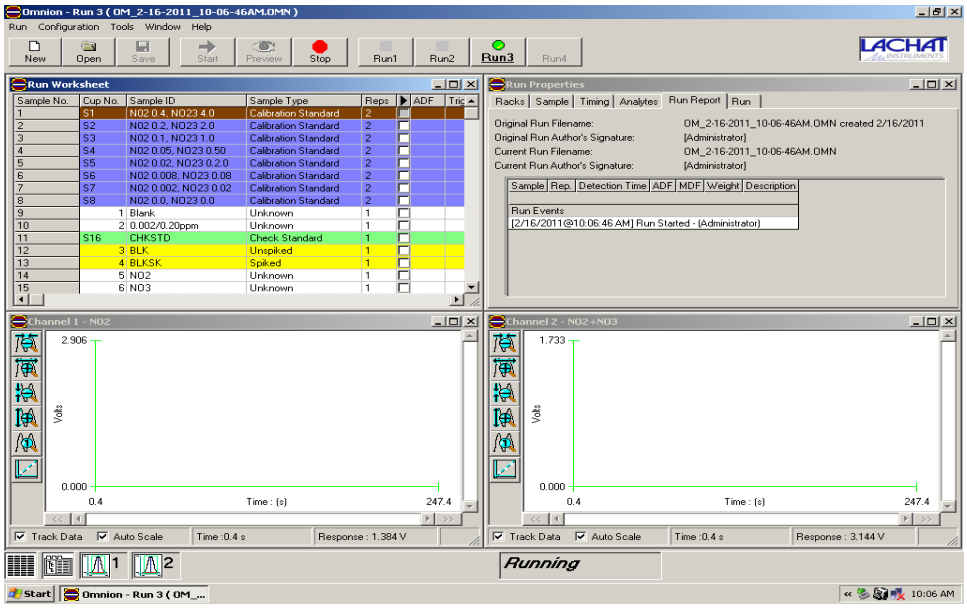
9.2.5 Enter all the sample, sample spike, QC and standard information in the run worksheet and print out the list.

9.2.6 Click on **"Window"** tab and then, click on **"Tile"** to return to the screen with three windows (9.2.3).

9.2.7 Place standards in standard vials in the standard rack in order of decreasing concentration in positions 1 to 8. Place the check standard vial in position 16 (S16) of the standard rack. Pour samples and quality control samples into 13 x 100 mm test tubes and place them in the sample racks according to **"Sample Run Log**".

9.2.8 Pump deionized water through all reagent lines for 15 - 20 minutes and check for leaks and smooth flow. Switch to reagents, turn on the Cadmium switching valve on and allow the buffer to rinse it for 5 - 10 minutes (Note: Lachat columns come as ready to use and need to be flushed for about 10 minutes with buffer after installing on the system.) Click on **"Preview"** tab to monitor the baseline.

9.2.9 Once a stable baseline is achieved, click on **"Stop"** tab to stop monitoring the baseline. Click on **"Start"** tab to begin the analysis.



9.2.10 If the calibration passes, instrument will continue to analyze the samples. If it fails, take appropriate corrective actions and recalibrate before proceeding to analyze samples.

9.2.11 Auto dilution will trigger on to reanalyzed samples with concentration exceeding the calibrated range.

9.2.12 When the run is complete, remove the reagent lines and place them in DI water and rinse for about 15 minutes. For extra rinse a reagent of Disodium EDTA can be used followed by DI rinse. Then all the reagent lines should be air dried and released from the pump.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All the calculations are performed by the Omnion 3.0 software system. It uses a calibration graph of peak area versus concentration to calculate the "nitrate + nitrite nitrogen" concentrations in the samples. All standards are analyzed in duplicate, and these points are used to generate the calibration curve. A duplicate peak may be excluded from the calibration if it is determined to be faulty (i.e. corrupted, damaged, misshapen) Samples with "nitrate + nitrite nitrogen" concentrations greater than 4 ppm are automatically diluted and reanalyzed.

10.2 The reduction efficiency of the cadmium column is calculated as following:

$$\% \text{ Recovery} = (NO_3 / NO_2) \times 100$$

10.3 Calculate % of spike recovery of the laboratory fortified samples as follows:

$$\%\,SR = \frac{\text{spiked sample conc.} - \text{sample conc., ppm}}{\text{amount of spike added to sample, ppm}} \times 100$$

10.4 Calculate the relative percent difference for the duplicated samples as follows:

$$RPD = \frac{\text{difference between the two duplicates}}{\text{average of the duplicates}} \times 100$$

11.0 DATA AND RECORDS MANAGEMENT

11.1 All the results are reported on the sample request forms to three decimal places and for performance evaluation (PE) samples to three significant figures. Normal turnaround time for samples submitted to this lab is 2 to 10 days from receipt.

11.2 Completed data packages are scanned and stored electronically before being placed in the appropriate binders in the lab.

11.3 Results are reported in writing on a sample analysis request form. The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five years custody period.

12.0 WASTE MANAGEMENT

12.1 It is the laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume and bench operation.

12.2 Samples and standards are poured down the drain while large amount of water is running.

12.3 Compliance with state's sewage discharge permits and regulations is required. For more information consult the "Waste Management manual for Laboratory Personnel", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N. W., Washington D. C. 20036, (202) 872-4600.

13.0 REFERENCES

13.1 EPA Method 353.2, *Methods for the Determination of Inorganic Substances in Environmental Samples,* Revision 2.0*,* August 1993.

13.2 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater, 21st Edition, p. 4-125, Method 4500- NO_3^-, 2005*

13.3 Lachat Instruments, Methods Manual for the *Quikchem Automated Ion Analyzer*, Method 10-107-04-1-A

13.4 Division of Environmental Sciences, Maryland Department of Health, *Quality Assurance Plan*, SOP No. Chem-SOP-QAP.

13.5 Division of Environmental Sciences, Maryland Department of Health, *Quality Manual,* SOP No. QA-SOP-QM.

13.6 EPA Definition *and Procedure for the Determination of the Method Detection Limit, Revision 2* December 2016

APPENDIX **A**

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist – Nitrite, Nitrate + Nitrite Nitrogen (Low Level)

EPA Method 353.2; Revision 2.0

Lab Numbers: [1] _____

Analyst: _____

Dates Collected: _____ Date Analyzed: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	48 hours @ 4°C 28 days @ –20°C		
Calibration Curve	Corr. Coefficient. ≥ 0.9950		
Reagent Blank	< 0.02 ppm for NO23 and < 0.002 ppm for NO2		
Blank Spike	1 per batch		
	Recovery = 90 – 110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10 samples		
	Recovery = 90–110%		
External QC	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the run		
	Concentrations = 90–110% of the true value		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RPD ≤ 10%		
NO_3/NO_2 Cadmium Column Check	90–110%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.020–4.000 ppm for NO_2+NO_3; 0.002–0.400 ppm for NO_2)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

* Check (√) if criteria are met. [1]Include beginning and ending numbers, account for gaps by bracketing

_____ _____
Analyst's Signature & Date Reviewer's Signature & Date

_____
Supervisor's Signature & Date

Reagents	ID	External QC			
Ammonia Buffer		Identification =			
Color Reagent		True Value =	NO2	NO2+3	ppm
		Range =	NO2	NO2+3	ppm

MDH- Laboratories Administration
DIVISION OF ENVIRONMENTAL SCIENCES

SOP Title:	Determination of Particulate Phosphorus by Flow Injection Colorimetric Analysis (EPA Method 365.1)
SOP No.:	CHEM-SOP-EPA 365.1
Revision:	5.3 Replaces: 5.2 Effective: 07/15/2023
Laboratory:	Inorganics Analytical Laboratory
Author / POC:	Jewel Freeman-Scott jewel.freeman-scott@maryland.gov

Laboratory Supervisor:	Lara Phillips Signature	6/28/23 Date
QA Officer:	Mohamed Habeeb Signature	07/11/23 Date
Manager:	Cynthia Stevenson Signature	7/12/2023 Date
Division Chief:	 Signature	07/12/2023 Date

REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	6/3/2008	N/A	S. Ameli	6/2/2008
1.0	12/2009	Screen snapshots added to procedure, new Sample Run Log, tracking IDs for standards and reagents	S. Ameli	01/2010
2.0	8/7/2011	New SOP tracking number, editorial and technical changes	S. Ameli	8/18/2011
2.1	08/2013	Reviewed SOP	S. Ameli	8/18/2011
3.0	11/18/2014	Document control and editorial changes.	C. Stevenson S. Ameli R. Carpenter	12/1/2014
3.0	6/1/2015	Reviewed SOP	C. Stevenson S. Ameli R. Carpenter	7/1/2015
3.1	5/5/2016	Changes to include commercial standard 6.2.1	C. Stevenson S. Ameli R. Carpenter	7/1/2016
4.0	6/1/2016	Reviewed and made organizational name changes	C. Stevenson S. Ameli R. Carpenter	7/1/2017
5.0	6/13/2018	Reference new MDL requirements, 8.2	C. Stevenson S. Ameli R. Carpenter	7/1/2018
5.0	2/22/2019	Reviewed SOP	C. Stevenson S. Ameli R. Carpenter	3/4/2019
5.1	4/17/2020	Reviewed SOP and edited for clarity.	J. Freeman-Scott C. Stevenson	5/1/2020
5.2	3/19/2021	Reviewed SOP, Technical changes in section 10.1	J. Freeman-Scott I.Ji	5/1/2021
5.2	4/29/2022	Reviewed SOP, Modified 9.1.4	J. Freeman-Scott I. Ji	5/1/2022
5.3	6/28/2023	Reviewed SOP, updated 13.0	S. Azemati, J. Freeman-Scott L. Phillips	7/15/2023

TABLE OF CONTENTS

STANDARD OPERATING PROCEDURES

Particulate Phosphorus

EPA Method 365.1

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of particulate phosphorus in surface and saline waters.

1.2 The applicable range is 0.05 to 1.00 mg P/L.

2.0 SUMMARY OF METHOD

2.1 Samples for particulate phosphorus are collected by filtering known volumes of water samples through the filters in the field. The filters are folded, placed in aluminum foil pouches, and kept frozen until the analysis time.

2.2 Filters are combusted at 550 ºC for 1.5 hours and treated with 1 N hydrochloric acid for 24 hrs.

2.2 The supernatant is analyzed for orthophosphate using Lachat Method *12-115-01-1-F*, where ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

3.0 INTERFERENCES

3.1 High iron concentrations (Fe^{3+} greater than 50 mg/L) can cause precipitation of, and subsequent loss, of phosphorus.

3.2 Silica forms a pale blue complex, which also absorbs at 880 nm. This interference is generally insignificant as a silicate concentration of approximately 1 mg/L SiO_2/L would be required to produce a 0.3 µg P/L positive error in orthophosphate.

3.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus.

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

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during reagent preparation and instrument operation.

4.2 The use of a fume hood, protective eyewear and clothing and proper gloves are required when handling acids.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Flow injection analysis equipment (Lachat 8500 series, QuikChem), consisted of the following modules, designated to deliver and react sample and reagents in the required order and rations:

5.1.1.1 Sampler

5.1.1.2 Multi-channel proportioning pump

5.1.1.3 Reaction unit or manifold

5.1.1.4 Colorimetric detector with a 10 mm, 800 µL glass flow cell and an 880 nm interference filter

5.1.1.5 Computer with Omnion 3.0 Data System and Printer

5.1.2 Isotemp Muffle Furnace (Fisher Scientific cat. no. 10-505-10)

5.1.2 Analytical Balance

5.1.3 Automatic Shaker (Thermo Scientific MaxQ 2508)

5.2 Supplies

5.2.1 Test tubes, 13 x 100 mm (Fisher Scientific cat. no. 14-961-27)

5.2.2 Volumetric flasks, Class A

5.2.3 Volumetric pipettes, Class A

5.2.4 Centrifuge tubes, 50 mL, with caps (Fisher Scientific cat. no. 14-432-22)

5.2.6 Test tubes, 16 x 125 mm (Fisher Scientific cat. no. 14-961-30)

5.2.7 Sera filters (TechniServe cat. no. 510-4055-P01)

5.2.8 Aluminum weighing pans (Fisher Scientific cat. no. 08-732)

5.2.9 Glass Microfiber Filters, Whatman GF/F; 47 mm, 0.7 μm pore size (Fisher Scientific cat. no. 1825-047)

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Reagent Water - Use deionized (18 megohm) water when preparing all reagents and standards. Degas deionized water and all reagents, except standards, to remove dissolved gases.

6.1.2 Stock Ammonium Molybdate Solution - In a 1 L volumetric flask, dissolve 40.0 g ammonium molybdate tetrahydrate [$(NH_4)6Mo7O_{24}.4H_2O$] in approximately 800 mL DI water. Dilute to the mark and let stir for four hours. Store in a plastic container and refrigerate. May be stored up to two months when kept refrigerated.

6.1.2 Stock Antimony Potassium Tartrate Solution - In a 1 L volumetric flask, dissolve 3.22 g antimony potassium tartrate Trihydrate $K(SbO)C_4H_4O_6.3H_2O$) or dissolve 3.0 g antimony potassium tartrate hemihydrate $K(SbO)C_4H_4O_6.1/2H_2O$), in approximately 800 mL DI water. Dilute to the mark and let stir for few minutes. Store in a dark bottle and refrigerate. This stock may be used up to two months when kept refrigerated.

6.1.4 Molybdate Color Reagent - Add 106.5 mL stock ammonium molybdate and 36.0 mL stock antimony potassium tartrate to about 250 mL of deionized water in a 500 mL volumetric flask. Dilute to the mark with deionized water and invert to mix, store in dark container and prepare weekly. Degas with helium.

6.1.5 Ascorbic Acid Reducing Solution - Dissolve 60.0 g ascorbic acid in about 800 mL deionized water in a 1 L volumetric flask. Mix on a magnetic stirrer and dilute to the mark with deionized water. Prepare fresh weekly.

6.1.6 1.0 M Hydrochloric Acid (Carrier/Diluent for Standards) - Add 83.0 mL of concentrated hydrochloric acid (37%, ACS Reagent Grade, d=1.200) to about 800 mL of deionized water in a 1 L volumetric flask. Dilute to mark with deionized water after cooling to room temperature. Mix well, prepare monthly.

6.1.7 Sodium Hydroxide - EDTA Rinse Solution – Dissolve 65.0 g sodium hydroxide and 6g tetrasodium ethylenediamine tetraaceticacid (Na_4EDTA) in about 800 mL of deionized water in a 1 L volumetric flask. Mix on a magnetic stirrer until it is completely dissolved. Dilute to the mark with deionized water and mix.

6.2 Standards

6.2.1 Phosphorous standard (1000 mg P/L) - Purchased from an approved source. If this stock is not available prepare 100 ppm P/L as detailed in (standard 6.2.2).

6.2.2 Stock Standard 100 mg P/L in 1.0 M Hydrochloric Acid - Add 10 mL of Phosphorus 1000 ppm stock standard (standard 6.2.1) to about 60 mL of 1.0 M Hydrochloric Acid in a 100 mL volumetric flask, dilute to mark, and mix well. If the 1000 ppm P stock is not available, prepare the 100 ppm stock by dissolving 0.4394 g potassium phosphate monobasic (KH_2PO_4) that has been dried for two hours at 110 ^oC, in about 800 mL of 1 M hydrochloric acid (reagent 6.1.6) in a 1 L volumetric flask. Dilute to the mark with 1.0 M hydrochloric acid and mix. Prepare monthly.

6.2.3 Intermediate Standard Solution (10 mg P/L) - Add 10 mL of stock standard (standard 6.2.2) to 60 mL of 1 M hydrochloric acid (reagent 6.1.6) in a 100 mL volumetric flask and dilute to 100 mL mark and mix. Prepare weekly

6.2.4 Working standards – Prepare the standards according to the following chart; dilute each with 1.0 M hydrochloric acid (reagent 6.1.6) and mix. Prepare every 48 hours.

6.2.5 Spiking solution – Use stock standard, 100 mg P/L (standard 6.2.2) to spike 10 ml of blank (1 M HCl) with 50 µL of this solution (Blank Spike)

Concentration mg N/L	**Intermediate Std 10ppm, mL**	**Final Volume, mL**
1.0	10 mL	100 mL
0.5	5 mL	100 mL
0.4	4 mL	100 mL
0.3	3 mL	100 mL
0.2	2 mL	100 mL
0.1	1 mL	100 mL
0.05	500µL	100 mL
0.00	0	100 mL

7.0 COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected by the field personnel on Whatman GF/F filters (47 mm; 0.7 µm pore size) by filtering known volumes of water samples through the filters. The filters are folded, placed in aluminum foil pouches, and kept frozen until analysis.

8.0 QUALITY CONTROL

8.1 A demonstration of capability study is performed by each analyst performing the test by analyzing four replicates of an external quality control sample during one or two analytical runs.

8.2 The U.S. EPA MDL procedures (40 CFR Part 136, Appendix B) including the EPA *Definition and Procedure for the Determination of the Method Detection Limit*, Revision 2 (2016); EPA *Methods Update Rule* (Final rule - August 28, 2017); EPA *Method Detection Limit - Frequent Questions*; and EPA Part 136 *Method Update Rule Revisions to Appendix B – MDL Procedure as Applied to Drinking Water* (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.

8.3 In the analytical run, every tenth sample is duplicated followed a blank. The accepted value for the relative percent difference (RPD) is ± 10%.

8.4 Blank filters are processed and analyzed when provided by the field personnel.

8.5 One mid-range standard (0.40 mg P/L) is analyzed for every 10 samples.

8.6 An external quality control sample is analyzed at the beginning and at the end of each analytical run.

8.6.1 For each analytical run prepare the external quality control sample.
8.6.2 Ignite MESS-4 marine sediment in a 550 ºC for 90 minutes. When cool, store in desiccator for up to a year.
8.6.3 Weigh out 0.025 g of the ignited MESS-4 in the desiccator and add 10 mL of 1M HCl in a capped centrifuge tube.
8.6.4 Shake all samples well manually to have all filters soaked in the solution. Place the samples on the automatic shaker overnight along with the QC sample. After shaking overnight allow sediment to settle to the bottom of the tube.
8.6.5 Prepare a x10 dilution of the QC by pipetting off 5 mL of the top layer from the centrifuge tube mixture, making sure to avoid the sediment, and adding it to a 50 mL volumetric flask.
8.6.6 Bring up to volume with 1M HCl. Invert to mix well.

8.7 Blank used for PP is 1M HCl is analyzed at the beginning of each run and after every 10th samples.

9.0 PROCEDURE

9.1 Sample Preparation

8.7.1 Place filters (samples and blanks, if provided) in labeled aluminum weighing pans and combust in a muffle oven at 550 oC for 1½ hours. Label the pans by impressing numbers on the bottom of the pan. Any ink would burn off.

.

9.1.2 Cool to ambient temperature, then transfer the combusted filters to labeled 50 mL screw cap centrifuge tubes. Use forceps to insert the pad into the bottom of the conical tube to ensure digestion.

9.1.3 Add 10 mL 1 M hydrochloric acid to each tube

9.1.4 Cap tubes and shake well, making sure that all filters are soaked in the solution. Shake all tubes before placing them on the automatic shaker. Place the tubes on an automatic shaker for a 12 hour period/overnight.

9.1.5 Pour samples into 16 x 125 mm tubes and filter using Sera filters.

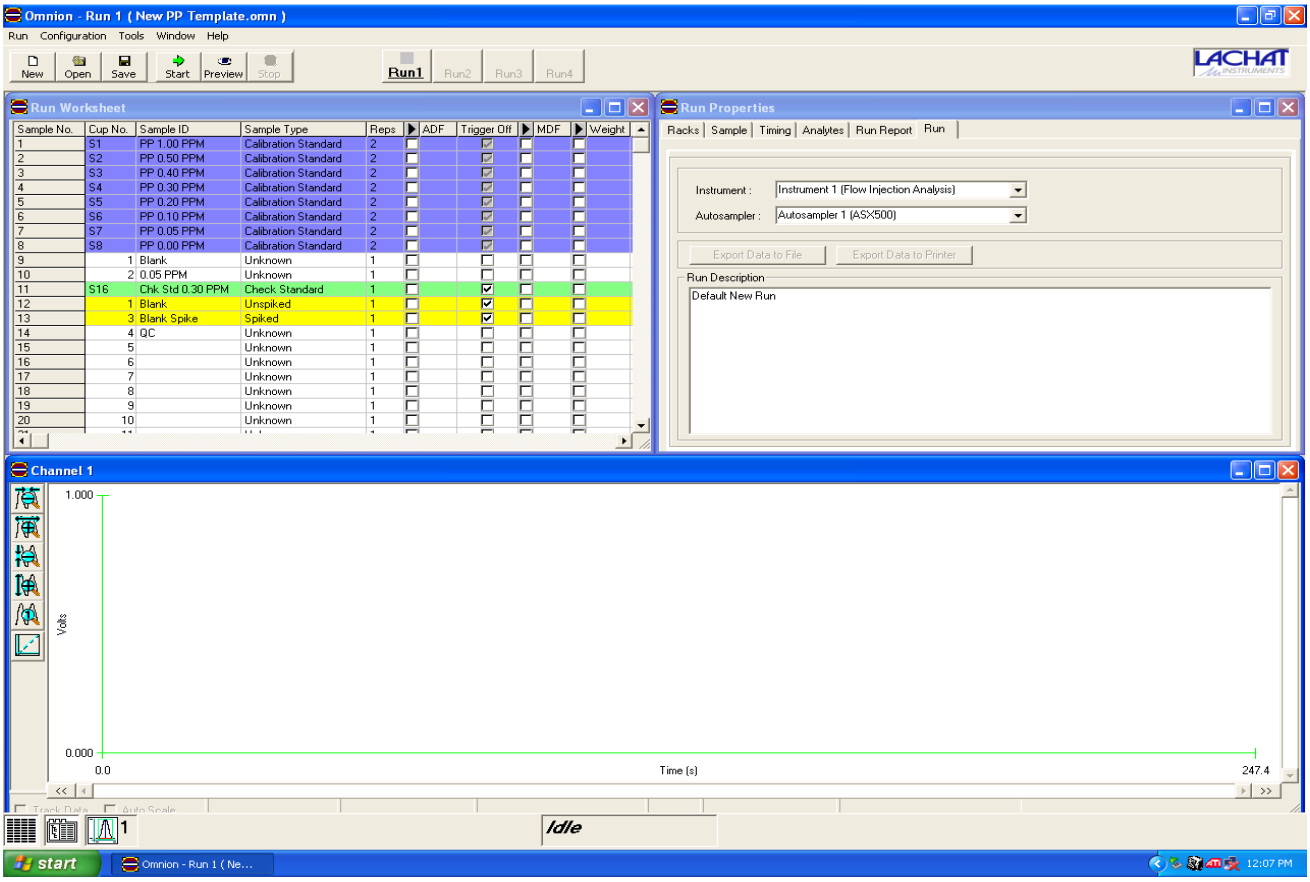
9.1.6 Transfer the filtrate to auto sampler tubes following the order of the run worksheet.

9.2 Instrument set-up and sample analysis

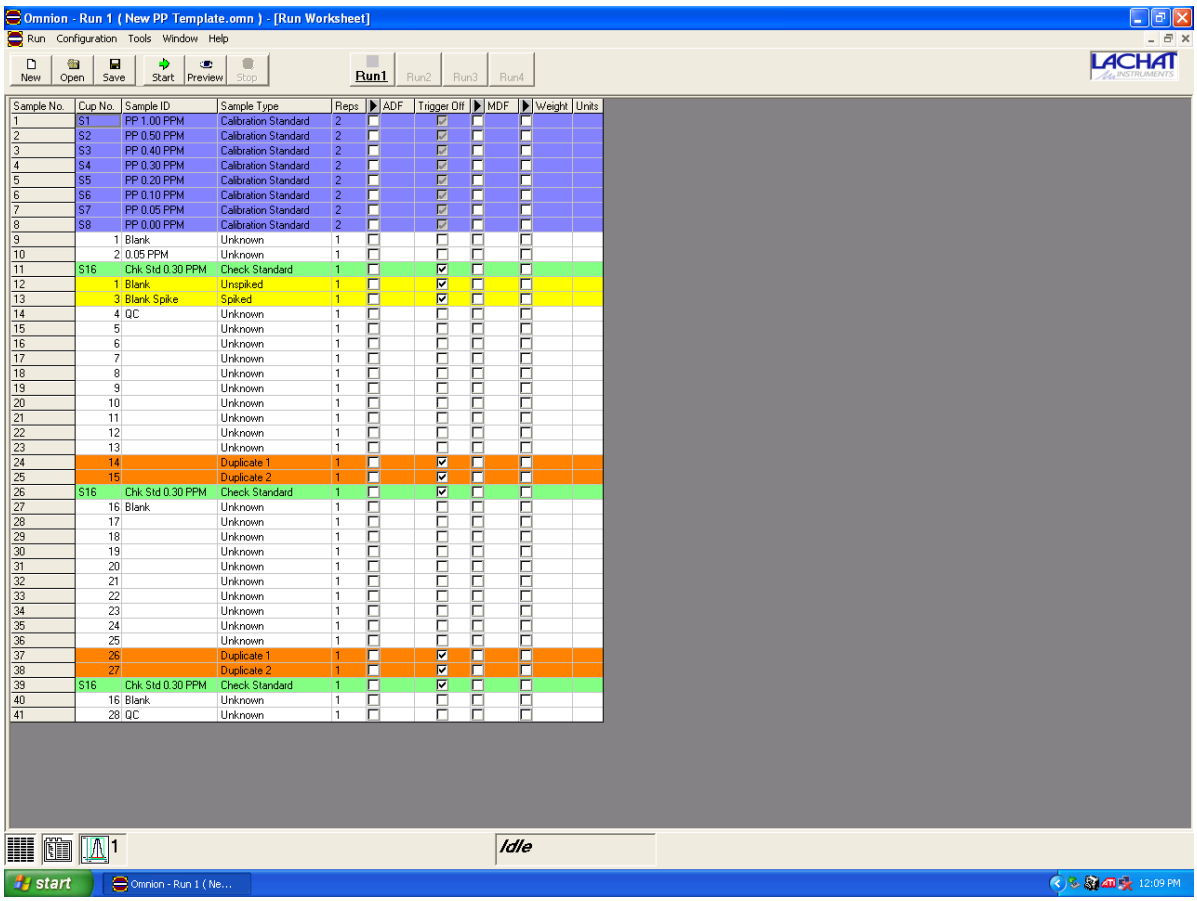
9.2.1 Set up manifold as described in the method.

9.2.2 Turn on the Lachat instrument, computer, monitor, and printer.

9.2.3 Double click on Omnion and then double click on **"LL PP"** to open the template, which consists of three windows.



9.2.4 Maximize the **"Run Worksheet"** window at the top left hand corner of the screen by clicking on the middle square on that screen to open the worksheet template. Enter sample identifications in the sample identification column, making sure that all duplicates are entered in the appropriate locations of the worksheet. Identifications of the quality control samples analyzed at the beginning of the run and the locations of the duplicates and the spiked have been saved on the template. Press the **"Enter"** key after each entry in order to save all entries.



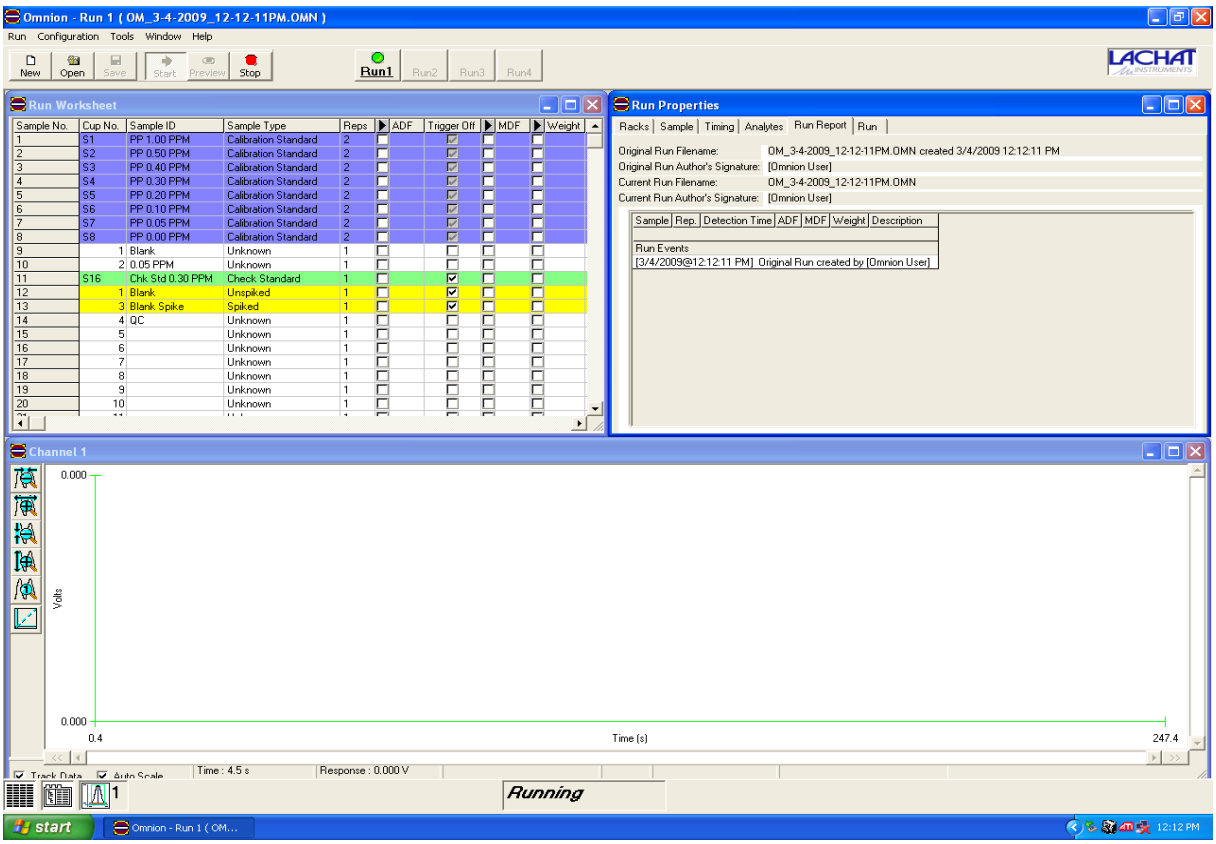
Sample No.	Cup No.	Sample ID	Sample Type	Reps	ADF	Trigger Off	MDF	Weight	Units
1	S1	PP 1.00 PPM	Calibration Standard	2					
2	S2	PP 0.50 PPM	Calibration Standard	2					
3	S3	PP 0.40 PPM	Calibration Standard	2					
4	S4	PP 0.30 PPM	Calibration Standard	2					
5	S5	PP 0.20 PPM	Calibration Standard	2					
6	S6	PP 0.10 PPM	Calibration Standard	2					
7	S7	PP 0.05 PPM	Calibration Standard	2					
8	S8	PP 0.00 PPM	Calibration Standard	2					
9	1	Blank	Unknown	1					
10	2	0.05 PPM	Unknown	1					
11	S16	Chk Std 0.30 PPM	Check Standard	1					
12	1	Blank	Unspiked	1					
13	3	Blank Spike	Spiked	1					
14	4	QC	Unknown	1					
15	5		Unknown	1					
16	6		Unknown	1					
17	7		Unknown	1					
18	8		Unknown	1					
19	9		Unknown	1					
20	10		Unknown	1					
21	11		Unknown	1					
22	12		Unknown	1					
23	13		Unknown	1					
24	14		Duplicate 1	1					
25	15		Duplicate 2	1					
26	S16	Chk Std 0.30 PPM	Check Standard	1					
27	16	Blank	Unknown	1					
28	17		Unknown	1					
29	18		Unknown	1					
30	19		Unknown	1					
31	20		Unknown	1					
32	21		Unknown	1					
33	22		Unknown	1					
34	23		Unknown	1					
35	24		Unknown	1					
36	25		Unknown	1					
37	26		Duplicate 1	1					
38	27		Duplicate 2	1					
39	S16	Chk Std 0.30 PPM	Check Standard	1					
40	16	Blank	Unknown	1					
41	28	QC	Unknown	1					

9.2.5 Print a copy of this worksheet by first double clicking on **"Run"** icon and then selecting **"Export Worksheet Data"**.

9.2.6 Click on **"Window"** tab and then, click on **"Tile"** to return to the screen with three windows.

9.2.7 Place standards in standard vials, then in the standard rack in the order of decreasing concentration from positions 1 to 8. Place the check standard vial in position 16 (S16) of the standard rack. Pour samples and quality control samples into 13 x 100 mm test tubes and place them in the sample racks according to the worksheet prepared in 9.2.4.

9.2.8 Pump deionized water through all reagent lines for 5 – 10 minutes and check for leaks and smooth flow. Switch to reagents and continue pumping for about 10 minutes. Click on **"Preview"** tab to monitor the baseline.



9.2.9 Once a stable baseline is achieved, click on **"Stop"** tab to stop monitoring the baseline. Click on **"Start"** tab to begin the analysis.

9.2.10 If the calibration passes, instrument will continue to analyze the samples. If failed, take appropriate corrective actions and recalibrate before proceeding to analyze samples.

9.2.11 Samples with concentration exceeding the calibrated range will be manually diluted by 1 M HCl and reanalyzed.

9.2.12 After the run is complete, remove the reagent lines and place them in DI water and rinse for about 15 minutes. If necessary, rinse the system with the NaOH – EDTA rinse solution (6.1.7) for not more than 5 minutes followed by DI water of 10 – 15 minutes. Pump the tubes dry, release the pump tubing, and turn off the pump.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All the calculations are performed by the Omnion 3.0 software system. The amount of color is plotted against the known concentrations and the line that best fits among the data points is the calibration curve. The concentration of unknown samples are determined automatically by plugging the amount of color (response)

in the calibration curve equation. All standards are analyzed in duplicate, and these points are used to generate the calibration curve. A duplicate peak may be excluded from the calibration if it is determined to be faulty (i.e. corrupted, damaged, misshapen) Samples with phosphorous concentrations greater than 1.00 ppm are diluted manually by 1 M HCl and reanalyzed.

10.2 Calculate the actual concentration of particulate phosphorus in samples (mg/L) by multiplying the concentration of sample mg /L X10mL / volume of sample (mL) used in the filtrate. Use the template below for calculations.

			Particulate Phosphorus Calculation					Date:		
	(concentration*10)/volume of sample= result									
Sample #	**conc.**	**volume**	**value**			**Sample #**	**conc.**	**volume**	**value**	
			#DIV/0!	###					#DIV/0!	###
			#DIV/0!	###					#DIV/0!	###
			#DIV/0!	###					#DIV/0!	###
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10.3 Calculate the relative percentage difference for the duplicated samples as follows:

$$\% RPD = \frac{\text{difference between the duplicates}}{\text{average of the duplicates}} \times 100$$

10.4 The reporting level for this method is the concentration of the lowest standard, which is 0.05 ppm.

10.5 Report results for all routine samples to three decimal places and for performance evaluation (PE) samples to three significant figures.

11.0 DATA AND RECORDS MANAGEMENT

11.1 The analysis data for the calibration blank, external QC and instrument performance check solution (IPC), i.e. the mid-range check standard, is kept on file with the sample analysis data.

11.2 Normal turnaround time for samples submitted to this lab is 2 to 10 days from the receipt. Results are reported in writing on the sample analysis request form.

11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five years custody period.

12.0 WASTE MANAGEMENT

12.1 It is laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume and bench operation.

12.2 Samples and standards are poured down the drain and flushed with running water.

13.0 REFERENCES

13.1 United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Waste, EPA/600/R-93/100, Method 365.4, May 1993.*

13.2 Lachat Instruments, *Determination of Total Phosphate in Ashed Soil Samples by Flow Injection Analysis, Method 12-115-01-1-F, September 2003.*

13.3 Chesapeake Biological Laboratories, *Particulate Phosphorus Method, February 2004.*

13.4 EPA Method 365.1, *Methods for the Determination of Inorganic Substances in Environmental Samples*, August 1993.

13.5 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 21st Edition, Method 4500- P E, 2005.

13.6 Lachat Instruments, *Operating Manual for the Quikchem Automated Ion Analyzer*

13.7 Division of Environmental Sciences, Maryland Department of Health, *Quality Assurance Plan*, SOP No. QA-SOP-QAP.

13.6 Division of Environmental Sciences, Maryland Department of Health, *Quality Manual,* SOP No. QA-SOP-QM.

13.7 EPA Definition *and Procedure for the Determination of the Method Detection Limit, Revision 2* December 2016

APPENDIX A

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist- Particulate Phosphorus

EPA Method 365.1

Lab Numbers[1]:_____ Analyst: _____

Date Collected: _____ Date Digested: _____ Date Analyzed: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	28 days @ –15ºC		
Calibration Curve	Corr. Coeff. $\geq$ 0.9950		
Reagent Blank	< Reporting level (0.05 ppm)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RPD ≤ 10%		
Check Standard	After every 10th sample and at the end of the run		
	Recovery = 90–110%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.05– 1.00 ppm)		
Diluted Samples	Correct final calculations		
External QC[2]	Beginning and end of each run		
	Within acceptance range		
Changes/Notes	Clearly stated		

* Check (✓) if criteria are met. [1]Include beginning and ending numbers, account for gaps by bracketing

_____ _____
Analyst's Signature & Date Reviewer's Signature & Date

_____
Supervisor's Signature & Date

Reagents	ID
1M HCl	_____
Ascorbic Acid	_____
Color Reagent	_____

External QC

Identification = _____
True Value = _____ ppm
Range = _____ ppm

MDH- Laboratories Administration
DIVISION OF ENVIRONMENTAL SCIENCES

Title: Determination of Total Dissolved Nitrogen
Flow Injection Colorimetric Analysis
(EPA Method 353.2)

SOP No.: (CHEM-SOP-EPA 353.2 TDN)

Revision: 5.2 Replaces: 5.1 Effective: 7/15/2023

Laboratory: Inorganics Analytical Laboratory

POC: Chengyuan Cao
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Laboratory Supervisor:	Lara Phillips Signature	7/11/2023 Date
QA Officer:	Mohamed Habeeb Signature	07/11/23 Date
Manager:	Cynthia Stevenson Signature	7/12/2023 Date
Division Chief:	 Signature	07/12/2023 Date

REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	6/3/2008	N/A	S. Ameli	6/2/2008
1.0	12/2009	Screen snapshots added to procedure, new Sample Run Log, tracking IDs for standards and reagents	S. Ameli	01/2010
2.0	08/2011	New SOP tracking number, technical and editorial changes	S. Ameli	8/18/2011
2.1	08/2013	Reviewed SOP	S. Ameli	8/18/2011
3.0	11/2014	New tracking numbers, technical and editorial changes	S. Ameli C. Stevenson	12/2014
3.0	6/1/2015	Reviewed SOP	C. Stevenson	7/1/2015
4.0	5/5/2016	Technical and editorial changes. Added commercial stock standard (6.2.1)	S. Ameli C. Stevenson J. Freeman-Scott	7/1/2016
4.1	6/1/2016	Reviewed and made organizational name changes	S. Ameli C. Stevenson J. Freeman-Scott	7/1/2017
5.0	6/13/2018	Reference new MDL requirements, 8.9	S. Ameli C. Stevenson J. Freeman-Scott	7/1/2018
5.0	2/22/2019	Reviewed SOP	S. Ameli C. Stevenson J. Freeman-Scott	3/4/2019
5.1	4/17/2020	Edited for clarity, added carrier	C. Stevenson C. Cao	5/1/2020
5.2	3/19/2021	Reviewed SOP, Technical changes in section 10.1	I. Ji C. Cao	5/1/2021
5.2	4/29/2022	Reviewed SOP	I. Ji C. Cao	5/31/2022
5.2	6/30/2023	Reviewed SOP	C. Cao, L.Phillips	7/15/2023

TABLE OF CONTENTS

STANDARD OPERATING PROCEDURES

DETERMINATION OF TOTAL DISSOLVED NITROGEN IN ALKALINE PERSULFATE DIGESTS BY AUTOMATED COLORIMETRY

EPA Method 353.2

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to seawater, brackish water, and non-saline water.

1.2 The applicable range is 0.1 to 5.0 mg N/L.

2.0 SUMMARY OF METHOD

The nitrate is quantitatively reduced to nitrite by passing the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide under acidic conditions followed by coupling with N-(1-naphthyl) ethylene diamine dihydrochloride (Marshall's reagent) to form a reddish-purple azo dye which is measured colorimetrically at 520 nm. Per manufacture's recommendation, water samples are digested for one hour with alkaline persulfate to oxidize all the nitrogen compounds present in the sample to nitrate (NO_3^-). A single multi-analyte standard is prepared for nitrate, nitrite and phosphorus as they are analyzed concurrently on the same instrument.

3.0 INTERFERENCES

3.1 Total carbon concentrations in excess of 20 mg C/L or Chemical Oxygen Demand (COD) concentrations in excess of 50 mg/L will result in complete oxidation of nitrogen compounds.

3.2 The presence of sulfide and chloride produced by seawater oxidation would reduce the column life as compared to non-saline samples.

3.3 Turbidity and colored samples that absorb at 520 nm will interfere in the colorimetric determination. Turbidity of the samples can be removed by filtration prior to analysis.

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during reagent preparation and instrument operation. The use of a fume hood, protective eyewear, lab coat and proper gloves are required when preparing reagents.

4.2 Sodium hydroxide, hydrochloric acid, and phosphoric acid used in this determination have the potential to be highly toxic or hazardous. Consult Safety Data Sheets (SDS) for detailed explanations.

4.3 Each employee is issued a *Laboratory Safety Manual* and is responsible for adhering to the recommendations contained therein.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat QuickChem 8500 Automated Ion Analyzer, which includes the following:

5.1.1.1 Automatic sampler

5.1.1.2 Multi-channel proportioning pump

5.1.1.3 Injection module with a 12.5 cm x 0.5 mm ID sample loop

5.1.1.4 Manifold

5.1.1.5 Colorimetric detector

5.1.1.5.1 Flow cell, 10 mm path length

5.1.1.5.2 Interference filter, 520 nm

5.1.1.6 Computer with Omnion 3.0 Data system and printer

5.1.2 Analytical balance capable of accurately weighing to the nearest 0.0001 g

5.1.3 Top loading balance for weighing chemicals for reagents

5.2 Supplies

5.2.1 Class A volumetric flasks, 50 - 1,000 mL

5.2.2 Class A volumetric pipettes, 1 - 10 mL

5.2.3 Automatic pipetters, 100 µL - 10 mL

5.2.4 Digestion tubes - 40 mL vials (Fisher 14-959-37C or equivalent) with autoclavable caps lined with Teflon liners (Kimble Caps Cat # 03-340-77E)

5.2.5 Beakers, disposable, polypropylene, 50 mL (Fisher 01-291-10)

5.2.6 Test tubes, glass, 13 x 100 mm and 16 x 125 mm

5.2.7 Reagent storage bottles, plastic or glass

5.2.8 Cadmium Reduction Column (Lachat Part No. 50237A)

5.2.9 Ultra High Purity Helium gas for degassing

6.0 REAGENTS AND STANDARDS

6.1 Reagents

Use deionized water (DI) for preparing all solutions. Prevent the bubble formation by degassing deionized water and all reagents with helium for one minute and half.

6.1.1 15 N Sodium Hydroxide - Gradually add 150 g NaOH in a beaker of about 200 mL DI water. Mix well and ensure dissolution. Let the solution reach to room temperature, and store in a plastic container**.**

6.1.2 Ammonium Chloride Buffer, pH 8.5 - While working In a fume hood, dissolve 85.0 g ammonium chloride (NH_4Cl) and 1.0g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA.2H_2O$) in about 800 mL DI water, in a 1L volumetric flask. Mix well and dilute to the mark. Adjust the pH to 8.5 with 15 N sodium hydroxide solution and then filter the reagent and refrigerate. This solution is stable for one month.

6.1.3 Sulfanilamide Color Reagent - Add about 600 mL of DI water into a 1 L volumetric flask. Then add 100 mL 85% phosphoric acid (H_3PO_4), 40.0 g sulfanilamide, and 1.0 g N- (1-naphthyl) ethylenediamine dihydrochloride (NED). Stir for about 30 minutes until dissolved. Dilute to the mark, filter and store in a dark bottle in a refrigerator. This solution is stable for one month.

6.1.4 Alkaline Persulfate Oxidizing Reagent - In a 1 L volumetric flask, dissolve 20.1 g potassium persulfate ($K_2S_2O_8$), and 3 g sodium hydroxide (NaOH) in about 600 mL DI water. Dilute to mark and mix. Prepare fresh daily before use.

6.1.5 Borate Buffer, 1.0 M, pH 7.5 - dissolve 61.8 g boric acid and 8.0 g sodium hydroxide in about 800 mL DI water in a 1 L volumetric flask. Mix for about four hours until it is completely dissolved. Dilute to the mark with DI water and mix. This solution is stable for two months.

6.1.6 Carrier - Use degassed deionized water for carrier.

6.2 Standards

6.2.1 Nitrate standard (1000 mg N/L) - Purchased from an approved source. If this stock is not available prepare by dissolving 0.722 g of potassium nitrate (dried in the oven for two hours at 110 ºC) in about 60 mL of DI water in a 100 mL volumetric flask. Dilute to mark and mix. Prepare monthly.

6.2.2 Phosphorous standard (1000 mg P/L) - Purchased from an approved source. If this stock is not available, prepare in lab as described in TDP SOP.

6.2.3 Stock phosphorous (100 mg P/L) - Standard Solution Add 10 mL of Phosphorus 1000 ppm stock standard 6.2.2 to about 60 mL of DI water in a 100 mL volumetric flask, dilute to mark, and mix well. Prepare monthly.

6.2.4 Combined Intermediate Standard Solution (1 mg P/L and 10 mg N/L) – Add 10 mL of standard 6.2.3, 100 mg P/L (stock standard solution for total dissolved phosphorus determination) and 10 mL of 1000 mg N/L stock nitrate standard 6.2.1 to about 800 mL DI water in a 1L volumetric flask. Dilute to mark and mix. Prepare weekly.

6.2.5 Combined Working Standard Solutions (5.0, 2.0, 1.0, 0.5, 0.2, 0.1 and 0.0 ppm) - Use the following table to prepare standards. Prepare per run and standards are good for 48 hours.

Concentration, mg N/L	Combined Working Standard, mL	Final Volume, mL
5.0	50 mL	100 mL
2.0	20 mL	100 mL
1.0	20 mL	200 mL
0.5	5 mL	100 mL
0.2	2 mL	100 mL
0.1	1 mL	100 mL
0.0	0 mL	100 mL

Note: ***The analyst may save a set of standards from a previous run for troubleshooting purposes only***

6.2.6 Stock Nitrite Standard Solution for Cadmium check (1000 mg N/L) - Purchased from an approved source. If not available, weigh and dissolve 0.6072 g potassium nitrite in about 80 mL of DI water in a 100 mL volumetric flask. Dilute to mark and mix. Prepare monthly.

6.2.7 Nitrite working standard for Cadmium check (2.5 ppm N/L) - Pipette 0.5

ml of standard 6.2.6 into 200 mL volumetric flask. Mix and dilute to mark. Prepare weekly

6.2.8 Nitrate working Standard for Cadmium check (2.5 mg N/L) - Pipette 0.5 mL of standard 6.2.1 to about 100 mL DI water in a 200 ml volumetric flask. Dilute to mark and mix. Prepare monthly.

6.2.9 Spiking Solution - Pipette 50 µL of a combined solution of 5 mL of 1000 mg/L N (standard 6.2.1) and 5 mL of 100 mg/L P (standard 6.2.3) into 10 mL of sample (sample spike) or 10 mL of DI water (blank spike). Prepare monthly.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are filtered in the field, collected in plastic bottles or cubitainers, and are preserved by cooling to 4 ºC.

7.2 Samples are analyzed within 48 hrs after collection. If they cannot be analyzed within this time period, they may be frozen at -20 ºC as soon as possible at the laboratory. The holding time for frozen samples is 28 days.

8.0 QUALITY CONTROL

8.1 An initial Demonstration of Performance (IDP) to establish the instrument's capability is required prior to its use in analyzing client's samples. The linearity of calibration range (LCR) and the ability to quantify correctly Quality Control Samples are used to assess performance.

8.2 A mid-range check standard and a calibration blank is analyzed immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. The acceptable concentrations for the check standard must be within ± 10% of the actual concentration of the check standard. If a check standard fails, the samples between the last satisfactory check standard and the unsatisfactory standard are re-analyzed. Blank concentration must be less than the reporting level of 0.1 ppm. Blanks that do not meet this criterion are reanalyzed.

8.3 Every tenth sample is duplicated (analyzed from two different tubes) and spiked. The accepted values for the relative percent difference (RPD) must fall within ± 10 % and for spike recovery between 90 - 110%. If these do not fall within the accepted ranges, the corresponding analyses are repeated.

8.4 A QC sample with a known concentration and a known range is analyzed at the beginning and at the end of each analytical run. Follow the vendor's procedure for preparation of solution. QC samples that do not fall within the accepted range are repeated.

8.5 Samples with a concentration exceeding the calibrated range are diluted manually and reanalyzed.

8.6 Data acceptance criteria are listed on the data review checklist. (page 15)

8.7 The laboratory annually participates in USGS, Chesapeake Bay Laboratory (CBL), Water Supply (WS) and Water Pollution (WP) proficiency studies.

8.8 The U.S. EPA MDL procedures (40 CFR Part 136, Appendix B) including the EPA *Definition and Procedure for the Determination of the Method Detection Limit*, Revision 2 (2016); EPA *Methods Update Rule* (Final rule - August 28, 2017); EPA *Method Detection Limit - Frequent Questions*; and EPA Part 136 *Method Update Rule Revisions to Appendix B – MDL Procedure as Applied to Drinking Water* (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.

8.9 A demonstration of capability study is performed by each analyst performing the test by analyzing four replicates of an external quality control sample during one or two analytical runs.

8.10 The efficiency of the cadmium column before and after sample run is calculated by running 2.5 ppm NO_2-N (standard 6.2.6) and 2.5 ppm NO_3-N (standard 6.2.7) standards and using the formula (NO_3-N/NO_2-N) x 100. The accepted range for the cadmium column efficiency is 90 - 110%. If the efficiency is out of this range, new standards are prepared and efficiency is re-evaluated. If the efficiency is still out of range then the column is replaced.

9.0 PROCEDURE

9.1 Sample preparation

9.1.1 Make a list of samples to be analyzed and pour aliquots of samples into labeled 16 mm x 125 mm test tubes.

9.1.2 Pipette 10 mL of each standard or sample into digestion tubes.

9.1.3 Pipette 10 mL of a mid-range (0.1 mg P/L and 1.0 mg N/L) standard, a blank, a blank spike, and an external quality control sample into digestion tubes. With each tray prepare a duplicate and a spike of every 10^{th} sample.

9.1.4 Pipette 10 mL of the nitrate and nitrite standards for cadmium column check (standard 6.2.6 and standard 6.2.7) into digestion tubes.

9.1.5 Add 5 mL of digestion solution to each tube, screw the caps on tightly and mix each. Digest the standards, samples, and all the quality control

samples in the autoclave for 60 minutes at 121 ºC (250 ºF) @ 17 psi after it reaches the set temperature and pressure.

For Autoclave Operation please see the manual

9.1.6 After one hour, turn off the autoclave and let the digests cool for 5 minutes. Remove the tubes from the autoclave and let the digests come to room temperature. Add 1 mL of borate buffer, vortex, and pour into 13 x 100 mm culture tubes analyze them as soon as possible.

9.1.7 If samples cannot be analyzed same day, do not add the borate buffer. Refrigerate the digests at 4 ºC. Refrigerated digests will be brought up to room temperature, and subsequently 1 mL borate buffer (standard 6.1.5) is added to each tube and mixed thoroughly by a vortex.

9.1.8 Analyze the digests using the procedure described in 9.2.

9.2 Instrument Calibration and Sample Analysis

9.2.1 Set up manifold according to the manifold diagram.

9.2.2 Pump deionized water through all reagent lines and check for leaks and a smooth flow. Switch to reagents and allow the system to stabilize and a stable baseline is achieved.

9.2.3 Enter sample information required by the data system.

9.2.4 Place standards, blanks, samples, quality controls, etc. in the auto sampler according to the run table.

9.2.5 Initiate the analytical run.

9.2.6 At the end of the run, review the calibration curve statistics and the results for the quality control samples. Acceptable values for the correlation coefficient are ≥ 0.9950. Other quality control criteria are described in 8.0.

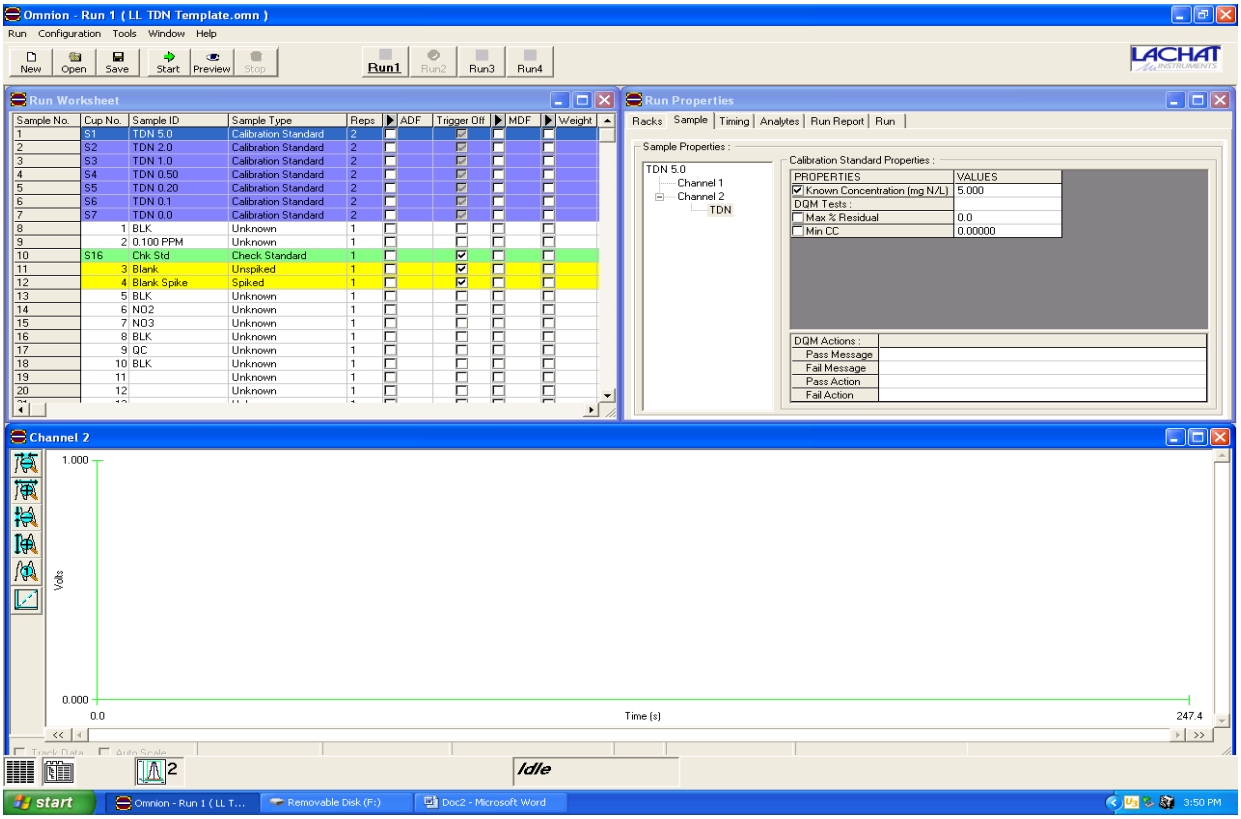
9.2.7 Get the data reviewed by a designated scientist, and then, report the results on the Analysis Request Forms.

9.3 Instrument set-up and sample analysis

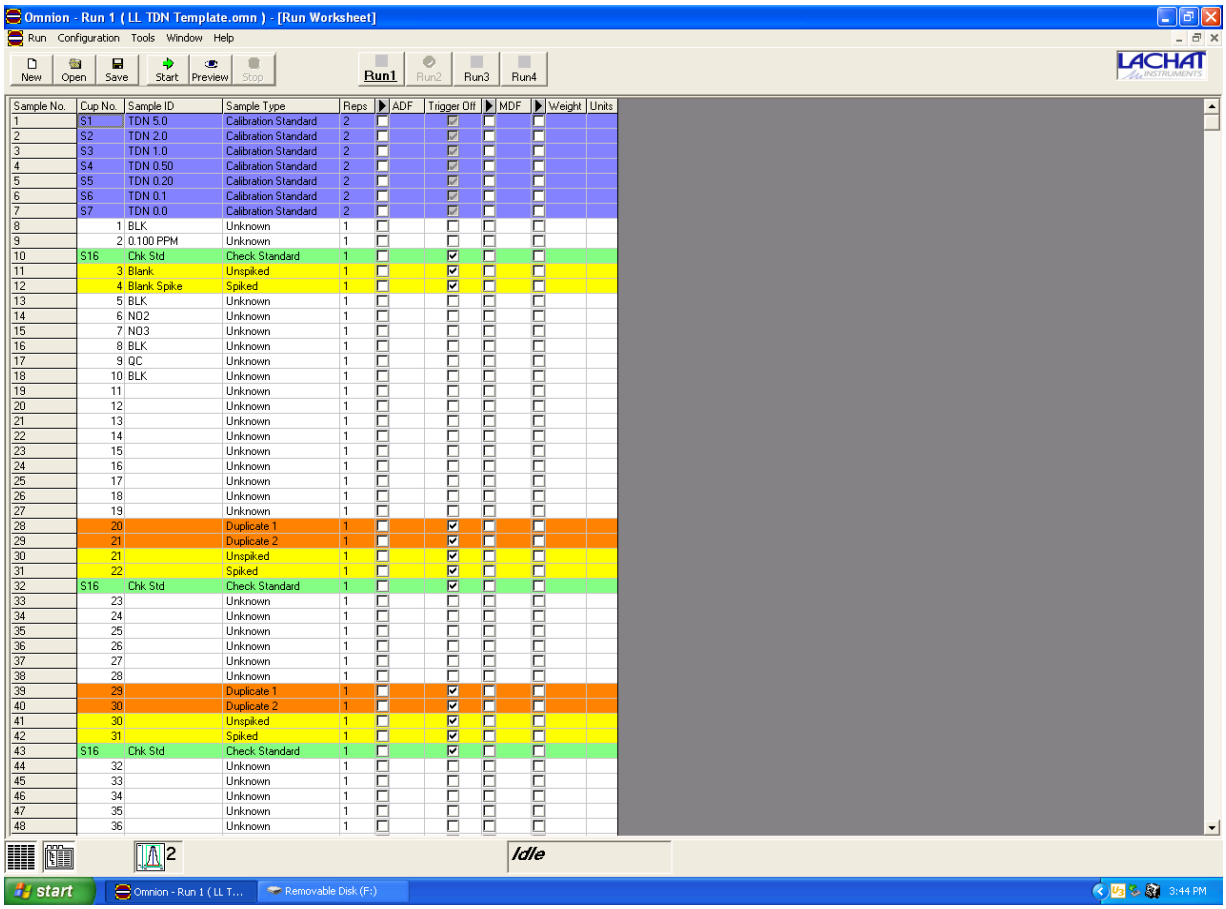
9.3.1 Set up manifold as in the diagram.

9.3.2 Turn on the Lachat instrument, computer, monitor, and printer.

9.3.3 Double click on Omnion and then on **"LL TDN"** to open the template, which consists of three windows.



9.3.4 Maximize the **"Run Worksheet"** window at the top left hand corner of the screen by clicking on the middle square on that screen to open the worksheet template. Enter sample identifications in the sample identification column, making sure that all duplicates and spikes are entered in the appropriate locations of the worksheet. Identifications of the quality control samples analyzed at the beginning of the run and the locations of the duplicates and the spiked have been saved on the template. Make sure that **"Enter"** key is pressed after each entry in order to save all entries.

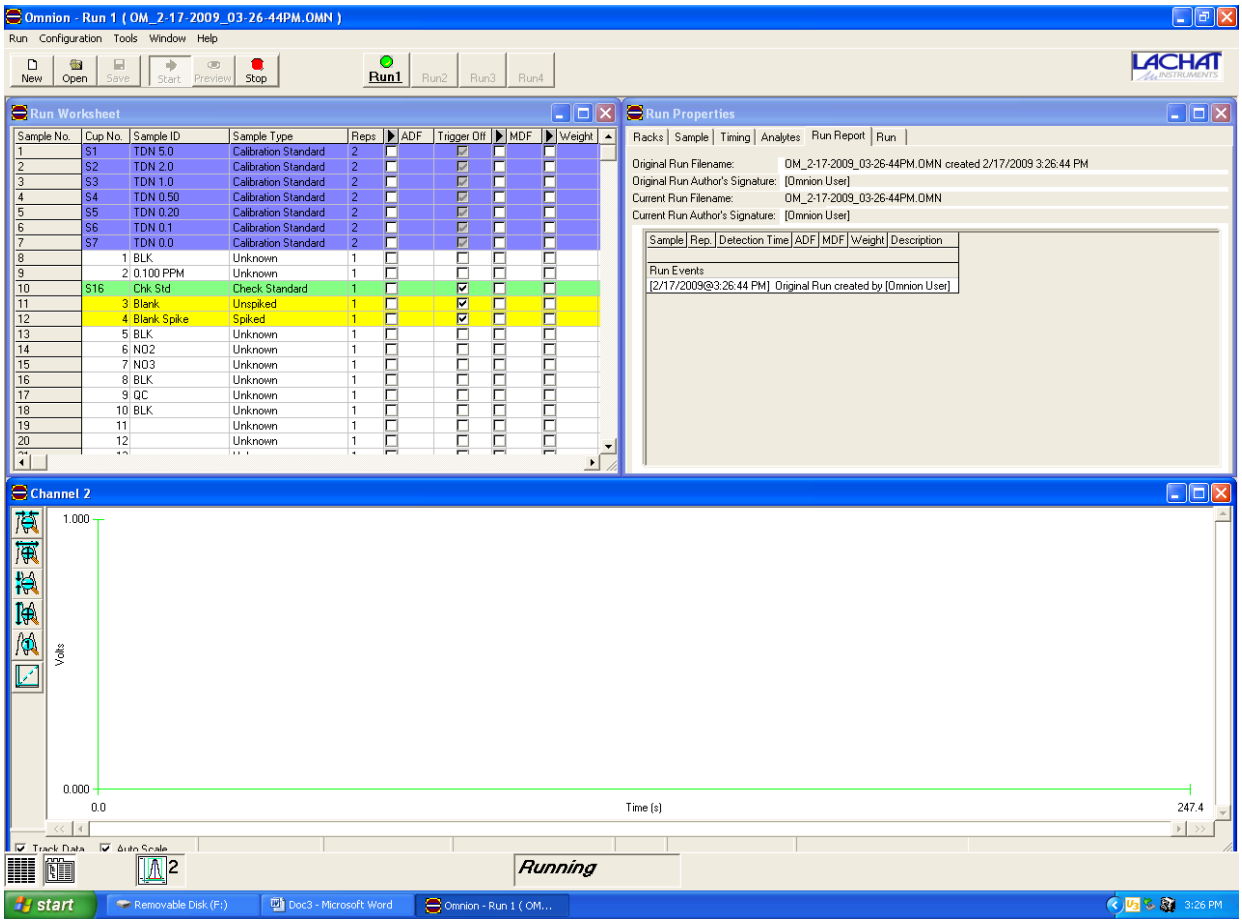


9.3.5 Print a copy of this worksheet by first double clicking on **"Run"** icon and then selecting **"Export Worksheet Data"**.

9.3.6 Click on **"Window"** tab and then, click on **"Tile"** to return to the screen with three windows.

9.3.7 Place standards in standard vials in the standard rack in order of decreasing concentration in positions 1 to 7 (STD 7 is DI water -0.00 mg/L). Place the check standard vial in position 16 (S16) of the standard rack. Pour samples and quality control samples into 13 x 100 mm test tubes and place them in the sample racks according to the worksheet.

9.3.8 Pump deionized water through all reagent lines for 10 - 15 minutes and check for leaks and smooth flow. Switch to reagents and continue pumping for about 10 minutes. Click on **"Preview"** tab to monitor the baseline.



9.3.9 Once a stable baseline is achieved, click on **"Stop"** tab to stop monitoring the baseline. Click on **"Start"** tab to begin the analysis.

9.3.10 If the calibration passes, curve fit of calibration solutions/response based on regression, the instrument will continue to analyze the samples. If it fails, take appropriate corrective actions and recalibrate before proceeding to analyze samples.

9.3.11 Manual dilution will be performed to reanalyze samples with concentrations exceeding the calibrated range.

9.3.12 After the run is complete, remove the reagent lines and place them in DI water and rinse for about 15 minutes. If necessary, rinse the system with the NaOH – EDTA rinse solution for not more than 5 minutes, followed by DI water rinse for 10 - 15 minutes. Pump the tubes dry, release the pump tubing, and turn off the pump.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All the calculations are performed by the Omnion 3.0 software system. The amount of color is plotted against the known concentrations and the line that best fits among the data points is the calibration curve. The concentration of unknown samples is determined automatically by plugging the amount of color (response) in the calibration curve equation. All standards are analyzed in duplicate, and these points are used to generate the calibration curve. A duplicate peak may be excluded from the calibration if it is determined to be faulty (i.e. corrupted, damaged, misshapen) Samples with total dissolved nitrogen concentrations greater than 5.00 ppm are diluted manually by 1 M HCl and reanalyzed.

10.2 The reduction efficiency of the cadmium column is calculated as followings:

$$\% \text{ RE} = (NO_3/NO_2) \times 100$$

10.3 Calculate the percentage spike recovery of the laboratory fortified samples as follows:

$$\% \text{ SR} = \frac{\text{(spiked sample conc. - sample conc.), ppm}}{\text{amount of spike added to sample, ppm}} \times 100$$

10.4 Calculate the relative percentage difference for the duplicated samples as follows:

$$\% \text{ RPD} = \frac{\text{difference between the duplicates}}{\text{average of the duplicates}} \times 100$$

10.5 The reporting level for this method is the concentration of the lowest standard, which is 0.1 ppm.

10.6 Report results for all routine samples to three decimal places and for performance evaluation (PE) samples to three significant figures.

11.0 DATA AND RECORDS MANAGEMENT

11.1 The analysis data for the calibration blank, external QC and instrument performance check solution (IPC), i.e. the mid-range check standard, is kept on file with the sample analysis data.

11.2 Normal turnaround time for samples submitted to this lab is 2 to 10 days from the receipt. Results are reported in writing on the sample analysis request form.

11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be

responsible for retrieving, copying, or transferring laboratory records exceeding the five years custody period.

12.0 WASTE MANAGEMENT

12.1 It is laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume and bench operation.

12.2 Samples and standards are poured down the drain and flushed with running water.

13.0 REFERENCES

13.1 EPA Method 353.2, *Methods for the Determination of Inorganic Substances in Environmental Samples*, August 1993.

13.2 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 21st Edition, Method 4500- P E, 2005.

13.3 Lachat Instruments, *Methods Manual for the Quikchem Automated Ion Analyzer,* Method 10-107-04-4-A.

13.4 Lachat Instruments, *Operating Manual for the Quikchem Automated Ion Analyzer*.

13.5 Division of Environmental Sciences, Maryland Department of Health, *Quality Assurance Plan*, SOP No. Chem-SOP-QAP.

13.6 Division of Environmental Sciences, Maryland Department of Health, *Quality Manual,* SOP No. QA-SOP-QM.

13.7 EPA Definition *and Procedure for the Determination of the Method Detection Limit, Revision 2* December 2016.

APPENDIX A

Division of Environmental Sciences

INORGANICS ANALYTICAL LABORATORY

Data Review Checklist Total Dissolved Nitrogen (TDN)/Alkaline Persulfate Digestion

EPA Method 353.2

Lab Numbers[1]:_____ Analyst: _____

Date Collected: _____ Date Digested: _____ Date Analyzed: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	48 hours @ 4ºC; 28 days @ –20ºC		
Calibration Curve	Corr. Coefficient. $\geq$ 0.9950		
Reagent Blank	< Reporting level (0.100 ppm)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10		
	Recovery = 90–110%		
External QC	Beginning and end of each run		
	Within acceptance range		
Check Standard	After every 10th sample and at the end of the run		
	Recovery = 90–110%		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RPD ≤ 10%		
Cadmium Column Check	NO_3/NO_2 X 100=90-110%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.100–5.00 ppm)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

[1]Include beginning and ending numbers, account for gaps by bracketing.

_____ _____

Analyst's Signature & Date Reviewer's Signature & Date

_____

Supervisor's Signature and Date

Reagents	ID	Reagents	ID	External QC	
Ammonia Buffer		Oxidizing Reagent		Identification =	
Color Reagent		Borate Buffer		True Value =	ppm
				Range =	ppm

APPENDIX B

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist LL Total Dissolved Phosphorus TDP/ LL Total Dissolved Nitrogen TDN

EPA Method 353.2 and EPA 365.1

Lab Numbers: [1] _____ Analyst: _____

_____ Date Digested: _____

Dates Collected: _____ Date Analyzed _____

Procedure	Acceptance Criteria	Status (√)	Comments
Holding Time	48 hours @ 4ºC; 28 days @ –20ºC		
Calibration Curve	Corr. Coeff. ≥ 0.9950		
Reagent Blank	< Reporting Level (0.010 ppm for TDP; 0.100 ppm for TDN)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10 samples		
	Recovery = 90–110%		
External QC	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the run		
	Recovery = 90–110%		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RPD ≤ 10%		
Cadmium Column Check	NO_3/NO_2 X 100=90-110%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.010–0.500 ppm for TDP; 0.100–5.000 ppm for TDN)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

[1]Include beginning and ending numbers, account for gaps by bracketing.

_____ _____
Analyst's Signature and Date Reviewer's Signature and Date

_____
Supervisor's Signature and Date

Reagents	ID	Reagents	ID
Ammonia Buffer		Sulfanilamide	
Ascorbic Acid		Color Reagent	
Borate Buffer		Molybdate	
1M HCl		Color Reagent	
Oxidizing Reagent			

External QC

Identification = _____
True Value = TDN /TDP ppm
Range = TDN ppm
Range = TDP ppm

MDH- Laboratories Administration
DIVISION OF ENVIRONMENTAL SCIENCES

SOP Title:	Determination of Total Dissolved Phosphorus Flow Injection Colorimetric Analysis (EPA Method 365.1)
SOP No.:	CHEM-SOP-EPA 365.1 TDP
Revision:	6.0 Replaces: 5.3 Effective: 8/31/2023
Laboratory:	Inorganics Analytical Laboratory
POC:	Chengyuan Cao chengyuan.cao@maryland.gov

Laboratory Supervisor:	Lara Phillips Signature	8/29/23 Date
QA Officer:	Mohamed Habeeb Signature	08/29/2023 Date
Manager:	Cynthia Stevenson Signature	8/29/2023 Date
Division Chief:	 Signature	8/29/23 Date

REVISION RECORD

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0.0	6/3/2008	N/A	S. Ameli	6/2/2008
1.0	12/2009	Screen snapshots added to procedure, new Sample Run Log, tracking IDs for standards and reagents	S. Ameli	01/2010
2.0	01/2011	New SOP tracking number, technical and editorial changes	J. Freeman-Scott S. Ameli	8/18/2011
2.0	01/2013	Reviewed the SOP	S. Ameli	1/13/2013
3.0	10/09/2014	New SOP tracking number, technical and editorial changes, formatting changes	C. Stevenson S. Ameli	12/2014
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5.3	4/29/2022	Reviewed SOP and edited for clarity	C. Cao I.Ji	5/31/2022
5.3	6/30/2023	Reviewed SOP, updated 5.2.4	C. Cao, L.Phillips	7/15/2023
6.0	8/22/2023	Updated 5.2.4, Updated 9.1.2 and 9.1.3	C. Cao, L.Phillips	8/31/23

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STANDARD OPERATING PROCEDURES

TOTAL DISSOLVED PHOSPHORUS IN ALKALINE PERSULFATE DIGESTS

EPA Method 365.1

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to seawater, brackish water, and non-saline water.

1.2 The applicable range is 0.01 to 0.5 mg P/L.

2.0 SUMMARY OF METHOD

Water samples are digested for one hour with alkaline persulfate to convert all of the phosphorus present in the sample to orthophosphate (PO_4^{3-}). Approximately 1.3 mL of this digest is injected onto the manifold, where orthophosphate reacts with ammonium molybdate and antimony potassium tartrate under acidic condition and then reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. Per manufacture's recommendation, water samples are digested for one hour with alkaline persulfate to oxidize all the phosphorus compounds present in the sample to orthophosphate (PO_4^{3-}). The absorbance is directly proportional to the concentration of phosphorus in the sample.

3.0 INTERFERENCES

3.1 Silica forms a pale blue complex which also absorbs at 880 nm. A silica concentration of 4000 ppm would produce a 1 ppm positive error in orthophosphate.

3.2 Glassware should be washed with 1:1 HCl and rinsed with deionized water in order to prevent possible contamination problems in low level phosphorus determinations.

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during reagent preparation and instrument operation.

4.2 The use of a fume hood, protective eyewear, lab coat and proper gloves must be used when preparing reagents.

4.3 Sodium hydroxide, hydrochloric acid, and sulfuric acid used in this determination have the potential to be highly toxic or hazardous. Consult SDS for detailed explanations.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat QuickChem 8500 Automated Ion Analyzer, which includes the following:

5.1.1.1 Automatic sampler

5.1.1.2 Multi-channel proportioning pump

5.1.1.3 Injection module with a 12.5 cm x 0.5 mm ID sample loop

5.1.1.4 Manifold

5.1.1.5 Colorimetric detector

5.1.1.5.1 Flow cell, 10 mm path length

5.1.1.5.2 Interference filter, 880 nm

5.1.1.6 Computer with Omnion 3.0 Data system and printer

5.1.2 Analytical balance capable of accurately weighing to the nearest 0.0001 g

5.1.3 Top loading balance for weighing chemicals for reagents

5.2 Supplies

5.2.1 Class A volumetric flasks, 50 - 1,000 mL.

5.2.2 Class A volumetric pipettes, 1 - 10 mL.

5.2.3 Automatic pipetters, 100 µL - 10 mL

5.2.4 Digestion tubes - 40 mL vials (Fisher 14-959-37C or equivalent) with autoclavable caps lined with Teflon liners (Kimble Caps Cat # 03-340-77E), pre-wash tubes and caps prior to use in dishwasher acid-wash cycle.

5.2.5 Beakers, disposable, polypropylene, 50 mL (Fisher 01-291-10)

5.2.6 Test tubes, glass, 13 x 100 mm and 16 x 125 mm

5.2.7 Reagent storage bottles, plastic or glass

5.2.8 Ultra High Purity Helium gas for degassing

6.0 REAGENTS AND STANDARDS

6.1 Reagents

Use deionized water (DI) for preparation of all solutions. Prevent the bubble formation by degassing deionized water and all reagents except the standards with helium for two minutes.

6.1.1 Alkaline Persulfate Oxidizing Reagent - In a 1 L volumetric flask, dissolve 20.1 g potassium persulfate ($K_2S_2O_8$), and 3g sodium hydroxide (NaOH) in about 600 mL DI water. Dilute to mark and mix. Prepare fresh daily before use.

6.1.2 Hydrochloric Acid, 1.0 M - Add 83.3 mL concentrated hydrochloric acid (37%, ACS Reagent Grade, d = 1.200) to about 800 mL of DI water in a 1L volumetric flask in a fume hood. Dilute to mark, mix well and prepare monthly.

6.1.3 Stock Ammonium Molybdate Solution - Dissolve 40.0 g ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}$, $4H_2O$) in about 800 mL DI water in a 1 L volumetric flask. Dilute to the mark and stir until completely dissolved; this may take about 4 hours. Store in plastic and refrigerate. This stock may be used up to two months when kept refrigerated.

6.1.4 Stock Antimony Potassium Tartrate Solution - Dissolve 3.22 g antimony potassium tartrate trihydrate ($K(SbO)C_2H_4O_6.3H_2O$) in about 600 mL DI water in a 1 L volumetric flask. Dilute to mark and mix. Store in a dark bottle and refrigerate. This stock may be used up to two months when kept refrigerated.

6.1.5 Molybdate Color Reagent - In a hood, carefully add 70.0 mL concentrated sulfuric acid to about 500 mL water in a 1 L volumetric flask and mix well. Then, add 72.0 mL stock antimony potassium tartrate (reagent 6.1.4) and 213 mL stock ammonium molybdate (reagent 6.1.3). Dilute to the mark with DI water. Prepare weekly and degas with helium.

6.1.6 Ascorbic Acid Reducing Solution - Dissolve 75.0 g ascorbic acid in about 800 DI water in a 1 L volumetric flask. Mix on a magnetic stirrer and dilute to the mark with DI water. Prepare fresh weekly.

6.1.7 Borate Buffer, 1.0 M, pH 7.5 - Dissolve 61.8 g boric acid and 8.0 g sodium hydroxide in about 800 mL DI water in a 1 L volumetric flask. Mix on a magnetic stirrer until it is completely dissolved. Dilute to the mark with DI water. This stock may be used up to two months

6.1.8 Carrier Solution - Combine 300 mL of oxidizing reagent (reagent 6.1.1), 60.0 mL 1 M hydrochloric acid (reagent 6.1.2), and 60.0 mL borate buffer (reagent 6.1.7) in a 1 L volumetric flask, dilute to volume, and stir well. Degas the solution with helium. It is recommended that the carrier is degassed within 4 hours of use and prepared same day of analysis.

6.1.9 Sodium Hydroxide - EDTA Rinse - In a 1L flask, dissolve 65.0 g sodium hydroxide (NaOH) and 6 g tetrasodium ethylenediamine tetraacetic acid (Na_4EDTA) in about 800 mL deionized water. Mix on a magnetic stirrer until it is completely dissolved. Dilute to the mark with deionized water. Prepare as needed.

6.2 Standards

6.2.1 Phosphorous standard (1000 mg P/L) - Purchased from an approved source with expiration date. If this stock is not available, prepare 100 ppm P/L as detailed in standard 6.2.2 below.

6.2.2 Stock Standard Solution (100 mg P/L) - Add 10 mL of Phosphorus 1000 ppm stock standard (standard 6.2.1) to about 60 mL of DI water in a 100 mL volumetric flask, dilute to mark, and mix well. If the 1000 ppm P stock is not available, prepare the 100 ppm stock by dissolving 0.4394 g of anhydrous potassium dihydrogen phosphate (KH_2PO_4) which has been dried for two hours at 110 ^oC in about 800 mL deionized water. Dilute to the mark and invert to mix. Prepare monthly.

6.2.3 Combined Intermediate Standard Solution (1 mg P/L and 10 mg N/L) - Add 10 mL of stock standard (standard 6.2.2) and 10 mL of 1000 mg N/L (stock standard solution for total dissolved nitrogen determination) to about 800 mL DI water in a 1 L volumetric flask. Dilute to mark and mix. Prepare weekly.

6.2.4 Spiking Solution - Mix 5 mL of 1000 mg/L N and 5 mL of 100 mg/L P (standard 6.2.2) in a small vial with cap. Mix well and pipette 50 µL of this solution into 10 mL of sample (sample spike) or 10 mL of DI water (blank spike). Prepare monthly.

6.2.5 Combined Working Standard Solutions - Use the following table to prepare standards. Dilute each to 100 mL and mix well. DI water is used as the last standard (0.00 ppm). Prepare per run and standards are good for 48 hours.

Concentration mg P/L	Combined Working Standard, mL	Final Volume, mL
0.50	50 mL	100 mL
0.20	20 mL	100 mL
0.10	20 mL	200 mL
0.05	5 mL	100 mL
0.02	2 mL	100 mL
0.01	1 mL	100 mL
0.00	0 mL	100 mL

Note: ***The analyst may save a set of standards from a previous run for troubleshooting purposes only.***

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are filtered in the field, collected in plastic bottles or cubitainers and preserved by cooling to 4 ^{o}C.

7.2 Samples are analyzed within 48 hours after collection. If they cannot be analyzed within this time period, they may be frozen at -20 ^{o}C as soon as possible at the laboratory. The holding time for frozen samples is 28 days.

8.0 QUALITY CONTROL

8.1 An initial Demonstration of Performance (IDP) to establish the instrument's capability is required prior to its use in analyzing client's samples. The linearity of calibration range (LCR) and the ability to quantify correctly Quality Control Samples are used to assess performance.

8.2 A mid-range check standard and a calibration blank are analyzed Immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. The acceptable concentrations for the check standard must be within ±10% of the true value. If a check standard fails, the samples between the last satisfactory check standard and the unsatisfactory standard are re-analyzed. Blank concentration must be less than the reporting level of 0.01 ppm. Blanks that do not meet this criterion are reanalyzed.

8.3 Every tenth sample is duplicated (analyzed from two different tubes) and spiked. The accepted values for the relative percent difference (RPD) must fall within ±10 % and for spike recovery between 90 - 110%. If these do not fall within the accepted ranges, the corresponding analyses are repeated.

8.4 A QC sample with a known concentration and a range is analyzed at the beginning and at the end of each run. QC samples that do not fall within the accepted range are repeated.

8.5 Samples with a concentration exceeding the calibrated range are diluted manually and reanalyzed.

8.6 Data acceptance criteria are listed on the data review checklist (Appendix A).

8.7 The laboratory annually participates in USGS, CBL, ERA Water Supply (WS) and Water Pollution (WP) proficiency studies.

8.8 A demonstration of capability study is performed by each analyst performing the test by analyzing four replicates of an external quality control sample during one or two analytical runs.

8.9 The U.S. EPA MDL procedures (40 CFR Part 136, Appendix B) including the EPA *Definition and Procedure for the Determination of the Method Detection Limit*, Revision 2 (2016); EPA *Methods Update Rule* (Final rule - August 28, 2017); EPA *Method Detection Limit - Frequent Questions*; and EPA Part 136 *Method Update Rule Revisions to Appendix B – MDL Procedure as Applied to Drinking Water* (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.

9.0 PROCEDURE

9.1 Sample preparation

9.1.1 Make a list of samples to be analyzed and pour aliquots of samples into labeled 16 mm x 125 mm test tubes.

9.1.2 Pipette 10 mL of each standard or sample into pre-washed digestion tubes.

9.1.3 Pipette 10 mL of a mid-range standard (0.3 mg P/L and 3.0 mg N/L), a blank, a blank spike, and an external quality control sample into pre-

washed digestion tubes with each tray of 24 samples. Prepare a duplicate and a spike of every 10th sample.

9.1.4 Pipette 10 mL of the nitrate and nitrite standards for cadmium column check (standard 6.2.5) into pre-washed digestion tubes. DONE FOR TDN ONLY

9.1.5 Add 5 mL of Alkaline Persulfate Oxidizing Reagent (reagent 6.1.1) to each tube, screw the caps on tightly and mix each. Digest the standards, samples, and all the quality control samples in the autoclave for 60 minutes after the autoclave reaches the set temperature and pressure of 121 ºC (250 ºF) @ 17 psi. *Please see the manual for Autoclave Operation.*

9.1.6 The autoclave will turn off automatically. Allow the digests to cool for 5 minutes. Remove the tubes from the autoclave and let the digests come to room temperature. Add 1 mL of borate buffer, vortex, and pour into 13 x 100 mm culture tubes analyze them as soon as possible.

9.1.7 If samples cannot be analyzed same day, **do not add the borate buffer**, refrigerate the digests at 4 ºC. Refrigerated digests will be brought up to room temperature, and then 1 mL borate buffer (reagent 6.1.7) is added to each tube and mixed.

9.1.8 Analyze the digests using the procedure described in 9.2.

9.2 Instrument Calibration and Sample Analysis

9.2.1 Set up manifold according to the manifold diagram.

9.2.2 Pump deionized water through all reagent lines and check for leaks and a smooth flow. Switch to reagents and allow the system to stabilize and a stable baseline is achieved.

9.2.3 Enter sample information required by the data system.

9.2.4 Place standards, blanks, samples, quality controls, etc. in the auto sampler according to the run table.

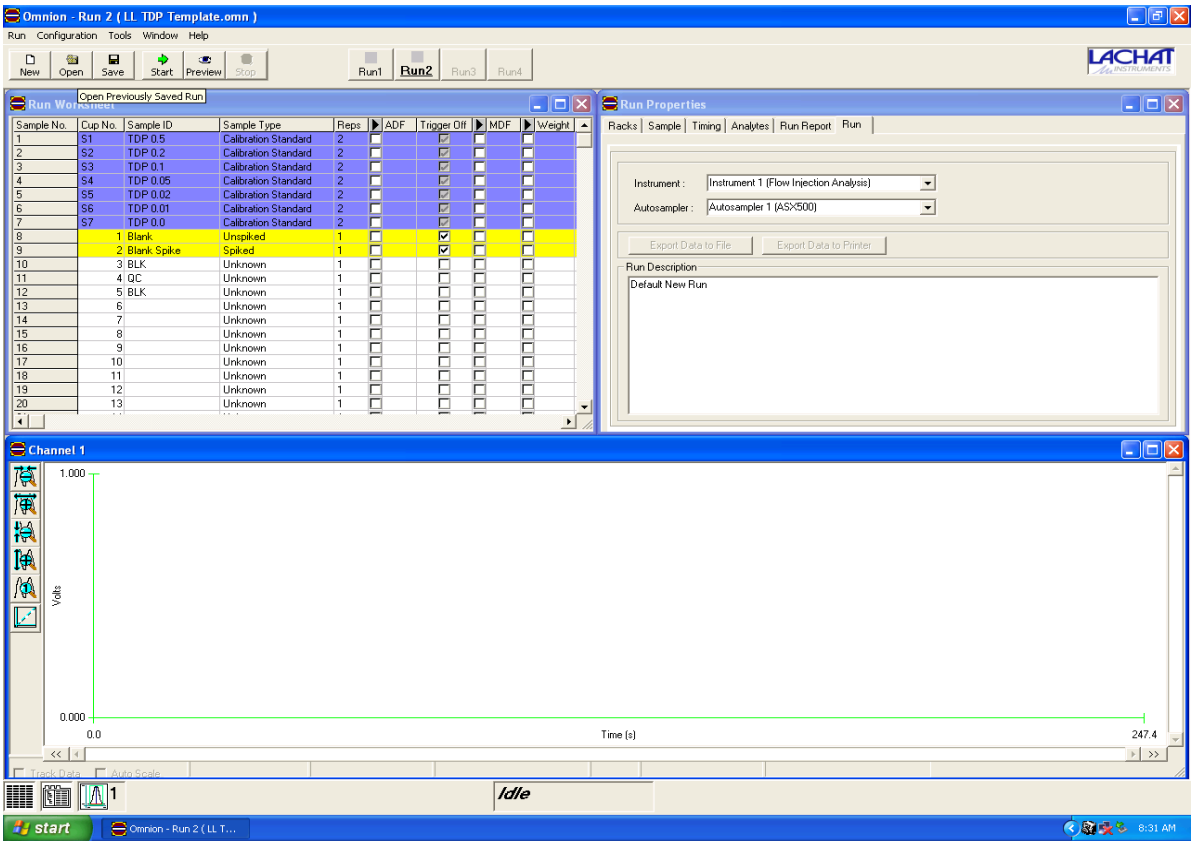
9.2.5 Click on **"Start"** tab to begin the analysis.

9.3 Instrument set-up and sample analysis

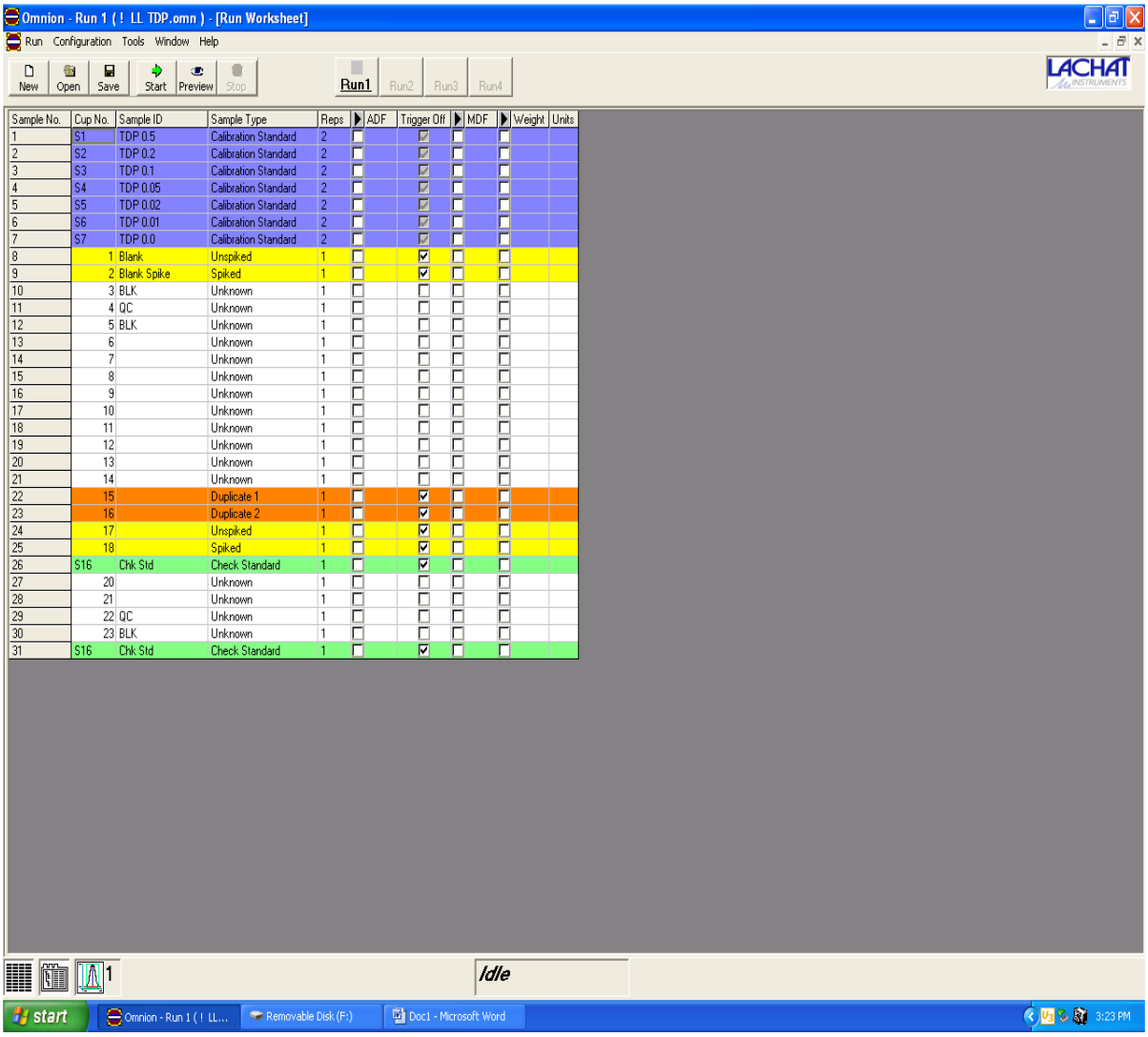
9.3.1 Set up manifold as in the diagram.

9.3.2 Turn on the Lachat instrument, computer, monitor, and printer.

9.3.3 Double click on the short-cut for **"LL TDP"** to open the template, which consists of three windows.



9.3.4 Maximize the **"Run Worksheet"** window at the top left hand corner of the screen by clicking on the middle square on that screen to open the worksheet template. Enter sample identifications in the sample ID column, making sure that all duplicates and spikes are entered in the appropriate locations of the worksheet. Identifications of the quality control samples analyzed at the beginning of the run and the locations of the duplicates and the spiked have been saved on the template. Press **"Enter"** key after each entry in order to save all entries.



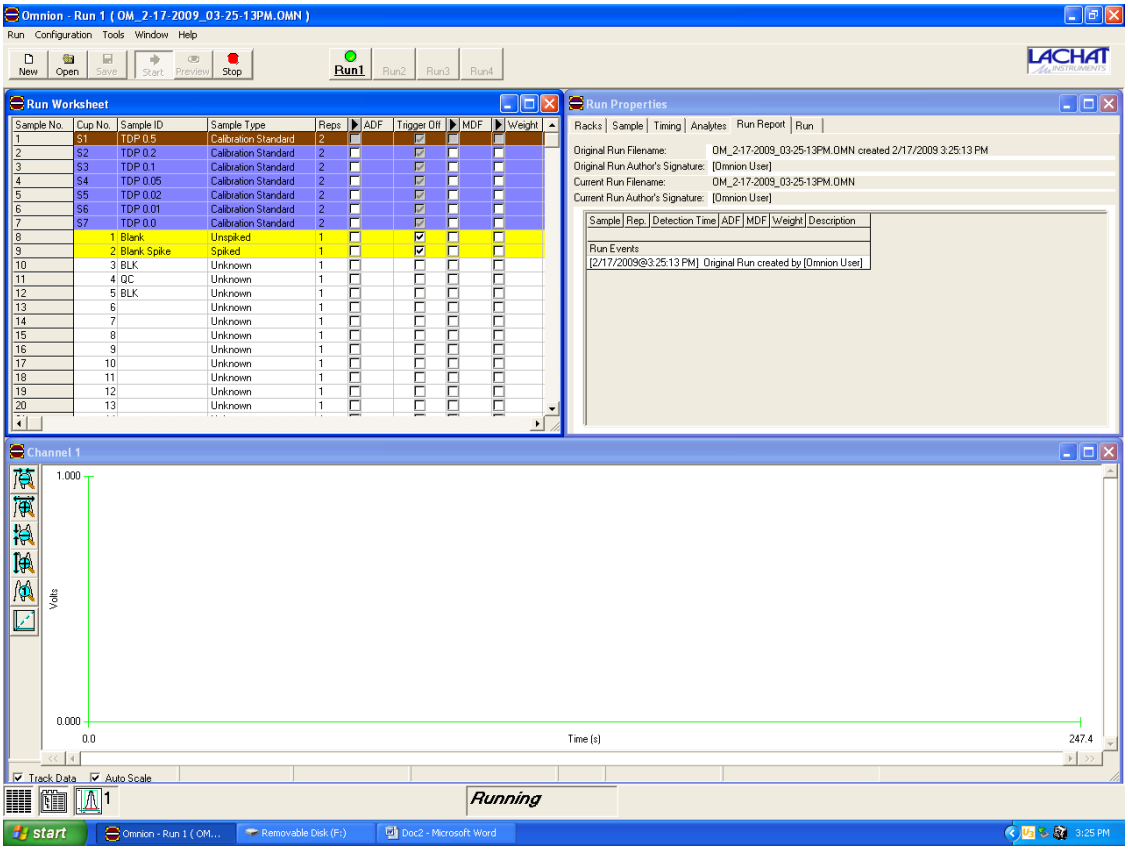
Sample No.	Cup No.	Sample ID	Sample Type	Reps	ADF	Trigger Off	MDF	Weight	Units
1	S1	TDP 0.5	Calibration Standard	2					
2	S2	TDP 0.2	Calibration Standard	2					
3	S3	TDP 0.1	Calibration Standard	2					
4	S4	TDP 0.05	Calibration Standard	2					
5	S5	TDP 0.02	Calibration Standard	2					
6	S6	TDP 0.01	Calibration Standard	2					
7	S7	TDP 0.0	Calibration Standard	2					
8	1	Blank	Unspiked	1					
9	2	Blank Spike	Spiked	1					
10	3	BLK	Unknown	1					
11	4	QC	Unknown	1					
12	5	BLK	Unknown	1					
13	6		Unknown	1					
14	7		Unknown	1					
15	8		Unknown	1					
16	9		Unknown	1					
17	10		Unknown	1					
18	11		Unknown	1					
19	12		Unknown	1					
20	13		Unknown	1					
21	14		Unknown	1					
22	15		Duplicate 1	1					
23	16		Duplicate 2	1					
24	17		Unspiked	1					
25	18		Spiked	1					
26	S16	Chk Std	Check Standard	1					
27	20		Unknown	1					
28	21		Unknown	1					
29	22	QC	Unknown	1					
30	23	BLK	Unknown	1					
31	S16	Chk Std	Check Standard	1					

9.3.5 Print a copy of this worksheet by first double clicking on **"Run"** icon and then selecting **"Export Worksheet Data"**.

9.3.6 Click on **"Window"** tab and then, click on **"Tile"** to return to the screen with three windows.

9.3.7 Place standards in standard vials in the standard rack in order of decreasing concentration in positions 1 to 7 (STD 7 is 0.00 mg/L). Place the check standard vial in position 16 (S16) of the standard rack. Pour samples and quality control samples into 13 x 100 mm test tubes and place them in the sample racks according to the worksheet prepared in 9.2.4.

9.3.8 Pump deionized water through all reagent lines for 15 – 20 minutes and check for leaks and smooth flow. Switch to reagents and continue pumping for about 10 minutes. Click on **"Preview"** tab to monitor the baseline.



9.3.9 Once a stable baseline is achieved, click on **"Stop"** tab to stop monitoring the baseline. Click on **"Start"** tab to begin the analysis.

9.3.10 If the calibration passes, instrument will continue to analyze the samples. If it fails, take appropriate corrective actions and recalibrate before proceeding to analyze samples.

9.3.11 Manual dilution using the digested blank will be performed to reanalyze samples with concentrations exceeding the calibrated range.

9.2.12 After the run is complete, remove the reagent lines and place them in DI water and rinse for about 15 minutes. If necessary, rinse the system with the NaOH - EDTA rinse solution (reagent 6.1.5) for about 5 minutes followed by DI water for 10 - 15 minutes. Pump the tubes dry, release the pump tubing, and turn off the pump.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All the calculations are performed by the Omnion 3.0 software system. It uses a calibration graph of peak area versus concentration orthophosphate concentrations in the samples. All standards are analyzed in duplicate, and these points are used to generate the calibration curve. A duplicate peak may be excluded from the calibration if it is determined to be faulty (i.e. corrupted, damaged, misshapen) Samples with orthophosphate concentrations greater than 0.5 ppm are manually diluted and reanalyzed.

10.2 Calculate the percentage spike recovery of the laboratory fortified samples as follows:

$$\%\,SR = \frac{(\text{spiked sample conc.} - \text{sample conc.}),\text{ppm}}{\text{amount of spike added to sample, ppm}} \times 100$$

10.3 Calculate the relative percentage difference for the duplicated samples as follows:

$$\%\,RPD = \frac{\text{difference between the duplicates}}{\text{average of the duplicates}} \times 100$$

10.4 The reporting level for this method is the concentration of the lowest standard, which is 0.01 ppm.

10.5 Report results for all routine samples to three decimal places and for performance evaluation (PE) samples to three significant figures.

11.0 DATA AND RECORDS MANAGEMENT

11.1 The analysis data for the calibration blank, external QC and instrument performance check solution (IPC), i.e. the mid-range check standard, is kept on file with the sample analysis data.

11.2 Normal turnaround time for samples submitted to this lab is 2 to 10 days from the receipt. Results are reported in writing on the sample analysis request form.

11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five years custody period.

12.0 WASTE MANAGEMENT

12.1 It is laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume and bench operation.

12.2 Samples and standards are poured down the drain and flushed with running water.

13.0 REFERENCES

13.1 EPA Method 365.1, *Methods for the Determination of Inorganic Substances in Environmental Samples*, August 1993.

13.2 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 21st Edition, Method 4500- P E, 2005.

13.3 Lachat Instruments QuickChem Method 30-115-01-4-A, *Determination of Total Phosphate by Flow Injection Analysis.*

13.4 Lachat Instruments, *Operating Manual for the Quikchem Automated Ion Analyzer*.

13.5 Division of Environmental Sciences, Maryland Department of Health, *Quality Assurance Plan*, SOP No. Chem-SOP-QAP.

13.6 Division of Environmental Sciences, Maryland Department of Health, *Quality Manual,* SOP No. QA-SOP-QM.

13.7 EPA Definition *and Procedure for the Determination of the Method Detection Limit, Revision 2* December 2016

APPENDIX A
Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist LL Total Dissolved Phosphorus (TDP)/Alkaline Persulfate Digestion

EPA Method 365.1

Lab Numbers: [1] _____ Analyst: _____

_____ Date Digested: _____

Dates Collected: _____ Date Analyzed _____

Procedure	Acceptance Criteria	Status (✓)	Comments
Holding Time	48 hours @ 4ºC 28 days @ –20ºC		
Calibration Curve	Corr. Coeff. ≥ 0.9950		
Reagent Blank	< Reporting level (0.010 ppm)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10		
	Recovery = 90–110%		
External QC	Beginning and end of each run		
	Within acceptance range		
Check Standard	After every 10th sample and at the end of the run		
	Recovery = 90–110%		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RPD ≤ 10%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.010–0.500 ppm)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

[1]Include beginning and ending numbers, account for gaps by bracketing.

_____ _____
Analyst's Signature & Date Reviewer's Signature & Date

_____
Supervisor's Signature & Date

Reagents	ID	Reagents	ID
Color Reagent		Oxidizing Reagent	
Ascorbic Acid		Borate Buffer	
1M HCl			

External QC
Identification = _____
True Value = _____ ppm
Range = _____ ppm

SOP Title:	Determination Particulate Carbon and Particulate Nitrogen (Exeter Analytical CE 440)
SOP No.:	CHEM-SOP-CE 440
Revision:	2.5 Replaces: 2.4 Effective: 7/15/2023
Laboratory:	Inorganics Analytical Laboratory
Author / POC:	Jake Kilczewski Jacob.Kilczewski@maryland.go

Laboratory Supervisor:	Lara Phillips Signature	7/10/2023 Date
QA Officer:	Mohamed Habeeb Signature	07/11/23 Date
Manager:	Cynthia Stevenson Signature	7/12/2023 Date
Division Chief:	 Signature	07/12/2023 Date

REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	12/09	N/A	Taiyin Wei	1/10
1.0	1/11	New SOP tracking number	Asoka Katumuluwa	1/2010
1.1	8/11	Technical and editorial changes	Shahla Ameli	7/2011
2.0	10/14	Reviewed SOP-document control, editorial and technical changes	Shahla Ameli Lara Phillips	12/2014
2.1	6/10/15	Reviewed, Revised procedure, section 8.3	Lara Phillips Shahla Ameli	7/1/2015
2.2	5/9/16	Formatting changes, reviewed SOP	L Phillips J. Freeman-Scott S. Ameli	7/1/2016
2.3	7/1/17	Formatting changes, reviewed SOP, Revised sections 2.0, 4.2, 5.1.4,6.1, 9.2.6, 9.3.4.4.5, 9.4 and appendix B	L Phillips J. Freeman-Scott S. Ameli	7/1/2017
2.4	6/4/18	Reviewed document, updated section 8.7 and 13.3	L Phillips J. Freeman-Scott S. Ameli	7/1/18
2.4	3/1/19	Reviewed document	L Phillips S. Ameli	3/4/19
2.5	4/21/20	Reviewed document and updated contact information.	L Phillips I. Ji	5/1/20
2.5	4/9/21	Reviewed document	L Phillips C. Stevenson	5/1/21
2.5	5/13/22	Reviewed document	L Phillips	5/23/22
2.5	6/30/23	Reviewed document	L Phillips	7/15/23

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STANDARD OPERATING PROCEDURES

DETERMINATION OF PARTICULATE CARBON & PARTICULATE NITROGEN

Exeter Analytical CE 440

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the carbon and nitrogen content in organic and inorganic compounds in surface and saline waters.

1.2 This instrument performs elemental analysis of material retained on filters used in water filtration applications.

2.0 SUMMARY OF METHOD

Particulate material on a pre-ignited glass fiber filter is combusted in an oxygen-helium atmosphere at 980°C. The products of combustion are passed over suitable reagents to undergo complete oxidation and removal of undesirable by-products. The remaining gas proceeds to a mixing chamber. This uniform gas mixture, then passes through a series of traps each bracketed with a pair of thermal conductivity detectors. The difference in the signals from each of these pairs of detectors is proportional to the amount of hydrogen (H in H_2O) and carbon (C in CO_2) present in each sample. The only remaining sample gas, nitrogen (N in N_2), is measured against the pure helium carrier gas.

3.0 INTERFERENCES

3.1 Sampling is the single largest determination of data quality. Duplicates or even triplicates sampling is recommended.

3.2 Filter blanks should be treated the same as filter samples in all respects.

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during instrument operation.

4.2 Combustion and reduction tubes are heated to 980°C and 650°C respectively. Wear heat resistant gloves and work on a heat resistant bench top when changing these tubes.

4.3 Wear insulated gloves and use tongs to remove hot crucibles from the furnace, and place them on a metal tray.

4.4 Each employee is issued a *Laboratory Safety Manual* and a *Quality Assurance Plan* and is responsible for adhering to the recommendations contained therein.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 CE-440 Elemental Analyzer

5.1.2 CEC-490 interface unit

5.1.3 PC computer

5.1.4 Drying oven, 45°C-55°C

5.1.5 Muffle furnace

5.1.6 Microbalance, Sartorius ME 5

5.2 Chemicals

5.2.1 Silver Tungstate-Magnesium Oxide on Chromosorb-A, 20 - 30 mesh

5.2.2 Silver Oxide-Silver Tungstate on Chromosorb-A, 20 – 30 mesh

5.2.3 Silver Vanadate on Chromosorb, 20 – 30 mesh

5.2.4 Ascarite, 20 mesh

5.2.5 Magnesium Perchlorate - slightly crush the irregular chunks to approx. 1/16” to 3/32” diameter

5.2.6 Copper wire

5.2.7 Compressed Oxygen gas

5.2.8 Compressed Helium gas

5.3 Supplies

5.3.1 Filters – Whatman GF/F glass fiber, 25 mm diameter, 0.7 µm particle retention

5.3.2 Nickel sleeves – 7 x 5 mm

5.3.3 Tin capsules – smooth, 6 x 2.9 mm

5.3.4 Desiccators and Desiccants

5.3.5 Microspectula – Hayman style, meets ASTM E 124, Fisher cat. no. 21-401-25A

5.3.6 Microforceps – smooth tips

5.3.7 Pinning forceps

5.3.8 Quartz wool

5.3.9 Vacuum grease

5.3.10 Gloves – heat resistant

5.3.11 Crucible dishes – 3" diameter

5.3.12 Crucible tongs

6.0 REAGENTS AND STANDARDS

6.1 Standard

Acetanilide ($C_6H_5NHCOCH_3$), Acros Organics or Exeter Analytical

6.2 External quality control samples

6.2.1 Domestic Sludge – Standard Reference Material 2781, National Institute of Standards & Technology

6.2.2 Marine Sediment Reference Materials (PACS-2) – National Research Council Canada

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

The filter pads (9.2.1 – 9.2.4) are kept frozen and dried pads (9.2.6) must be desiccated.

8.0 QUALITY CONTROL

8.1 The calibration series must be placed at the beginning of the wheel. (9.3.1)

8.2 Continue the sample run only after the calibration standards have been analyzed and confirmed that the calculated K_C and K_N are acceptable. KC = 18 – 25
KN = 7 – 10

8.3 Every tenth sample should be duplicated and followed by an Acetanilide standard.

8.4 The relative percent difference (RPD) for field and sample duplicates need to be calculated.

8.5 A standard series (standard, blank) should also be placed at the end of the wheel.

8.6 Data acceptance criteria are listed on the data review checklist (Appendix A).

8.7 The U.S. EPA MDL40 procedures CFR Part 136, Appendix B) including the EPA *Definition and Procedure for the Determination of the Method Detection Limit*, Revision (2016); EPA *Methods Update Rule* (Final rule - August 28, 2017); EPA *Method Detection Limit - Frequent Questions*; and EPA Part 136 *Method Update Rule Revisions to Appendix B – MDL Procedure as Applied to Drinking Water* (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.

9.0 PROCEDURE

9.1 Preparation for Analysis

9.1.1 Filters – Place the filters in ceramic crucibles/dishes, combust at a temperature of 450 – 500°C for one hour, remove from oven and then place them in a desiccator to be cooled. Remove from the desiccator and store in a closed container. These filters are sent to the field for sample collection.

9.1.2 Nickel sleeves – Place the nickel sleeves in stainless cups and muffle at 900°C for one hour. Remove, cool down in a desiccator, and store in a capped glass jar. Pre-muffled sleeves can be purchased from Exeter Analytical, Cat # 6703-0499M.

9.2 Sampling, Filtration and Preparation (performed in the field)

9.2.1 Place a pre-combusted filter pad, with rough side up, in a vacuum filtration assembly.

9.2.2 Mix each sample well before pouring a known volume of sample (anywhere from 10 to 500 mL depending on the density of sample) and quickly pour sample into the filtration assembly.

9.2.3 Filter at a low pressure (15 inches Hg); vacuum to dryness and then break the seal of the vacuum.

9.2.4 Fold the filter in half (exposed surface inside), wrap in aluminum foil and label the sample with the date, ID, volume filtered, and scientist signature.

9.2.5 Freeze at –10°C until ready for analysis.

9.2.6 Prior to analysis, samples should be placed in a drying oven at

45°C-55°C for at least 12 hours. Once dried, leave samples in a desiccator until ready to use.

9.3 Sample Measurements

9.3.1 Prepare a sample run log (Appendix B) starting with a calibration series that is consisting of 1 nickel sleeve blank, 1 condition, 1 tin capsule blank, 1 condition, and then followed with 3 acetanilide standards.

9.3.2 Standard Preparation

9.3.2.1 Weigh out approximately 1500 µg of acetanilide into a tin capsule for each standard.

9.3.2.2 Quarterly; Weigh out 200 to 250 µg of domestic sludge into a pre-weighed tin capsule as the reference standard for particulate nitrogen (PN).

9.3.2.3 Quarterly; Weigh out about 1000 µg of PACS-2 into a pre-weighed tin capsule as a reference standard for particulate carbon (PC).

9.3.3 Sample Preparation

9.3.3.1 On a clean surface, place a 7 x 5 mm nickel sleeve into the filter loading die with a plastic loading funnel.

9.3.3.2 Fold the filter and squeeze it into the sleeve with a microforceps. Carefully pull out the microforceps. Use the 4 mm loading plunger to force the compressed filter into the nickel sleeve. Make sure no excess filter protrudes above the lip of the sleeve.

9.3.3.3 Transfer the standards and samples into the 64 sample wheel according to the run log (9.2.1).

9.3.4 Instrument Operation

9.3.4.1 On the main menu, click “Run” and select “Carbon, Hydrogen, Nitrogen” in the pull down list. Enter date (ddmmyy) as the run name, then click “Run” to open the sample information box.

9.3.4.2 Enter sample name and sample weight according to the run log. Enter 100 for the weight of the filter samples. Double check all entries.

9.3.4.3 Click “Run” to open the list of instructions.

9.3.4.4 Installation of the sample wheel

9.3.4.4.1 Open the manual purge valve on the injection box. Loosen the 4 cover screws and lift the lid. Remove the empty wheel if necessary.

9.3.4.4.2 Insert the loaded sample wheel with the locking pin in place (position 24). Tilt the wheel slightly, line up the scribe mark on the wheel with the ratchet in the housing. Make sure the mark on the tray is touching the triangular marker on the instrument. Lower the wheel, and make sure that it is properly seated. Place the locking pin in the center hole.

9.3.4.4.3 Close the cover, and tighten equally on all four screws.

9.3.4.4.4 Open and remove any spent capsules in the capsule receiver. Re-install the cover.

9.3.4.4.5 Check the helium pressure to be sure there is adequate gas to perform the run. Adjust the helium pressure to allow for a fill time near 30 (not < 20). The oxygen pressure is set around 25 psi with enough gas available to complete the run. The combustion temperature is set to 980°C, and reduction temperature at 650°C.

9.3.4.4.6 Close the valve. Click “OK” to start the run.

9.3.5 Data Analysis

9.3.5.1 Arrange the data print outs in order.

9.3.5.2 Open the Excel work book template from PCPN / Calculations / Year / Month.

9.3.5.3 Update the sample names and volumes in the spread sheet.

9.3.5.4 Enter the concentrations for PC and PN in their respective columns.

9.5.3.5 Confirm that the calculations are right and the formulae are ok and consistent. Save the file.

9.5.3.9 Double check all entries and print out the results.

9.4 Instrument maintenance

Replace and pack (Appendix C) reduction tube after 300 to 400 runs; combustion tube after 1000 runs; CO_2 or H_2O trap after 500 runs, and helium or oxygen scrubber after 2000 runs or sooner if necessary.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Calculate the concentrations of PC or PN using the following formula:

$$\text{PC/PN, ppm} = \frac{\text{PC/PN, ug}}{\text{sample volume filtered, mL}}$$

10.2 Calculate the relative percent difference (RPD) for the duplicated samples as follows:

$$\text{RPD} = \frac{\text{difference between the duplicates}}{\text{average of the duplicates}} \text{ x } 100$$

11.0 DATA AND RECORDS MANAGEMENT

11.1 Instrument maintenance, instrument calibration, and quality control data are kept in binders and test results are kept in the file cabinet.

11.2 Normal turnaround time for samples submitted to this lab for analysis will be 2 to 10 days from receipt. Results are reported in writing on a sample analysis request form.

11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five years custody period.

12.0 WASTE MANAGEMENT

All spent capsules, combustion tube, reduction tube, and absorbent tubes are disposed of as regular trash.

13.0 REFERENCES

13.1 Exeter Analytical, Inc., *Model 440 CHN/O/S Elemental Analyzer Manual,* 1994.

13.2 Division of Environmental Sciences, Maryland Department of Health, *Quality Assurance Plan,* SOP No. CHEM-SOP-QAP

13.3 Division of Environmental Sciences, Maryland Department of Health, *Quality Manual,* SOP No. QA-SOP-QM

13.4 EPA *'Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. Dec 2016.*

APPENDIX A

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist – PC & PN

Exeter Method 440

Lab Numbers[1]:_____

Date Collected: _____ Date Analyzed: _____ Analyst: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	28 days @ – 20°C		
2 Acetanilide Calibration Standards	KC = 18 – 25 KN = 7 – 10		
Blank	BC < 500 BN < 250		
Check Standard	After every 10th sample and at the end of the run		
	%C = 71.09 (Range = 70.005 – 71.569) %N = 10.36 (Range = 9.934 – 10.914)		
External PC QC[2] Analyze Quarterly	Within acceptable range		
	Last date analyzed:		
External PN QC[3] Analyze Quarterly	Within acceptable range		
	Last date analyzed:		
Field Filter Blank	PC < 25 µg; PN < 2 µg		
Field and Sample Duplicates	RPD Calculated		
Decimal Places Reported	3		
Sample Calculation	Done correctly		
Changes/Notes	Clearly stated		

* Check (√) if criteria are met. [1]Include beginning and ending numbers; account for gaps by bracketing.

_____ _____
Analyst's Signature & Date Reviewer's Signature & Date

_____
Supervisor's Signature & Date

[2]PC QC Sample: PACS-2 Tracking ID: _____

True Value = _____ Acceptable Range =_____

[3]PN QC Sample: D. Sludge Tracking ID: _____

True Value = _____ Acceptable Range =_____

APPENDIX B

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Sample Run Log – Excel Template Particulate Carbon and Particulate Nitrogen

Exeter Method CE 440

Pos	Sample Name	wt (µg)	C-Result	H-Result	N-Result
1	Blank (B)	-			
2	cond (%)	1500			
3	Sleeve Blank (B)	-			
4	cond (%)	1500			
5	STD1 (K)	1500			
6	STD1 (K)	1500			

Position	Sample Name/No.		Sample wt (ug)	Sample vol (mL)	PC(ug)	PN(ug)	ppm PC	ppm PN	avg. PC	avg. PN
7	Acetanilide		1500	-			%C=		%N=	
8	Filter	a	-	-			ug PC=	#DIV/0!	ug PN=	#DIV/0!
9		b	-	-						
10			-				#DIV/0!	#DIV/0!		
11			-				#DIV/0!	#DIV/0!		
12			-				#DIV/0!	#DIV/0!		
13			-				#DIV/0!	#DIV/0!		
14			-				#DIV/0!	#DIV/0!		
15			-				#DIV/0!	#DIV/0!		
16			-				#DIV/0!	#DIV/0!		
17			-				#DIV/0!	#DIV/0!		
18			-				#DIV/0!	#DIV/0!		
19	SampleDup	a	-				#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
20		b	-				#DIV/0!	#DIV/0!		
21	Acetanilide		1500	-			%C=		%N=	
22			-				#DIV/0!	#DIV/0!		
23			-				#DIV/0!	#DIV/0!		
24			-				#DIV/0!	#DIV/0!		
25			-				#DIV/0!	#DIV/0!		
26			-				#DIV/0!	#DIV/0!		
27			-				#DIV/0!	#DIV/0!		
28			-				#DIV/0!	#DIV/0!		
29			-				#DIV/0!	#DIV/0!		
30			-				#DIV/0!	#DIV/0!		
31	SampleDup	a	-				#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
32		b	-				#DIV/0!	#DIV/0!		
33	Acetanilide		1500	-			%C=		%N=	
34	Blank		-	-	BC=		BH=		BN=	

APPENDIX C

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Tube Replacement – PC & PN

Exeter Method 440

CHN Mode Combustion Tube

Silver tungstate / Magnesium oxide on chromosorb

Silver Oxide / Silver tungstate on chromosorb

Silver vanadate on chromosorb

Silver gauze

Quartz wool

Platinum gauze

CHN Mode Reduction Tube

Copper wire

APPENDIX C (continued)

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Tube Replacement – PC & PN

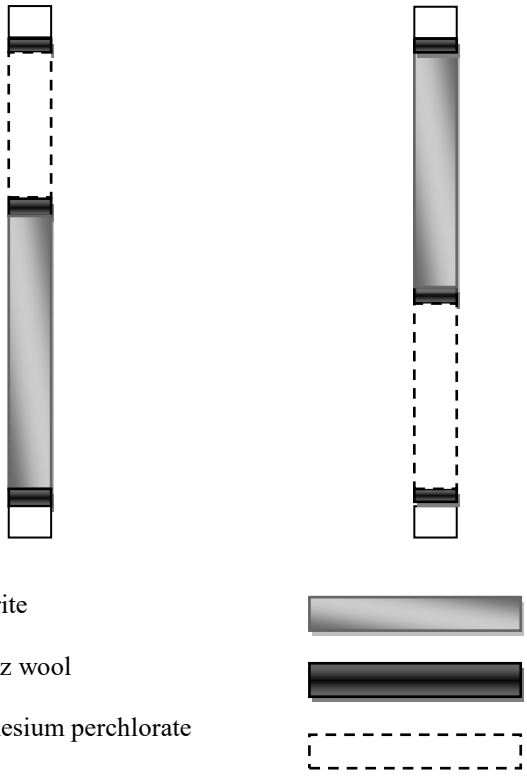
Exeter Method 440

CHN Mode Helium & Oxygen Scrubbers

CHN Mode CO_2 Trap

(This end up)

CHN Mode H_2O trap



Ascarite

Quartz wool

Magnesium perchlorate

MDH- Laboratories Administration
DIVISION OF ENVIRONMENTAL SCIENCES

Title:	Determination of Ammonia – Low Level Flow Injection Colorimetric Analysis EPA Method 350.1
SOP No.:	CHEM-SOP-EPA 350.1
Revision:	5.2 Replaces: 5.1 Effective: 7/15/2023
Laboratory:	Inorganics Analytical Laboratory
POC:	Jacob Kilczewski Jacob.kilczewski@maryland.gov

Laboratory Supervisor:	Lara Phillips Signature	7/11/2023 Date
QA Officer:	Mohamed Habeeb Signature	07/11/23 Date
Manager:	Cynthia Stevenson Signature	7/12/2023 Date
Division Chief:	 Signature	07/12/2023 Date

REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	6/3/2008	N/A	S. Ameli	6/2/2008
1.0	12/2009	Screen snapshots added to procedure, new Sample Run Log, tracking IDs for standards and reagents	S. Ameli	01/2010
2.0	08/2011	New SOP tracking number and technical and editorial changes	C. Vares S. Ameli	08/18/2011
2.1	12/12/2012	Section 6.0 and technical and editorial changes	C. Vares S. Ameli	12/12/2012
2.1	8/20/2013	Reviewed SOP	C. Stevenson S. Ameli	12/12/2012
3.0	10/09/2014	New SOP tracking number and technical and editorial changes	C. Stevenson C. Vares S. Ameli	12/01/2014
3.0	6/1/2015	Reviewed SOP	C. Stevenson	7/1/2015
3.1	5/5/2016	Reviewed and formatted SOP	C. Stevenson	7/1/2016
3.2	6/1/2017	Reviewed and organizational name changes	S. Ameli C. Vares C. Stevenson	7/1/2017
4.0	3/15/2018	Adopted Salicylate Method	S. Ameli C. Vares C. Stevenson	3/26/2018
5.0	6/13/2018	Reference new MDL requirements, 8.7	S. Ameli C. Vares C. Stevenson	7/1/2018
5.0	2/22/2019	Reviewed SOP	S. Ameli C. Vares C. Stevenson	3/4/2019
5.1	4/17/2020	Edited for clarity	I. Ji C. Stevenson	5/1/2020
5.2	3/19/2021	Reviewed SOP, Technical changes in section 10.1	I. Ji	5/1/2021
5.2	4/21/2022	Reviewed SOP	I. Ji	5/31/2022
5.2	6/30/2023	Reviewed SOP	J.Kilczewski/L.Phillips	7/15/2023

TABLE OF CONTENTS

STANDARD OPERATING PROCEDURE

DETERMINATION OF AMMONIA (LOW LEVEL) FLOW INJECTION COLORIMETRIC ANALYSIS

EPA Method 350.1

1.0 SCOPE AND APPLICATION

1.1 This method determines Ammonia in industrial samples, drinking, ground and surface waters.

1.2 The applicable range of this method is 0.008 to 0.500 mg N/L.

2.0 SUMMARY OF METHOD

2.1 The salicylate method is a variation of the Berthelot-Phenate method but does not require the use and disposal of toxic phenol. When ammonia is heated with salicylate and hypochlorite in an alkaline phosphate buffer an emerald green color is produced which is proportional to the ammonia concentration. The color is intensified by the addition of sodium nitroprusside.

The salicylate method involves a three-step reaction sequence. The first reaction step involves the conversion of ammonia to monochloroamine by the addition of chlorine. The monochloroamine then reacts with salicylate to form 5-aminosalicylate. Finally, the 5-aminosalicylate is oxidized in the presence of sodium nitroferricyanide (a catalyst) to form a blue-green colored dye that absorbs light at 650nm. In the assay described below, the colorimeter uses an ammonia standard curve to determine the amount of ammonia in samples.

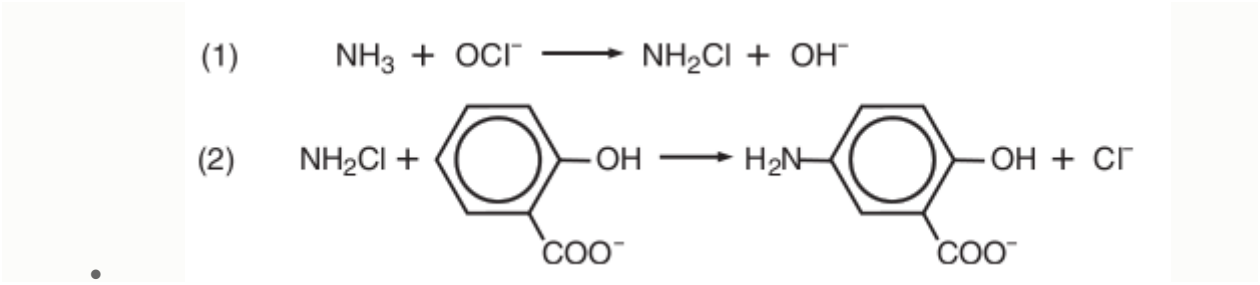


Fig 1: Ammonia compounds are initially combined with hypochlorite to form monochloramine (1), which then reacts with salicylate to form 5-aminosalicylate (2).

3.0 INTERFERENCES

3.1 In alkaline solution, calcium and magnesium will interfere by forming a precipitate, which scatters light. EDTA is added to the buffer to prevent this interference.

3.2 Non-volatile amines such as cysteine, ethanolamine and ethylenediamine cause a decrease in ammonia sensitivity.

3.3 Lauryl sulfate and some detergents can cause low ammonia recoveries.

3.4 Color, turbidity and certain organic species may interfere. Turbidity is removed by filtration and sample color can be corrected for by running the samples through the manifold without color formation.

3.5 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that can bias analyte response, especially in low level detection of Ammonia. To eliminate this problem, wash glassware with 1:1 HCl and rinse with DI water.

4.0 HEALTH AND SAFETY

4.1 Accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Use of gloves, eye protection, and lab coat are required when preparing reagents.

4.2 The following chemicals have the potential to be highly toxic or hazardous.

3.3.1. Sodium Hydroxide

3.3.2. Sodium Nitroprusside

4.3 A reference file of Safety Data Sheets (SDS) is available to all personnel involved in the chemical analysis.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat Quick Chem FIA 8500 series.

5.1.1.1 XYZ Auto sampler ASX-520 series with sample, standard and dilution racks

5.1.1.2 Manifold or reaction unit

5.1.1.3 Multichannel Reagent Pump RP-100 series

5.1.1.4 Colorimetric Detector

5.1.1.4.1 Flowcell, 10 mm, 80uL, glass flow cell

5.1.1.4.2 660 nm interference filter

5.1.1.5 Computer, monitor, printer and The Flow Solution software.

5.2 Supplies

5.2.1 13 x 100 mm test tubes, Fisher # 14-961-27

5.2.2 16 x 125 mm test tubes, Fisher # 14-961-30

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Buffer - In a 1 L volumetric flask dissolve 30.0 g sodium hydroxide (NaOH), 25.0 g ethlylenediaminetetraacetic acid, disodium salt dihydrate, and 67 g sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$) in about 900 mL DI water. Dilute to the mark with DI water and mix well. Prepare monthly.

6.1.2 Salicylate Nitroprusside Color Reagent - In a 1 L volumetric flask, dissolve 144 g sodium salicylate [salicylic acid sodium salt, $C_6H_4(OH)(COO)Na$] and 3.5 g sodium nitroprusside [sodium nitroferricyanide dihydrate, $Na_2Fe(CN)_5NO.2H_2O$] in about 800 mL DI water. Dilute to the mark with DI water and invert to mix. Store in a light proof bottle. Prepare weekly.

6.1.3 Hypochlorite Reagent (0.315%) - In a 1 L volumetric flask, dilute 52.5 mL of 6% sodium hypochlorite (NaOCl), to the mark with DI water. Invert to mix. If 6% NaOCl is not available, adjust volume of sodium hypochlorite used in order to create a 0.315% final concentration. Prepare weekly.

6.1.4 Sodium Hydroxide – EDTA Rinse - In a 1 L volumetric flask, dissolve 65 g sodium hydroxide (NaOH) and 6 g tetrasodium ethylenediamine tetraacetic acid (Na4EDTA) in 800 mL of water. Dilute to the mark after all is dissolved. This is used for cleaning both OP and NH_3 manifold.

6.1.5 Diluent/Carrier for non-preserved samples - Use Millipore ultra pure water as carrier. Degas for one minute. Containers for carrier should be acid washed with 6M HCl before each use.

6.2 Standards

6.2.1 Ammonia Stock Standard (1000 mg N/L) - This standard is pre-made and purchased from an approved commercial supplier with expiration date. If this stock standard is not available, prepare it by dissolving 0.3819 g ammonium chloride (NH_4Cl) that has been dried in the oven for two hours at 105 ºC, in about 80 mL of DI water. Bring up to the 100 mL mark with DI water and store at 4 ºC. Prepare this reagent monthly.

6.2.3 Intermediate Standard (100 mg N/L) - Pipette 10 mL of standard 6.2.1 into a 100 mL volumetric flask. Bring up to mark with DI water. Store at 4 ºC. Prepare weekly.

6.2.4 Spiking Solution (100 mg N/L) - This is the same as the intermediate standard, which is used to spike the samples. Pipette 30 uL of the spiking solution (standard 6.2.2) into 10 mL of DI water or 10 mL of sample, in order to make the blank spike and sample spike. The concentration of spiking solution is 0.30 mg/L.

6.2.5 Working Standards - The working standards are prepared according to the following table and they are good for 48 hours:

Ammonia ppm	Combined Intermediate Std	Final Volume
0.000	DI water	100 mL
0.008	2.67 mL of Std 0.30 ppm	100 mL
0.020	20 mL std 0.100 ppm	100 mL
0.100	100 µL	100 mL
0.200	200 µL	100 mL
0.300	600 µL	200 mL
0.400	400 µL	100 mL
0.500	500 µL	100 mL

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in plastic or glass bottles. All bottles must be thoroughly clean.

7.2 Never use acid preservation for samples to be analyzed for Low Level Ammonia.

7.3 Samples to be analyzed for ammonia only are cooled to 4 ºC and analyzed within 48 hours. For short-term preservation, freeze at –20 ºC for no more than 28 days.

8.0 QUALITY CONTROL

8.1 An Initial Demonstration of Performance (IDP) to establish the instrument's capability is required prior to its use in analyzing samples. The Linearity of Calibration Range (LCR) and the ability to quantify the Quality Control Samples correctly are used to assess performance.

8.2 A demonstration of capability study is performed by each analyst performing the test by analyzing four replicates of an external quality control sample during one or two analytical runs.

8.3 All the standards are run in duplicates: that is, two analyses from each tube. A linear calibration is done daily before the sample run. See the attached checklist for the acceptance criteria.

8.4 A mid-range check standard and a calibration blank is analyzed immediately following daily calibration, after every ten samples (or more frequently, if required) and at the end of run. If a check standard fails, the samples between the last satisfactory check standard and the unsatisfactory standard are re-analyzed.

8.5 Every tenth sample is duplicated (analyzed from two different tubes) and spiked. The accepted value for the relative percent difference (RPD) or spike recovery is ± 10 %. If these do not fall within the accepted ranges, the corresponding analyses are repeated.

8.6 A known QC is analyzed for ammonia in the beginning and at the end of each run.

8.7 The U.S. The U.S. EPA MDL procedures (40 CFR Part 136, Appendix B) including the EPA *Definition and Procedure for the Determination of the Method Detection Limit*, Revision 2 (2016); EPA *Methods Update Rule* (Final rule - August 28, 2017); EPA *Method Detection Limit - Frequent Questions*; and EPA Part 136 *Method Update Rule Revisions to Appendix B – MDL Procedure as Applied to Drinking Water* (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.

9.0 PROCEDURE

9.1 Sample preparation

9.1.1 Prepare a list of samples to be analyzed and pour samples into labeled tubes (16 mm x 125 mm test tubes).

9.1.2 Spike every tenth sample by adding 30 uL of 100 ppm N/L (standard 6.2.3) into 10 mL DI water (blank spike) or 10 mL of sample (sample spike).

9.1.3 Filter the turbid samples by inserting the Sera Filter inside the 16 x 125 mm test tubes containing the sample. Press the filter down and pour the filtered sample collected on the top inside a 13 x 100 mm test tube for analysis.

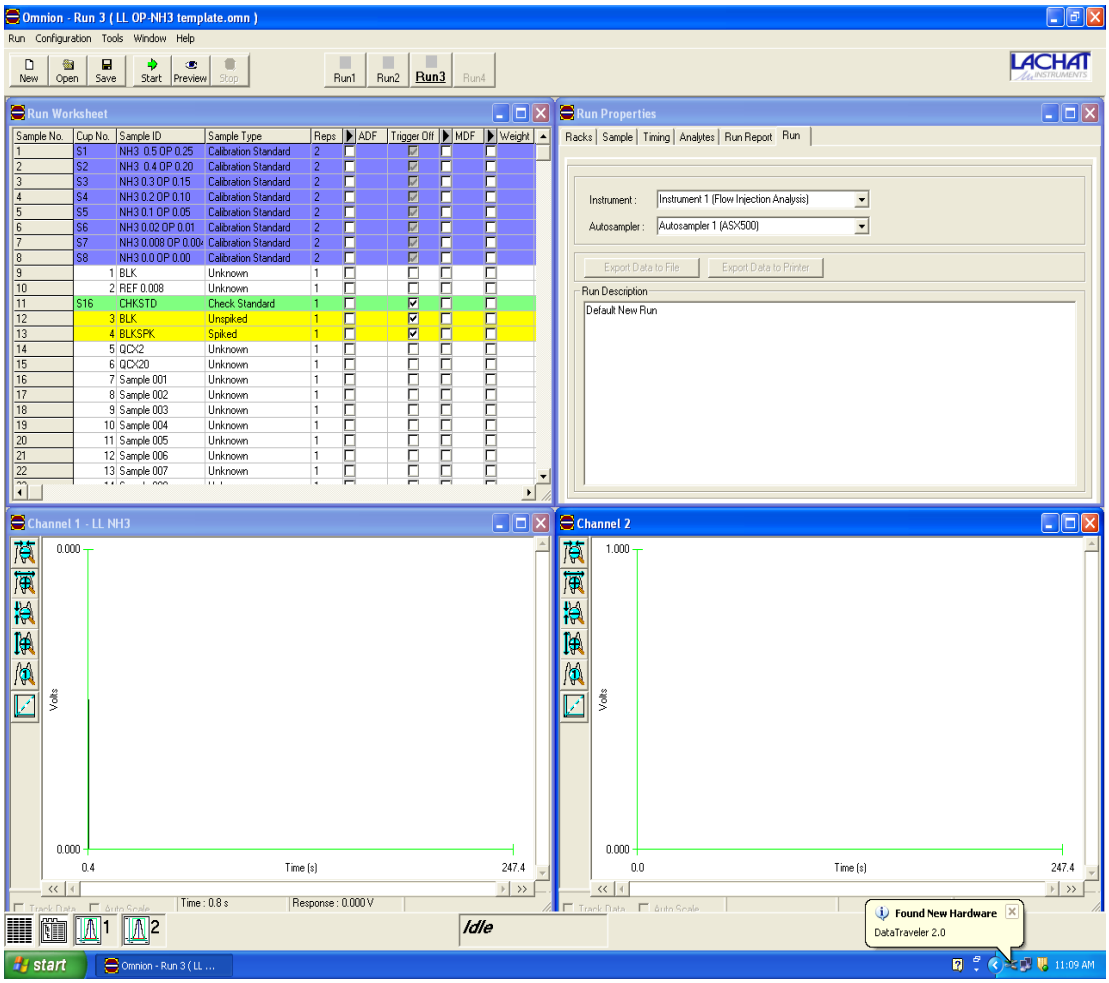
9.1.4 To prevent bubble formation, degas all reagents except for hypochlorite with helium for one minute.

9.2 Instrument set-up and sample analysis

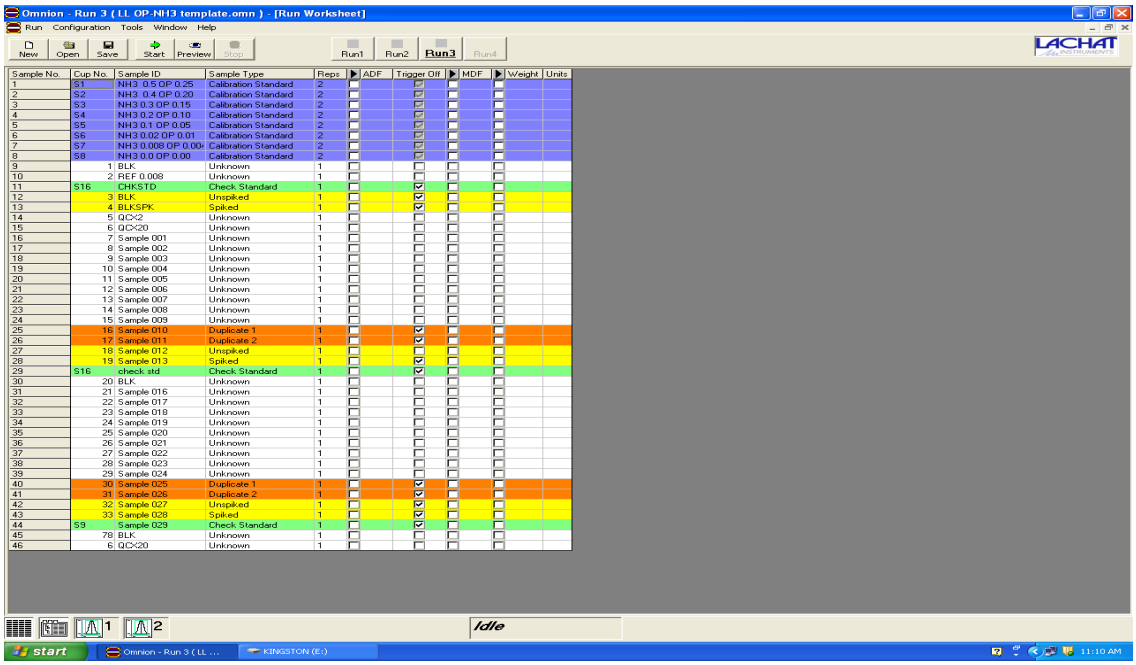
9.2.1 Set up manifold as in the diagram.

9.2.2 Turn on the Lachat instrument, computer, monitor, and printer.

9.2.3 Double click on **"LL OP/NH_3"** to open the template, which consists of four windows. Samples are analyzed consecutively for orthophosphate and ammonia on the same system.



9.2.4 Maximize the **"Run Worksheet"** window at the top left hand corner of the screen, by clicking on the middle square on that screen to open the worksheet template. Enter sample identifications in the sample ID column, making sure that all duplicates and spikes are entered in the appropriate locations of the worksheet. Identifications of the quality control samples analyzed at the beginning of the run and the locations of the duplicates and the spiked have been saved on the template. Press **"Enter"** key after each entry in order to save all entries.

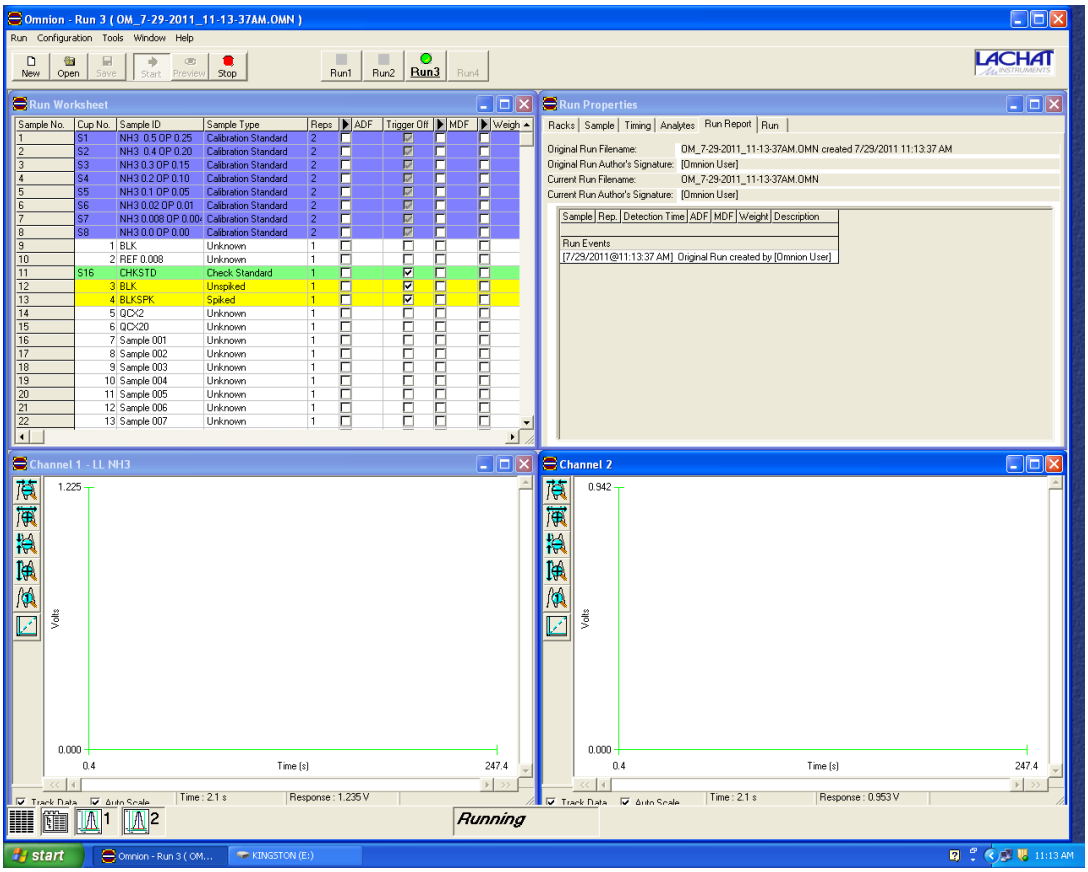


9.3.5 Print a copy of this worksheet by first double clicking on **"Run"** icon and then selecting **"Export Worksheet Data"**.

9.3.6 Click on **"Window"** tab and then, click on **"Tile"** to return to the screen with four windows.

9.3.7 Place standards in standard vials in the standard rack in order of decreasing concentration in positions 1 to 8 (STD 8 is DI water-0.00 mg/L). Place the check standard vial in position 16 (S16) of the standard rack. Pour samples and quality control samples into 13 x 100 mm test tubes and place them in the sample racks according to the worksheet prepared in 9.2.4.

9.3.8 Pump deionized water through all reagent lines and check for leaks and smooth flow. Switch to reagents in the order of 1. Buffer, 2. Salicylate Nitroprusside Color Reagent, 3. Hypochlorite. If analyzing for orthophosphate, then include; 5. Ascorbic Acid and 6. Color Reagent and continue pumping for about 10 minutes. Click on **"Preview"** tab to monitor the baseline.



9.3.9 Once a stable baseline is achieved, click on **"Stop"** tab to stop monitoring the baseline. Click on **"Start"** tab to begin the analysis.

9.3.10 If the calibration passes, the instrument will continue to analyze the samples. If it fails, take appropriate corrective actions and recalibrate before proceeding to analyze samples.

9.3.11 Manual dilution will be performed to reanalyze samples with concentrations exceeding the calibrated range.

9.3.12 After the run is complete, remove the reagent lines in the reverse order that they were inserted and place them in DI water and rinse for about 15 minutes. For extra rinse of NH_3 channel, a reagent of Sodium Hydroxide – EDTA Rinse can be used for 5 minutes followed by DI rinse for 10 – 15 minutes. Pump the tubes dry, release the pump tubing, and turn off the pump.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All the calculations are performed by the Omnion 3.0 software system. It uses a calibration graph of peak area versus concentration to calculate the ammonia nitrogen concentrations in the samples. All standards are analyzed in duplicate, and these points are used to generate the calibration curve. A duplicate peak may be excluded from the calibration if it is determined to be faulty (i.e. corrupted, damaged, misshapen) Samples with nitrogen concentrations greater than 0.500 ppm are manually diluted and reanalyzed.

10.2 Calculate the percentage spike recovery of the laboratory fortified samples as follows:

$$\%\,SR = \frac{(\text{spiked sample conc.} - \text{sample conc.}),\ \text{ppm}}{\text{amount of spike added to sample, ppm}} \times 100$$

10.3 Calculate the relative percentage difference for the duplicated samples as follows:

$$\%\,RPD = \frac{\text{difference between the duplicates}}{\text{average of the duplicates}} \times 100$$

11.0 DATA AND RECORDS MANAGEMENT

11.1 Completed data packages are scanned and stored electronically before being placed in the appropriate binders in the lab.

11.2 Report only those results that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard are manually diluted and reanalyzed.

11.3 Sample results for are reported in mg N/L. Report results to three decimal places. Report results below the lowest calibration standard as < 0.008. For the Chesapeake Bay Program only, report all calculated results with the “L” sign for concentrations less than that of the lowest standard.

12.0 WASTE MANAGEMENT

12.1 It is laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume and bench operation. Compliance with all sewage discharge permits and regulations is also required.

12.2 Samples and standards are poured down the drain while a large amount of water is running. Reagent waste lines are also washed down through the drain with water running.

12.3 For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N. W., Washington D. C. 20036, (202) 872-4477.

13.0 REFERENCES

13.1 EPA Method 350.1, *Methods for the Determination of Inorganic Substances in Environmental Samples*, August 1993

13.2 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 21st Edition, Method 4500- NH3 H, 2005

13.3 *Lachat Instruments QuickChem Method 10-107-06-2-O,* Determination of Ammonia by Flow Injection Analysis

13.4 Lachat Instruments, *Operating Manual for the Quikchem Automated Ion Analyzer*

13.5 Division of Environmental Sciences, Maryland Department of Health, *Quality Assurance Plan*, SOP No. Chem-SOP-QAP.

13.6 Division of Environmental Sciences, Maryland Department of Health, *Quality Manual,* SOP No. QA-SOP-QM.

13.7 EPA Definition *and Procedure for the Determination of the Method Detection Limit, Revision 2* December 2016

APPENDIX A

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist-LL Ammonia

EPA Method 350.1

Lab Numbers: [1] _____ **Analyst:** _____

Dates Collected: _____ **Date Analyzed:** _____

Procedure	Acceptance Criteria	Status (√)	Comments
Holding Time	48 hours @ 4ºC 28 days @ –20ºC		
Calibration Curve	Corr. Coeff. ≥ 0.9950		
Reagent Blank	< Reporting level (0.008 ppm)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10 samples		
	Recovery = 90–110%		
External QC	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the run		
	Concentration = 90–110% of the true value		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RPD ≤ 10%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.008–0.500 ppm)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

[1]Include beginning and ending numbers, account for gaps by bracketing.

_____ Analyst's Signature & Date

_____ Reviewer's Signature & Date

_____ Supervisor's Signature and Date

Reagents	ID	Reagents	ID	External QC
Buffer				Identification =
Salicylate Nitroprusside				True Value = ppm
Sodium Hypochlorite				Range = ppm

APPENDIX B

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

Data Review Checklist LL Orthophosphate/ LL Ammonia

EPA Method 365.1/ EPA Method 350.1

Lab Numbers: [1] _____

Analyst: _____

Dates Collected: _____ **Date Analyzed:** _____

Procedure	Acceptance Criteria	Status (√)	Comments
Holding Time	48 hours @ 4ºC; 28 days @ –20ºC		
Calibration Curve	Corr. Coeff. $\geq$ 0.9950		
Reagent Blank	< Reporting Level (0.004 ppm for OP; 0.008 ppm for NH_3)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10		
	Recovery = 90–110%		
External QC	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the		
	Concentration = 90–110% of the true value		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10		
	RPD ≤ 10%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.004–0.250 ppm for OP; 0.008–0.500 ppm for NH_3)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

[1]Include beginning and ending numbers, account for gaps by bracketing.

_____ _____
Analyst's Signature & Date Reviewer's Signature & Date

_____
Supervisor's Signature and Date

NH_3 Reagents	ID	OP Reagents	ID
Buffer		Color Reagent	
Salicylate Nitroprusside		Ascorbic Acid	
Sodium Hypochlorite			

External QC

Identification = _____
True Value = $_{NH_3}$ /$_{OP}$ ppm
NH_3 Range = ppm
OP Range = ppm