INDIGENOUS OBSERVATION NETWORK
QUALITY ASSURANCE PROJECT PLAN

Prepared by
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Prepared for
U.S. Environmental Protection Agency

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APPROVAL PAGE

10/28/2022

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10/28/2022

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10/28/22

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The YRITWC would like to thank the members of the technical advisory committee for advice during the development of this QAPP. We would also like to thank Paul Schuster of the U.S. Geological Survey (USGS) for the invaluable information provided by him on the dynamics of the Yukon River and also the sampling materials put together and provided by USGS.

We would like to thank the YRITWC Executive Council members for their vision and wisdom in the project. We would like to thank the Indigenous communities of the Yukon River watershed for sharing their knowledge and insight on water quality and contaminants issues in the watershed. Finally, we would like to thank the U.S. Environmental Protection Agency for their longstanding support and the National Science Foundation for funding this project.

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LIST OF ABBREVIATIONS

ADEC	Alaska Department of Environmental Conservation
ASTM	American Society for Testing and Materials
AWQMS	Ambient Water Quality Monitoring System
CWA	Clean Water Act
COC	Chain of Custody
DQO	Data Quality Objective
DO	Dissolved Oxygen
EPA	Environmental Protection Agency
ET	Environmental Technician
TET	Tribal Environmental Technician
GPS	Global Positioning System
ISO/IEC	General Requirements for the Competence of Testing and Calibration
IDL	Instrument Detection Limit
LCS/LCSD	Laboratory Control Check/Laboratory Control Check Duplicate
LOD	Limit of Detection
MQO	Measurement Quality Objective
MDL	Method Detection Limit
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MSDS	Material Safety Data Sheet
µS/cm	microsiemens/centimeter
mg/L	milligrams/liter
µg/L	micrograms/liter
PE Sample	Performance Evaluation Sample
PM	Project Manager
PT Sample	Performance Test Sample
PQL	Practical Quantification Limit
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QAO	Quality Assurance Officer
QC	Quality Control
RL	Reporting Limit
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SOP	Standard Operating Procedure
STORET	Storage and Retrieval System
TA	Technical Advisor
UAF	University of Alaska Fairbanks
USGS	United State Geological Survey
WQS	Water Quality Standards
WOP	Water Quality Portal
WQX	Water Quality Exchange
YRB	Yukon River Basin
YRITWC	Yukon River Inter-Tribal Watershed Council

I. DISTRIBUTION LIST

Table 1: List of names and contact information of those who received an official copy of the Quality Assurance Project Plan and any subsequent revisions will be provided to:

Distribution List				
NAME	**POSITION**	**AGENCY/ Company**	**DIVISION/ BRANCH/SECTION**	**CONTACT INFORMATION**
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Donald Brown	QA Officer	EPA	Region 10	Phone: (206) 553-0717 Email: brown.BonaldM@epa.gov

Copies of this Quality Assurance Project Plan will be made available to the Alaska Tribes of the Yukon River watershed, Executive Committee, EPA, USGS, and Technical Advisory Committee. Other interested parties may review the plan at the Yukon River Inter-Tribal Watershed Council's website at www.yritwc.org.

II. PROJECT MANAGEMENT

1. Project Task & Organization

Specific Role and Responsibilities of key individuals and organizations participating in the Yukon River Inter-Tribal Watershed Council (YRITWC) Indigenous Observation Network (ION) water quality monitoring program include:

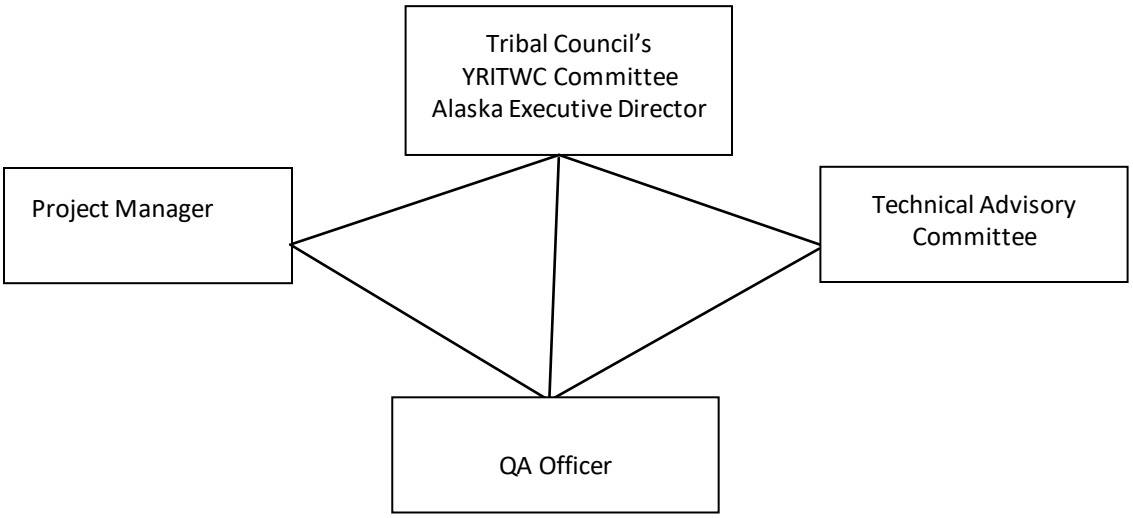

Figure 1: YRITWC QAPP Organizational Chart

2. Responsibilities:

Alaska Tribal Councils' & YRITWC Executive Committee

The Alaska Tribes and the YRITWC Executive Committee main responsibility is to be the primary point of contact to guide the Indigenous Observation Network to provide historical and cultural information about the water resources and advise the community relevant water quality monitored program with their local knowledge and observations of the water resources and surrounding natural environment.

Theresa Clark, YRITWC Alaska Executive Director **– Program Director (PD)**

The PD has the oversight responsibility of all the financial and contractual management aspects on the project.

Dr. Edda Mutter, YRITWC Science Director **– Project Manager (PM)**

The PM is the primary contact point and responsible for the overall technical, logistical, financial and contractual management of the project. The PM is responsible for preparation of sampling plan, sample collection, verifies sample data, data management and analysis, quality control and production of reports, administrative support and grant implementation. The PM is also responsible reporting of QA reviewed data to EPA and DEC project QAPP revisions.

Kari Young, YRITWC **– Environmental Technician (ET)**

The ET is responsible for ensuring that all field logistics and data collection activities are carried out according to this QAPP. The ET is familiar with this QAPP and its contents.

Indian Environmental General Assistant Program (IGAP) Tribal Environmental Technician - TET
The TETs are responsible for data collection activities are carried out according to this QAPP. The TETs are familiar with this QAPP and its contents.

Paul Schuster, USGS **- Quality Assurance Officer (QAO)**
The QAO is responsible for technical support to review and verify the validity of sample data results as specified in the QAPP and appropriate EPA approved analytical methods. The QAO ensures all monitoring complies with the QAPP specified criteria. This is accomplished through routine technical assessments of the sample collection, analysis and data reporting process. Assessments may include, but are not limited to: on-site field audits, data audits, QA review of laboratory and sampling performance evaluation samples, laboratory audits, etc. These assessments are performed independent of overall project management.

Nicole Herman-Mercer, USGS – **Technical Advisor (TA)**
Dr. Ryan Toohey, USGS – **Technical Advisor (TA)**
Dr. Jennifer Guerard, University of Alaska Fairbanks **- Technical Advisor (TA)**
The TAs are responsible for coordinating with YRITWC to help with data interpretation and reporting. The TAs will provide technical expertise in data reporting to participating Alaska Tribes within the Yukon River watershed. The TAs are also advise and oversee data release at USGS ScienceBased and the EPA sponsored National Water Quality Monitoring Council's Water Quality Portal (WQP) and Water Quality Exchange (WQX) online platform. Primary data users will be the Alaska Tribes and First Nations of the Yukon River Basin and local, state and federal agencies involved in support of this project.

Laboratory Manager, UAF, USGS and SGS Laboratory (LM)
Responsible for the overall review and approval of contracted laboratory analytical work, responding to sample result inquiries and method specific details. Responsible for QA/QC of laboratory analysis as specified in the QAPP and reviews and verifies the validity of sample data results as specified in the QAPP and appropriate EPA approved analytical methods.

III. BACKGROUND & PROBLEM IDENTIFICATION

1. Problem Definition

The Yukon River Inter-Tribal Watershed Council's (YRITWC) Indigenous Observation Network (ION) Quality Assurance Project Plan (QAPP) is designed to respond to Alaska Tribes concerns about environmental and anthropogenic impacts to water resources within the Yukon River Basin (YRB). The Umbrella ION QAPP will support Alaskan Tribes with assessing local and regional water quality condition through a standardized water quality monitoring plan to collect long-term baseline data to ascertain for the conservation and protection of the YRB water resources.

This QAPP was drafted using guidance documents from the EPA [1,2].

2. *Project Background*

The Yukon River Basin (YRB) is the fourth largest draining basin in North American, spanning across 330,000 square miles (855,000 km^2) and originates in British Columbia, Canada flows across the entire state of Alaska. The watershed is fundamental as one of the largest sources of freshwater to the Bering Sea ecosystem with a discharge of 6,457 m^3/s (Brabets et al. 2000, 2009). Overall, the Yukon River flows from east to west through 20 different ecosystems, each with unique geological features and mostly underlain by discontinuous permafrost.

The Yukon River and its tributaries are home to the Indigenous Cup'ik, Yup'ik, Koyukon, Athabaskan, and Tlingit Tribes and First Nations, which rely on these river systems for their subsistence foods, drinking water resource, household use, and as a major transportation system. Hence, water quality is essential for Alaska Tribes' and First Nations' traditional way of life and their stewardship to protect and preserve the health of the watershed.

Water quality plays an important role in the overall ecosystem and human health and impaired water quality resulting from microbial or chemical pollutants in the form of bacteria, algae, heavy metals, pesticides and other trace elements from natural or anthropogenic sources can have significant impacts. Water quality is currently undergoing change by trends specific to the basin's response to a warmer climate (Toohey et al. 2016). Trends such as organic matter and sedimentation influx resulting from river erosion and permafrost thawing, wildfire increase and associated influx of nutrients, lakes warming and drying-up, and infestation and spread of invasive aquatic species (i.e. Elodea) are responses to warming water temperature and landscape changes.

Furthermore, pollutants in the form of organics (i.e. plastic material, petroleum products and person hygiene and cleaning products), heavy metals and other trace elements from historical and present mineral exploration operations and atmospheric deposition are directly linked to impact water quality and pose a risk to indigenous peoples and citizens of the region that depend on the river systems for food sources through fish and wildlife and drinking water resources. For example: Bioaccumulation or biomagnification of certain pollutants occurs in the fish and higher forms of wildlife (birds and mammals) harvested and hunted as an important food source for the people within the basin. Under this Umbrella ION QAPP, the Alaska Tribes collaborate with the YRITWC, the USGS and the University of Alaska Fairbanks to establish a water quality monitoring program that allows coordination of data collection for local and regional water quality baselines, critical to understanding changes and impacts to water and aquatic subsistence food resources, and the watershed as a whole. The following secondary data sources will be utilized to enhance ION database.

Table 2. List of Secondary Data Sources that may be included (but not limited to)

Data Type	Data Source	Data Uses Relative to Current Project
Geology/Hydrology	United States Department of the Interior Geological Survey (USGS) Topographic and Geologic Maps, State Agencies/EPA My WATERS Mapper	Identify area Geology, topography, surface water bodies, hydrologic units/watersheds, water quality, water quantity, etc.
Streams/Drainages	EPA WATERS GeoViewer and USGS Topographic Maps	Topography, surface water bodies, hydrologic units/watersheds, water quality, etc.
Water Quality	National Water Quality Monitoring Council – Water Quality Portal National Water Information Systems (NWIS) U.S. and State Fish & Wildlife Service	Identify surface water quality and quantity, drinking water systems and sample parameters

	National Park Services Alaska Department of Environmental Conservation (ADEC) – Alaska's Water Quality Map, Drinking Water Watch, & Drinking Water Source Protection Areas Map Bureau of Land Management	
Registered Wells	State and Tribal Databases Yukon Government Water Well Registry	Identify well locations, drinking water wells, and groundwater use
Meteorological	National Weather Service	Precipitation, Wind, and Air Temperature, humidity, etc.
Environmentally Sensitive Areas	U.S. and State Fish & Wildlife Service Maps, Publications, and Databases	Identify sensitive and endangered species and environments potentially present on or in removal action/emergency response area
Wetlands	USDA NRCS Web Soil Survey and Soil Data Mart (Hydric Soils List), and U.S. and State Fish & Wildlife	Identify wetlands and associated sensitive and endangered species and environments potentially present on or in removal action/emergency response area

IV. PROJECT DESCRIPTION

1. Introduction

The Umbrella ION QAPP provides the framework of a standardized monitoring design that includes training availability, equipment choices, defines sampling design, describes collected parameters, defines QA/QC activities, describes sampling handling, describes sample shipment, and database management practices used to implement as a part of YRITWC ION water monitoring program. Data generated under this QAPP will be used for Alaska Tribes to assess water quality condition (non-point source/climate change indicators and point-source/natural and anthropogenic indicators) at water resources and within the YRB. One of the main responsibilities of the YRITWC will be to provide logistical and technical support to Alaska Tribes water quality programs to ensure consistent water quality monitoring, data processing, and data management to maintain data cohesion. The availability of Alaska Indian Environmental General Assistant Program (IGAP) Tribal Environmental Technicians (TETs) to support data collection is crucial to the long-term success of this program.

2. Project Objectives

In order to accomplish a coordinated water quality monitoring program, the YRITWC established the following objectives:

1. Establish a water-quality reference against which to measure any future changes in the YRB that allows for special and temporal trend analysis for water quality assessment.

2. Identify spatial and temporal trends to help predict future changes that will act as a reference for any changes seen in the YRB river systems in the future.

3. Establish local site-specific water quality monitoring programs to address local concerns by assessing potential point-source pollution as a result of surface water runoff or leachate from sewage lagoons, outhouses, solid waste sites, historical or current placer mining activities, or leaking heating storage tanks. Community site specific monitoring database serves as a water quality reference to measure against Alaska Department of Environmental Conservation (ADEC) and Environmental Protection Agency (EPA) Water Quality Standards (WQS).

4. Establish local site-specific water quality monitoring programs to address Tribal Councils' concerns about traditional drinking water sources and Environmentally Sensitive Habitat Areas (ESHAs) such as king salmon spawning areas. Community site specific monitoring database serves as a water quality reference to measure against ADEC and EPA WQS.

5. Establish environmental observation records to assess spatial and temporal water condition and ecological changes.

6. Support Alaska Tribes in developing water quality code recommendations to guide the best possible management practices to address local point source pollution.

7. Provide water quality monitoring top-level training workshops, seminars, and on-site training workshops to environmental technicians from Alaska Tribal communities within the YRB; the trained technicians will be well versed in proper water quality sampling techniques, procedures and protocols. These skills will aid technicians in the development of their local program.

8. Provide logistical and technical support, as well as data management capacity to Alaska Tribal water quality sampling/monitoring programs. The YRITWC PM, USGS and UAF researchers will complete data quality and control procedures, data analysis, interpretation, mapping, and record keeping in order to assist Alaska Tribes with data reporting.

3. Project Implementation Schedule

As we increase our understanding of the most effective water quality sampling strategy for the ION water quality data collection, refinements in methods or additional testing parameters may be incorporated to enhance project goals. Any changes will be submitted to the EPA for approval.

The ION monitoring sampling sites are corresponding either with existing ION YRB established or local identified sampling sites starting in 2006 and have continued based on funding availability through subsequent years. Physical water parameter measurements, surface water grab samples and environmental observations are collected by the PM, ET or TETs that resides along the Yukon River and its tributaries. The PM or ET are responsible to collect surface water samples at the Yukon Bridge, the Tanana River above Nenana, the upper and lower Chena River sites at Fairbanks, the upper and lower Tanana River sites at Fairbanks, Tanana River at Delta Junction, Tanana River at Tok, Hess Creek, Tolovana East and West Fork, Tatalina River, Clearwater Creek, and any of the other established sites as needed to fill in when the TET is not available. Sampling methodology will follow YRITWC protocols and adhere to the standards of quality set by USGS in TWR book 9 protocols. In order to address ION QAPP objectives three Tier sampling strategies have been developed to observe potential climate change indicators or local point source concerns such as:

Tier I Sample Sites: Surface water quality sampling at 42 strategically located sites to measure climate change indicators within the YRB such that they: 1) provide maximum spatial coverage, 2) are co-located with USGS or other state or federal agencies gaging stations, and 3) are sites with historical water quality data. The collected long-term baseline data serves to address objectives 1, 2 and 5. The strategically located sites are monitored throughout open water season starting June until ice freeze-up forms, resulting in 6 monthly sampling events. In addition, 9 sites are selected to conduct under ice water quality monitoring within the YRB. The purposes of collecting water quality data during winter season is to achieve a better understanding of seasonal dynamics of groundwater and surface water. Under ice water quality monitoring starts in January, when river ice thickness is safe to access the samples sites and ends when river ice break-up/water

overflow initiates (maximum of 4 additional sampling events). Physical parameters are measured in the field and surface water grab samples are analyzed at the USGS or UAF laboratory. The following listed sites in Table 3 representing Tier I sample sites.

Table 3: List of Tier I Sample Sites for ION Monitoring Program Participating Alaska Tribes

River System	Organization/Tribal Councils	Year Established	Reason
Alatna River	Alatna Village Council	2019	Climate Change
Anvik River	Anvik Tribal Council	2006	Climate Change
Andreafski River	Yupiit of Andreafski & Algaaciq Native Village Tribal Governance	2006	Climate Change
Chena River	YRITWC - Fairbanks	2006	Climate Change
Clearwater Creek	YRITWC	2006	Climate Change
Delta River	YRITWC	2020	Climate Change
Draanjik Gwich'in	Chalkyitsik Village Council	2014	Climate Change
Hess Creek	YRITWC	2008	Climate Change
Huslia River	Huslia Tribal Council	2007	Climate Change
Hogatza River	Huslia Tribal Council	2007	Climate Change
Koyukuk River	Hughes Village Council	2019	Climate Change
Koyukuk River	Huslia Tribal Council	2007	Climate Change
Koyukuk River	Allakaket Traditional Council & Alatna Village Council	2019	Climate Change
Koyukuk River	Koyukuk Tribal Council	2013	Climate Change
Nenana River	YRITWC – Cantwell & Nenana	2018	Climate Change
Nome Creek	YRITWC	2019	Climate Change
Porcupine River	Council of Athabascan & Gwichyaa Zhee Gwich'in Tribal Government	2007	Climate Change
Tanana River	YRITWC - Fairbanks	2006	Climate Change
Tanana River	YRITWC – Fort Eielson	2006	Climate Change
Tanana River	YRITWC- Delta Junction	2020	Climate Change
Tanana River	YRITWC - Tok	2016	Climate Change
Tanana River	Nenana Native Council	2006	Climate Change
Tatalina River	YRITWC	2020	Climate Change
T'ee Drin Jik River	Venetie Village Council & Tribal Government	2007	Climate Change
T'ee Drin Jik River	Arctic Village Council	2016	Climate Change
Tolovana River	Native Village of Minto/YRITWC	2017	Climate Change
Yukon River	Alakanuk Traditional Council	2016	Climate Change
Yukon River	Anvik Tribal Council	2013	Climate Change
Yukon River	YRITWC - Dalton Highway Bridge	2006	Climate Change
Yukon River	Beaver Tribal Council	2013	Climate Change
Yukon River	Native Village of Stevens	2013	Climate Change
Yukon River	Circle Village Council	2002	Climate Change
Yukon River	Eagle Traditional Council	2006	Climate Change
Yukon River	Emmonak Traditional Council	2017	Climate Change
Yukon River	Council of Athabascan & Gwichyaa Zhee Gwich'in Tribal Government	2006	Climate Change
Yukon River	Louden Tribal Council	2008	Climate Change
Yukon River	Kaltag Tribal Council	2012	Climate Change
Yukon River	Native Village of Kotlik	2008	Climate Change
Yukon River	Yupiit of Andreafski & Algaaciq Native Village Tribal Governance	2006	Climate Change
Yukon River	Marshall Traditional Council	2007	Climate Change
Yukon River	Nulato Tribal Council	2012	Climate Change
Yukon River	Rampart Village Council	2018	Climate Change
Yukon River	Ruby Tribal Council	2006	Climate Change
Yukon River	Iqurmiut Tribal Council	2006	Climate Change
Yukon River	Pilot Station Tribal Council	2006	Climate Change
Yukon River	Tanana Tribal Council	2003	Climate Change

***Tier II* Sample Sites**: Alaska Tribes water quality monitoring programs to assess water quality conditions for established traditional water resources and Environmentally Sensitive Habitat Areas (ESHAs) within the YRB. Tier II samples sites are established to address ION QAPP objective 4. In local sampling programs using TETs measure physical parameter at the site and collect surface water grab samples for chemical analysis conducted at the USGS or UAF laboratory. Surface water samples are collected during open water season starting June till ice freeze-up forms (October), resulting in 6 monthly sampling events. The Tier II ION monitoring sites are listed in Table 4.

Table 4: List of Tier II Sample Sites for ION Monitoring Program Participating Alaska Tribes

River System	Organization/Tribal Councils	Year Established	Reason
Akuliqutaq Slough	Hooper Bay Native Village	2010	ESHA
Alakanuk Slough	Alakanuk Traditional Council	2016	ESHA
American Creek	Eagle Traditional Council	2020	Traditional Water Resource
Airport Lake	Arctic Village Council	2021	ESHA
Arctic Village Slough	Arctic Village Council	2021	ESHA
Bear Creek	Tanana Tribal Council	2016	Traditional Water Resource
Big Lake	Hooper Bay Native Village	2010	ESHA
Bone Pond	Hooper Bay Native Village	2010	ESHA
Freshwater Creek	Algaaciq Native Village	2021	Drinking Water Resource
Glacial Creek	Arctic Village Council	2015	Traditional Water Resource
Hay Slough	Tanana Tribal Council	2004	ESHA
Kwiguk River	Emmonak Traditional Council	2017	ESHA
Minto Flats	Native Village of Minto	2017	ESHA
Mouth of Kakolade	Iqurmiut Tribal Council	2016	ESHA
Naparyaraq Slough	Hooper Bay Native Village	2010	ESHA
Ninglivvak River	Chevak Traditional Council	2007	ESHA
Richards Slough	Huslia Tribal Council	2019	ESHA
T'ee Drin Jik River	Venetie Village Council & Tribal Government	2012	ESHA
Yukon River at Lower Birch Creek Slough	Beaver Tribal Council	2021	ESHA

Tier III Sample Sites: Alaska Tribal surface water quality sampling programs to assess point-source pollutant impacts to water resources resulting from landfill and historical or current existing mining operations. Tier III surface sample are collected twice a year during snow-melt and at major rain events late summer when runoff water and leachate are present at the established sites. Except the monitoring sites at American and Fish Creek in Tanana, sites will be only sampled once a year in June due to water level accessibility. Field parameters are measured by the TETs at the site and surface water grab samples are analyzed at the certified professional SGS laboratory. The Tier III ION monitoring sites are listed in Table 5.

Table 5: List of Tier III Sample Sites for ION Monitoring Program Participating Alaska Tribes

River System	Organization/Tribal Councils	Year Established	Reason
Alakanuk	Alakanuk Traditional Council	2017	Landfill
American Creek	Tanana Tribal Council	2020	Mining
Birch Creek	Circle Village Council	2019	Mining
Fish Lake	Tanana Tribal Council	2020	Mining
Blueberry Creek	Hughes Village Council	2019	Landfill
Landfill Pond	Venetie Village Council & Tribal Government	2018	Landfill
Big Lake	Venetie Village Council & Tribal Government	2018	Landfill

The following parameters listed in Table 6 are measured for ION QAPP water quality sampling for each Tier.

Table 6: List of the Analytical Parameters to be Measured & Recorded

Field Measurements	Analytical Parameters Measurements	Tier
Temperature	Aluminum (AL)	I & II & III
pH	Antimony (Sb)	I & II & III
Conductance	Arsenic (As)	I & II & III
Dissolved Oxygen	Barium (Ba)	I & II & III
Turbidity	Beryllium (Be)	I & II & III
	Calcium (Ca)	I & II & III
	Cadmium (Cd)	I & II & III
	Copper (Cu)	I & II & III
	Chromium (Cr) (total)	II & III
	Cobalt (Co)	I & II & III
	Iron (Fe)	I & II & III
	Lead (Pb)	I & II & III
	Magnesium (Mg)	I & II & III
	Manganese (Mn)	I & II & III
	Mercury (Hg)	II & III
	Molybdenum (Mo)	I & II & III
	Nickel (Ni)	I & II & III
	Phosphorus (P)	I & II & III
	Potassium (K)	I & II & III
	Selenium (Se)	I & II & III
	Silicon (Si)	I & II & III
	Silver (Ag)	I & II & III
	Sodium (Na)	I & II & III
	Thallium (Tl)	I & II & III
	Tin (Sn)	II & III
	Titanium (Ti)	I & II & III
	Vanadium (V)	I & II & III
	Zinc (Zi)	I & II & III
	Bromide (Br^-)	II & III
	Chloride (Cl^-)	I & II & III
	Fluoride (F^-)	I & II & III
	Nitrite (NO_2^{2-})	II & III
	Nitrate (NO_3^{2-})	I & II & III
	Sulfate (SO_4^{2-})	I & II & III
	Alkalinity	I & II & III

Previous Data Collection: Surface water data collected by the ION program from 2006 to 2014 is publicly available at the USGS ScienceBased (https://www.sciencebase.gov/catalog/item/59efa7d3e4b0220bbd99b69e) and EPA WQX (https://www.epa.gov/waterdata/water-quality-data) and National Water Quality Monitoring Council (https://acwi.gov/monitoring/) online platform. The data from 2014 to 2018 has not been through the full process of quality assurance (QA) and quality control (QC) and will be added to the existing online platform as soon as completed.

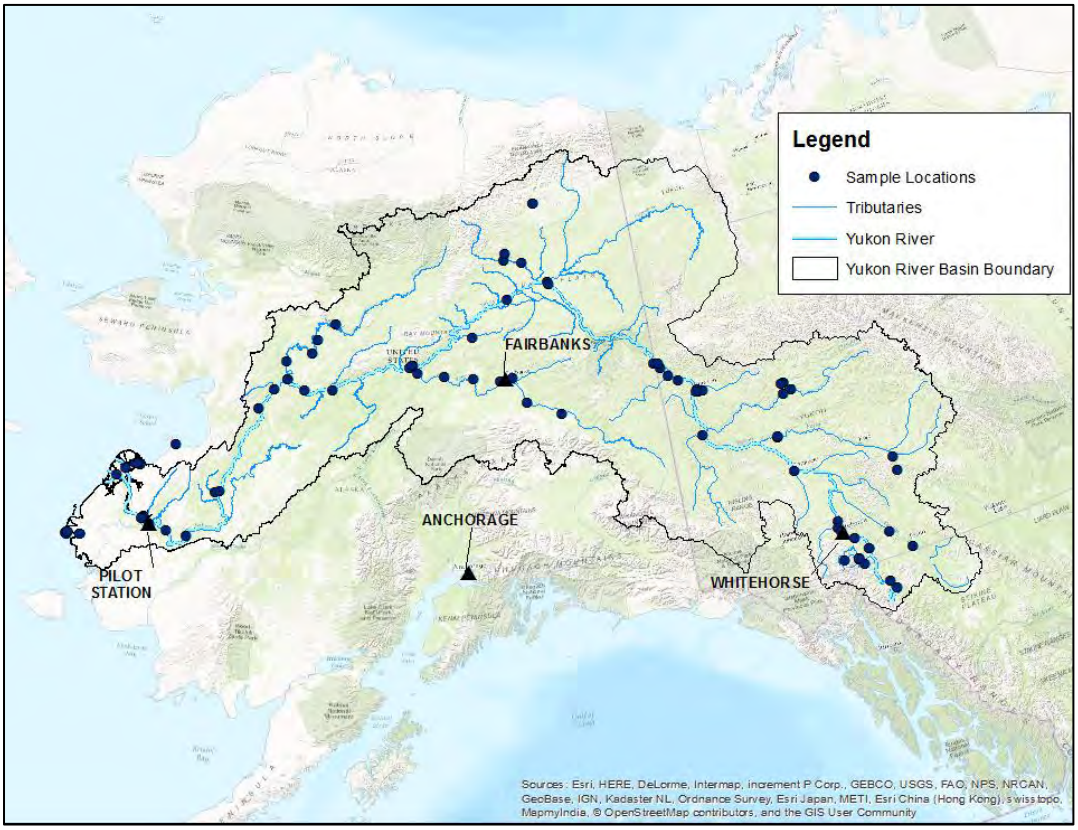

Figure 2: YRITWC's Water Quality Sampling Sites for 2014 Season (Nicole Herman-Mercer, 2017).

The annual schedule of tasks and the personnel conducting the tasks for this project is listed in Table 7. The parameters measured, methods used, applicability, laboratories used when applicable, method reference in Section V. All personnel will follow the required SOPs for training, sample collection, sample analysis, data collection, QC/QA, data management, and water quality equipment

Table 7: Project Timeline of Tasks

MAJOR TASK CATEGORIES	PERSON RESPONSIBLE	J	F	M	A	M	J	J	A	S	O	N	D
Water Quality Monitoring Training & Re-certification	YRITWC			x	x	x	x						
Testing for Water Quality Physical & Chemical Parameters	PM / ETs /TETs	x	x	x	x		x	x	x	x	x		
Collecting Field Duplicates for both Physical & Chemical Analysis (one per ~10 total samples collected or once per year whichever is more frequent)	PM / ETs /TETs			x	x		x	x	x				
Collecting Environmental Observations	PM / ETs /TETs	x	x	x	x		x	x	x	x	x		
Conducting Chemical Analysis (cations, anions, water isotopes, and dissolved organic carbon)	USGS, UAF or SGS LM	x	x	x	x	x	x	x	x	X	x	x	x
Complete QA/QC Review	PM/QAO/ LM	x	x	x	x								
Data Entry	PM / ETs	x	x	x	x								
Annual Data Verification & Validation	PM / QAO / TAs	x	x	x								x	x
Annual Analysis Report	PM / QAO / TAs	x	x	x	x								x
Annual QAPP Review/QAPP Revision	PM / QAO / TAs	x	x	x	x								
Annual Project Report	PM / TAs			x	x	x							

V. DATA QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

1. Data Quality Objectives (DQOs)

The Data Quality Objectives (DQO's) have been established to ensure that the project meets its overall qualitative and quantitative objectives as described under section IV.2 (Table 17 to 18) The project DQOs may be revised in the future if funding becomes available for additional equipment or for testing additional parameters, or if it becomes evident that other objectives would be more effective in meeting program goals.

2. Measurement Quality Data Objectives (MQOs)

The Measurement Quality Data Objectives (MQO's) are designed to evaluate and control field and laboratory analysis of the measurement process to ensure that analytical accuracy and precision meet the DQOs (see Table 15 -16). Precision and accuracy for each parameter to be tested are listed in SGS's, USGS's, and UAF's SOPs for laboratory analysis (Appendices D) and Table 16 and Table 15 for field screening parameters. The MQO's quality indicators are detectability, precision, accuracy, representativeness, comparability and completeness are summarized in below sections. In each case the sampling matrix is water.

Detectability is the ability of the method to reliably measure a pollutant concentration above background. Two components are used to define detectability: Detection Limit (DL) and Limit of Quantification (LOQ) or Reporting Limit (RL).

- The DL is the minimum value which the instrument can discern above background but with no certainty to the accuracy of the measured value. For field measurements, the manufacturer's listed Instrument Detection Limit (IDL) can be used.
- The LOQ or RL is the minimum value that can be reported with confidence (usually 3 times of the DL).

Note: The measurement method of choice should at a minimum have a LOQ 3 times more sensitive than the respective ADEC WQS and/or permitted pollutant level (for permitted facilities).

When sample results are below ½ LOQ they are reported as non-detect ND. Analytes detected above ½ LOQ and below LOQ are reported as estimates and flagged by the lab with a J. Analytes reports above LOQ are reliable unless otherwise decided by the QA officer.

Precision and Accuracy: Precision is the degree of agreement among repeated measurements of the same characteristic or parameter, and gives information about the consistency of methods. Precision is expressed in terms of the Relative Percent Difference (RPD) between two measurements (A and B). Accuracy is a measure of confidence that describes how close a measurement is to its "true" value. Accuracy is used to describe the agreement between an observed value and an accepted reference or true value. The goal is to maintain a level of accuracy consistent with the DQOs and method SOPs.

The QC samples for laboratory accuracy and precision include the following analysis: duplicate samples, Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCS/LCSD). The LCS/LCSD analyses are laboratory blank samples spiked with a certain amount of analyte. The RPD between sample and duplicate are used to track method accuracy. Required RPD s and recoveries for specific analytes are provided in appropriate laboratory SOPs (see Attachment).

Field Precision will be evaluated by the RPD between field duplicate samples and/or replicate readings for field screening using the following formula:

$$RPD = 100 * \frac{(A - B)}{\left(\frac{(A + B)}{2}\right)}$$

Where: RPD = relative percent difference
A = primary sample
B = replicate field sample or laboratory duplicate sample

Replicate field measurements will be performed on one out of each ten measurements. The variation of duplicate values, for each parameter, must not exceed the range of precision specified in Table 15. Replicate measurements that fall outside the specified precision range will be marked and not considered for data analysis. Additional replicate field measurements may be scheduled in cases where data quality objectives are not met.

Laboratory Accuracy will be routinely checked according to the instrument and analytical method accuracy requirements of each parameter (see Table 16). Field duplicate samples are submitted blind to the laboratory. The RPD gives the overall precision that reflects the homogeneity of sample matrix, sampling technique and laboratory performance. RPDs are 20% for water as listed in ADEC regulations.

Data Representativeness is the extent to which measurements actually represent the true environmental condition. Representativeness of data collected is considered in project design and plan (e.g. sampling site selection and sampling frequency) and sampling techniques. Sampling sites are, in part, selected for representativeness of the main stream channel of the river. Samples will be collected from mid-stream when facing upstream, by grab samples from a few inches below the water's surface. Surgical powder free nitrile or latex gloves will be used to avoid sample contamination. YSI Professional Pro Plus Multiparameter, YSI EXO2 Multiparameter Probe, YSI Sonde 600 Probe, YSI 556 Mulitprobe System, YSI DSS, Hanna Combo Meter, LaMotte 2020we Portable Turbidity Meter, and Hach Digital Titrator Model 16900 will be used on site to gather basic water quality data.

Sampling equipment will be calibrated according to the manufacturer's instructions. A summary of accuracy and calibration requirements is in Table 8 to 14. Notes on calibration will be documented in the field notebook. Any issues with the equipment will be documented, and addressed as soon as possible. Physical data will be flagged as unreliable if equipment is malfunctioning, or suspected to be malfunctioning. All water quality instrumentations will be calibrated according to the manufacture instructions prior to each use. Results of the calibration will be recorded on the field sheet. Handheld Global Information Systems (GPS) will be used to identify coordinates of selected sites for mapping and resampling purposes.

Table 8: Method References: Professional Pro Plus Multiparameter Instrument Manual

Parameter	Sensor Type	Range	Accuracy	Resolution	Calibration
Temperature (°C, °F, K)	Thermistor	-5 to 70 °C	±0.2 °C	0.1 °C	None
pH (mV, pH units)	Glass Combination Electrode	0 to 14 units	±0.2 units	0.01 units	1,2 or 3 point
Conductance (µS/cm,	Four Electrode	0 – 0.2 µS/cm	± 0.5% of reading or 1.0	Standard	1 point

mS/cm)	Cell	(auto-range)	µS/cm	Solutions Method	
Dissolved Oxygen (DO) % saturation, temp comp range -5 to 50 °C	Polargraphic	0-500%	0 – 200 % + 2% of reading or 2% air saturation	0.1% to 1% air saturation	1 or 2 point with zero
Barometer (mmHg, inHg, mbar, psi, kPa, ATM)	Peizoresistive	375 to 825 mmHg	± 1.5 mmHg from 0 to 50 °C	0.01 mmHg	1 point

Manual is available at https://www.ysi.com/file%20library/documents/manuals/605596-ysi-proplus-user-manual-revd.pdf

Table 9: Parameters Analyzed in the Field using YSI EXO Probe

Parameter	Sensor Type	Range	Accuracy	Resolution	Calibration
Temperature (°C, °F, K)	Conductivity / Temperature	-5 to 50°C	±0.01°C[1]; ±0.05°C[1]	0.001 °C	None
pH (mV, pH units)	pH/ORP	0 to 14 units	±0.1 pH units within ±10˚C of calibration temp	0.01 units	1,2 or 3 point
ORP (mV)	pH/ORP	-999 to 999 mV	±20 mV in Redox standard solution	0.1 mV	1 point
Dissolved Oxygen (DO) % saturation, temp comp	Optical Dissolved Oxygen	0 to 500% air saturation	0 to 200%: ±1% of reading	0.1% air saturation	1 or 2 point with zero
Conductivity (µS/cm, mS/cm)	Conductivity / Temperature	0 to 200 mS/cm	±0.5% of reading or .001 mS/cm	0.001 to 0.1 mS/cm (range dependent)	1 point
Salinity (ppt)	Calculated from Conductivity and Temperature[2]	0 to 70 ppt	±1.0% of reading or 0.1 ppt	0.01 ppt	
Turbidity[3] (FNU or NTU)	Turbidity	0 to 4000 FNU	0 to 999 FNU: 0.3 FNU or ±2% of reading	0 to 999 FNU = 0.01 FNU	1,2 or 3 point
Total Dissolved Solids (TDS) mg/L	Calculated from Conductivity and Temperature[3]	0 to 100,000 mg/L Cal constant range 0.30 to 1.00 (0.64 default)	Not Specified	Variable	
Total Suspended Solids (TSS) mg/L	Calculated from Turbidity and user reference samples	0 to 1500 mg/L	Not Specified	Variable	
Barometric Pressure mmHg, inHg, mbar, psi, kPa, ATM	Integral Barometer	375 to 825 mmHg	±1.5 mmHg from 0 to 50°C	0.1 mmHg	1 point

[1] Temperature accuracy traceable to NIST standards
[2] Values are automatically calculated from conductivity according to algorithms found in Standard Methods for the Examination of Water and Wastewater (Ed. 1989).
[3] Calibration: 1-, 2-, or 3-point, user-selectable

Manual is available at https://www.ysi.com/File%20Library/Documents/Manuals/EXO-User-Manual-Web.pdf

Table 10: Method References: YSI 556 Multiparameter Instrument

Parameter	Sensor Type	Range	Accuracy	Resolution	Calibration
Temperature (°C, °F, K units)	TM thermistor	-5 to 45ºC	±0.15°C	±0.1°C	None
pH (mV, pH units)	Glass combination	0 to 14 units	±0.2 units	±0.01 pH units	1,2 or 3 point

	electrode				
ORP (mV)	Platinum button	-999 to +999 mV	± 20 mV	0.1 mV	1 point
Dissolved Oxygen (DO) % saturation, temp comp	Polarographic	0 to 500% air saturation	± 2% of the reading or 2% air saturation; whichever is greater	0.1% air saturation	1 point or 2 point with zero
Conductivity (µS/cm, mS/cm)	4-electorde cell with auto-ranging	0 to 100 mS/cm	±0.5% of reading + 0.001 mS/cm	0.001 mS/cm to 0.1 mS/cm (range-dependent)	1 point
Salinity (ppt)	Calculated from conductivity and temperature	0 to 70 ppt	± 1.0% of reading or 0.1 ppt, whichever is greater	±0.01ppt	
Barometer (mmHg, inHg, mbar, psi, kPa, ATM)		500 to 800 mmHg	± 3 mm Hg within ± 15°C temperature range from calibration point	0.1 mm Hg	1 point

Manual is available at https://www.ysi.com/File%20Library/Documents/Manuals/655279-YSI-556-Operations-Manual-RevD.pdf

Table 11: Method References: YSI DSS Multiparameter Probe

Parameter	Sensor Type	Range	Accuracy	Resolution	Calibration
Temperature (°C, °F, K)	Thermistor; Combination Sensor with Conductivity	-5 to 70°C	±0.2°C	±0.1°C	None
pH (mV, pH units)	Glass Bulb Combination Electrode; Ag/AgCl Reference Gel	0 to 14 units	±0.2 units	±0.01 pH nits	1, 2, or 3 points
ORP (mV)	Platinum Button; Ag/AgCl Reference	-1999 to +1999 mV	±20 mV	0.1 mV	1 point
Dissolved Oxygen % saturation, temp comp	Optical Luminescence	0 to 500%, 0 to 50 ppm	0 to 200% (±1% of reading or 1% air saturation, whichever is greater)	0.1 or 0.01 ppm; 0.1 or 1% saturation	1 or 2 points
Salinity (ppt)	Calculated from Conductivity and Temperature	0 to 70 ppt	±1.0% of reading or ±0.1 ppt, whichever is greater	0.01 ppt	1 point
Conductivity (µS/cm, mS/cm)	Four Nickel Electrode Cell	0 to 200 mS/cm	0 to 100 mS/cm (±0.5% of reading or 0.001 mS/cm, whichever is greater)	0.001, 0.01 or 0.1 mS/cm (range dependent)	1 point
Turbidity (FNU or NTU)	Nephelometric - Optical, 90° Scatter	0 to to 4000 FNU	0 to 999 (0.3 or ±2% of reading, whichever is greater)	±0.1 FNU	1, 2, or 3 points
Barometer (mmHg, inHg, mbar, psi, kPa, ATM)	Piezoresistive	375 to 825 mmHg	±1.5 mmHg from 0 to 50°C	0.1 mm Hg	1 point

Manual is available at https://www.ysi.com/File%20Library/Documents/Manuals/ProDIGITAL-User-Manual-English.pdf

Table 12: Method References: Hanna Combo Meter HI 98129

Parameter	Sensor Type	Range	Accuracy	Resolution	Calibration
Temperature (°C, °F, K unit)	HI 98129	0 to 60°C	±0.5°C	±0.1°C	None
pH (mV, pH units)	HI 73127	0 to 14 units	±0.01 units	±0.01 pH nits	1 or 2 point
Conductivity (µS/cm, mS/cm)	HI 98129	0 to +3999 µS	±2% f.s.	1 µS/cm	1 point

Manual is available at https://docs.rs-online.com/1a16/0900766b801ee160.pdf

Table 13: Method References: LaMotte 2020we Portable Turbidity Meter

Parameter	Sensor Type	Range	Accuracy	Resolution	Calibration
Turbidity	Tungsten Filament Bulb	0.00 to 1100 NTU	±2% for reading below 100 NTU, ±3% above 100 NTU	0.01 from 0.00 -10.99 NTU 0.1 from 11.0 - 109.9 NTU 1 from 110 -1100 NTU	3 point standards within ±1% accuracy 1 NTU; 10 NTU 100 NTU

Manual is available at https://www.geotechnical.net/Technical%20PDF%20Files/1799.pdf

Table 14: Method Hach 8203 Digital Titrator Model 16900 - Alkalinity

Parameter	Indicators	Sulfuric Acid Titration	Range	Accuracy
Total Alkalinity	Phenolphthalein & Bromcresol Green-Methyl Red	0.1600 N H_2SO_4	10 to 4000 mg/L $CaCO_3$	Standard Additions Method

Manual is available at file:///C:/Users/Edda/Downloads/DOC316.53.01166_9ed.pdf

Data Comparability is the degree to which data can be compared directly to similar studies. Using standardized sampling and analytical methods and units of reporting with comparable sensitivity helps ensure comparability. For the parameters included in this project ION has selected testing methods that are USGS, EPA and DEC approved. For the ION water quality monitoring program, high quality equipment and laboratories are used to ensure the comparability to other data collected by using standardized methods of sampling and analysis. In addition, the ION monitoring program selected sample site at Pilot Station coincides with the USGS and the Woodwell Climate Center, Arctic Great Rivers Observatory projects, which allows a direct dataset comparison to additionally assure of ION data precision, accuracy, and comparability.

Data Completeness is the comparison between the amounts of usable data collected versus the amount of data called for in the sampling plan. In this project, completeness will be measured as the percentage of total samples collected and analyzed as a whole and for individual parameters and sites as compared to the goals set out by the project design. The target completeness goal for this project shall be 75% or better. Percent Completeness is calculated using the following formula:

$$\% \text{ Completeness (per parameter)} = \frac{\text{\# of valid results}}{\text{\# of sample taken}} * 100$$

The parameters measured, analytical methods used, method sensitivity, QC samples, holding times, preservative, and containers needed for this project are listed in Table 19 - 20. A summary of DQOs is illustrated in Tables 17 - 18, and will be used as the criteria for evaluating and determining the quality, bias, and usability of the data generated for the project conducted. This will be performed during the data validation process.

Table 15: Project Measurements Quality Objectives (MQOs)

Group Method	Method	Analyte	Alaska Water Quality Standards[8]			Precision (RPD)	Accuracy (% Recovered)
			Aquatic Life	Recreation	Drinking Water (MCL)		
Water Quality	YSI	Dissolved oxygen (DO)	> 7 mg/L[1] > 5 mg/L[2] < 17 mg/L[3]	> 4.0 mg/L	> 4.0 mg/L	± 10%	N/A
		pH	6.5 - 8.5 [4]	6.5 - 8.5	6.0 - 8.5	± 0.1	± 0.2
		Temperature	< 20°C [5] < 15°C [6] < 13°C [7]	< 30° C	< 15° C	± 10%	± 0.2°C
		Conductivity	N/A	N/A	N/A	± 10%	± 10%
	LaMotte 2020we	Turbidity[11]	> 25 NTU above natural conditions	> 5 NTU above natural conditions when the natural turbidity is 50 NTU, not to exceed max. increase of 15 NTU	> 5 NTU above natural conditions when the natural turbidity is 50 NTU or > 10% increase in turbidity when the natural turbidity is < 50 NTU, not exceed an increase of 25 NTU	± 10%	±2% for reading below 100 NTU, ±3% above 100 NTU
	Digital Titrator Model 16900	Alkalinity	20,000 [9, 10]	N/A	N/A	± 10%	N/A

[1] For anadromous fish
[2] For non-anadromous fish
[3] All other
[4] Not vary by 0.5 from natural condition
[5] Never to exceed
[6] For migration routes and rearing areas
[7] Spawning areas, egg and fry incubation
[8] AK DEC (2020) 18 AAC 70 Water Quality Standards
[9] Minimum as CaCO3 except where natural alkalinity occurs
[10] Chronic

Table 16: Project Measurements Quality Objectives for Laboratory analyses (MQOs) for Water, units = µg/L

Method	Analyte	LOQ Goals	LOQs Laboratory	Alaska Water Quality Standards[1]	
				Aquatic Life	Drinking (MCL)
Inorganic Cations EPA 6020A & EPA 200.8	Aluminum (AL)	40	40	750[5], 87[4]	N/A
	Antimony (Sb)	0.6	0.6	N/A	6
	Arsenic (As)	1.0	1.0	340[5], 150[4]	10
	Barium (Ba)	0.6	0.6	N/A	2,000
	Beryllium (Be)	0.2	0.2	N/A	4

[1] AK DEC (2008) Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances

	Calcium (Ca)	100	100	N/A	N/A
	Cadmium (Cd)	0.4	0.4	Hardness Dependent[7]	5
	Copper (Cu)	1.2	1.2	Hardness Dependent[7]	1,300
	Chromium (Cr)	0.8	0.8	Hardness Dependent[7]	100
	Cobalt (Co)	0.2	0.2	N/A	N/A
	Iron (Fe)	100	100	1000 [4]	3001
	Lead (Pb)	0.2	0.2	Hardness Dependent[7]	15
	Magnesium (Mg)	100	100	N/A	N/A
	Manganese (Mn)	0.4	0.4	100	50[1]
	Mercury (Hg)	0.04	0.04	0.051	2
	Molybdenum (Mo)	1.0	1.0	N/A	N/A
	Nickel (Ni)	0.4	0.4	Hardness Dependent[7]	610[1]
	Phosphorus (P)	200	200	0.1[4]	N/A
	Potassium (K)	200	200	N/A	N/A
	Selenium (Se)	4.0	4.0	5.0 [4]	50
	Silicon (Si)	1000	1000	N/A	N/A
	Silver (Ag)	1	1	N/A	N/A
	Sodium (Na)	200	200	N/A	N/A
	Thallium (Tl)	1	1	N/A	2
	Tin (Sn)	1	1	N/A	N/A
	Titanium (Ti)	2.0	2.0	N/A	N/A
	Vanadium (V)	20	20	N/A	N/A
	Zinc (Zi)	5.0	5.0	Hardness Dependent[7]	7400
EPA 415.3	Dissolved Organic Carbon (DOC)	0.2	0.2	N/A	N/A
Hydrogen Equilibration Technique (Coplen et al., 1991; Revesz & Coplen, 2008)*	Deuterium & Oxygen Isotopes ($_2H$,$_{18}O$)	0.2/2	0.2/2	N/A	N/A
Mercury LL /1631E	Mercury (Hg)	1.0	1.0	0.77[5], 1.4[4]	2
Inorganic Anions EPA 300.0 & EPA 300.1	Alkalinity[6]	10,000	10,000	20,000 [3, 4]	N/A
	Bromide (Br^-)	0.20	0.20	N/A	250[1]
	Chloride (Cl^-)	0.20	0.20	860,000[5], 230,000[4]	N/A
	Fluoride (F^-)	0.20	0.20	N/A	4,000
	Nitrite (NO_2^{2-})	0.20	0.20	N/A	10,000
	Nitrate (NO_3^{2-})[8]	0.20	0.20	N/A	1,000
	Sulfate (SO_4^{2-})	0.20	0.20	N/A	250[1]

[1] *Secondary drinking water*

[2] *Freshwater*

[3] *Minimum as $CaCO_3$ except where natural alkalinity occurs*

* *Full citation available upon request*

[4] *Chronic*
[5] *Acute*
[6] *Measured with SM21 2320B for SGS, USGS via Kramer, 1982*, & Hach 8203 Digital Titrator Method*
[7] *Metal standards for the protection of aquatic life are hardness dependent, the formulas for calculating the appropriated stan dard are available at: htpp://dec.alaska.gov/water/wqsar/wqs/index.htm Water Quality Criteria Manual for Toxics (December 12, 2008) Appendix A*
[8] *Dissolved organic carbon and nitrogen analysis measured with EPA 415.3*

Table 17: Summary of Analytical and Data Quality Objectives (DQO) Field Screening Data

Analytical Group	# of QA Samples/Rep/ Dup/MS/MSD	EPA Method/ Instrument	Accuracy Project Goal (% recovery)	Precision Project Goal (RPD)	Target Completeness	Preservation	Holding Time
Turbidity	1:10 rep or 1 per day	EPA 180.1	20%	10%	95%	None	Analyze Immediately
Alkalinity	1:10 rep or 1 per day	Hach 8203	20%	10%	95%	None	Analyze Immediately
Dissolved Oxygen	1:10 rep or 1 per day	YSI	20%	10%	95%	None	Analyze Immediately
Temperature	1:10 rep or 1 per day	YSI	0.2 °C	10%	95%	None	Analyze Immediately
Conductivity	1:10 rep or 1 per day	YSI	N/A	10%	95%	None	Analyze Immediately
pH	1:10 rep or 1 per day	YSI	0.1	10%	95%	None	Analyze Immediately

Table 18: Summary of Analytical and Data Quality Objectives (DQO) Laboratory Data

Analytical Group	QA Sample Field Blank	QA Sample Field Duplicate	Matrix	EPA Method/ Instrument Used	Accuracy Project Goal (% recovery)	Precision Project Goal (RPD)	Target Completeness
Alkalinity	10%	10%	Water	SM 21 2320B (SGS), Incremental Endpoint Point Titration (USGS)	75-125% [1]	25% [1]	95%
Anions	10%	10%	Water	EPA 300.1 (USGS & UAF), EPA 300 (SGS) Ion Chromatograph (IC)	75-125% [1]	25% [1]	95%
Cations	10%	10%	Water	EPA 6020A (SGS), EPA 200.8 (USGS & UAF) Inductively Coupled Plasma Mass Spectrometer (ICP- MS)	75-125% [1]	25% [1]	95%
Deuterium & Oxygen Isotopes	10%	10%	Water	Continuous Flow Isotope Mass Spectrometry (CF-IRMS)	75-125% [1]	25% [1]	95%
Dissolved Organic Carbon	10%	10%	Water	EPA 415.3 TOC Shimadzu TOC-L CSH ASI 40	75-125% [1]	25% [1]	95%

[1] Criteria may vary based on laboratory established control limit

Table 19: List of Parameters and Required Container, Holding Times and Preservation Methods for USGS & UAF Laboratory

Parameter	Container	Necessary Volume	Preservation & Filtration	Maximum Holding Time
Anions	125 mL HDPE*	75 mL	Filtered 0.45 µm**, Keep Cool (4°C)	30 days
Cations	125 mL HDPE	75 mL	Filtered 0.45 µm, Acidify, HNO_3, To pH < 2	6 months
Alkalinity	125 mL HDPE	30 ml	Filtered 0.45 µm, Refrigerate (4°C)	14 days
Dissolved Organic Carbon	40 mL Amber Glass	15 ml	Filtered 0.45 µm, Refrigerate (4°C)	14 days
Deuterium & Oxygen Isotopes	60 mL Glass with Polyseal cap	60 ml	N/A	Indefinite

* High-density polyethylene (HDPE); fluorocarbon polymer

** 0.45 µm Glass Micro Fiber syringe filter

Table 20: List of Parameters and Required Holding Times and Preservation Methods for SGS Laboratory

Analyte	Container	Necessary Volume	Preservation and Filtration	Maximum Holding Time
Alkalinity, mg $CaCO_3$/L	250 mL HDPE*	200 mL	None Required, Keep Cool (4°C)	14 days
Bromide	50 mL HDPE	10 mL	None Required, Keep Cool (4°C)	28 days
Chloride	50 mL HDPE	10 mL	None Required, Keep Cool (4°C)	28 days
Fluoride	50 mL HDPE	10 mL	None Required, Keep Cool (4°C)	28 days
Nitrate-N	50 mL HDPE	10 mL	None Required, Keep Cool (4°C)	48 hours
Nitrite-N	50 mL HDPE	10 mL	None Required, Keep Cool (4°C)	48 hours
Otho-Phosphate-P	50 mL HDPE	10 mL	None Required, Keep Cool (4°C)	48 hours
Sulfate (SO4)	50 mL HDPE	10 mL	None Required, Keep Cool (4°C)	28 days
Al, Sb, As, Ba, B, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Mn, K, Se, Na, U, Zn, -	250 mL HDPE	200 mL	3 mL 1:3 HNO_3, Filtered within 15 minutes of collection using a 0.45 µm filter, Keep cool (4°C)	6 months

* High-density polyethylene (HDPE); fluorocarbon polymer

VI. TRAINING REQUIREMENTS & CERTIFICATION

Water quality sampling training of Alaska TETs will be provided by the PM. Dr. Mutter has 15 years of environmental sampling experience. Anyone collecting samples for this project will be required to complete the YRITWC training. The trainer will make note of each participant's precision and accuracy for all testing methods and comment on the overall understanding of procedures. This training program meets the EPA's Office of Grant and Debarment requirement for field competency.

VII. DOCUMENTATION & RECORDING

All data gathered during this water quality program will be recorded on write-in-the-rain-paper field data sheets (see example Appendix A). The sampler will complete each data sheet with the minimum data requirement identified in each method's SOP. Data is entered using an indelible marker. If a mistake is made, one line is drawn through the characters in question and the new characters are entered to the immediate right of the lined-out entries with the initial of the sampler. Data sheets are sent with the water sample to the YRITWC office at 201 E 3rd Avenue, Suite 100, Anchorage AK 99501.

The sampler will use the "Additional Comments" section of the data sheet for any equipment or procedural problems. All records and documents are kept at the YRITWC office and are available to EPA for inspection at any time. Copies of all records and documents may also be sent to the Quality Assurance Officer (QAO) for QA/QC procedure upon request.

Monitoring equipment is inspected by the PM before shipped to the TETs annually. Equipment inspection forms and corresponding SOPs for each method are kept up-to-date for each piece of equipment. The person collecting samples will be responsible for calibrated monitoring equipment before every sampling event and calibration data are documented on field datasheets. The maintenance history for all monitoring equipment will be recorded in a separate maintenance log for each instrument.

1. Publications & Ownership

After all QC/QA review is completed the data resulting from the ION water quality monitoring program will be shared between the YRITWC, USGS, UAF, and Alaska Tribes. The data is also becoming public domain through the USGS ScienceBase, the National Science Foundation Arctic Data Portal, the National Quality Monitoring Council Data Portal (EPA WQX), the BSCS Science Learning FieldScope, and the YRITWC website. In addition, data will be made available by the PM through personal request and partnerships for scientific journal publications. Our goal is to provide free and easy access to the data so that stakeholders of the YRB can better understand water quality conditions and potential impacts on the health of the river.

VIII. MEASUREMENTS & DATA ACQUISITION

1. Sampling Process Design

Sample Site Selection: In order to obtain useful information and address Tribal Councils concerns, sample sites are selected strategically as best practice approach to capture climate change impacts to the Yukon River and its tributaries (hydrological, geographical, and environmental physical conditions), flow direction of the river/stream location relative to the community, drinking water resource location relative to perceived

source point pollution impacts, location of the ESHA within the YRB, safe accessibility, representativeness of the water body and repeatability. Adjustments will be made if physical constraints on planned field events occur due to weather, safety considerations, or problems that may impact the technical quality of the measurements.

Each site is assigned a site name and identified by a site number as well as a location description, in addition by latitude, longitude and elevation using a Geographic Information System (GIS) mapping program (i.e. ArcGIS), USGS topographical maps or GPS. Table 21 lists the Tier I, Tier II and Tier III samples locations, site identifications, and GPS information.

Table 21: ION Monitoring Program Sample Sites

Site ID	River Name	Latitude	Longitude	Elevation (m)	Sample Frequency
akhpb1a	Akuliqutaq Slough at Hooper Bay	61.5381	-166.1117	0	Open Water
alauk2a	Alakanuk Landfill	62.6821	-164.6592	5	May & August
alauk3a	Alakanuk below Landfill	62.6748	-164.4535	7	May & August
alarc1a	Airport Lake at Arctic Village	66.4784	-145.4784	131	Open Water
asarc1b	Arctic Village Slough	68.1294	-145.5348	622	Open Water
asauk1a	Alakanuk Slough	62.6970	-164.6898	3.1	Open Water
aceaa1a	American Creek at Eagle	64.7265	-141.2626	429	June & September
actan1a	American Creek at Tanana	65.0504	-151.3225	73	June
araet1a	Alatna River above Alatna	66.5710	-152.6269	124	Open Water
ananv1a	Anvik River	62.6667	-160.2817	30	Open Water
anksm1a	Andreafski River	62.0536	-163.1325	20	Open Water/Under Ice
bctal1a	Bear Creek at Tanana	65.2612	-151.9392	364	Open Water
bccrc1a	Birch Creek at Circle	65.7095	-144.3335	192	Open Water
bihpb1a	Big Lake at Hooper Bay	61.5047	-166.1254	0	Open Water
bchus1a	Blueberry Creek - Hughes Landfill	66.0347	-154.2401	370	June & September
blcik1a	Draanjik Gwich'in at Chalkyitsik	66.6543	-143.7163	158	Open Water
bohpb1a	Bone Pond at Hooper Bay	61.5004	-166.1102	2	Open Water
chfai1b	Chena River at Fairbanks	64.8025	-147.9153	137	Open Water/Under Ice
chfai6a	Chena River above Fairbanks	64.8470	-147.4074	137	Open Water/Under Ice
chvee1a	T'ee Drin Jik (Chandalar River) above Venetie	67.0191	-146.4304	175	Open Water
chvee2a	T'ee Drin Jik River at Venetie	67.0219	-146.5330	201	Open Water
crarc1b	T'ee Drin Jik River at Arctic Village	68.1297	-145.5378	648	Open Water
ccdjn1a	Clearwater Creek	64.0541	-145.4334	316	Open Water
drdjn1a	Delta River	64.0709	-145.7529	338	Open Water
fctan1a	Fish Creek at Tanana	65.0422	-151.3636	71	June
gcarc1b	Glacial Creek at Arctic Village	68.1231	-145.4930	657	Open Water
hefai1a	Hess Creek	65.6658	-149.0966	137	Open Water/Under Ice
huhsl1a	Huslia River	65.7316	-156.5498	67	Open Water
hohsl2a	Hogatza River	65.9998	-155.3455	62	Open Water
hstal1a	Hay Slough at Tanana	65.1625	-151.9488	68	Open Water
kwenm1a	Kwikguk River at Emmonak	62.7738	-164.5098	0	Open Water
kwenm2a	Kwikguk River at Emmonak	62.7774	-164.5514	0	Open Water
koaet1a	Koyukuk River above Allakaket	66.5678	-152.6234	124	Open Water
koaet1b	Koyukuk River below Allakaket	66.5451	-152.7165	122	Open Water
kohus1a	Koyukuk River above Hughes	66.0735	-154.2276	85	Open Water
kohsl1a	Koyukuk River above Huslia	65.7007	-156.4280	161	Open Water
kohsl1b	Koyukuk River below Huslia	65.6767	-156.3805	161	Open Water

kokyu1a	Koyukuk River at Koyukuk	64.9221	-157.5414	36	Open Water
tomnt3a	Tolovana River at Minto	65.1624	-149.1282	103	Open Water
tomnt4a	Minto Flats at Minto	65.1436	-149.0389	97	Open Water
mkrsh1a	Mouth of Kakolade at Russian Mission	61.9708	-161.3442	8	Open Water
rmlrsh1a	Mouth of Russion Mission Lake	61.7667	-161.4325	8	Open Water
nahpb1a	Naparyaraq Slough at Hooper Bay	61.5421	-166.0789	0	Open Water
nettw1a	Nenana River at Cantwell	63.4543	-148.8062	603	Open Water
nenen1b	Nenana River at Nenana	64.5564	-149.1160	106	Open Water/Under Ice
nivak1a	Ninglivvak River above Chevak	61.5461	-165.5741	9.1	Open Water
ncfai1a	Nome Creek at Fairbanks	65.3413	-146.7113	656	Open Water
rshsl1b	Richards Slough at Huslia	65.6589	-156.4719	160	Open Water
pofyu1a	Porcupine River above Fort Yukon	66.5928	-145.2786	164	Open Water
pofyu2a	Porcupine River at Hubert Camp	66.9898	-143.1396	164	Open Water
tafai1b	Tanana River below Fairbanks	64.7936	-147.9554	133	Open Water/Under Ice
tafai2a	Tanana River above Fairbanks	64.5469	-147.0539	188	Open Water/Under Ice
tadjn1a	Tanana River above Delta Junction	64.1565	-145.8484	301	Open Water
tafai3a	Tanana River above Eielson	64.5325	-147.0149	337	Open Water
tanen1a	Tanana River at Nenana	64.5546	-149.0599	107	Open Water/Under Ice
tatal1a	Tanana River above Tanana	65.1591	-151.9561	75	Open Water
tatok1a	Tanana River above Tok	63.3172	-142.6482	493	Open Water
tatfai1a	Tataline River at Fairbanks	65.3285	-148.3115	157	Open Water
tdksm1a	Traditional Drinking Water above Gravel Pit at St Mary's	62.0576	-163.1946	31	Open Water
tdksm1b	Traditional Drinking Water below Gravel Pit at St Mary's	62.0520	-163.1747	30	Open Water
diaet1a	Allakaket Drinking Water Intake	66.5488	-152.6631	402	Open Water
tomnt1a	Tolovana River	65.4709	-148.2689	185	Open Water
tomnt2a	Tolovana River (Elliott Hwy)	65.4657	-148.6672	127	Open Water
yuanv1a	Yukon River above Anvik	62.6717	-160.1970	36	Open Water
yuauk1a	Yukon River at Alakanuk	62.6847	-164.6184	10	Open Water
yubri1a	Yukon River at Dalton Highway Bridge	65.8760	-149.7179	80	Open Water/Under Ice
yucrc1a	Yukon River at Circle	65.8246	-144.0537	211	Open Water
yueaa1a	Yukon River at Eagle	64.7828	-141.1767	268	Open Water
yuemn1a	Yukon River at Emmonak	62.7588	-164.4790	0	Open Water
yufyu1a	Yukon River at Fort Yukon	66.5588	-145.2776	130	Open Water/Under Ice
yugal1a	Yukon River at Galena	64.7198	-156.7526	142	Open Water
yukal1a	Yukon River above Kaltag	64.3440	-158.7103	37	Open Water
yukot1a	Yukon River above Kotlik	63.0414	-163.6697	3	Open Water
yuksm1a	Yukon River at St. Mary's	62.0282	-163.2381	4	Open Water
yukyu1b	Yukon River below Koyukuk	64.8746	-157.7192	34	Open Water
yumll1a	Yukon River at Marshall	61.8387	-162.1418	4	Open Water
yunul1a	Yukon River above Nulato	64.7277	-158.0550	32	Open Water
yupqs1a	Yukon River above Pilot Station	61.9438	-162.8609	7	Open Water
yupqs1b	Yukon River below Pilot Station	61.9304	-162.8801	5.9	Open Water/Under Ice
yurby1a	Yukon River at Ruby	64.7454	-155.4887	42	Open Water
yurmp1a	Yukon River above Rampart	65.5197	-150.1434	205	Open Water
yursh1a	Yukon River at Russian Mission	61.8419	-161.3053	8	Open Water
yusvs1a	Yukon River above Stevens Village	65.9930	-149.0564	87	Open Water
yuwbq2a	Yukon River at Lower Birch Creek Slough	66.3775	-147.1004	108	Open Water
yuwbq1a	Yukon River above Beaver	66.3511	-147.3270	108	Open Water
yuwbq1b	Yukon River below Beaver	66.3463	-147.4511	105	Open Water

yutal1a	Yukon River above Tanana	65.1757	-151.9692	63	Open Water
yutal2a	Yukon and Tanana River confluence	65.1647	-152.0195	61	Open Water
vlveet1a	Venetie Landfill Pond	67.0206	-146.3937	181	Open Water
vlveet2a	Venetie Big Lake	67.0381	-146.3448	168	Open Water

Sampling Parameters: As described in Table 6, selected parameters are based on their usefulness in inventorying water quality and projecting the general "health" of the water bodies in question. Water quality physical data is obtained by the using YSI Mutliparameter probes. TETs are trained in the use of YSI Professional Pro Plus Multiparameter and Hanna Meter data collection and YRITWC staff collecting data via YSI Professional Pro Plus Multiparameter, YSI EXO2 Multiparameter Probe, YSI Sonde 600 Probe, YSI 556 Mulitprobe System, YSI DSS. Physical data collected in the field are: Dissolved Oxygen (DO), pH, Conductivity, air and water Temperature. Surface water samples are measured for Turbidity with a LaMotte 2020we Portable and Total Alkalinity using a Hach Digital Titrator Model 16900 in the YRITWC office as soon as samples arrive. Surface water sample for chemical analysis are send directly to the laboratory. Tier I and II samples are analyzed for major ions, Dissolved Organic Carbon (DOC), nutrients, selected trace metals, and isotopes of oxygen at the UAF or USGS laboratory. Tier III samples are sent directly to the certified SGS laboratory for cation, anion, alkalinity, and mercury analysis. Environmental observations are collected on historical and current changes to river channel, bank, vegetation, and water body flow rate to better understand the dynamics (transport, sources, sinks) of the river system during open water and freeze up time.

Water Sampling Frequency*: Tier I Baseline Data:* The YRITWC will coordinate efforts with TETs to ensure environmental observation, physical data measurements and surface water sample collection is performed monthly during the open water season (June to October). Under ice sampling will be attempted at 11 strategically selected sites within the YRB, logistics or weather will play a major role in the ability to obtain these samples. For both logistical and geochemical reasons, under ice sampling will only occur monthly from the time the rivers are completely frozen to the time when spring snow melt begins (tentatively January through March). Replicate field measurements will be performed on one out of each ten measurements. The tentative sampling schedule is dependent on discharge, which is in turn, dependent on snow melt and is determined by the PM utilizing the USGS real-time discharge data from: Yukon River at Eagle (http://waterdata.usgs.gov/ak/nwis/uv?15356000); Yukon River near Stevens Village (http://waterdata.usgs.gov/ak/nwis/uv?15453500); and Yukon River at Pilot Station (http://waterdata.usgs.gov/ak/nwis/uv?15565447).

Tier II Baseline Data: The YRITWC will coordinate efforts with TETs to ensure environmental observation, physical data measurements and surface water sample collection is completed monthly during open water season starting June till ice freeze-up forms (October). Replicate field measurements will be performed on one out of each ten measurements.

Tier III Baseline Data: The YRITWC will coordinate efforts with TETs to ensure environmental observation, physical data measurements and surface water sample collection is completed twice a year during snow-melt and at major rain events in late summer when runoff water and leachate are present at the established sites.

The PM and TETs will strive to maintain a regular monitoring schedule under consideration of weather conditions and safety. The PM will make efforts to reschedule sampling events as weather allows. The ION sample frequency for all sample sites is listed in Table 21.

2. Site Health and Safety Plans

The following safety precautions discussed below do not constitute a safety plan, and approval of this QAPP doesn't constitute a safety plan approval. Sampling sites are selected, in part, because they are safely accessible. The TETs and YRITWC personnel are instructed to use safe access routes and will be warned of site-specific hazards. The TETs and YRITWC will use appropriate safety equipment while collecting samples such as rubber boots, life vest and appropriately clothing to be prepared for variable weather conditions. All CDC recommendations with regards to COVID-19 and restrictions from the Tribal Councils, will be adhered to.

3. Sampling Methods Requirements

Only trained TETs and YRITWC personnel will conduct sampling for this project. To obtain the best representation of the entire river system, at each site, a grab sample will be collected manually at mid-channel using a boat (when available). Samples will be obtained from approximately six to twelve inches beneath the water surface. Samples will be collected and sent to the laboratory within the analytical holding times. Sampling method is descripted in the 2022 ION Field Manual (Appendix A).

Sample Collection, Container and Equipment: All sampling equipment and sample containers must be cleaned according to the equipment specifications and/or the analytical laboratory. Bottles supplied by a laboratory are pre-cleaned, must never be rinsed, and will be filled only once with a sample. Individual sample containers, sample size, preservation, and maximum storage requirements for each parameter are provided by YRITWC or the analytical laboratory.

Sample Handling and Custody Requirements: All monitoring and field procedures will be conducted by the trained YRITWC PM or ET or TETs. All collected samples will be labeled at the time of collection. The date, time, and site name will be recorded directly on the sample bottles. When samples are collected the following chain of custody procedure will be followed:

- Samples will be labeled (date, time, and site name, see Figure 3) directly on the bottles and field data will be recorded on field datasheet (Appendix B) upon collection.
- In the field, surface water grab samples will be the responsibility of, and stay with the person who collected them.
- The sample procedure (2022 ION Field Manual, YRITWC field sheet and COC, see Appendix A-C) or one provided by the laboratory will be used to record all transport and storage information.
- Samples will travel with the person who collected them (in a cooler with ice packs) and be sent immediately either to the YRITWC office or to the UAF or SGS laboratory for analysis as indicated on the chain of custody (COC).
- Trained YRITWC or UAF or certified SGS laboratory personnel will record the date, time, site name, and temperature of the samples upon their arrival.
- Trained YRITWC or UAF personnel will conduct secondary filtering of major ion samples using a GMF or nylon 0.45 μm filter.
- Samples will be refrigerated or kept in a cooler to maintain preservation temperature given in Table 19 and Table 20.
- Trained YRITWC personnel will complete Turbidity measurement and Alkalinity titration immediately

when sample arrives at the office.

- At this point the samples will become the responsibility of the certified laboratory and will be subject to their sample custody and quality control procedures.
- Laboratory personnel will record the date and time the sample arrives at the laboratory.
- All results from the laboratory will be documented, and kept on a hard drive, along with a cloud back-up, at the YRITWC office.

Analyte Sample Date: Time: Sample ID:

Figure 3: Sample Container Label

4. Shipping Requirements

Surface water samples are shipped from remote YRB communities. Packaging, marking, labeling, and shipping of samples will comply with all regulations promulgated by the U. S. Department of Transportation in 49 CFR 171-177. YRITWC staff have had training for shipping samples and consult with the laboratory for additional shipping instructions.

Temperature preservation method and holding time limitations illustrated in Table 19 and 20 must be considered when decisions are made regarding sampling and shipping times for time and temperature sensitive sample analyses.

IX. ANALYTICAL METHODS REQUIREMENTS

Analysis shall be conducted in accordance with USGS or EPA-approved analytical procedures and in compliance with 40 CFR Part 136, Guidelines Establishing Test Procedures for Analysis of Pollutants. Reference the Project's MQO Table 15 and Table 16 of this QAPP for list of parameters of concern, approved analytical methods, method-specific detection and reporting limits, and accuracy and precision values applicable to this project. The project's QAO will verify that only USGS or EPA CWA approved methods are used.

For Tier III samples the maximum laboratory turnaround time from sample receipt to providing analytical results shall be 30 days of sampling receipt date.

X. QUALITY CONTROL REQUIREMENTS

Quality Control (QC) is the overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the monitoring project's data quality objectives.

All personnel directly involved with the monitoring program and this project are required to complete the YRITWC water quality monitoring training to be eligible to collect data.

1. QC for Field Measurements

- Proper cleaning of sample containers and sampling equipment.
- Maintenance, cleaning, and calibration of field instrument/s per the manufacturer's and/or laboratory's specifications and field SOPs.
- Standard certified reference solutions used prior to expiration dates.
- Proper field sample collection and analysis techniques.
- Correct sample labeling and data entry.
- Proper sample handling and shipping/transport techniques
- Field replicate samples (blind to the laboratory, e.g. 1 replicate/10 samples).
- Replicate measurements shall be performed in the field for every 10 sample measurements. Precision of the replicate analyses shall be within the acceptable criteria set forth by the instrument or the method SOP. Only replicate measurements that meet the precision criteria will be entered in the project database. Should a problem arise due to unacceptable precision results, no other measurements for the parameter will be conducted until the cause of the problem is identified and resolved. Problems encountered will be documented in the field data sheet (Appendix A). Deviations from the QAPP shall be documented in the field data sheet.
- Calculation of precision, accuracy, and completeness are outlined in Section V.
- Depending on the frequency of the sample collection and measurement activities, duplicates and blank samples may be collected and analyzed by a laboratory. Duplicate confirmatory samples may also be sent to the commercial laboratory in case questionable/anomalous high results were obtained in the field. The contracted laboratory must meet EPA or USGS Competency Policy.

Field Instrument QC includes the following:

- All field instruments are calibrated appropriately using manufacturers manual periods prior to use.
- Check field instrument/s calibration solution illustrated in Tables 8 to 14.
- Record observed values on field sheets and any additional comments.
- If observed values are more than +/- 10% of expected values, repeat calibration steps.

If results vary by more than +/- 10 %, a third test will be performed. If no two successive readings fall within the +/- 10 % precision objective, contact the QAO for equipment check immediately. All results will be recorded on the field sheet, however only the final determined value will be entered into the project data system.

- Record environmental observations on field sheet and any additional comments.

2. QC for Laboratory Chemical Analysis

Laboratory analytical equipment will remain within the domain of the respective certified testing laboratory ISO/IEC standards, and testing inspection and maintenance is the responsibility of the analytical laboratory. Contracted laboratories will provide analytical results after verification and validation by the laboratory QAO. The laboratory report in PDF format shall include data concentration, DLs, PQLs, units, surrogate recovery, and qualifier (if applicable), blanks, laboratory QC samples such as LCS/LCSD, method blanks, sample receiving documentation and a written report summary discussing QC issues. The Laboratory data will then

be evaluated by the QAO for laboratory performance and correctness. The PM, and QAO will review these data to ensure that the required QC measurement criteria have been met. If a QC concern is identified in the review process, the PM, and QAO will seek additional information from the contracted laboratory to resolve the issue and take appropriate corrective action.

XI. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, & MAINTENANCE REQUIREMENTS

The manufacturer's manual for the Alkalinity titrator, YSI and turbidity instrumentation describe the proper handling and maintenance of equipment. Proper equipment handling and maintenance is also emphasized during all training and QC sessions. The initial inspection, testing and assurance that all of the sample collection and measurements meet the technical specifications as specified by the method and/or SOP are the responsibilities of the PM.

1. Instrument/Equipment Testing and Maintenance

- Prior to a sampling event, the sampler shall inspect and test all field instruments and equipment in accordance with the manufacturers' specifications.
- If any instrument/equipment is found to be defective in any way, the person sampling shall contact the PM to arrange for immediate replacement or repair.
- Whenever a faulty instrument/piece of equipment is replaced, the PM shall document in the maintenance log kept at the YRITWC's office.
- The project PM shall maintain an adequate supply of expendable supplies for the project (e.g., calibration standards, parts, tools, etc.) located at the YRITWC office. The quantity of reagent maintained in the office shall be carefully estimated to assure that replenishments are received before exhaustion of the supply and that stored supplies do not exceed expiration dates.
- All sample collection devices and equipment will be appropriately cleaned prior to use in the sampling project.
- All sample containers, tubing, filters, etc. provided by a laboratory or by a commercial vendor will be certified clean for the analyses of interest. The sampler will take note of the information on the certificate of analysis that accompanies sample containers to ensure that they meet the specifications and guidance for contaminant-free sample containers for the analyses of interest.
- UAF, USGS and SGS (the contracted laboratory for this project) will follow procedures in their laboratorys' QAP and SOPs for inspection/acceptance of supplies and consumables.

2. Instrument/Equipment Calibration and Frequency

All field instruments and equipment shall be calibrated before use following the calibration procedures described in each method SOP and the manufacturer's manual. Field instruments will be calibrated each day prior to use.

All commercial laboratory instrumentation and equipment used in the analysis for this project shall be calibrated prior to sample analysis in accordance with the technical specifications and procedures specified in the analytical method used and laboratory SOPs.

3. Inspection and Acceptance Requirements for Supplies

Monitoring equipment and supplies are ordered from various manufacturers and are inspected upon arrival by project personnel. Broken bottles, incomplete kits and reagents or instruments that do not meet standards are shipped back to the manufacturer for replacement.

XII. DATA ACQUISITION REQUIREMENTS

Required longitude and latitude coordinates for monitoring sites is derived by using USGS topographic maps and confirmed using GPS coordinates taken at the site. Sites are plotted and spatially checked using a Geographic Information System (GIS) computer-mapping program (ArcView).

Additional water and physical river characteristics, and other data pertaining to the sample location will be gathered. Historical data will be analyzed to assess direct comparability and may be qualified or excluded from trend analyses in annual reports. Water quality data will be evaluated by comparison to state and federal WQS as applicable. Traditional and local knowledge will guide water quality monitoring and help with assessing current and historical conditions of the selected waterbodies.

XIII. DATA MANAGEMENT

The person sampling is responsible to document data on the field datasheet(s) (Appendix A) provided for this project. All environmental observational data, and water, and field measurements are recorded at the time of sampling. The person sampling will sign and date the field datasheets after each sampling event. The field data sheets are kept and maintained in an organized file in the YRITWC office.

Field data sheets and other sample documentation shall be initially reviewed by the PM, and peer reviewed by the QAO prior to data entry to the project database. Another review for transcription errors, precision, completeness, anomalous data, and other general problems shall be conducted after data entry to the database. The PM will ensure that data generated are accurately entered into an Excel database and made available for online access via the USGS ScienceBase, the National Science Foundation Arctic Data Portal, the National Quality Monitoring Council Data Portal (EPA WQX), the BSCS Science Learning FieldScope, and the YRITWC website. Data are reviewed regularly by the QAO and PM and will be reported to the ION monitoring program participating Tribal Councils annually.

XIV. ASSESSMENT AND OVERSIGHT

1. Assessment and Response Action

Project Level Assessments (Internal Project Assessments)

- All those collecting samples will be trained YRITWC personnel or TETs, or under the direct supervision of one.
- Depending on the frequency of the sample collection and measurement activities, field duplicate samples shall be collected and analyzed by a laboratory. Field duplicate samples shall also be sent to the laboratory in case questionable/anomalous high results were obtained in the field.
- Three levels of data verification shall be employed, i.e. during sample collection, data documentation,

and data entry and generation processes. Data that does not meet the DQ standards are appropriately flagged or qualified in the database during the data validation process.

- The YRITWC PM and QAO will review this QAPP and the overall project design annually and may suggest procedural refinements or additional testing procedures. This may include new parameters to be measured or changes to procedures currently in use. Any such changes will be subject to EPA approval. The project is open to EPA management or technical system audits at their discretion.

Program Level Assessments (External Project Assessment)

- Upon request a TSR of the project may be conducted by EPA to assess the progress and effectiveness of the program.
- A performance evaluation sample may be submitted blind to the contract laboratory to test proficiency.

Response and Corrective Actions: Problems encountered during sample collection and data generation shall be documented and handled accordingly and as soon as possible in a Corrective Action Form (see Appendix C). No measurements will be generated by an instrument or piece of equipment that did not meet the technical specifications of the manufacturer or the method SOP. Problems that may have a big impact on data quality shall be properly documented and resulting data will be flagged accordingly.

Any failure to meet DQO will be evaluated. If the cause is found to be equipment failure, calibration and maintenance procedures will be reassessed and improved. If the problem is found to be personnel error, that person will work with the PM to resolve the problem. If accuracy and precision goals are frequently not being met, QC sessions will be scheduled more often.

If failure to meet program specifications is found to be unrelated to equipment, methods, or personnel error, the QAPP may be revised. Revisions and subsequent modifications and amendments to this QAPP shall be submitted to the EPA Quality Assurance Manager for review and approval.

2. Community Reports

The PM is responsible for the preparation and distribution of the annual report to the Tribal Councils. The annual reports will be produced each year and will include:

- Spreadsheets detailing all data collected
- Graphs depicting test results for each parameter tested
- Review of historical data from each site
- Discussion of discernable trends
- Photographs of each sampling site
- GIS maps showing land use and other relevant information
- Results of QC audits and internal assessments
- Conclusions with recommendations for futures sampling and monitoring efforts.

XV. DATA VALIDATION AND USABILITY

1. Data Review, Validation and Verification

All data collected by project personnel is subject to review by the project QAO, PM, and Laboratory Managers to determine if the data meet QAPP objectives. Decisions to reject or qualify data are made by the QAO.

2. Validation and Verification Methods

Data Verification Requirement: Field datasheets and chain-of custody forms must be filled out completely and signed by the sampler at the time of sampling and analysis. There will be at least three levels of data verification for this project, (1) field datasheet and data generation documentation, (2) peer review by a PM other than the ET or TET samplers and (3) data review and evaluation by the project QAO. During this process, the field datasheet for calibration and measurements and COC records shall be checked and evaluated for precision, accuracy, missing or illegible information, errors in transcription and calculation, and values outside of the expected range.

When review is completed and any concern addressed, each field data sheet and chain-of custody form is signed and dated by the QAO and PM. If data quality questions cannot be adequately resolved, data will not be entered into the data system and the PM will arrange for corrective measures (i.e. re-training, equipment re-calibration, etc.). Any changes made to data are documented, initialed and dated, and any action taken as a result of the data review is specifically recorded on the datasheet below with the reviewers' signatures and dates of signatures.

Data Validation Requirement: Data validation shall be conducted on all environmental data generated for this project by the QAO and the TAs in accordance with the specifications and QC acceptance criteria set forth by the analytical methods and SOPs used for each environmental measurement. Data that did not meet the DQO of the project are appropriately flagged or qualified in the database during the data validation process.

On an annual basis, the QAO and TAs will print the data and proofread it against the original data sheets. Errors in data entry are corrected and inconsistencies are flagged for further review. Data shall be documented in an annual report. The report will identify deficiencies in data collection or program design.

XVI. RECONCILIATION WITH DATA QUALITY OBJECTIVES

Data generated by this project shall be evaluated and assessed in accordance with the DQO requirements listed in Tables 17 and 18 and the technical specifications and QC acceptance criteria set forth by the analytical methods and SOPs used for each environmental measurement. All data generated shall be reported in the annual report. Data that were slightly outside the DQO goals of the project shall be appropriately flagged or qualified in the database with a short narrative defining the qualifier and its effect on the quality of the data.

XVII. REFERENCES

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YSI EXO Probe Manual. https://www.ysi.com/File%20Library/Documents/Manuals/EXO-User-Manual-Web.pdf

YSI 556 Multiparameter Manual. https://www.ysi.com/File%20Library/Documents/Manuals/655279-YSI-556-Operations-Manual-RevD.pdf

YSI DSS Multiparameter Manual. https://www.ysi.com/File%20Library/Documents/Manuals/ProDIGITAL-User-Manual-English.pdf

Hanna Combo Meter HI 98129 Manual. https://docs.rs-online.com/1a16/0900766b801ee160.pdf

LaMotte 2020e Portable Turbidity Meter Manual. https://www.geotechnical.net/Technical%20PDF%20Files/1799.pdf

Hach 8203 Digital Titrator Model Manual. file:///C:/Users/Edda/Downloads/DOC316.53.01166_9ed.pdf

Appendix A

Water Quality Monitoring Field Manual

Yukon River Inter-Tribal Watershed Council • Science Department • 2022

"to once again drink water directly from the Yukon as our ancestors did"

ONE PEOPLE-ONE RIVER

Yukon River Inter-Tribal Watershed Council

www.yritwc.org

Yukon River Inter-Tribal Watershed Council

The Yukon River Inter-Tribal Watershed Council (YRITWC) is an Indigenous grassroots organization, consisting of 74 First Nations and Tribes, dedicated to the protection and preservation of the Yukon River watershed. The YRITWC accomplishes this by providing Canadian First Nations and Alaskan Tribes in the Yukon watershed with technical assistance, such as facilitating the development and exchange of information, coordinating efforts between First Nations and Tribes, undertaking research, and providing training, education and awareness programs to promote the health of the watershed and its Indigenous peoples.

Manual Overview

This manual is a reference tool for technicians conducting water sampling under the YRITWC protocols. The YRITWC protocols were developed using the United States Geological Survey (USGS) protocols as a benchmark for quality (USGS, TWR Book 9). The structure set forth here will be one that focuses on end-user functionality. Throughout the manual key points will be noted with special characters and text boxes in the body of the text. This will highlight essential material and give resources for additional research.

Acknowledgements

This work would not be possible without the collaboration of many individuals, communities, government agencies and funding sources. Through this collaboration, the YRITWC has established a long-term database of water quality monitoring that covers the entire Yukon River Watershed. At several sites, monitoring began as early as 2001. Through consistent sampling you benefit your community and also other communities upstream and downstream. The YRITWC greatly appreciates all the hard work and dedication of the Environmental Coordinators, Lands and Resources Departments, and their staff to collect water quality samples throughout the summer and winter. Without their (your) dedication, this network would not exist. The YRITWC would also like to recognize the contribution of the Environmental Protection Agency's Indian General Assistance Program that funds many of the Environmental Programs to collect and report this data. The YRITWC also greatly appreciates the collaboration with the USGS Water Resource Mission Area and Alaska Climate Adaptation Science Center. For over ten years now, the USGS has provided an immense contribution to this network by providing almost all of the laboratory analysis for the water quality samples. Since, 2019 we have been delighted to welcome the University of Alaska Fairbanks (UAF) project partners with their expertise that will contribute to the Indigenous Observation Network (ION) chemical laboratory analysis and active layer dynamics research capacity. The National Science Foundation, Administration for Native Americans, Health Canada, Yukon Government, Environment Canada, and the Gordon Foundation have all provided substantial funding to assure the sustainability of the ION and its water quality program. Finally, we would like to thank USGS, National Geographic, and BSCS Science Learning for the development of our water quality database.

TABLE OF CONTENTS

Getting Started

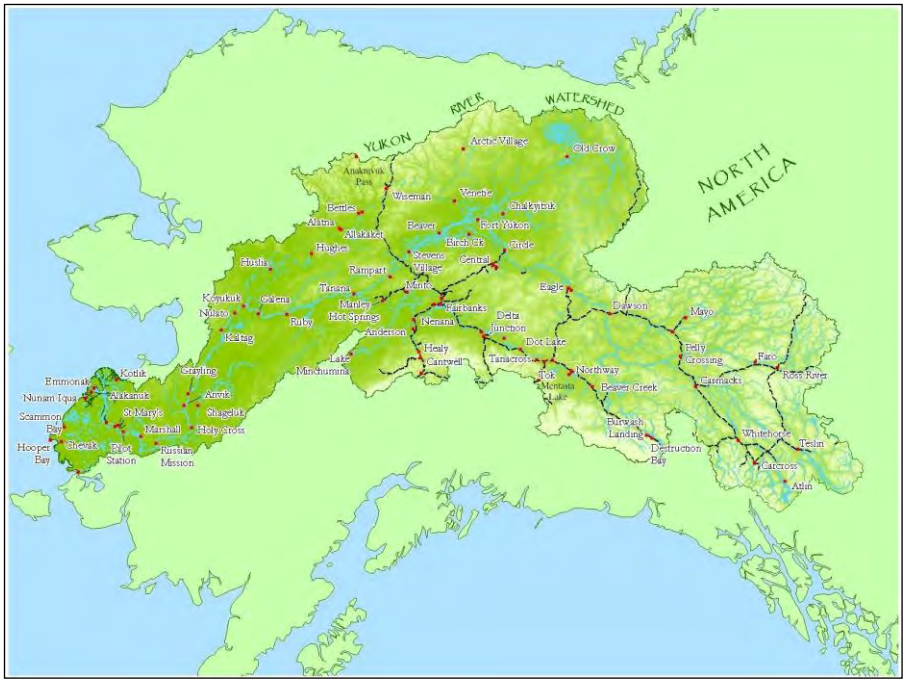
Asking a Question

All science research starts by someone asking a question. Most questions that we receive revolve around water and if you are reading this manual the odds are that you and your community are interested in what is going on in the Yukon River watershed.

The Water Quality Monitoring Program managed by the YRITWC Science Department was started because people of the Yukon River Watershed asked questions about the water. ***What is happening to the fish? Is the water safe to drink? Why is the water changing?*** All these questions, and more, led to the development of a baseline watershed study that has been operating continuously since 2006.

Developed through collaboration and assistance by the USGS, the baseline Water Quality Monitoring Project has spread to over 54 communities across the entire Yukon River watershed.

Map of communities in the Yukon River Watershed



Yukon River Basin Map with YRITWC signatory Tribes/First Nations highlighted

This project focuses on collecting information on basic water quality parameters (see Appendix D) that give a picture of the overall health of the water system, including fish habitat and responses to climate change. Long-term baseline studies are important for several reasons. They provide a basis for comparison against possible contaminants in the river, as well as document long-term trends that can be useful in highlighting natural versus unnatural changes in the water system. You can access the ION database for

the long-term baseline data at the USGS ScienceBase https://www.sciencebase.gov/catalog/item/573f3b8de4b04a3a6a24ae28 or check out the FieldScope online platform site at http://yukon.fieldscope.org/. All community water quality reports and USGS factsheets and reports can be uploaded directly from YRITWC website https://www.yritwc.org/reports.

If you have a question about the ION database or community reports, please feel free to contact us. We would also like to hear from you, if there are any water quality concerns around your community to explore how we help to find answers to those concerns. Maybe you can even help start a new initiative in the watershed. Sometimes answers take time to reveal themselves, but be patient and have fun taking observations and learning more about the environment you live in!

Quality Assurance Project Plan (QAPP)

The YRITWC Science Department has revised a Quality Assurance Project Plan (QAPP) for the ION water quality baseline project that covers the sampling conducted by communities and YRITWC staff in spring 2020. A QAPP is specifically required by projects funded through the Environmental Protection Agency (EPA) to ensure that the project and tasks are documented and reviewed before work is started.

If your project is addressing additional questions or requires protocols for site specific contaminant sampling, please contact us and we help you to develop your own QAPP or amend the existing one to include all the criteria within your project.

The QAPP describes the quality assurance procedures, quality control specifications and other technical activities that must be implemented to ensure that the results of the project or task to be performed will meet project specifications (https://www.epa.gov/r10-tribal/quality-assurance-project-plans-tribes-region-10 and https://www.epa.gov/quality/quality-assurance-project-plan-development-tool).

Contact YRITWC

Once you have asked a question and desire to pursue projects that will help to give insight to the topic, contact the YRITWC! We can assist at multiple levels to help you meet your community goals. Whether you need to develop your project or would like to take part in the ION program, the YRITWC will do our best to assist communities in answering their question(s).

The YRITWC office in Anchorage is staffed with knowledgeable employees who are eager to talk with you about ways your community can participate in YRITWC programs. The Science Department will assist in guiding you towards programs that will best answer the questions from your community.

Anchorage Office:
Science Staff:
Edda Mutter (emutter@yritwc.org)
Kari Young (kyoung@yritwc.org)

Address:
201 E 3rd Avenue, Suite 100
Anchorage, AK 99501
Phone: (907) 258-3337; Fax: (907) 258 3339

Next Steps

Training

Once you have your question and have decided which projects best fit your community needs, it's time to attend training! The Science Department offers annual training in water quality sampling. Contact the YRITWC to find out when the next training opportunity will be. Generally, the water quality trainings are held in spring. We are often able to work around schedules and provide on-site training in a community if necessary.

Purchasing Equipment & Supplies

Your equipment and supply needs will be met through participation in the Science Department's projects. The YRITWC can typically provide equipment and basic maintenance, as well as provide most of the necessary supplies to complete project goals. This service is entirely funded through grant opportunities, which vary from year to year. If your project budget is designed to support (even partially) the equipment, supply and shipping needs you can be assured that your project will be sustainable throughout your participation (***see budget recommendation in Appendix F***). We are constantly seeking new funding to support the long-term projects and goals of the YRITWC and the Science Department, so please do not let shortfalls in your budget stop you from participating.

There are several manufacturers of water quality instruments currently on the market. Manufacturers include: Hydrolab, YSI Inc., Eureka, Oakton, Hanna, and Hatch. Each manufacturer produces several types of equipment, from single parameter probes to multi-parameter and sondes*. The level of sophistication of each probe depends on the type of parameters being measured and the needs of the user (see Appendix D for explanation of parameters). The type of probe selected for each project will depend on the time and frequency of data collection. This manual explains how to calibrate the meter you will be using this field season. Calibration directions begin on page 8 of this manual. Also, technical manuals can often be found online for each meter.

If you are considering buying equipment for your IGAP program please talk with the YRITWC Science Department staff and we will be glad to explore options on equipment that will fit the long term needs of your community (see Appendix E for equipment suppliers).

Choosing a Site

Site location is extremely important when collecting water samples. The flow of the river, the location relative to the community, potential contaminants, accessibility and the question(s) you are asking all need to be taken into consideration when choosing the site.

Leah Mackey, collects water sample by canoe on the Tanana River in

When participating in the baseline project, YRITWC staff will assist in choosing a site that best meets all criteria. The initial site will be located above the community in the main channel of the river. This sample will provide the most accurate information on the water flowing past your community.

Naming the Site

Each site is assigned a unique name based on the river, community and location relative to the community (see Appendix B for list of current sites). The naming convention was developed as a method to efficiently identify the river, the community, and the site through a single reference. The structure of the system is in four distinct parts. First, the river is identified using the first two letters of the river from which the sample was taken. Second, the community is identified by the three-letter airport code from where the sample will be shipped. Third, the site number is identified using chronological numbers starting at 1. The fourth component is the letter **"a"** or **"b"**, which identifies the site as being **above** the community**, "a",** or **below** the community, **"b",** from where the sample was taken**.**

An example of the naming convention would be: Yukon River (**yu**), Village of Eagle (**eaa**), site number (1), above Eagle (**a**). This site would be written on the field sheet as: **yueaa1a**.

Calibration

Introduction

Calibration is the act of comparing the readings of an instrument with those of a known/reference standard to check the instrument's accuracy. Adequate documentation of standards and procedures is essential for any use of environmental instrumentation to conduct physical measurements. Correctly following the calibration procedures and providing accurate documentation allows the measured data to be checked using quality assurance methods and is essential to assuring high quality data.

When to Calibrate: Calibration of the YSI 63 and 550 instruments will occur once just right before using the instrument in the field to collect the measurements/readings from the river or water source. Documenting the calibration is equally important as going through the calibration procedures. Documentation is completed on the field sheet that is provided with the sample kits sent to you. On the field sheet you will find a designated section for recording the calibration data (see Appendix C). Carefully follow the instructions described in the following pages! While calibration and documentation are essential for collecting high quality and accurate data, basic care is equally important to ensure instruments performs high-level work.

The equipment we use are top-of-the-line scientific instruments that will display high quality data points when calibrated correctly and cared for respectfully. Instruments should be stored inside a heated building and care should be taken to protect and preserve all working parts. Further details will be outlined for each instrument in the following sections.

Hazel Lolnitz, Koyukuk Tribal Council, calibrates a YSI 63 during a water quality training in Fairbanks.

The calibration of equipment is essential to collecting physical field measurements accurately!

Bad Calibration = Bad Data

Instruments

YSI Professional Plus (YSI Pro)

YSI Professional Plus handheld multi-parameter instrument will measure pH, Dissolved Oxygen (DO), conductance, and water temperature.

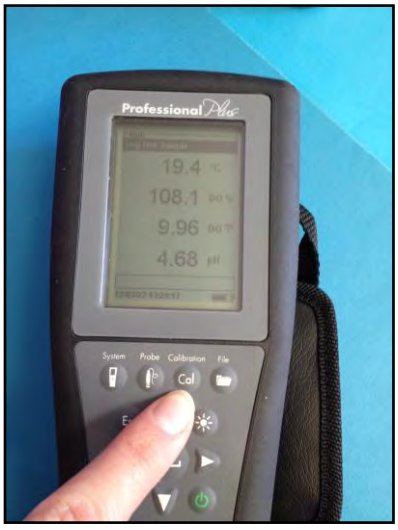
The YSI Pro meter will be stored with the calibration cup attached with a small amount of pH 4. Be sure to rinse and replace the calibration cup with a small amount of pH 4 when you finish sampling for the day. This protects the sensors from drying out.

Always use clean, properly stored calibration solutions (~25℃ or room temp.). Check expiry date before first use.

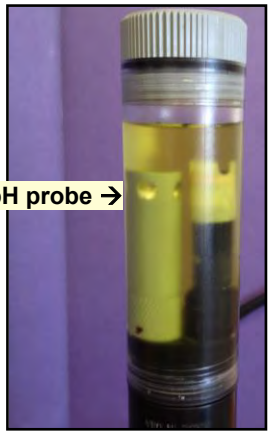
Calibrating pH

You will need: pH 7, pH 10, distilled water and the calibration cup.

1. Power on by pressing green button. 
2. Rinse calibration cup twice with distilled water.
3. Rinse calibration cup with small amount of pH 7.
4. Fill calibration cup with pH 7 to the “fill line” marked on the cup or just over half of the calibration cup.



5. Screw calibration cup onto probe and invert so gray cap is pointing up. (Be sure the pH probe is completely covered in solution.)



6. Press **CAL** and select **“ISE1 (pH)”** and press the Enter button.

7. Check the “Calibration value” on your screen with the Buffer Solution Temperature Chart (found in Appendix A ***OR*** on the side of the pH buffer solution bottle). If value needs adjusted proceed to step 8. If value is accurate skip to step 12.

8. Select **"Calibration value"** and press **Enter**. The screen will display a number pad.

9. Using the solution temperature (found on the screen under **"Actual Reading"**) find the corresponding pH 7 value in the chart. Using the arrow pad and enter button to put in the correct pH value. *Note: Select the decimal point as well. It can be difficult to see.

10. Once the value is correct, select **"Enter"** on the screen and press the **Enter** button on the keypad.

11. Allow value under **"Actual Reading"** to stabilize. Select **"Accept Calibration"** on the screen and press the **Enter** button.

12. Press **CAL** to finish. Once the display returns to the main screen record the pH and temperature values on the pH 7 section of the field sheet.

13. Discard pH 7 solution from calibration cup. Rinse cup twice with distilled water.

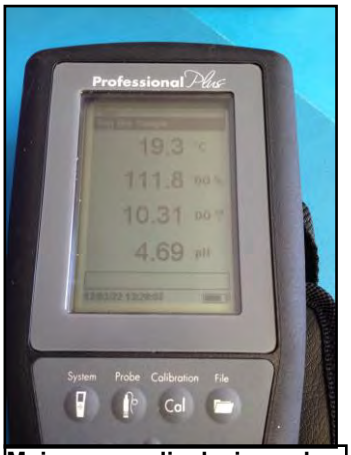
14. Rinse calibration cup with small amount of pH 10.

15. Fill calibration cup with pH 10 to the fill line or just over half of the calibration cup.

16. Follow steps 5 - 12 outlined above using the pH 10 temperature chart and values found in Appendix A.

17. Press **CAL** to finish. Once display returns to main screen

    record the pH and temperature values on the pH 10 section of the field sheet (see example below, in the Conductivity calibration section).



Main screen displaying values to record from calibration.

18. Discard solution and rinse calibration cup with distilled water.

Calibrating Conductivity

You will need: Conductance Standard 1413 µS/cm, the calibration cup and distilled water.

1. Rinse calibration cup twice with distilled water.

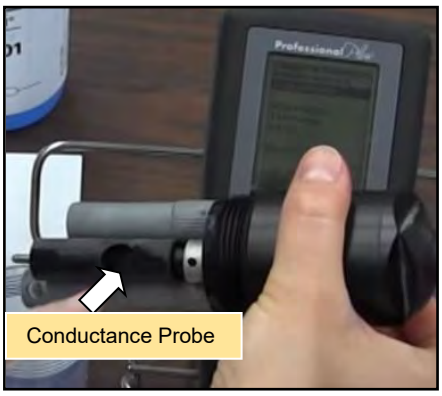
2. Rinse calibration cup with small amount of 1413 µS/cm Conductance solution.

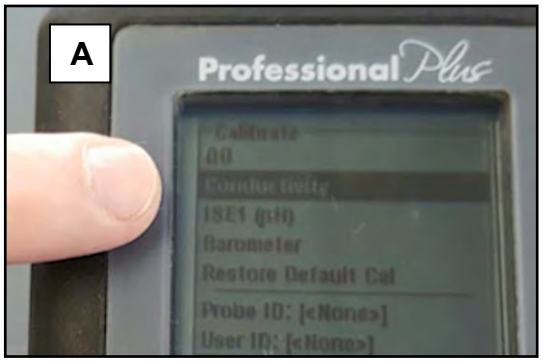
3. Fill calibration cup with 1413 µS/cm Conductance solution to the “fill line” marked on the cup or just over half of the calibration cup.

4. Screw calibration cup onto probe and invert so gray cap is pointing up. (Be sure the pH probe is completely covered in solution.)

5. After placing the probe into the 1413 µS

   Conductance solution, gently move the probe up and down to remove any air bubbles that may be trapped in the conductivity probe.





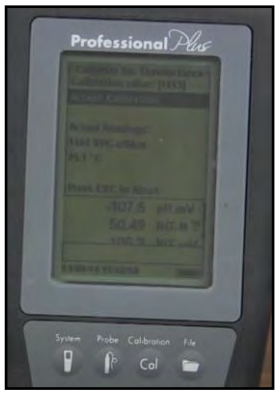
6. Press **CAL** and select “**Conductance**” picture A and select “**Conductance Unit – C µS/cm**” picture B. Press the **Enter** button after your selection.

7. Enter the “**Calibration value**” of the 1413 µS/cm Conductance solution as it is listed on the Temperature Chart (found in Appendix A OR on the back of the 1413 µS/cm Conductance solution bottle). If value needs adjusted proceed to step 8. If value is accurate skip to step 12.

8. Select “**Calibration value**” and press Enter. The screen will display a number pad.

9. If you receive a warning message stating that the calibration is questionable, do not continue with the calibration. Instead, select “**No**” and investigate what is causing the questionable results. If you accept a questionable calibration, your conductivity readings (and your DO mg/L readings) will be erroneous. Typical causes for this error message include: incorrect entries (entering 1413 µS/cm instead of 1.413 mS/cm), not using enough solution to cover the vent holes, air bubbles trapped in the sensor, calibrating in specific conductance instead of conductivity, dirty conductivity electrodes, and/or bad calibration solution.

10. Once the value is correct, select “**Enter**” on the screen and press the Enter button on the key pad.



11. Allow value under "**Actual Reading**" to stabilize. Select "**Accept Calibration**" on the screen and press the "**Enter**" button.

12. Once the calibration is finished and the display returns to main screen record the Conductance and Temperature values on the field sheet (see example below, in the Conductivity calibration section).

13. Discard solution and rinse calibration cup with distilled water.

Example of field sheet with calibration section completed

Calibration Data

pH Calibration *(YSI 63, YSI Pro, YSI 650, and Hanna)* *pH 7 and 10 need to be within 0.1 of buffer values, if not RECALIBRATE!*

pH 7 Buffer Reading: 7.01 pH 10 Buffer Reading: 10.00

pH 7 Buffer Temperature (°C): 24.7°C pH 10 Buffer Temperature (°C): 25.0°C

Dissolved Oxygen (DO) Calibration *(YSI Pro, YSI 650, 550A)*

Barometric Pressure (inHg *or* kPa): _____ DO Reading (%) Saturation: _____

In US, visit ***www.weather.gov*** *for air pressure in inHg* *DO % needs to be between 95 - 105%, if not RECALIBRATE!*

In Canada, visit ***www.weather.gc.ca*** *for air pressure in kPa* DO Reading (mg/L): _____

Conductivity Calibration *(YSI 63, YSI 650, Hanna)*

Conductivity Standard Used (µS/cm): 1413 us/cm Conductivity Solution Temperature (°C): 25.0°C

Conductivity Reading (µS/cm): 1414 us/cm

Calibrating the Barometer

The barometer of the YSI Pro will need to be calibrated to your location/elevation before the first sample. This is typically done only one time at the beginning of the season.

You will need: The barometric pressure in your location. This can be found online through a local weather report or by visiting ***www.weather.gov*** and type in your zip code for your community's air pressure in inches of mercury (inHg).

1. With power on, press **CAL**.

2. Select **"DO"** and press **Enter**. Then Select **"DO%"** and press **Enter**.

3. Highlight **"Barometer"** on the screen and press **Enter**. Manually enter the barometric pressure you obtained online for your location. This will mostly likely be shown as a value of **"inHg"** (inches of Mercury). Select **"Enter"** and press **Enter**.

4. Continue with Steps 4 - 8 listed below in the Calibrating DO% to complete calibration.

Calibrating Dissolved Oxygen (DO %)

You will need: small amount of distilled water and calibration cup.

1. With power on, press **CAL**.

2. Select **"DO"** and press **Enter**.

3. Select **"DO%"** and press **Enter**.

4. Fill clean calibration cup with a small amount of water (about a 1/2 inch).

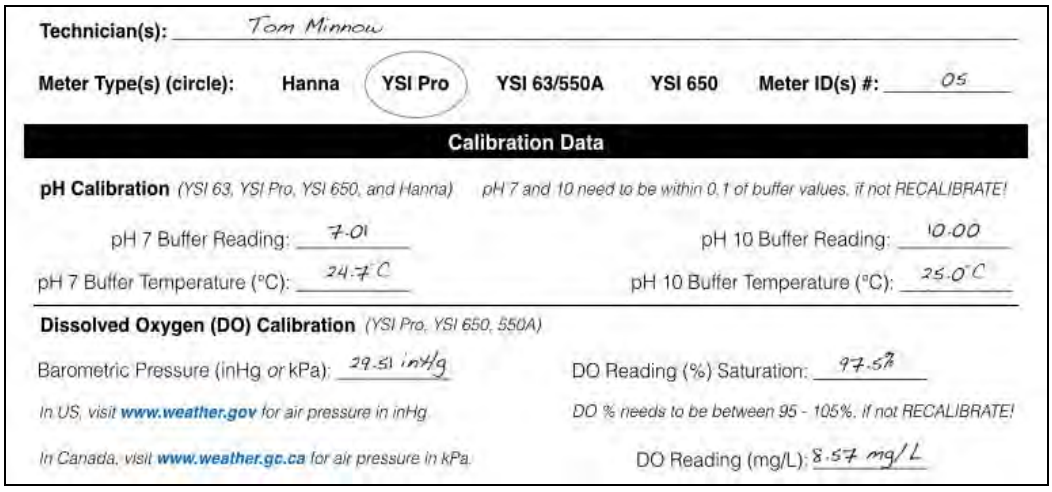
5. Screw calibration cup onto probe and shake for a few seconds. Unscrew the cap a few times, so that it is threaded loosely, but still connected.

6. When **"Actual Reading"** values are stable on the screen press **Enter**.

7. Screen says **"Calibrating channel"** at the bottom and returns to main screen display when complete.

8. Record the Barometer value inHg, **DO %** value and the **DO mg/L** value in the DO calibration section of the field sheet (see example below).

Example of field sheet with calibration section completed



Technician(s): Tom Minnow

Meter Type(s) (circle): Hanna (YSI Pro) YSI 63/550A YSI 650 **Meter ID(s) #:** 05

Calibration Data

pH Calibration *(YSI 63, YSI Pro, YSI 650, and Hanna)* *pH 7 and 10 need to be within 0.1 of buffer values, if not RECALIBRATE!*

pH 7 Buffer Reading: 7.01 pH 10 Buffer Reading: 10.00

pH 7 Buffer Temperature (°C): 24.7°C pH 10 Buffer Temperature (°C): 25.0°C

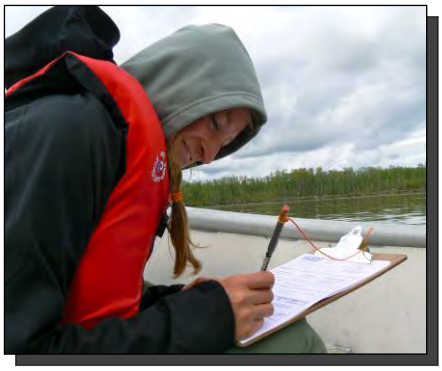
Dissolved Oxygen (DO) Calibration *(YSI Pro, YSI 650, 550A)*

Barometric Pressure (inHg *or* kPa): 29.51 inHg DO Reading (%) Saturation: 97.5%

In US, visit **www.weather.gov** *for air pressure in inHg* *DO % needs to be between 95 - 105%, if not RECALIBRATE!*

In Canada, visit **www.weather.gc.ca** *for air pressure in kPa* DO Reading (mg/L): 8.57 mg/L

Field Sample



Elli Matkin records sampling information on the field sheet.

Introduction

After successfully calibrating your instrument you are ready to go collect your water sample! There are several steps to take to ensure you are collecting the best sample possible.

Field Sheet (Appendix C)

Field Sheet Documentation:

Filling out the field sheet completely is very important. The field sheet serves as a quality assurance method by documenting the calibration and is also a hard copy documentation of the data collection. Keeping consistent and reliable records are important in long-term data collection. If you make any mistakes, remember not to erase, just draw a line through the mistake and write the correction as close as possible.

Date and Time:

To work toward the standardization of protocols across the watershed, the YRITWC Science Department uses the International Standards Organization (ISO) standard for date and time records. This standard is accepted as the format for international trade. In our application, Indigenous peoples of the Yukon Basin are engaging in the trade of information to sustain their traditional way of life.

The international standard for recording the date, as set by the ISO, ranks the priority of information from the most important to least important; the year being the most important, the month being second in priority, and the day being of the lowest priority. The format for the date would be: ***yyyy-mm-dd***. This format should be used when recording the date on the field sheet and sample bottles.

The use of 24-hour time is standard practice in scientific data collection. Using 24-hour time reduces the potential for transmission error when recording field data into a database and allows for accurate record keeping when samples are taken at multiple times in a single day. ***On the field sheet record the time you collected the water sample from your site***. Use this same time for documentation throughout the duration of your samples (i.e. labeling bottles).

Site Naming Convention:

The naming convention was developed as a method to efficiently identify the river, the community, and the site with a single reference. This method is described earlier in the manual under the "***Next Steps***" section (for list of all existing sites see Appendix B).

An example of the naming convention would be: Yukon River (**yu**), Eagle (**eaa**), site number (1), above Eagle (**a**). This site would be written on the field sheet as: **yueaa1a**.

General Information: Technicians, Waterbody Name, Meter and Elevation:

Fill out these sections of the field sheet completely. It is important to know who is taking the sample. The technicians are *you* and any volunteers, assistants, youth or boat drivers. The water body name refers to the name of the river, lake or slough that the sample is being taken from. In the example below, the sample is from the Tanana River. The meter type is important for us to know for many reasons, largely because the YRITWC has multiple kinds of meters that samplers use and different ones are capable of measuring different parameters. After you circle which type of meter you are using, locate the number written on the side of the meter with a permanent marker. This is the meter number. Every YRITWC meter has a different number; this helps us keep track of which specific meter is in what location in the watershed.

Site Coordinates: Latitude, Longitude, and Elevation:

Before you put your meter in the water, write down the coordinates and elevation of your site at each visit. The latitude, longitude and elevation for each site are listed in Appendix B. If you have a GPS (sorry, the YRITWC does not provide one) we recommend that you check the accuracy of the coordinates listed in the appendix, this way we can be sure that you are sampling in exactly the same place week after week, year after year. Fill out the Latitude/Longitude section on your field sheet - especially if you are sampling a new location, adding a site or need to alter your location for any reason. If you sample from the riverbank once or twice (due to weather, boat problems, etc.) it is also helpful for us to know the GPS coordinates of that shore location since it is different from your usual sample site.

Calibration:

The calibration section of the field sheet is explained in more detail for each meter in the Calibration section of the manual (starting on page 8). Your field sheet will look like one below:

Field Measurements:

The field measurements are the reward for all your work calibrating and collecting the samples. These measurements provide real-time information to supplement the water sample you collect.

Field Data

pH: 8.24	Air Temperature (°C): 15.3°C	Latitude: N 64.7828
Dissolved Oxygen (%): n/a	Water Temperature (°C): 11.4°C	Longitude: W 141.1767
Dissolved Oxygen (mg/L): n/a	Ice Thickness (cm): n/a	Elevation (m): 268 m
Conductivity (µS/cm): 172 uS/cm		

Comments & Observations:

The reverse side of the field sheet provides an opportunity for you to write any additional comments or observations that you have during your sample trip. There are some guided questions that you may find useful. Documenting observations alongside instrument data helps in explaining or understanding the numbers produced from the meters and laboratory analysis. Your first-hand experience, knowledge and observations are a very important part of the documentation process. To the right is an example of answers for questions on the field sheet.

RIVER AND WEATHER

Weather conditions now (circle): overcast / clear / partly cloudy / cloudy • heavy / steady / intermittent rain • calm / breezy / windy

Weather in past 24 hours (circle): overcast / clear / partly cloudy / cloudy • heavy / steady / intermittent rain • calm / breezy / windy

Sample location (circle): mid-channel / bank / other • riffle / pool / eddy

Flow description (circle): < 19 L (5 gal) per second / > 19 L (5 gal) per second / under ice

Water clarity (circle): clear / cloudy (greater than 4" visibility) / murky (less than 4" visibility)

Site odor (circle): none / fresh algae / chlorine / rotten eggs / sewage / other

Other (circle): litter / foams or suds / oily sheen / algae and/or aquatic plants

Anything different happening with the river since the last sample (flooding, erosion, flow change)?

First sample of the season. Ice still flooding down the river.

How does the river height compare to two weeks ago?

First sample of the year but it looks to be slightly higher by a few inches.

How does the river height compare to this time last year?

Similar in height.

Anything noteworthy happening with the weather?

Warm spring.

WILDLIFE

Any specific concerns the YRITWC should know about wildlife?

Bears disturbed by warm winter.

Any noteworthy wildlife or fish species traveling through your community or nearby?

Moose spotted in town.

CONTAMINANTS

Has anything occurred since the last sampling that might have affected the water quality at your site?

Fuel spill occurred upstream from site.

Is there any other site that your community wants monitored? Please explain why you're concerned.

South of Fairbanks.

OTHER

Anything else interesting? Please write your comments or observations.

Very excited to sample again!

Are there any issues with this sample that we should know about?

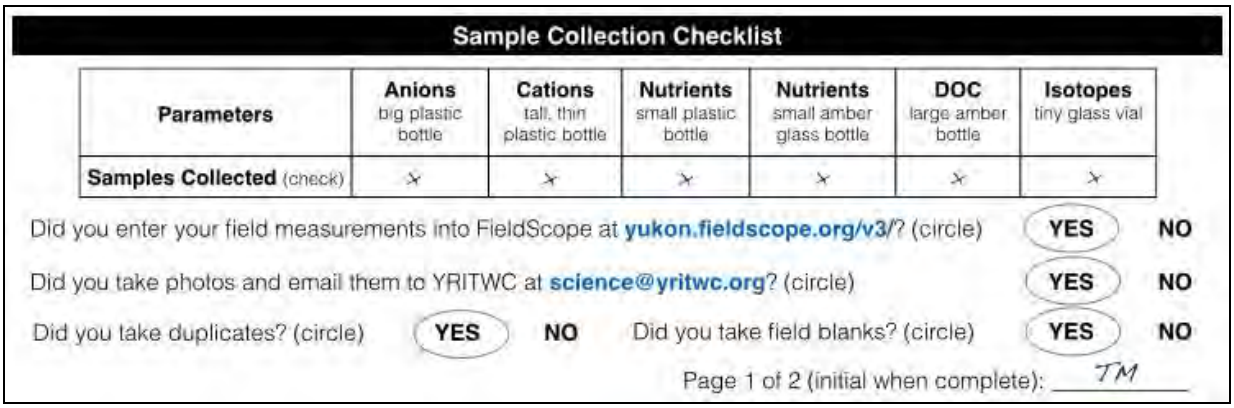
Had to recalibrate a couple of times but meter seems to be functioning okay.

Page 2 of 2 (initial when complete): TM

Bottle Check List:

The final section of the field sheet provides a space to double check that all the sample bottles were filtered and filled correctly. The checklist provides a description of each sample bottle and the parameter to be analyzed in the laboratory. Check off each bottle

as you complete the filtering process. If you encounter any issues during your sampling, please make a note on the field sheet.



Sample Collection Checklist

Parameters	Anions big plastic bottle	Cations tall, thin plastic bottle	Nutrients small plastic bottle	Nutrients small amber glass bottle	DOC large amber bottle	Isotopes tiny glass vial
Samples Collected (check)	✓	✓	✓	✓	✓	✓

Did you enter your field measurements into FieldScope at **yukon.fieldscope.org/v3/**? (circle) **YES** **NO**

Did you take photos and email them to YRITWC at **science@yritwc.org**? (circle) **YES** **NO**

Did you take duplicates? (circle) **YES** **NO** Did you take field blanks? (circle) **YES** **NO**

Page 1 of 2 (initial when complete): TM

FieldScope:

The YRITWC would like to introduce BSCS Science Learning FieldScope, an interactive online map and database. This new database stores your water quality field data and observations. This exciting tool allows you to add your site's pH, dissolved oxygen, conductivity, temperatures, photos, videos, field observations, and local knowledge. We hope FieldScope will be a very useful tool for samplers to share water quality data with all ION participants across the Yukon River watershed. You can choose to make your community's information private or open to all public viewers. Tell us what you think of FieldScope. We would love your feedback! Visit the Yukon River watershed at yukon.fieldscope.org/v3/.

Pictures:

Please take pictures while you are out in the field to record any changes occurring at the site and email them to Science staff at emutter@yritwc.org or kyoung@yritwc.org. We also love to see pictures from you in action! We really would appreciate it, if you are open to letting us use your pictures for reporting and publication purposes. Please clarify that in your email and we will send you a consent form. We hope to continue assisting the Indigenous Observation Network for years to come, and for funders, pictures are powerful evidence of the program's success! Feel free to add your photos to FieldScope as well.

Field Blanks and Duplicates:

Once or twice a season you will have to fill field Blanks and duplicates. This will usually happen at the very beginning of the open water sampling season and the very end. See section "***Open Water***", below, for specific instructions on how to complete this task.

Field Measurements

Open Water:

Gear Check List

- ✓ Meter
- ✓ Sample kit (cooler, bottles & frozen ice pack)
- ✓ Thermometer
- ✓ Field sheet
- ✓ Nitrile Gloves
- ✓ Clip board with pencil
- ✓ Holding bottles
- ✓ Syringe
- ✓ 3-way valve & rubber tubing (optional)
- ✓ Sampling Rod (optional – for safety and convenience)
- ✓ Filters
- ✓ Life jacket
- ✓ GPS (highly recommended if you have one!)
- ✓ Camera

From the Boat:

The ideal location to collect a water sample is from the main flow, typically in the middle of the river. If you have access to a boat to collect your water sample, your site will be located in the main channel and flow of the river. Position the boat as close to the center of the river as possible pointing the bow upstream and holding the same position. If the river velocity is high, you may have to let the boat drift with the current. Make all field measurements upstream from the boat and away from the motor, if the boat is equipped with one.

Once you have your boat or body positioned correctly and have recorded your latitude, longitude and elevation on your field sheet, you are ready to collect meter measurements.

From the Riverbank:

If you are unable to sample from the main flow of the river, a sample is better than no sample, so collecting from the riverbank is acceptable (make sure to note the location on your field sheet). Pick a location where river flow is not affected by eddies (straight river reach) or contaminated by upstream

point source pollution (sewage effluent, docks, boat landings, bridges, etc.). Wearing a life jacket, wade out into current as far, but as safely as possible. Always make field measurements with probes positioned upstream of you! This avoids influencing the water samples and field readings.

YSI Pro Meter Measurements:

1. Remove instrument from the pelican case.
2. Remove calibration cup from the end of the probe and carefully replace with the sampling cover.
3. Place probe in the water on the upstream side of the boat or your body (if sampling from shore); hold onto the handheld portion of the meter.
4. Power **On** the meter. This should take you to the main screen display and you will see values under each parameter.
5. Allow values to stabilize for at least 60 seconds.
6. Record the values from the screen in the **"Field Sample"** section of the field sheet (see page13 for example).

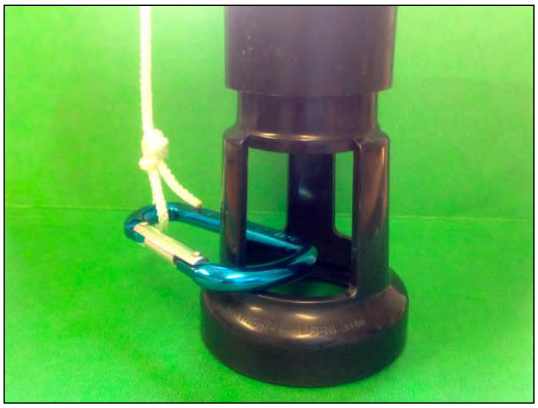
Water Sample Collection:

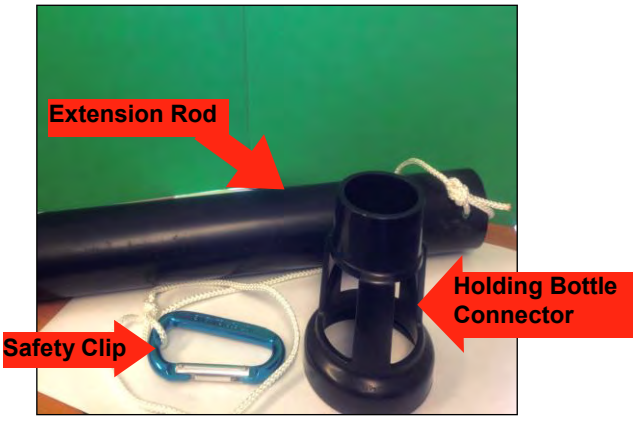
Wear Latex or Nitrile disposable gloves during water sample collection. Avoid touching the boat or anything besides sampling equipment. If the gloves become compromised, dispose and put on a new pair. The sample should be taken in the same location and similar manner as the meter values (see meter measurement descriptions from the boat and shore). Always collect the sample upstream from you and/or the boat engine.

Sample Rod Assembly:

If a sample rod is provided with your equipment, use this to collect a sample. By attaching the holding bottle to this extension you will be able to more easily collect the sample below the surface level. This method also allows for safer sample collection by reducing the amount of reach required over the side of the boat. The set-up with the 4-foot extension is also very useful for under-ice sampling.

To assemble the sample rod, slide the extension rod onto the holding bottle connector. Press firmly to secure the attachment. Attach the safety clip to the holding bottle connector (see picture below). ***The holding bottle will screw directly to the holding bottle connector.***





Collecting Water Sample from a Boat or Riverbank:

The sample will be collected using the holding bottle attached to a 4-ft plastic rod. It is important that the bottle fills with water from below the ice level.

1) Connect bottle to the sample rod (see picture and description on 27). Not applicable for glass jar.

2) Rinse the holding bottle/jar with river water and discard water three (3) times.

3) To fill the bottle/jar, submerge below the surface of the water (approximately 12 inches if possible) and allow the bottle to completely fill with water (large bubbles will stop rising to the surface when it is full).

4) Disconnect the holding bottle from the sample rod (if applicable).

5) Replace lid and get ready to transfer water into sample bottles (See **"Filling Sample Bottles"** section on page 31).

The water sample is now ready to be filtered into the sample bottles. If the weather is below freezing, this will be easier to complete inside. Take the sample back to a warm place and immediately filter and fill the sample bottles. Keep the sample refrigerated or chilled at all times.

**** This is a good time to rinse your syringe too! It must be rinsed three (3) times with river water before using it to fill your sample bottles. For detailed description on how to rinse your syringe see page 31.***

Under Ice:

Collecting samples in the winter only adds a few more steps (and several more layers of clothing!), but generally follows the same procedures as open water sampling. Safety is a top priority any time during sampling, but be especially careful when traveling on the ice. Be aware of ice conditions and safe routes to the sample location. If in doubt, don't go out!

Gear Check List

- ✓ Meter
- ✓ Sample kit (cooler, bottles & frozen ice pack)
- ✓ Thermometer
- ✓ Field sheet
- ✓ Nitrile Gloves
- ✓ Clip board with pencil
- ✓ Holding bottle
- ✓ Long Rod
- ✓ Syringe
- ✓ 3-way valve & rubber tubing (optional)
- ✓ Sampling Rod (optional – for safety and convenience)
- ✓ Filters
- ✓ GPS (highly recommended if you have one!)
- ✓ Camera
- ✓ Ice Auger with spare blades
- ✓ Auger fuel (Most augers take mixed fuel. Read instructions carefully)
- ✓ Warm Clothing

Drilling the Ice Hole:

1) Using an ice auger, drill a hole in the ice until you reach water.

2) Use the auger to **"clean the hole"** by dipping it into the water and pulling out several times. This pulls water up and out onto the ice and helps remove some of the ice chunks from the open hole.

Brendan Mulligan drills an ice hole on the Tanana River.

Meter Measurements:

The under ice measurement will be taken in the same location as the open water sample. Use a GPS or landmarks to find the sample location in the winter. You still want to be in the general location of the main flow of the river, even though it is under ice. Take care not to let the sensors on the instruments freeze, keep it warm! Ice build-up will cause inaccurate readings and has the potential to break the sensors.

Ice Thickness Measurements:

The thickness of the ice is important data to collect in the winter and it allows us to see if there are variations year after year. We are still perfecting the best method to measure how thick the ice is so you may be equipped with any number of measuring tools. However, the following instructions apply to all measuring rods.

1. You should have a long rod (up to 7 meters in length) with centimeters marked out. On one end of the rod there is a nail protruding outward. Lower this end down into your ice hole.

2. Hook the protruding nail under the bottom of the ice. Make sure it doesn't move.

3. Look at where the top of the ice (the surface on which you are standing) meets the rod. Using this as a reference, mark on your field sheet how many centimeters thick the ice is.

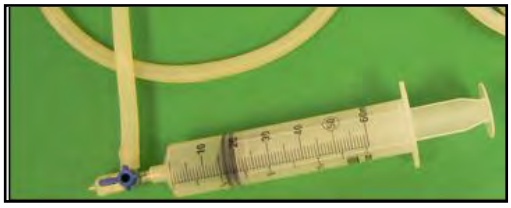
Filling Sample Bottles

Now that you have collected the water sample in the holding bottle, you are ready to transfer the water into the individual sample bottles. This can be done immediately on-site or as soon as possible in another location that may be more convenient (i.e. office, vehicle, riverbank, etc.).

The following method for filling the sample bottles will be the same for under-ice and open water sampling. ***Always wear Latex or Nitrile disposable gloves when handling and filling sample bottles***.

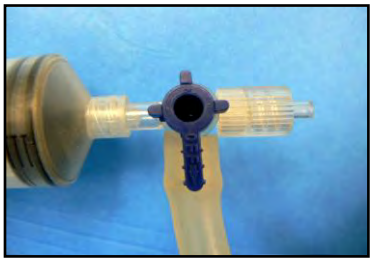
Rinsing the Syringe:

The syringe and connecting tube should be rinsed at the beginning of each new sample location. Do not stick the syringe directly into the holding bottle. If this is your only option (i.e., no tubing or valve), make sure the syringe is rinsed (inside and out) before proceeding.

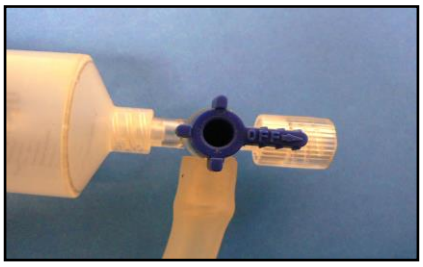


1) Connect the syringe to the 3-way valve & hose.

2) To rinse, place the end of the rubber tube into the river or holding bottle. Turn the 3-way valve position so that “off” is in-line with the dispensing tip.



When the “off” position is pointing towards the tube, water can be expelled through the dispensing tip.

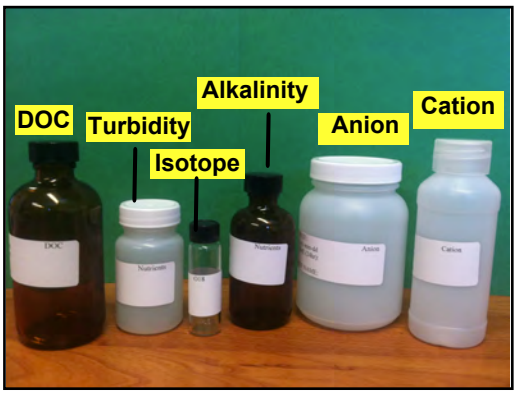


With the 3-way valve in this position, the syringe will draw water through the tube and into the syringe.

3) Draw a small amount of water (about 25 mL) into the syringe. Turn the valve position so that “off” is pointing towards the tube.

4) Continue to draw the syringe end all the way out. At this point only air should be entering the syringe. Shake to rinse the syringe, and then squirt all of the water out the dispensing tip. Repeat 2 more times.

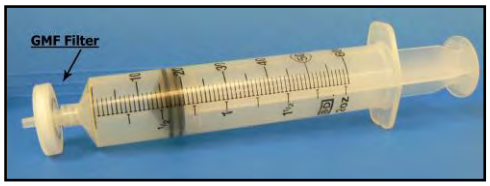
Filtered Bottles:



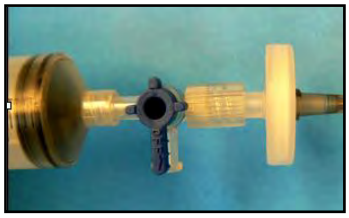
~ Alkalinity, DOC, Isotope, Anion and Cation

Most of the sample bottles will be filled with filtered water. The water is filtered using a GMF (glass microfiber) filter that is connected to the end of the syringe. The filter can either be connected directly to the syringe or to the 3-way valve connected to the syringe.

1) Fill the syringe completely from the holding bottle of sample water using the 3-way valve connection (if applicable).



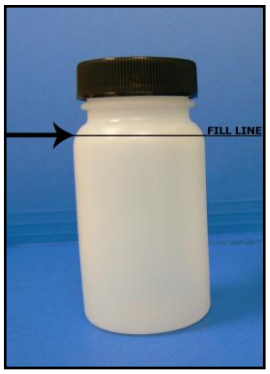
OR



2) Place the GMF filter onto the syringe.

3) Remove cap from bottle and place face-up in a safe place.

4) One at a time, fill each bottle with filtered water up to the shoulder (Anion, Cation, Alkalinity, DOC). Securely replace the cap on the bottle. Fill the Isoptope bottle completely to the top, secure the cap, and ensure there are no air bubbles.



The "shoulder" of the bottle is where it starts to curve at the top.

5) Re-fill the syringe as needed throughout the filtering process. Each filter can be used until it is too difficult to filter water through.

Always use new filters at a new site location.

6) Record any observations or procedural mishaps in the comment section of the field sheet.

Unfiltered Bottle:

~Turbidity

The turbidity sample bottle is the only bottle that should be filled with unfiltered water. Shake the water in the holding bottle and pour water into the sample bottle before any sediment has settled. Fill to the shoulder of the sample bottle and secure the cap.

Stable Water Isotopes ~ O18:

The isotopes glass vial is filtered, but is filled completely to the top until a meniscus forms (round curve of water). There should be no air bubbles in the vial.

1) Using the 3-way valve (if applicable), fill the syringe with sample water from the holding bottle.

2) Place a GMF filter on the syringe.

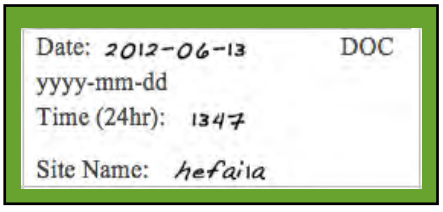
3) Remove cap from the vial and place face-up in a safe place.

4) Fill with filtered water completely to the top. Replace the cap carefully and securely. (There should be no air bubbles in this sample once the cap is in place; you can check by turning the bottle upside-down. No air bubbles should appear.)

5) Record any observations or procedural mishaps in the comments section of the field sheet.

Labeling Sample Bottles:

Labeling each bottle in the sample is very important. The bottles have white labels that need to be filled out with the Date, Time and Site Name. This label will be identical to the information on the top right hand corner of the field sheet. When the bottles are sent to the USGS lab they are split up and sent with hundreds of other bottles to different labs to be analyzed. The label is an important part of the tracking and identification of your sample, so writing clear and consistent information on each bottle is extremely helpful.



Jay Hootch & Earl Alstrom, Yupiit of Andreafski, assist with lab work at USGS Boulder, CO.

Quality Control

When we collect water samples, we always work to reduce any sources of error that might affect our measurements. There are two types of error that we work to reduce: **bias** and **variability**.

Bias is systematic, directional error. We can work to reduce bias by calibrating our field meters with reference materials (such as pH buffers and conductivity standard solutions) and by collecting blank samples.

Variability is random error. We can work to reduce variability by standardizing our methods and by collecting replicate samples.

The goal of quality control (**QC**) sampling is to identify, quantify, and document bias and variability in data that result from the collection, processing, shipping, and handling of samples. The bias and variability associated with environmental data must be known for the data to be interpreted properly and to be scientifically defensible!

Blank Samples

The primary purpose of a blank sample **("blank")** is to measure the concentration of anything that might have been introduced into the sample as a result of sampling-related activities: collection, processing, shipping, and handling. Blank water is specially prepared in a quality-controlled laboratory and always carries a special certificate. It is not the same as the distilled/deionized water we use to rinse our sampling equipment. It is really important to wear gloves and to use caution when working with blanks: blank water is expensive!

Blank Samples should be collected the first and last time we visit our sampling sites every season.

How to collect a Blank Samples?

1) Ensure that you're wearing gloves!

2) Rinse your sampling equipment (holding bottle, syringe, three-way valve, and tubing) three times with DI water.

3) Rinse your sampling equipment (holding bottle, syringe, three-way valve, and tubing) once with blank water.

4) Fill the holding bottle with blank water.

5) Follow the normal procedure for filtering water outlined on Page 32. Before filling your sample bottles, be sure to push some blank water through the filter.

Duplicate Samples:

The primary purpose of duplicate/replicate samples is to identify and/or quantify the variability associated with sample collection and processing. Duplicate samples are collected simultaneously or close in time with the associated water sample, using identical procedures.

Duplicate Samples should be collected from each sampling site once every season. Duplicate Samples should be collected twice from a site only if more than 10 samples are collected at the site in a single season.

How to collect Duplicate Samples?

1) Use identical sampling procedures and supplies to collect two samples, one immediately after the other, using the normal sampling procedure. Remember to rinse your sampling equipment (holding bottle, syringe, three-way valve, and tubing) before collecting the second sample, just as you did before you collected the first sample.

2) Label the samples using the site name you always use, but add **"DUP 1"** to the first sample collected and **"DUP 2"** to the second sample collected. It's that easy!

Shipping Samples

Pack samples **CAREFULLY**! Use foam sleeves for glass vials and place all bottles in the large Ziploc bag. Field sheets should be folded in quarters with the date, time, and site name facing out. Place the folded field sheet in the small Ziploc bag and place the small Ziploc bag inside the large Ziploc bag so the date, time, and site name is visible through the bags. Place a frozen ice pack in the bottom of the cooler with the sample! Turn the shipping label over so it reads **"TO: YRITWC Science Program"**. Tape the cooler shut and drop the sample off for the flight out. Give the YRITWC Science staff a call or email to let them know the sample is on the way and what flight it was sent on.

**** If you are unable to ship the sample the same day you collect it, please keep the sample refrigerated!***

***** Plan your field day so that you are sampling at the beginning of the week and shipping out your sample(s) by the middle of the week or early in the week for Yukon communities***.

1. Double check field sheet & bottle labels. Place glass bottles in protective sleeves & field sheet in Ziploc bag.

2. Pack gallon size bag with sample bottles and field sheet. Gather cooler and frozen ice pack.

3. Place a frozen ice pack in the bottom of the cooler. Place sample kit in the cooler with the field sheet facing out.

4. Secure shipping label to cooler and send via freight collect to YRITWC staff. Notify staff of shipment.

Appendices

Appendix A: Solution Temperature Chart

Conductance

Temp °C	Temp °F	µS
5	41	896
10	50	1020
15	59	1147
16	60.8	1173
17	62.6	1199
18	64.4	1225
19	66.2	1251
20	68	1276
21	69.8	1305
22	71.6	1332
23	73.4	1359
24	75.2	1386
25	77	1413
26	78.8	1440
27	80.6	1467
28	82.4	1494
29	84.2	1521
30	86	1548
31	87.8	1575

pH 10

Temp °C	Temp °F	pH
0	32	10.33
5	41	10.25
10	50	10.18
15	59	10.11
20	68	10.05
25	77	10.00
30	86	9.95
35	95	9.92
40	104	9.88
45	113	9.85
50	122	9.82
55	131	9.9
60	140	9.77
70	158	9.73
80	176	9.69
90	194	9.66

pH 7

Temp °C	Temp °F	pH
0	32	7.12
5	41	7.09
10	50	7.06
15	59	7.04
20	68	7.02
25	77	7.00
30	86	6.99
35	95	6.98
40	104	6.98
45	113	6.97
50	122	6.97
55	131	6.98
60	140	6.98
70	158	6.99
80	176	7.00
90	194	7.02

Appendices B: Field Data Sheet

Yukon River Inter-Tribal Watershed Council
Fairbanks: 907-451-2530 • Whitehorse: 867-393-2199

Date (yyyy-mm-dd): _____ - _____ - _____

Sample Time (24 hrs): _____

Site Name ID: _____

Waterbody Name: _____

Technician(s): _____

Meter Type(s) (circle): **Hanna** **YSI Pro** **YSI 63/550A** **YSI 650** **Meter ID(s) #:** _____

Calibration Data

pH Calibration *(YSI 63, YSI Pro, YSI 650, and Hanna)* *pH 7 and 10 need to be within 0.1 of buffer values, if not RECALIBRATE!*

pH 7 Buffer Reading: _____ pH 10 Buffer Reading: _____

pH 7 Buffer Temperature (°C): _____ pH 10 Buffer Temperature (°C): _____

Dissolved Oxygen (DO) Calibration *(YSI Pro, YSI 650, 550A)*

Barometric Pressure (inHg *or* kPa): _____ DO Reading (%) Saturation: _____

In US, visit ***www.weather.gov*** *for air pressure in inHg.* *DO % needs to be between 95 - 105%, if not RECALIBRATE!*

In Canada, visit ***www.weather.gc.ca*** *for air pressure in kPa.* DO Reading (mg/L): _____

Conductivity Calibration *(YSI 63, YSI 650, Hanna)*

Conductivity Standard Used (µS/cm): _____ Conductivity Solution Temperature (°C): _____

Conductivity Reading (µS/cm): _____

Field Data

pH: _____ Air Temperature (°C): _____ Latitude: _____

Dissolved Oxygen (%): _____ Water Temperature (°C): _____ Longitude: _____

Dissolved Oxygen (mg/L): _____ Ice Thickness (cm): _____ Elevation (m): _____

Conductivity (µS/cm): _____

Sample Collection Checklist

Parameters	Anions big plastic bottle	Cations tall, thin plastic bottle	Nutrients small plastic bottle	Nutrients small amber glass bottle	DOC large amber bottle	Isotopes tiny glass vial
Samples Collected (check)						

Did you enter your field measurements into FieldScope at **yukon.fieldscope.org/v3/**? (circle) **YES** **NO**

Did you take photos and email them to YRITWC at **science@yritwc.org**? (circle) **YES** **NO**

Did you take duplicates? (circle) **YES** **NO** Did you take field blanks? (circle) **YES** **NO**

Page 1 of 2 (initial when complete): _____

RIVER AND WEATHER

Weather conditions now (circle): overcast / clear / partly cloudy / cloudy • heavy / steady / intermittent rain • calm / breezy / windy
Weather in past 24 hours (circle): overcast / clear / partly cloudy / cloudy • heavy / steady / intermittent rain • calm / breezy / windy
Sample location (circle): mid-channel / bank / other • riffle / pool / eddy
Flow description (circle): < 19 L (5 gal) per second / > 19 L (5 gal) per second / under ice
Water clarity (circle): clear / cloudy (greater than 4" visibility) / murky (less than 4" visibility)
Site odor (circle): none / fresh algae / chlorine / rotten eggs / sewage / other:
Other (circle): litter / foams or suds / oily sheen / algae and/or aquatic plants

Anything different happening with the river since the last sample (flooding, erosion, flow change)?

How does the river height compare to two weeks ago?

How does the river height compare to this time last year?

Anything noteworthy happening with the weather?

WILDLIFE

Any specific concerns the YRITWC should know about wildlife?

Any noteworthy wildlife or fish species traveling through your community or nearby?

CONTAMINANTS

Has anything occurred since the last sampling that might have affected the water quality at your site?

Is there any *other* site that your community wants monitored? Please explain why you're concerned…

OTHER

Anything else interesting? Please write your comments or observations…

Are there any issues with this sample that we should know about?

Appendices C: Chain of Custody (COC) Form

Yukon River Inter Tribal Watershed Council / ION
201 E 3rd Avenue, Suite 100
Anchorage, Alaska 99501
(907) 258-3337 phone (907) 258-3339 Fax

Project Contact:	*Phone:*	*Page_____ of _____*
e-mail address:	*Fax:*	
Project ID:	*Comments:*	
Location:		
Sampled By:		

Sample ID	Sample Date/Time	Matrix	No. of Containers	Size of Container	Analysis Requested	Comments

Relinquished by:	*Date/Time*	*Received by:*	*To be completed by laboratory:*
Relinquished by:	*Date/Time*	*Received by:*	*Condition Sample received:*
Relinquished by:	*Date/Time*	*Received by:*	_____ *COC Seal Intact:____Yes_____No* *Temperature on Arrival_____ ℃* *Comments:*

Appendices D: Correction & Action List

EQUIPMENT AND SUPPLY INSPECTION FORM

Date:———————————— Initials:————————————

Parameter	Component	In Kit	Condition	Batch/ Lot #	Expire Date	Date Replaced	New Exp. Date
Temperature	YSI Professional Pro Plus						
	YSI EXO Probe						
	YSI 556 Multiparameter						
	YSI DSS Multiparameter						
	Hanna Combo Meter HI 98129						
	Temperature Calibration Solution						
Conductivity	YSI Professional Pro Plus						
	YSI EXO Probe						
	YSI 556 Multiparameter						
	YSI DSS Multiparameter						
	Hanna Combo Meter HI 98129						
	Conductivity 1413 μs/cm Calibration Solution						
pH	YSI Professional Pro Plus						
	YSI EXO Probe						
	YSI 556 Multiparameter						
	YSI DSS Multiparameter						
	Hanna Combo Meter HI 98129						
	pH 4 Calibration Solution						
	pH 7 Calibration Solution						
	pH 10 Calibration Solution						
Dissolved Oxygen	YSI Professional Pro Plus						
	YSI EXO Probe						
	YSI 556 Multiparameter						
	YSI DSS Multiparameter						
ORP	YSI Professional Pro Plus						
	YSI EXO Probe						
	YSI 556 Multiparameter						
	YSI DSS Multiparameter						
	ORP Calibration Solution						
Turbidity	LaMotte 2020we Portable Turbidity Meter						
	Vials						
	1 NTU Calibration Solution						
	10 NTU Calibration Solution						
	100 NTU Calibration Solution						
Alkalinity	Hach 8203 Digital Titrator						
	Phenophthalein						
	Bromocresol Green-Methly Red						
	Sulfuric Acid 1:1						

	Beaker 50 mL						
	Beaker, 100 ml						
	De-ionized water						

Inspected by: _____ Date:_____

Appendices 9: University of Alaska Fairbanks Laboratory SOPs

Sample Handling: All samples should be filtered through 0.45 μm filters. Samples for ICP-MS need to be in nitric acid washed or trace-metal clean polypropylene or HDPE containers (30 mL). Samples for IC need to be in HCl acid washed or trace clean polypropylene or HDPE containers (30 mL). Samples for absorbance/ fluorescence I will need ~ 10 mL total. ICP-MS and IC samples could be collected in one container that I split in my lab in Fairbanks, which I could also use for absorbance/fluorescence depending on transport time etc. ICP-MS samples will be preserved to 2% omnitrace nitric acid and stored at 4ºC. IC samples will be frozen at -80ºC until analysis with no preserving agent. Absorbance/fluorescence will be run as soon as possible after samples are processed in my lab in Fairbanks, and stored at 4ºC before then. Samples for DOC need to be in glass muffled or trace carbon clean glass containers (40 mL vials with PTFE/Silicone caps) and preserved to pH ≤ 2 with HCl prior to transport.

ICP-MS with Agilent 7500ce Inductively Coupled Plasma Mass Spectrometer for Trace Metal(loid) Quantification (EPA Method 200.8):
Instrument detection limits are ≤ 0.01 ppb with quantification up to 100 ppb for most elements (can run major cations with standards up to 2000 ppb). Actual detection limits for each element are determined off of calibration curves with each ICP-MS run. QA/QC: All samples are injected 3 times and %RSD is calculated for each sample. Matrix (acid) Blanks are run every 10 samples, with tolerance of 20%. Lab reagent blanks and field blanks as appropriate are also run. QC multi-element standard is run every 10 samples and checked against given concentrations, with tolerance of 15%. NIST SRM 1640A Trace Elements in Natural Water and SLRS-6 River Water Certified Reference Material are run with each run for additional QC.

ICP Sample Preparations:

- Special attention needs to be used in sample prep for low ppb analysis. You need to assume that everything is dirty unless you have cleaned it.
- Samples need to be placed in 15ml falcon tubes (with screw caps). For instrumental analysis 5ml to 10ml is a good volume. If there is a problem with the volume you have, less is OK but may not allow us to do a rerun.
- Use only the best 18 mOhm water from a filter unit for all steps.

Matrix Preparation: Samples need to be acidified so that the final concentration is 2%-5% nitric acid (2% if the most common concentration). Nitric acid is used for ICP analysis to keep elements stable in solution.

Recommended Dilution Process:

- Always use 10X dilution
- Make a 10-20% trace metal grade nitric acid solution. You will need enough for samples, standards and rinse.
- Determine how many ml sample + acid will be close to 2% final acid solution. All calculations are done by volume.
- Pipet sample + acid into tube. MIX WELL.

As a check on background concentration, please include another sample which is a blank of your acid diluted as if it were a sample.
Acidified sample MUST be filtered through 0.2um syringe filters. The reason for this is that the orifice in the nebulizer small and easily clogged.

Standard Preparation:

We supply some common elements to concentrated standards. If you are looking for some non-common elements, you have to purchase your own standards. These are often supplied in 1000 ppm million range because they are more stable. You need to prepare a standard curve that will bracket the expected range of your samples. Again, use 10X dilution to achieve the expected concentrations. For example, if the estimated concentration of your sample is 200 ppb, I will suggest to prepare 0 (blank), 5, 10, 50, 250, 500, 1000 ppb for your standards. For standards, there is no need to fill the tube. 10 - 20 ml will be plenty for the number of samples you will have. This volume is required because standards will be sampled multiple times. Standards must be same % acid as the samples so that the matrix is the same during the analysis.

Internal Standards Solution

Please bring 400 ml of matrix solution i.e., blank solution containing only nitric acid without samples. Results are best if all matrix is from same batch diluted with same source water.

Agilent 4200 Microwave Plasma-AES: The following communication outlines the plasma emission spectroscopy analysis of water samples, employed by the WERC laboratory. Much of this method is a reflection of the EPA method 200.7 as it applies to the quantitative analysis of trace elements. It is recommended that each analyst also review EPA 200.7. This outline is not intended as a sole teaching tool, and individuals will require training prior to using the WERC instrumentation.

I Chemical Safety, Storage Requirements, and Hazardous Waste Disposal

All standards and samples for this method are preserved through the addition of 2 % by volume concentrated nitric acid. The preservation must be done in the fume hood, and analysts must wear eye protection, nitrile gloves, and a lab coat. Nitric acid is both corrosive, and a strong oxidizer. An appropriate acid spill kit must be available while working with concentrated $HNO_{3(aq)}$.

Some of the elements analyzed by this technique are acutely toxic metals, such as arsenic and cadmium. Analysts working with such toxic compounds must review safety data sheets, and any samples or standards that contain toxic metals must be treated as hazardous waste once all work is completed. Collection in a 5 gallon polyethylene container is acceptable. The container should be clearly labeled with the identity of the contents, and approximate concentrations. Once the container is nearly full, the laboratory manager should be notified via email.

II Instrumentation and Method Parameters

The plasma emissions analysis is performed with an Agilent 4200 MP-AES instrument, utilizing an SPS 4 auto-sampler. This instrument is capable of analyzing for 71 different elements. Calibration range and detection limits, as well as some of the instrument parameters, are element specific. As such, each analyst will need to determine these parameters individually. The following common instrumental conditions are constant for all elements:

Replicates	3
Pump speed	15 rpm
Uptake time	45 seconds
Rinse time	45 seconds
Stabilization time	30 seconds
Number of Pixels	3

III Standards, Calibration and Quantitative Limits.

Standard stock solutions, at a concentration of 1000 ppm and of ICP-MS grade, are provided by VWR scientific. All calibration standards are made by dilution of the stocks, with type 1 DI water plus 2% by volume trace metal grade nitric acid. Calibration standards are made with class A volumetric glassware, then stored in HDPE bottles, and have a hold time of six months.

A minimum of five calibration standards are used, and the calibration must yield a minimum r^2 of 0.95. Also, the difference between calculated and known concentration, for the standard regression curve individual points, must not exceed 25%.

Any samples that give a result above the highest calibration curve standard must be repeated, after an appropriate level of dilution.

Defining an appropriate practical quantitation level (PQL) will be at the discretion of the analyst. When all samples give results above the lowest calibration standard, then all results may be considered above the PQL.

Samples that clearly show peaks, but at a level below the lowest standard, will require a more extensive look into PQL limits. A good estimate of PQL can be made by measuring a low level know concentration 7 to 10 times, with a signal to noise ratio between 2.5 and 10. The standard deviation of the results, multiplied by students T, gives a quality estimate of PQL.

I. Quality Control, Treatment, Storage, and Hold Times

Measurements must be taken to monitor for possible instrument drift during a sample run. Before and after every ten sample measurements, the calibration blank and midpoint calibration standard must be measured, as samples. These two, referred to as laboratory reagent blank (LRB) and continuous calibration verification (CCV) must pass specific. The LRB must give a result of 0 +/- PQL, and the CCV must give a result within 10% of the know value. If either the LRB of CCV fails, then the sample data is no valid, and the problem must be identified and fixed prior to reanalysis of the samples.

Steps must be taken to ensure the absence of matrix interference from the samples. A minimum of one in ten samples must be analyzed in duplicate, and augmented. The duplicate sample analyses must agree within 20%, and the augmented sample must give a spike recovery of 70-130%. When either of these two QC checks fail, the sample should be diluted and analyzed again, provided the dilution does not give results below the PQL. When dilution is not possible, the method of standard additions may be used.

All samples and standards are preserved by the addition of 2% by volume concentrated nitric acid. No further preservation or refrigeration is needed, and samples are viable for six months.

The following lower limits of detection (LOD) were determined with multiple samples from the provided inventory:

Analyte	LOD (ppm)
Calcium	0.01
Magnesium	0.01
Iron	0.5
Manganese	0.025
Sodium	0.05
Lithium	0.01
Potassium	0.01
Barium	0.01
Strontium	0.01

Ion Chromatography (IC) with Dionex ICS 3000 (EPA Method 300.1):
Instrument detection limits are ≤ 25 ppb with quantification up to 250 ppm for anions F^-, Cl^-, NO_3^-, NO_2^-, Br^-, $SO_4^=$, and PO_4^{3-} and cations Na+, K+, Mg+, NH4+, Ca+. QA/QC: MilliQ water blanks are run every 10 samples, with tolerance of 20%. Lab reagent blanks and field blanks as appropriate are also run. QC multi-element standard is run every 10 samples and checked against given concentrations, with tolerance of 15%.

II. Chemical Safety, Storage Requirements, and Hazardous Waste Disposal

The salts used to make the stock standards for this method are the primary hazard analysts must be aware of. All analysts must read SDS sheets for these chemicals prior to working with them. The nitrate and nitrite salts are strong oxidizers and are toxic. The fluoride salt is also toxic. Safety glasses and nitrile gloves must be used when handling these chemicals, and weighing should be done in the fume hood. Expired standards need to be treated as hazardous waste. Collection in a 5-gallon polyethylene container is acceptable. The container should be clearly labeled with the identity of the contents, and approximate concentrations. Once the container is nearly full, the laboratory manager should be notified via email.

All standards and samples for this method are preserved through the addition of 2 % by volume concentrated nitric acid. The preservation must be done in the fume hood, and analysts must wear eye protection, nitrile gloves, and a lab coat. Nitric acid is both corrosive, and a strong oxidizer. An appropriate acid spill kit must be available while working with concentrated $HNO_{3(aq)}$.

Some of the elements analyzed by this technique are acutely toxic metals, such as arsenic and cadmium. Analysts working with such toxic compounds must review safety data sheets, and any samples or standards that contain toxic metals must be treated as hazardous waste once all work is completed. Collection in a 5 gallon polyethylene container is acceptable. The container should be clearly labeled with the identity of the contents, and approximate concentrations. Once the container is nearly full, the laboratory manager should be notified via email.

III. Instrumentation and Method Parameters

The plasma emissions analysis is performed with an Agilent 4200 MP-AES instrument, utilizing an SPS 4

auto-sampler.

Instrument: Dionex Aquion

Columns: AG22-Fast 4 micron guard column and AS22-fast 4 micron analytical column. Both columns are housed in a column oven set to 30 degrees Celsius.

Suppressor: ADRS 600 - 2mm. Current set to 8uA.

Mobile Phase: 4.5mM sodium carbonate and 1.4mM sodium bicarbonate. Flow rate set to 0.3 mL per minute.

Detector: DS6 heated conductivity cell set to 30 degrees Celsius.

This instrument is capable of analyzing for 71 different elements. Calibration range and detection limits, as well as some of the instrument parameters, are element specific. As such, each analyst will need to determine these parameters individually. The following common instrumental conditions are constant for all elements:

Replicates	3
Pump speed	15 rpm
Uptake time	45 seconds
Rinse time	45 seconds
Stabilization time	30 seconds
Number of Pixels	3

IV. Standards, Calibration and Quantitative Limits

A high concentration standard stock solution is prepared, from dried salts, according to the table below. The final volume is 1000 ml.

Ion	Salt	Weight g	Concentration ppm
Fluoride	NaF	0.557	250
Chloride	NaCl	0.825	500
Nitrite	NaNO2	1.231	250
Bromide	NaBr	0.329	250
Nitrate	NaNO3	1.515	250
Phosphate	KH2PO4	4.396	1000
Sulfate	K2SO4	1.817	1000

The instrument is calibrated with 5 calibration standards, made by dilution of the above stack standard.

Calibration concentrations are shown in the table below:

Ion(s)	Stock volume ml	Final volume ml	Concentration ppm
F^-, NO_2^-, Br^-, NO_3^-,	1, 2, 3, 4, 5	250	1, 2, 3, 4, 5
Cl^-		250	2, 4, 6, 8, 10
PO_4^{2-}, SO_4^{2-}		250	4, 8, 12, 16, 20

All standards are made with class A volumetric glassware, then stored in HDPE bottles and refrigerated. Standards have a hold time of 3 months.

The instrument calibration must yield a minimum r^2 of 0.95. Also, the difference between calculated and known concentration, for the standard regression curve, must not exceed 25%.

Any samples that give a result above the highest calibration curve standard must be repeated, after an appropriate level of dilution.

Defining an appropriate practical quantitation level (PQL) will be at the discretion of the analyst. When all samples give results above the lowest calibration standard, then all results may be considered above the PQL.

Samples that clearly show peaks, but at a level below the lowest standard, will require a more extensive look into PQL limits. A good estimate of PQL can be made by measuring a low level know concentration 7 to 10 times, with a signal to noise ratio between 2.5 and 10. The standard deviation of the results, multiplied by students T, gives a quality estimate of PQL.

IV Quality Control, Treatment, Storage, and Hold Times

Measurements must be taken to monitor for possible instrument drift during a sample run. Before and after every ten sample measurements, the calibration blank and midpoint calibration standard must be measured, as samples. These two, referred to as laboratory reagent blank (LRB) and continuous calibration verification (CCV) must pass specific. The LRB must give a result of 0 +/- PQL, and the CCV must give a result within 10% of the know value. If either the LRB of CCV fails, then the sample data is no valid, and the problem must be identified and fixed prior to reanalysis of the samples.

Steps must be taken to ensure the absence of matrix interference from the samples. A minimum of one in ten samples must be analyzed in duplicate, and augmented. The duplicate sample analyses must agree within 20%, and the augmented sample must give a spike recovery of 70-130%. When either of these two QC checks fail, the sample should be diluted and analyzed again, provided the dilution does not give results below the PQL. When dilution is not possible, the method of standard additions may be used.

All samples must be stored between 0 and 4 deg. c. Nitrate, nitrite, and phosphate have a hold time of 48 hours. All other ions have a hold time of 28 days. When the temperature requirements and/or hold times cannot be met, the samples may be preserved by adding 3 drops per 100 ml of a saturated HgCl solution. Analysts using this method of preservation must familiarize themselves with the safety, storage, and disposal practices required for $HgCl_{(aq)}$.

Total organic carbon and nitrogen analysis with TOC Shimadzu TOC-L CSH ASI 40 and TN (from EPA method 415.3): Instrument detection limits are 4 μgC/L for non-purgable organic carbon and 0.2 μgN/L. QA/QC: All samples are injected at least 3 up to 5 times until a %RSD < 2 %. Field and lab reagent blanks are run to quantify leaching if any from containers and 0.45 μm filters. Blanks and QC purchased potassium hydrogen phthalate (KHP) or potassium nitrate (KNO_3) standards are injected every 10 samples, with tolerance of 20%.

Absorbance and Fluorescence Spectrometer with Horiba Aqualog (from USGS OFR 2018-1096): Instrumentation detection limits are ≤ 0.01 absorbance units (a.u.) for absorbance, and ~ 0.15 raman units (r.u.) for fluorescence. QA/QC: Upon initialization lamp and raman scans are run daily, quinine sulfate standard in 0.05 M sulfuric acid is run monthly and matched against NIST spectrum. Lab reagent and field blanks are collected to quantify leaching if any from containers and 0.45 μm filters. Fluorescence cuvettes are rinsed between every sample 3x, and washed with sample 3x for each run. Cuvettes are continually inspected for spots, and MilliQ water blanks are run every 10 samples to monitor cuvette cleanliness.

The employed ISO analytical procedures were performed for:

Inorganic Anions in Drinking Water by ION Chromatography EPA Method 300.1, 1997 Revision 1.0 by Daniel P. Hautman (USEPA, Office of Water) and David J. Munch (USEPA, Office of Water).

Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry EPA Method 200.8 Revision 5.4, 1994 by J.T. Creed, C.A. Brockhoff and T.D. Martin.

Procedure for Using the Horiba Scientific Aqualog Fluorometer to Measure Absorbance and Fluorescence from Dissolved Organic Matter by Hansen, A.M., Fleck, J.A., Kraus, T.E.C., Downing, B.D., von Dessonneck, T., and Bergamaschi, B.A., 2018, Procedures for using the Horiba Scientific Aqualog® fluorometer to measure absorbance and fluorescence from dissolved organic matter: U.S. Geological Survey Open-File Report 2018–1096, 31 p., https://doi.org/10.3133/ofr20181096.

Shimadzu 32356 TOC Analyzer Operating Instructions

Turning the TOC Analyzer On

1) Open the valve of the compressed air gas tank for liquid sample analysis, and open both the compressed air and oxygen air tank for solid samples.
2) Press the power button on if the red light is on (if no light is visible turn the instrument on towards the back right side of the instrument first)

Log into computer, software, and logbook

1) Log into logbook (record date, user name, initial air tank pressure and time, analysis type, estimated time of run 4 hours + 15 minutes / sample, stop time, and stop pressure
2) Select the **TOC-Control L Icon** on the desktop
3) Select **Sample Table Editor**
4) Under “enter username” prompt enter your name and click ok

To load an existing sequence

1) Click on the sample tab on left hand panel
2) Under the H/W Settings header double click on the desired existing sequence name
3) If you would like to reuse an existing sequence file but upload new data, Highlight existing data and right click on highlighted area, select **clear measured data**
4) Once everything is in sequence table select the **save** icon on the top left hand corner of the screen
5) Edit the file name such that the previous sequence data is not overwritten

To create a calibration curve file

1) Select the calibration curve tab on the left hand panel of the screen
2) Select **new**
3) Under system select TOC-TN
4) In the comment section specify standard solution concentrations
5) Select **next**, under the sample wizard page 2 select normal and check “use dilution from standard solution”
6) Select **next**, under analysis select NPOC
7) Under calculation method use linear regression
8) Create a file name and select **next**
9) Under number of injections set it to ⅗
10) Set number of washes to 2 and sparge time to 3
11) Set acid addition to 0
12) Select **next**
13) Select **add**, enter the existing standard solution concentration and the desired standard solution concentration (the dilution factor will be automatically calculated by the software)
14) Set number of injections to ⅗ and select **ok**

HORIBA Aqualog Instrument Operation

1. 20 minutes prior to running samples turn on the Aqualog, lamp will ignite
2. Place "USB Key" into the computer (Aqualog Jump Drive)
3. Open the program (Figure 1)

Figure 1: Aqualog Program on desktop

4. Wait for the program to load

Sample Prep:

1. Blank
    a. Milli-Q water MUST BE USED for Raman run
2. Fill cuvette up to the neck with Milli-Q (≥18.2 MΩ) water (3 mL)
3. Screw on cap
4. Invert
5. Dump in sink
6. Repeat steps 2-5 for 3x total
7. Remove bubbles by flicking or slowly inverting
8. Place in cuvette holder with **UV** pointed towards you
9. Sample prep for samples is similar
    a. Ensure sample is filtered through 0.45um syringe filters
    b. Dilution might be necessary if sample goes above an absorbance of 0.5
        i. Dilute with Milli-Q water

Running the Aqualog

1. Create a project

a. File
    i. Save Project as (figure 2)
        1. Name (Date_Project)
        2. Place it into your folder
    ii. Save
        1. Note the file name in your notebook

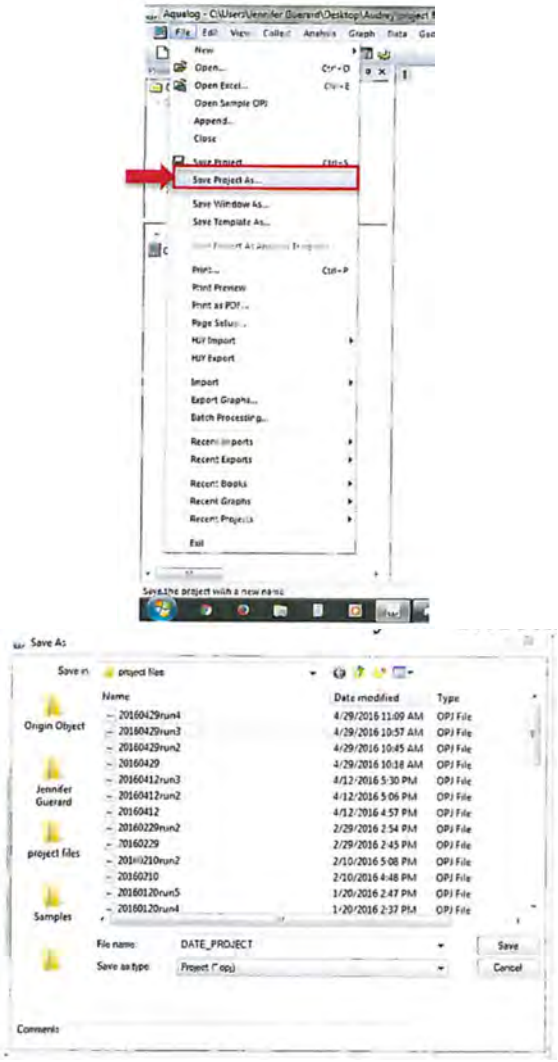


Figure 2: Save project

2. Run a Raman
    a. Milli-Q Cuvette
        i. Note that UV is forward, because all cuvettes in Guerard Lab are matched
        ii. Note no bubbles
    b. Click RU box up top (Red Arrow) (figure 3)

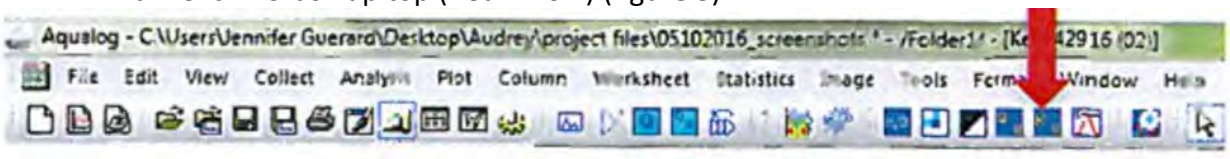


Figure 3: RU button

c. Run
d. Write in the Aqualog Log Book (figure 4)
    i. Date, User, Raman Peak, Area

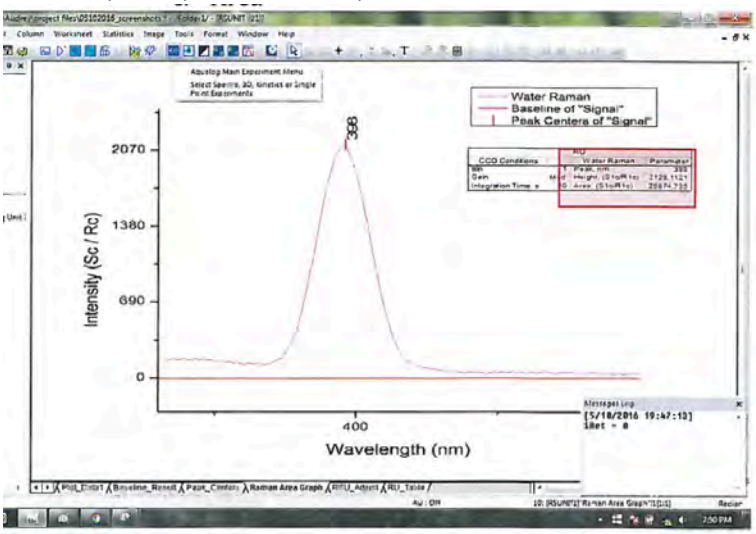


Figure 4: Write down Raman information

3. Run Blank Spectrum
    a. With Milli-Q Cuvette still in the Aqualog
    b. UV-Vis
        i. Click H2O Box (Blue Arrow) (figure 5)

Figure 5: Blue Arrow for H2O button

        ii. Select Spectra (UV-Vis) (figure 6)

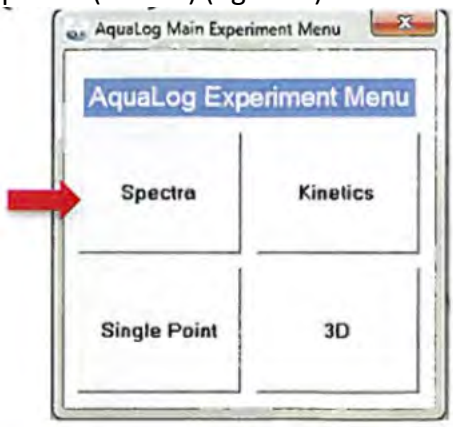


Figure 6: Spectra is for UV-Vis

        iii. Select Absorbance (Figure 7)

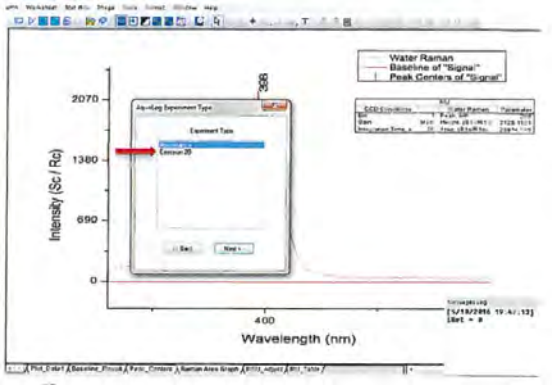


Figure 7: Absorbance for UV-Vis

iv. Figure 8
    1. Change increment to 1nm
    2. Make sure High is 800nm and low is 240nm
    3. Click Blank Only
        a. Save Blank as MonthDayYearUVvisBlank.blank
            i. This can be typed into empty box next to Blank
            ii. Alternatively, you can click the 3 dots to the right and a Save file As will pop up where you can name it MonthDayYearUVvisBlank
    4. Change Identifier to UVVis blank or leave as is

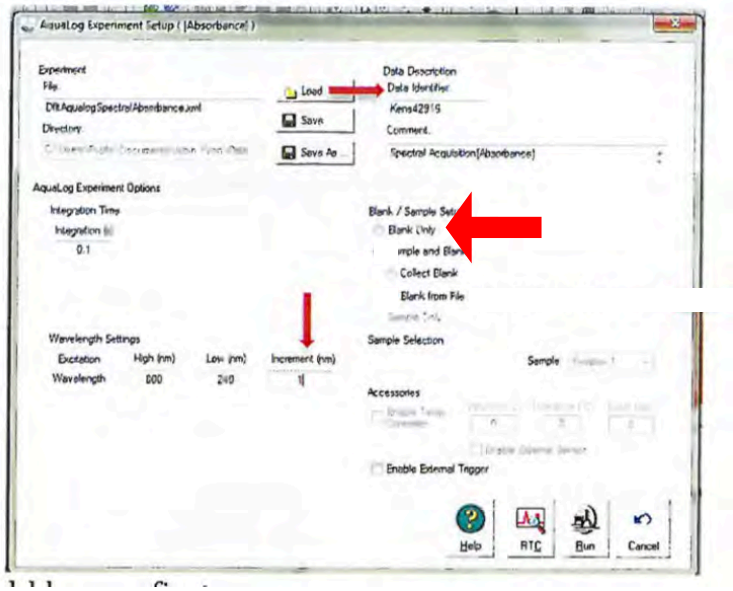


Figure 8: UV-Vis for blank sample

c. 3D EEMs
    i. Click H2O Box (Blue arrow) (Figure 9)

Figure 9: Blue Arrow for H2O button

ii. Select 3D (EEMS) (Yellow arrow) (figure 10)

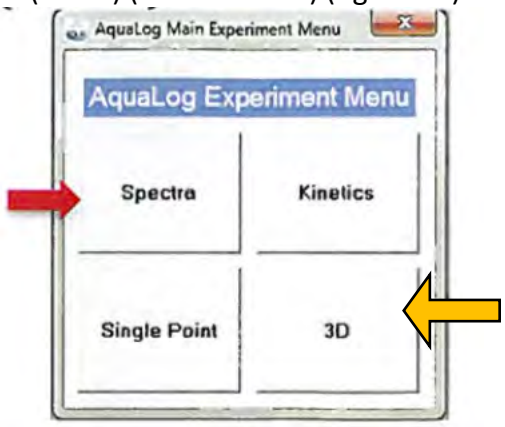


Figure 10: 3D for EEMs

iii. Select 3D CCD + Absorbance (figure 11)

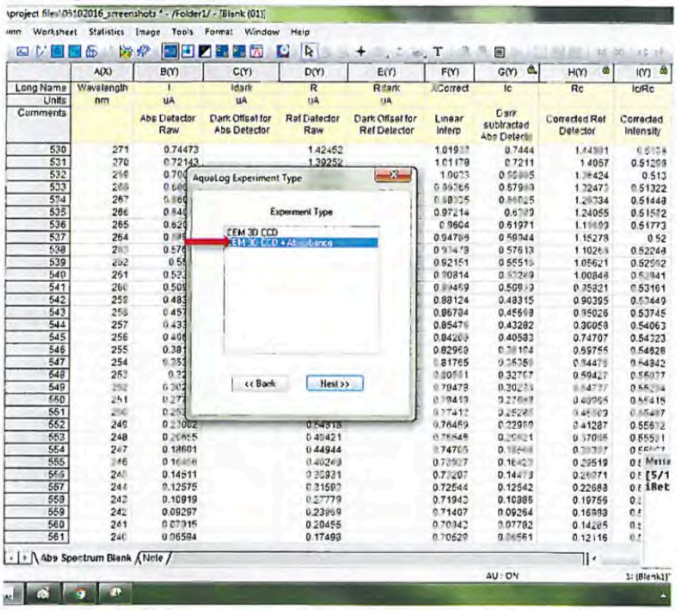


Figure 11: EEMs

iv. Click Next
v. Figure 12
    1. Change Wavelength (excitation)
        a. 600 → 240nm with 3nm increments
    2. Change Wavlength (emission)
        a. 4 pixel
    3. Gain = medium

4. Change Identifier to UVVis blank or leave as is
5. Click Blank Only
    a. Save Blank as MonthDayYearBlank.blank
        i. This can be typed into empty box next to Blank
        ii. Alternatively, you can click the 3 dots to the right and a Save file As will pop up where you can name it MonthDayYearBlank

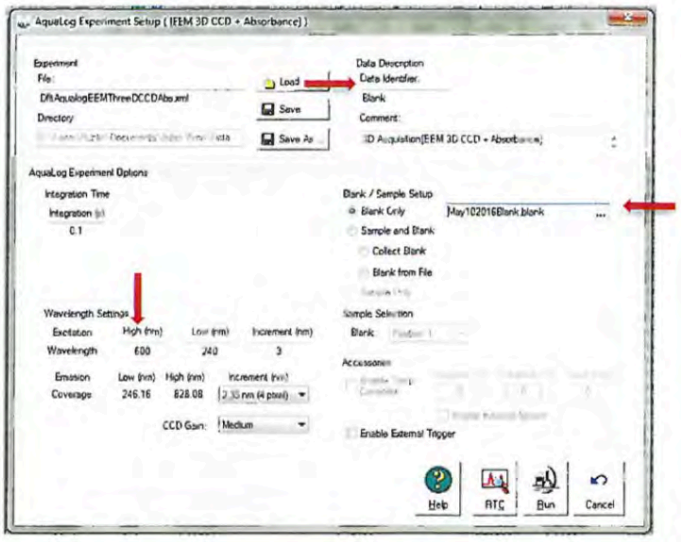


Figure 12: EEMs blank

4. Run Samples
    a. Change out blank with sample utilizing sample prep instructions
    b. UV-Vis first followed by EEMS to ensure proper dilution
    c. UV-Vis
        i. Click H2O Box (Blue Arrow) (figure 13)

Figure 13: H2O button

        ii. Select Spectra (UV-Vis) (figure 14)

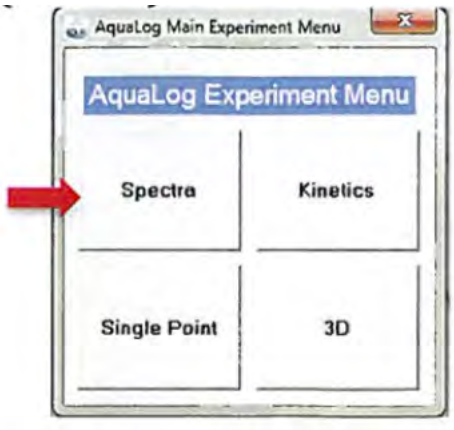


Figure 14: Spectra = UV-Vis

iii. Select Absorbance (Figure 15)

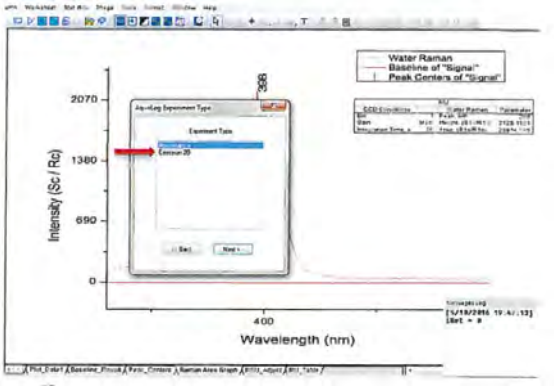


Figure 15: UV-Vis

d. Figure 16
   i. Change increment to 1nm
   ii. Make sure High is 800nm and low is 240nm
   iii. Change Data Identifier to sample name. Cannot exceed 9 characters
      1. Must be a combination of numbers and letter only
   iv. Instead of selecting blank only select **Sample + Blank**
      1. Blank from file
      2. Click on the 3 dots
      3. Select appropriate blank file

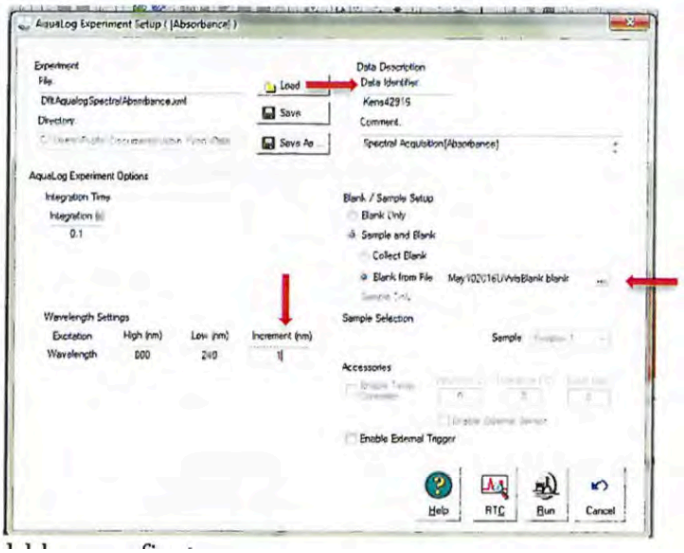


Figure 16: UV-Vis for Sample

5. Check 254nm and 280nm to ensure sample does not exceed 0.5 (Figure 17)
    a. If exceed rerun with a 10X dilution (or appropriate dilution to bring absorbance below 0.5 a.u.)
        i. 10X = 300uL sample and 2.7mL Milli-Q Water

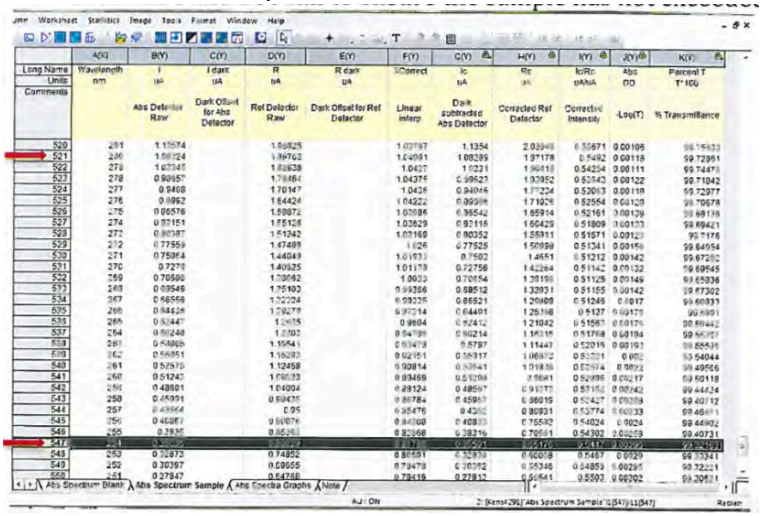


Figure 17: Sample check for dilution

    b. EEMs
        i. Click H2O Box (Blue arrow) (figure 18)

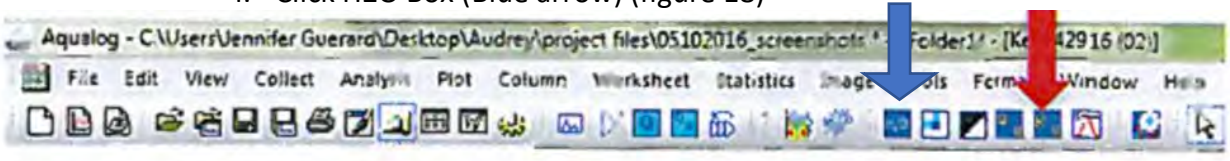


Figure 18: H2O button

        ii. Select 3D (EEMS) (Yellow arrow) (figure 19)

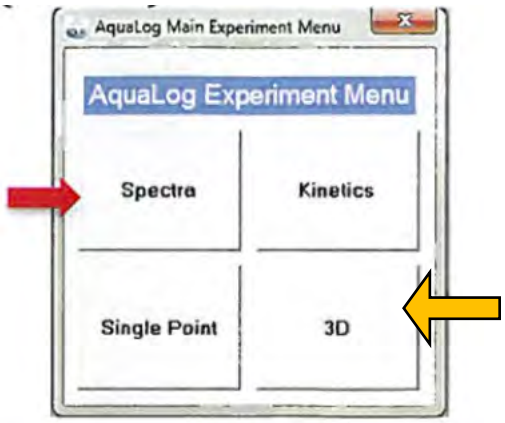


Figure 19: 3D is for EEMs

iii. Select 3D CCD + Absorbance (figure 20)

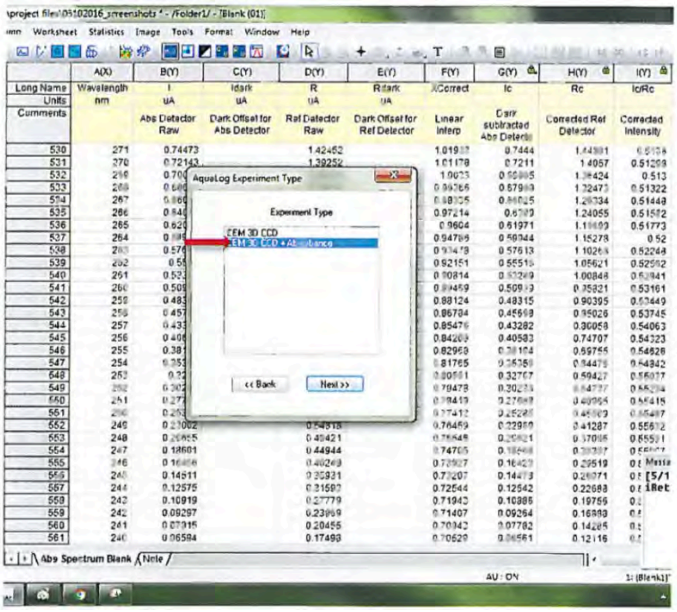


Figure 20: EEMs option

iv. Click Next

c. Figure 21
   i. Change Wavelength (excitation)
      1. 600 → 240nm with 3nm increments
   ii. Change Wavlength (emission)
      1. 4 pixel
   iii. Gain = medium
   iv. Change Data Identifier to sample name. Cannot exceed 9 characters
      1. Must be a combination of numbers and letter only
   v. Click **Blank + Sample**
      1. Click 3 dots and choose appropriate blank file

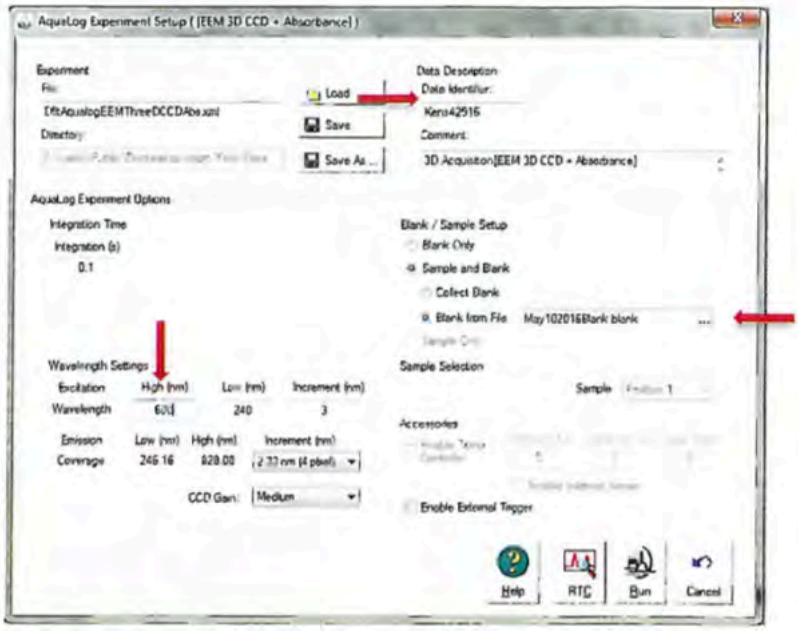


Figure 21: EEMs for sample

Sample Clean Up

1. Dispose of sample appropriately
2. Rinse cuvette with Milli-Q water twice
3. Submerge cuvette in methanol bath for 2-3 minutes
4. Remove cuvette from methanol bath.
5. Rinse cuvette with Milli-Q 3x
6. Set out to dry

Aqualog Data Processing and Exportation

1. With your fluorescence file selected make sure **Sample-Blank Waterfall Plot** is chosen (Figure 1).
2. Click **Inner Filter Effect** Icon (Figure 1 #1).
3. Click **Rayleigh Masking** Icon (Figure 1 #2).
    a. Mark **Mask 1st Order Rayleigh** and **Mask 2nd Order Rayleigh** (Figure 2).
    b. **SUM of slit widths (in bandpass)** should be changed to 12. (Figure 2).

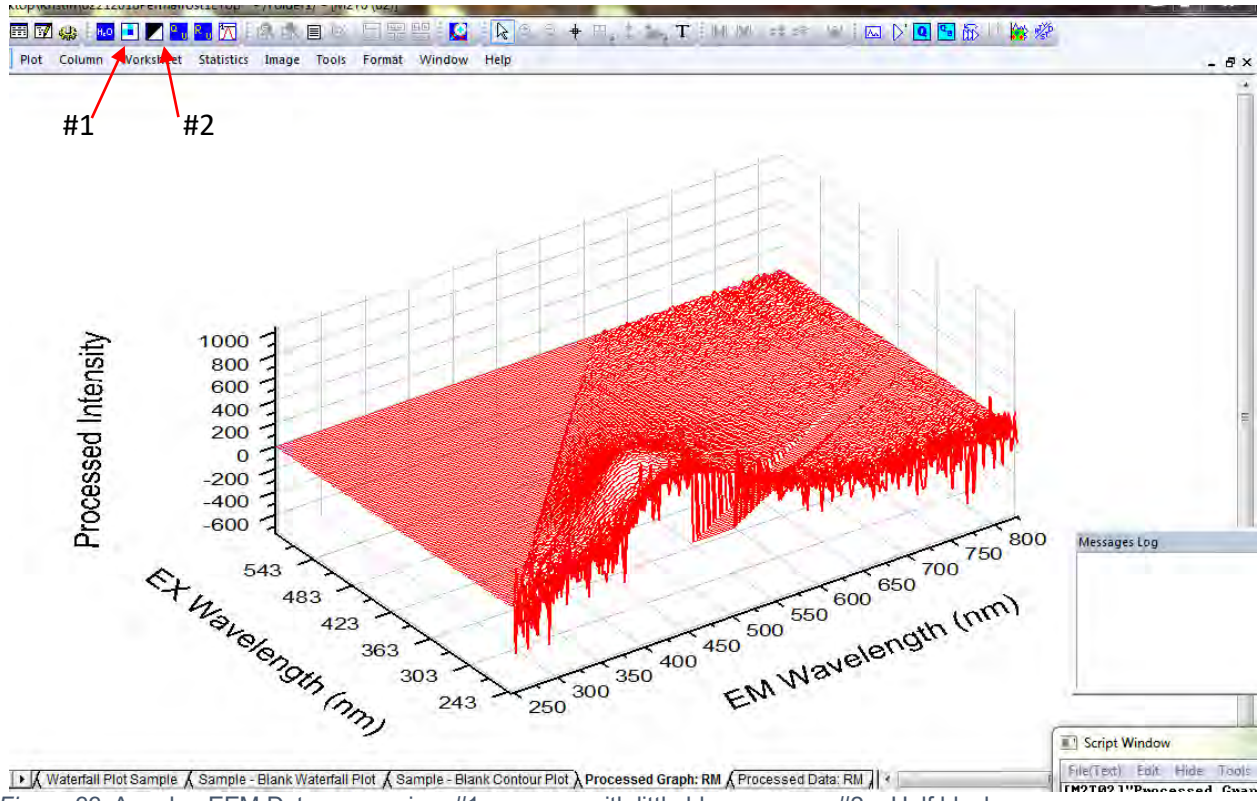


Figure 22: Aqualog EEM Data processing. #1 = square with little blue squares. #2 = Half black square

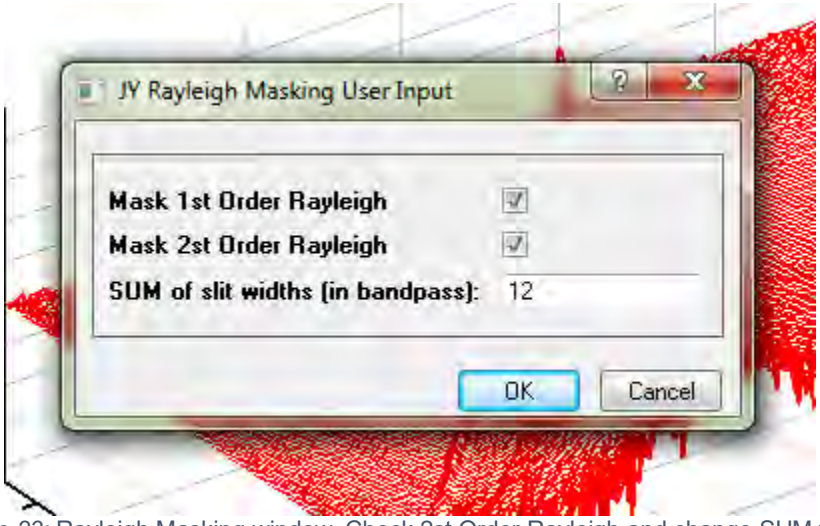


Figure 23: Rayleigh Masking window. Check 2st Order Rayleigh and change SUM to 12.

4. **File**
    a. **Export**
    b. **As image file**
5. In “Import and Export window” (Figure 3).
    a. Set Image type to **JPG**
    b. Name file accordingly
    c. Set Path to your specific folder
    d. Hit **OK**

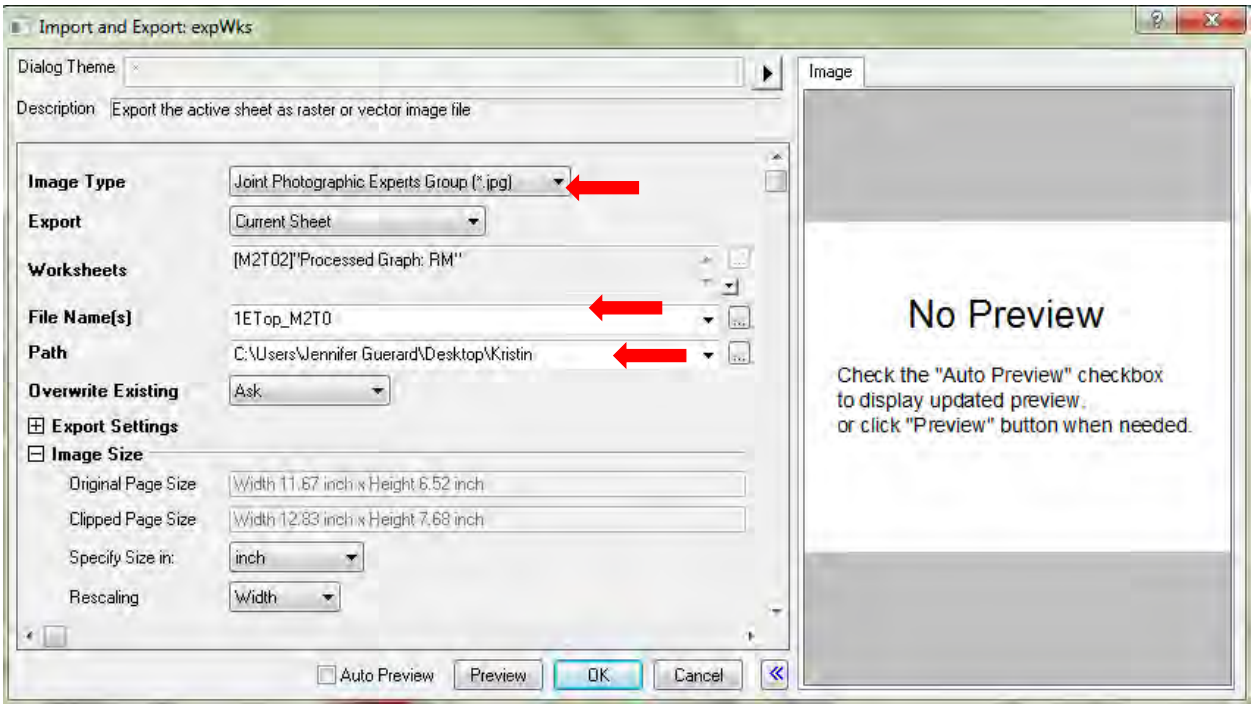


Figure 24: Image export window. Arrows indicate changes that need to be made.

6. Click on the last tab labeled **Processed Contour: RM**
    a. Repeat 4 and 5
7. **Processed Data: RM** Tab
    a. Make sure nothing is highlighted in black by clicking on a single cell
8. **File**
    a. **Export**
    b. **ASCII**
    c. In desired folder save file as a **.csv** (Figure 4)
        i. Ie. 02212018Permafrost1ETopM1T0.csv
9. Select your UV-Vis File
10. **Abs Spectrum Sample** Tab
    a. Make sure nothing is highlighted in black by clicking on a single cell

11. **File**
    a. **Export**
    b. **ASCII**
    c. In desired folder save file as a **.csv** with ABS following the name. (Figure 4)
        i. ie. 02212018Permafrost1ETopM1T0ABS.csv

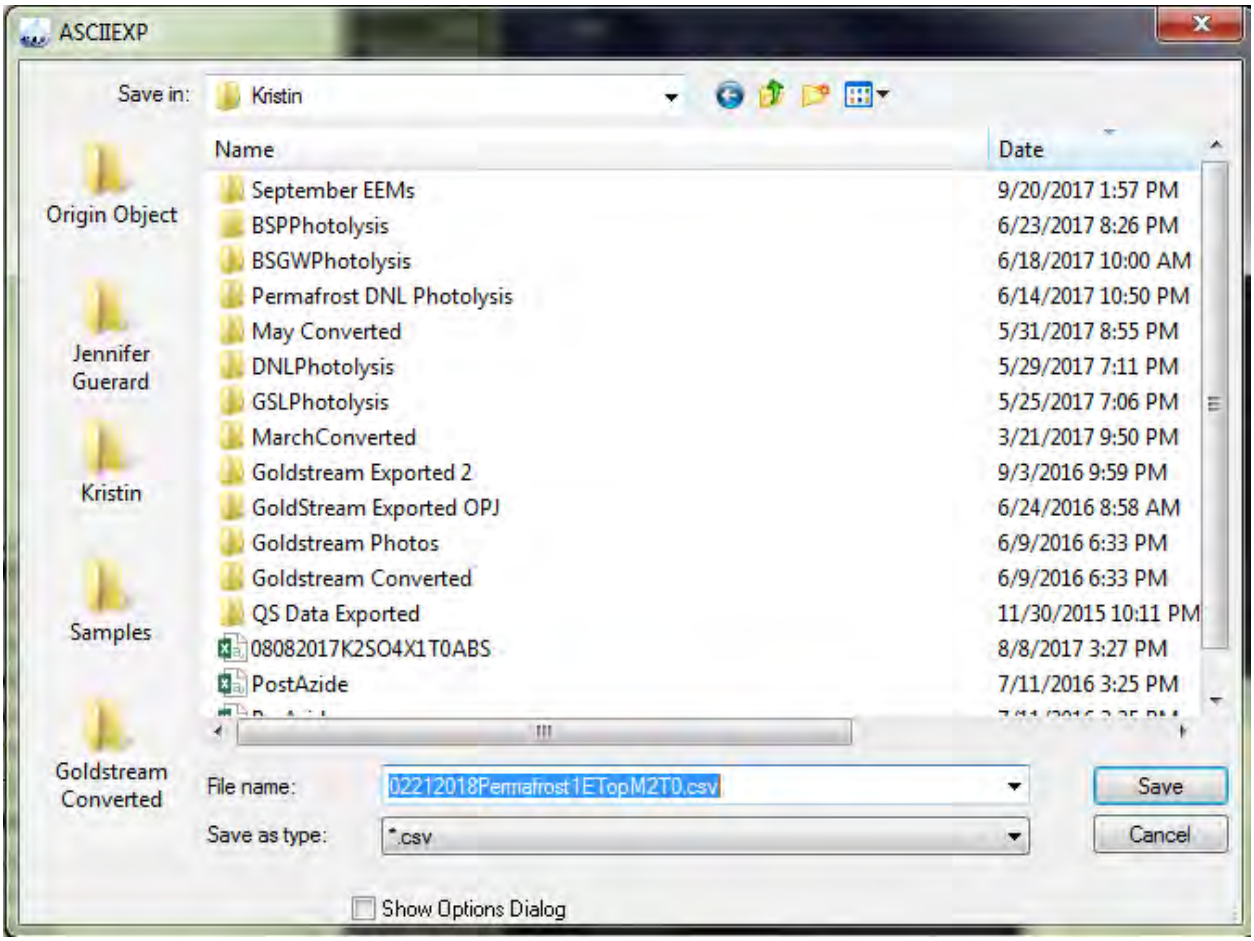


Figure 25: File saving window. Make sure the type in .csv

12. Keep a Master List of your file names for PARAFAC utilization. (Figure 5).

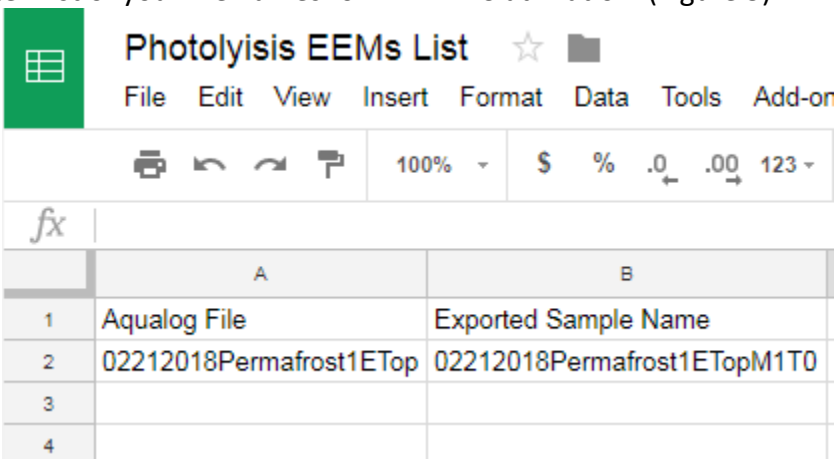


Figure 26: Example of a master list for file names.

13. Check file size to make sure all files have exported properly.
    a. ABS files should be ~82 KB
    b. EEMS files should be ~347 KB

15) Repeat step 13 for each point in the calibration curve that you would like to have for carbon analysis
16) Select **next**, select **finish**
17) If running a nitrogen analysis repeat steps 6-16 but under analysis for step 6 select TN
18) To load calibration standards onto sequence table select a number on left hand column of spreadsheet and right click
19) Select **Insert-calibration curve**

To create a new sequence

1) Click on the sample tab on the left hand panel
2) Select **New**
3) Set system to TOC-TN
4) Set table type to normal and click **ok**
5) Right click on a number on the numbered column to the left and select **Insert-Sample**
6) Under the method section select desired method (Default: NPOC_TN_GUERARD.met) and click **open**
7) Select **next**, select **next**
8) Analysis should say NPOC
9) Under “calibration curve 1” select desired calibration curve file (Default ends in: NPOC-100ppm.cal)
10) Select **next**, select **next**, select **next**
11) On sample wizard page 6 Analysis should say TN
12) Under “calibration curve 1” select desired calibration curve file (Default ends in: TN-28.cal)
13) Select **next**, select **next**
14) On sample wizard page 9 under pharmaceutical water testing select none
15) Select **finish**
16) Right click on number on left numbered column and select **copy**
17) Paste row of information into spreadsheet for the number of desired blanks, samples, and QC’s
18) Highlight all rows and click on the **view vial settings** icon on the top right corner of the screen
19) Under the vial column select your desired row and double click on the vial number on the right auto sample wheel icon (If blank is solution from TOC reservoir type 0 in place of an auto sample number) you can sequentially double click on the auto sample number that pertains to the following row on your sequence table
20) Select a sample and click on **view measurement parameters** icon on the top left of spreadsheet
21) Select NPOC tab and edit the dilution factor to desired value and select **ok.** Highly colored samples will likely need more dilution, want to give a dilution factor that puts samples in middle of calibration curve if possible.
22) Once everything is in sequence table select the **save** icon on the top left hand corner of the screen

23) Then on the top left side of the screen select **connect**, select shut down instrument when finished, and select **start** to run experiment

Appendices F: USGS Standard Analytical Methods and Instrument Detection Limits

Determination of Selected Trace and Major Elements, Dissolved Iron and Silica in Aqueous Media by Inductively Coupled Plasma-Optical Emission Spectroscopy

Revised Feb 9, 2014

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Scope and Application:
This inductively coupled plasma-optical emission spectroscopy (ICP-OES) method is primarily for the quantitative determination of Ca, Fe, K, Mg, Na, S, and SiO_2, including Cr, P, and Ti for digestates, in aqueous media (natural waters and precipitation samples, and with appropriately diluted digestates) at concentrations of less than 500 mg/L. The inclusion of Cr, P, and Ti are primarily for the determination of those elements in digestates of sediment, soil, vegetation and animal tissue due to the higher concentrations found in those liquids. In general, using clean handling techniques and purified reagents, method detection limits in the range of 0.002 - 0.05 mg/L for the major elements and a range of 0.3 – 13 µg/L the trace elements Cr, P, and Ti are routinely attainable. The trace elements Al, B, Ba, Cd, Co, Cu, Li, Mn, Mo, Ni, Sr, V, and Zn are also quantified using this method; however the reported concentrations are generally taken from alternant instrumental determinations using inductively coupled plasma-mass spectrometry (ICP-MS) methodology due to reduced interferences or better sensitivity. Detection limits for these elements range from 0.02 - 23 µg/L. As and Sc are also quantified against calibration standards but both suffers from a lack of an appropriate standard reference material (SRM) and cannot be properly quality control (QC) checked. Results for As and Sc will not normally be reported until a suitable SRM becomes available and it has been thoroughly tested. A single argon wavelength is monitored throughout the run as a global gage to indicate how well the analysis is progressing. The argon wavelength's intensity is an indicator of nebulizer performance, as it becomes clogged the intensity will show a significant positive deviation from its starting value. All wavelengths are monitored in the axial configuration except K, which is monitored both the axial and radial configurations. The quantifiable elements and their measured wavelengths are listed in

Table 1. Spectroscopic wavelengths, in nanometers (nm), of elements used in the concentration determinations for the quantifiable elements and argon.

Element	Wavelength (nm)	Line Type		Element	Wavelength (nm)	Line Type
Argon[1,2]	420.069	Atom		Magnesium	285.213	Atom
Aluminum	394.401	Atom		Manganese	257.610	Ion
Aluminum	396.153	Atom		Manganese	260.568	Ion
Arsenic	188.979	Atom		Molybdenum	204.597	Ion
Arsenic	193.696	Atom		Molybdenum	281.616	Ion
Boron	208.957	Atom		Sodium	330.237	Atom
Boron	249.772	Atom		Sodium	588.995	Atom
Barium	455.403	Ion		Sodium	589.592	Atom
Barium	493.408	Ion		Nickel	231.604	Ion

Cadmium	214.440	Ion		Nickel	232.003	Atom
Cadmium	226.502	Ion		Phosphorous	213.617	Atom
Calcium	315.887	Ion		Phosphorous	214.914	Atom
Calcium	317.933	Ion		Potassium[3]	766.490	Atom
Calcium	396.847	Ion		Sulfur	180.669	Atom
Cobalt	228.616	Ion		Sulfur	181.975	Atom
Cobalt	230.786	Ion		Scandium[1]	361.383	Ion
Chromium	267.716	Ion		Scandium[1]	424.683	Ion
Chromium	357.869	Atom		Silica	251.611	Atom
Copper	224.700	Ion		Silica	288.158	Atom
Copper	324.752	Atom		Strontium	407.771	Ion
Copper	327.393	Atom		Strontium	460.733	Atom
Iron	238.204	Ion		Titanium	334.940	Ion
Iron	239.562	Ion		Titanium	336.121	Ion
Iron	259.939	Ion		Vanadium	292.402	Ion
Lithium	670.784	Atom		Vanadium	311.071	Ion
Magnesium	279.077	Ion		Zinc	206.200	Ion
Magnesium	279.553	Ion		Zinc	213.857	Atom

[1] Currently no reference standard available for these elements.

[2] Argon wavelength is used to indicate problems associated with the analytical run.

[3] This wavelength for potassium is analyzed in both the axial mode and the radial mode to expand the linear range of the instrument.

Summary of Method

Samples are collected using ultra-clean sample handling protocols into rigorously cleaned polyethylene bottles and are preserved with 1% (v/v) double quartz-distilled nitric acid. Analysis is performed on a Perkin Elmer Optima 3300 DV ICP-OES using techniques based on those described by Garbarino and Taylor (1979), except as modified below.

Reagents

Water: 18 megohm ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. This water is produced from a Barnstead Nanopure II mixed bed deionizer. Both trace ionic species and trace organic compounds are removed from the processed water.

Nitric Acid: Trace-metal purified reagent HNO_3 is purchased and doubly-distilled in a quartz still in the laboratory (Kuehner, et al, 1972). At monthly intervals, aliquots are sampled for quality-control purposes.

Stock standard solutions: Certified 10 mg/mL and 1 mg/mL standards are used as the basis of all lower concentration laboratory stock solutions. These solutions are commercially available.

Stock secondary mixed solutions: Six multi-element standards and three single element standards are prepared from the single element stock standard solutions, in 18 megohm ultra-pure deionized water and quartz-distilled nitric acid. Standard WMixA contains majors at 200 mg/L Na and 150 mg/L Ca, trace elements at 20 mg/L for Al, Li, and Sr, and 10 mg/L Ni and Cu. Standard WMixB contains majors at 100 mg/L Mg and 50 mg/L SiO_2, and trace elements at 20 mg/L Mn, 10 mg/L Fe and Zn, and 2 mg/L B and Ba. Standard WMixT contains only trace elements at 10 mg/L Be, Cd, Co, and Mo. These standards are then diluted 1/10, 1/50, and 1/250 to make up the calibration sets. The high major standard WC1 contains 250 mg/L Mg and 500 mg/L Na which is analyzed directly only. All of these stock solutions are prepared on a

regular basis, usually about six times per year as needed. A single element set of 4 standards with a concentration range of 0.1 to 5 mg/L K are prepared from the certified stock for the calibration of K, and an additionally multi-element standard containing 10 mg/L K and 25 mg/L Fe is used when sample concentrations exceed 5 and 10 mg/L respectively. Four Sulfur standards ranging in concentration from 3 to 100 mg/L are prepared from a 1000 mg/L certified stock solution and a single 2 mg/L P standard (for a one-point calibration, blank and 2 mg/L standard) is also prepared from a commercial certified stock solution. Lastly a single multi element standard for the trace elements As, Sc, and Ti at concentrations of 10, 1, 10 mg/L respectively is prepared and run as a single point calibration.

Mixed working standards: The mixed working standards described above for instrument calibration are prepared on a monthly basis from the stock secondary mixed solutions by simple dilution and acidification of the secondary standards.

Ionization Buffer: The ionization buffer is prepared from 99.999% CsCl solid by adding 1 gram CsCl solid to 1L of 1% HNO_3 (10 mL double distilled HNO_3 diluted to approximately 1L) with 18 megohm ultra-pure deionized water.

QC SRM Samples: A variety of quality control (QC SRM) samples are used during each analysis run to insure the accuracy of the analytical results. Generally, these QC SRM samples include 4 U.S. Geological Survey Standard Reference Water Samples (USGS SWRS) run six times, 3 USGS SRWS run 4 times and 4 USGS SRWS run 3 times per run. Occasionally (about every other month) a National Institute of Standards and Technology (NIST) standard is analyzed. In addition, these USGS SWRS standards are traceable to NIST certified samples (see Peart, et al, 1998). The QC standards are changed as new ones become available. Additionally, two laboratory made reference samples are run 17 times each during the run to monitor and account for drift during the run.

Argon: Ultra-high purity argon is fractionally distilled from liquid argon stored in a cryogenic cylinder.

Equipment

The equipment and analytical methodology are described in Garbarino and Taylor (1979) and are summarized here. Samples are analyzed on a Perkin Elmer Optima 3300 DV Inductively-Coupled Plasma Optical Emission Spectrophotometer, equipped with a Perkin Elmer AS-91 autosampler. The sample stream and ionization buffer (mixed real time at approximately a 9:1 ratio) are pumped with a Perkin Elmer 3-channel peristaltic pump from the autosampler to a Burgener Teflon T2100 nebulizer and a cyclonic spray chamber. Aerosol produced by the nebulizer is then transported through an alumina injector and quartz plasma torch. Wavelengths and emission transition type (i.e. atom line vs ion line) used for the determination of the five elements were listed previously in Table 1. The typical system operating conditions for this method are listed below in Table 2.

Table 2. System operating conditions

Plasma	
Incident RF Power	1300 W
Coolant argon flow rate	15 L/min
Sample argon flow rate	0.850 L/min
Auxiliary argon flow rate	0.6 L/min
Sample pumping rate	1.25 mL/min
Vertical/Horizontal observation position	Mn optimized
Shear Gas	Purified Air

Spectrometer	
Purge Gas	Argon
UV detector range	165 – 403 nm
VIS detector range	404 – 782 nm
Grating (UV/VIS)	Echelle
Secondary dispersion device (UV)	Schmidt Cross Disperser
Secondary dispersion device (VIS)	Prism
Detectors (UV/VIS)	Segmented array CCD
Controller	
Min/Max Exposure time	0.2 – 20 sec
Replicate exposure/determination	5
Resolution	High

Calibration

Typical calibration data consists of four to six calibrants and a reagent blank covering the following ranges: major ions Ca: 0.6-150 mg/L; K: 0.1-10 mg/L; Mg: 0.4-250 mg/L; Na: 0.8-500 mg/L; S: 3.0-100 mg/L; and SiO_2: 0.2-50 mg/L. For trace elements B and Ba: 0.008-2 mg/L; Be, Cd, Co, Cr, Cu, Mo, Ni and Zn: 0.04-10 mg/L; Al, Li, Mn, and Sr: 0.08-20 mg/L; and e: 0.04-25 mg/L. Only one calibrant and a reagent blank are used for P, As, Sc, and Ti (concentrations for these elements can be found in the reagents section). For these calibration standards, regression r^2 values are determined, achieving values greater than 0.999. On those occasions upon which r^2 values are below 0.999, the calibration curves are scrutinized and incorrect calibrants are remade. Calibration standards are analyzed producing a calibration curve for each analysis run. Samples whose concentrations fall above these ranges are diluted and reanalyzed. Table 3 shows typical r^2 values from eleven different analysis runs.

Table 3. Mean and median calibration r^2 values from indicated number of analysis runs.

Element	**Wavelength**	**Mean r^2**	**Median r^2**	**n**
Aluminum	394.401	0.99991	0.99990	11
Aluminum	396.153	0.99998	0.99998	11
Arsenic	188.979	2 point	calibration	
Arsenic	193.696	2 point	calibration	
Barium	455.403	0.99998	0.99999	11
Barium	493.408	0.99998	0.99999	11
Boron	208.957	0.99999	1.00000	10
Boron	249.772	0.99999	1.00000	10
Cadmium	214.440	0.99996	0.99998	11
Cadmium	226.502	0.99998	0.99999	11
Calcium	315.887	0.99998	0.99999	11
Calcium	317.933	0.99996	0.99998	11
Calcium	396.847	Experimental	Wavelength	
Chromium	267.716	0.99999	1.00000	11
Chromium	357.869	1.00000	1.00000	11
Cobalt	228.616	0.99999	1.00000	11

Cobalt	230.786	0.99996	1.00000	11
Copper	224.700	0.99970	0.99962	11
Copper	324.752	0.99985	0.99988	11
Copper	327.393	0.99987	0.99987	11
Iron	238.204	0.99969	0.99991	11
Iron	239.562	0.99958	0.99991	11
Iron	259.939	0.99967	0.99980	11
Lithium	670.784	0.99985	0.99996	11
Magnesium	279.077	0.99988	0.99996	11
Magnesium	279.553	Experimental	Wavelength	
Magnesium	285.213	0.99807	0.99811	11
Manganese	257.610	0.99994	0.99995	11
Manganese	260.568	0.99997	0.99998	11
Molybdenum	204.597	0.99997	0.99998	11
Molybdenum	281.616	0.99997	0.99998	11
Nickel	231.604	0.99998	0.99998	11
Nickel	232.003	0.99999	1.00000	11
Phosphorous	213.617	2 point	calibration	
Phosphorous	214.914	2 point	calibration	
Potassium (axial)	766.490	0.99991	0.99992	10
Potassium (radial)	766.490	0.99958	0.99971	10
Scandium	361.383	2 point	calibration	
Scandium	424.683	2 point	calibration	
Silica	251.611	0.99938	0.99999	11
Silica	288.158	0.99938	0.99999	11
Sodium	330.237	0.99988	0.99989	11
Sodium	588.995	0.99993	0.99995	11
Sodium	589.592	0.99974	0.99975	11
Strontium	407.771	0.99999	0.99999	11
Strontium	460.733	0.99992	0.99993	11
Sulfur	180.669	0.99930	0.99970	11
Sulfur	181.975	0.99950	0.99983	11
Titanium	334.940	2 point	calibration	
Titanium	336.121	2 point	calibration	
Vanadium	292.402	0.99999	1.00000	11
Vanadium	311.071	0.99999	1.00000	11
Zinc	206.200	0.99995	0.99997	11
Zinc	213.857	0.99990	0.99992	11

Blanks

Eighteen laboratory blanks are analyzed during each analysis run to monitor instrument stability, contamination issues, and carry-over problems. The blanks are interspersed throughout the analysis run. Additionally, these blanks are used to calculate detection limits for each analyte for each analysis run.

Detection Limits

The "Minimum Detection Limit" (MDL) is calculated according to the method of Skogerboe and Grant (1970). This method calculates the MDL as the standard deviation of n blanks multiplied by the Student t-statistic at the 97.5% confidence level for (n-1) degrees of freedom. Table 4 shows calculated detection limits and number of blanks analyzed for eight separate analysis runs.

Table 4. Mean and Median detection limits for eleven separate analysis runs (n). Number of blanks used to calculate the detection for each run is 18.

Element	Wavelength	Mean	Median	Units	n
Aluminum	394.401	4	3	µg/L	11
Aluminum	396.153	2	2	µg/L	11
Arsenic	188.979	18	17	µg/L	11
Arsenic	193.696	24	23	µg/L	11
Barium	455.403	0.04	0.04	µg/L	11
Barium	493.408	0.05	0.05	µg/L	11
Boron	208.957	3	2	µg/L	11
Boron	249.772	0.8	0.5	µg/L	11
Cadmium	214.440	0.4	0.3	µg/L	11
Cadmium	226.502	0.4	0.4	µg/L	11
Calcium	315.887	0.008	0.008	**mg/L**	11
Calcium	317.933	0.006	0.005	**mg/L**	11
Calcium	396.847	experimental	wavelength	**mg/L**	
Chromium	267.716	0.3	0.3	µg/L	11
Chromium	357.869	1	1	µg/L	11
Cobalt	228.616	0.6	0.6	µg/L	11
Cobalt	230.786	1	1	µg/L	11
Copper	224.700	2	2	µg/L	11
Copper	324.752	2	2	µg/L	11
Copper	327.393	0.8	0.2	µg/L	11
Iron	238.204	4	4	µg/L	11
Iron	239.562	4	4	µg/L	11
Iron	259.939	3	2	µg/L	11
Lithium	670.784	0.05	0.05	µg/L	11
Magnesium	279.077	0.003	0.002	**mg/L**	11
Magnesium	279.553	experimental	wavelength	**mg/L**	11
Magnesium	285.213	0.002	0.002	**mg/L**	11
Manganese	257.610	0.09	0.08	µg/L	11
Manganese	260.568	0.1	0.1	µg/L	11
Molybdenum	204.597	8	7	µg/L	11
Molybdenum	281.616	6	5	µg/L	11
Nickel	231.604	1	1	µg/L	11
Nickel	232.003	3	2	µg/L	11
Phosphorous	213.617	13	10	µg/L	11
Phosphorous	214.914	14	13	µg/L	11

Potassium (axial)	766.490	0.004	0.003	**mg/L**	11
Potassium (radial)	766.490	0.2	0.1	**mg/L**	11
Scandium	361.383	0.1	0.1	µg/L	11
Scandium	424.683	0.1	0.1	µg/L	11
Silica	251.611	0.006	0.005	**mg/L**	11
Silica	288.158	0.02	0.02	**mg/L**	11
Sodium	330.237	0.3	0.3	**mg/L**	11
Sodium	588.995	0.02	0.009	**mg/L**	11
Sodium	589.592	0.02	0.007	**mg/L**	11
Strontium	407.771	0.03	0.02	µg/L	11
Strontium	460.733	0.7	0.5	µg/L	11
Sulfur	180.669	0.05	0.05	**mg/L**	11
Sulfur	181.975	0.09	0.08	**mg/L**	11
Titanium	334.940	0.4	0.3	µg/L	11
Titanium	336.121	0.4	0.4	µg/L	11
Vanadium	292.402	0.3	0.2	µg/L	11
Vanadium	311.071	0.6	0.2	µg/L	11
Zinc	206.200	1	1	µg/L	11
Zinc	213.857	0.5	0.6	µg/L	11

Quality Control

QC SRM samples are analyzed at a frequency which exceeds 30% of all analyses. These check standards are interspersed throughout the analysis run to determine precision, accuracy and instrument stability. Table 5 presents typical precision and accuracy results from various USGS SRWS standards for trace elements and major ions for eleven separate analysis runs. For the elements B and Mn, NIST SRM 1643d water reference sample is used to determine accuracy and precision. For Ti a NIST SRM sediment (8704) is used due to no suitable water reference samples. The median value for each QC sample is determined and is compared against its published "most probable value" (MPV) to establish the accuracy of the results. As can be seen, accuracy is better than 5% as the percent recoveries are between 98 and 102 percent with the exception of Ti which used the digested NIST Buffalo River 8704 reference standard. Precision is evaluated by the % Rmad which is a robust analog to % relative standard deviation (% RSD). Over the course of these 11 analysis runs, the % Rmad is less than 4% for each of the elements evaluated.

Table 5. Accuracy and precision results for this method; Mad is the median absolute deviation which is a robust analogue for standard deviation (Rousseeuw, 1990) and % Rmad is the percent relative median absolute deviation, an analogue for %RSD. Italicized elements indicate those elements which SRMs are in the evaluation phase or the SRM search is ongoing. All concentration in µg/L unless noted.

Element	MPV[3]	Median	Mad	% Recovery	% Rmad	Reference Standard
Aluminum	62.9	61.7	0.5	98	0.9	USGS SRWS T187
Arsenic						*No standard available*
Barium	29.9	29.9	0.08	100	0.3	USGS SRWS T195
Boron	14.48	14.5	0.01	100	0.1	NIST 1643d (1/10 dilution)
Cadmium	8.2	8.34	0.07	102	0.8	USGS SRWS T175
Calcium[2]	3.90	3.89	0.02	100	0.4	USGS SRWS T187
Chromium	2.62	2.68	0.06	102	2.2	USGS SRWS T211
Cobalt	5.55	5.47	0.11	99	2.0	USGS SRWS T197
Copper	7.50	7.37	0.08	98	1.1	USGS SRWS T173
Iron	66.9	67.1	1.29	100	1.9	USGS SRWS T205

Lithium	17.1	16.8	0.09	98	0.5	USGS SRWS T173
Magnesium[2]	4.91	4.88	0.06	99	1.3	USGS SRWS T209
Manganese	3.766	3.77	0.09	100	2.3	NIST 1643d (1/10 dilution)
Molybdenum	41.4	41.2	1.5	99	3.7	USGS SRWS T159
Nickel	18.9	19.1	0.3	101	1.6	USGS SRWS T197
Phosphorous	162	166	1	102	0.6	USGS SRWS M206
Potassium[2]	2.66	2.62	0.06	99	2.1	USGS SRWS T209
Scandium						*No standard available*
Silica[2]	8.78	8.68	0.04	99	0.5	USGS SRWS T205
Sodium[2]	6.56	6.46	0.07	98	1.1	USGS SRWS T195
Strontium	23.5	24.0	0.1	102	0.6	USGS SRWS T187
Sulfur[2]	10.8	11.0	0.2	102	2.1	USGS SRWS M206
Titanium[1]	0.457	0.49	0.01	108	2.3	*NIST Buff. R. Sed. 8704*
Vanadium	4.31	4.33	0.06	100	1.5	USGS SRWS T173
Zinc	71.6	71.5	1.6	100	2.3	USGS SRWS T175

[1] Reference standard used is a digested sediment standard due to lack of water standard availability. Concentration is in µg/g except for Ti which is in wt%.

[2] Concentration is in mg/L.

[2] MVP is Most Probable Value, except for NIST concentrations which are certified.

Sample Analysis

Each sample is analyzed in triplicate, again interspersed throughout the analysis run such that one replicate for each sample is analyzed in every third of the analysis run. The concentration value for each sample is the mean of these three separate analyses and the precision of the measurement is calculated as the standard deviation of the three analyses. Each of the three replicate analyses are compared for consistency. On those occasions for which one of the replicates substantially disagrees with the other two, it is discarded and the average and standard deviation of the remaining two are used for the concentration and precision. For those rare times when all three values substantially disagree, the sample is reanalyzed.

Sample Pre-Processing

The raw sample data are run through a pre-processing macro to get the analytical results in to a suitable matrix form that has elements along the top of the table and sample (in chronological order) down the right side column. It is during this process that the run is initially evaluated using preliminary data to warrant passing it on the next processing step.

Sample Processing

After analysis, the initial results from the instrumentation need to be processed to yield final results. These post-analysis processing steps are complex and thorough and will be briefly described below. The wavelengths are chosen so that interferences are minimized and multiple wavelengths are analyzed for each analyte so at least one of the wavelengths will be generally unaffected by the same interfering substance.

The initial step is to convert the raw instrument values into a preliminary concentration. For analyses performed on the ICP-OES, there are generally more than one wavelength of sufficient intensity per element to provide concentration values, and therefore there is generally more than one estimate of concentration per element. The instrument yields wavelength intensities that are “counts per second” (cps) and they are generally proportional to the concentration of the element. These cps are converted to initial concentrations by using the calibration standards which are analyzed at the beginning of each analysis run. For most elements, the cps of the calibrants are regressed against their known concentrations; concentrations of the standards are biased towards the lower end of the calibration

curve, extend for more than two orders of magnitude, and span the range found in most samples. Regression R^2 values are normally at least 0.9995. Using the regression parameters from these, all values for all elements are converted into a preliminary concentration.

The next step in the post-analysis processing is referred to as "blank subtraction". In each analysis run, between 10 and 20 laboratory blank samples are analyzed, these blanks being interspersed throughout the run. The initial concentrations of these are regressed against the sample order (this latter being directly proportional to the time at which the sample was analyzed). The regression parameters from this step are used to "blank-subtract": the initial concentrations of all samples (including these blanks) are adjusted by subtracting the sum of the slope value times the sample order number and the intercept value. It is thus the case that after this step the average value of the blanks throughout the run has a concentration of zero, and that there is no drift amongst the blanks across the run. The standard deviation of these blanks is used to calculate a detection limit for each line and is unique to the analysis run.

The third step is called "drift-correction" and is a fine-tuned adjustment to account for instrument drifts. In each analysis run, two separate "consistency standards" (C-standards) are analyzed as samples between ten and twenty times interspersed throughout the run. These C-standards are prepared in the laboratory from single-element NIST-traceable standards; there are two C-standards because not all elements are compatible with each other. The ratios of the known concentration of the C-standard to its blank-subtracted values within the analysis run are regressed against the sample number (proportional to the time at which the sample was analyzed). Under ideality, the slope of this regression is 0 (no instrument drift) and the intercept is 1; however, there is almost always a non-zero slope indicating an instrument drift. To correct for this drift (the "QC correction"), blank subtracted concentrations of each sample are multiplied by the sum of the intercept and the product of the slope and the sample number. The consequence of this action insures that each element has been corrected so that there is no drift over the course of the analysis run.

The fourth step is called the "final-adjustment". In addition to the C-standards, every analysis run has six to twelve different USGS, Environment Canada, and/or NIST standard reference water samples (SRWS) each of which is analyzed between three and six times interspersed throughout the run. The median value of every SRWS is calculated and this is plotted against its respective certified or most-probable value (MPV). Under ideality, these median observed values (MOVs) should match the MPVs, and normally this is what is seen; however, at times there is either a positive or negative bias in which the MOVs are systematically greater or less than the MPVs. In this case, the MOVs are regressed against the MPVs by forcing the intercept through zero (since the blank-subtraction step has insured this), and the slope is used to adjust the concentrations of all samples to remove the bias.

The final step is referred to as "outlier removal". Every sample is analyzed in triplicate, once in the first third of the analysis run, once in the middle third and once in the last third. In this step, the agreement of these is examined for each sample. In those cases in which one of the three is substantially different than the other two, it is removed. Whether a value has been removed or not, the mean and standard deviation are calculated for the sample either from the three values or from two if one has been removed. For those samples whose averaged concentration is less than the detection limit value calculated in the blank-subtraction step, the concentration is replaced by a "less than the detection limit value". Thus for all samples and all lines, both an average concentration and a standard deviation are calculated.

The laboratory normally reports the concentrations of an element not an isotope or an analysis line. In the case in which the element has been analyzed using only on one wavelength, this is what is reported. However, many elements have more than one wavelength which has been analyzed; in addition, many elements are also analyzed other techniques such as ICP-MS as well as on the ICP-OES. In these cases there is frequently one emission wavelength or atomic mass that is "preferred", either because it has the greatest sensitivity or because it has the least amount of interferences, and this line is what is reported. This cross check using two different analysis techniques greatly enhances the confidence in the final result, but the analyst must be aware of the limitations and strengths of each technique. In spite of these generalizations, the analyst has to determine which of the multiple values represents the best one to report, and since the qualities of the various data are not equal, they simply cannot be averaged. Thus, the analyst must use his/her experience and judgment to select the one he/she feels represents the "best" value to report, and because of the intricacies of the analyses, there is no hard or fast rules which can be applied.

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USGS Standard Analytical Methods and References Summary

Constituent	Publication	Method of analysis
Calcium, dissolved	ISO 14911 – 1 (1998[1])	Ion chromatography
Magnesium, dissolved	ISO 14911 – 1 (1998*)	Ion chromatography
Potassium, dissolved	ISO 14911 – 1 (1998*)	Ion chromatography
Ammonium, dissolved	ISO 14911 – 1 (1998*)	Ion chromatography
Sodium, dissolved	ISO 14911 – 1 (1998*)	Ion chromatography
Manganese, dissolved	ISO 14911 – 1 (1998*)	Ion chromatography
Alkalinity	USGS (1997 – 1999)	Incremental endpoint point titration
Chloride, dissolved	Fishman and Friedman (1989) ; Fishman (1993)	Ion chromatography
Sulfate, dissolved	Fishman and Friedman (1989) ; Fishman (1993)	Ion chromatography
Dissolved Organic Carbon	Brenton and Arnett (1993)	Wet-chemical oxidation, Nondispersive infrared detector
UV absorbance, 254 nm	Chin and others (1994)	UV absorbance, 254 nm
Deuterium	Coplen, Wildman, and Chen (1991)	Gaseous hydrogen equilibration
Oxygen-18	Epstein and Mayeda (1953)	Carbon dioxide-water equilibration

The employed ISO analytical procedures were performed for dissolved Na+, NH4+, K+, Mn2+, Ca2+, Mg2+ according to the current Polish standards issued by the Polish Committee for Standardization using ion chromatography method (ISO 14911-1:1998)

[UV, Ultraviolet; nm, nanometer; USGS, U.S. Geological Survey; ISO, International Organization for Standardization]

Appendices G: SGS Standard Analytical Methods and Instrument Detection Limits

SGS	SGS North America, Inc. - Alaska Division Standard Operating Procedure
NOTE: This document contains CONFIDENTIAL business information and is not intended for distribution.	
S.O.P. Title: Mercury in Water and Soil by Oxidation, Purge & Trap, and CVAFS	**Revision Date**: March 2020
Method No: EPA 1631E	**SOP No**: 354r13
Page: 1 of 18	**Supersedes**: 354r12

Signatures below reflect periodic review of Standard Operating Procedures. If the procedure is found adequate with little or no editing necessary, this page is signed and dated. An Addendum may be issued for minor changes that need to be implemented immediately. If it is determined that major edits are required, a new revision will be released with a new signature page.

Technical Director	Date	Quality Assurance (QA) Manager, QA Staff or their Designee	Date
Stephen C. Ede	4/1/20	Samara Bentz	4/1/2020

Original cover pages with wet signatures and the digitally signed electronic SOP versions are available in the Quality Assurance Office.

This document will be converted into a PDF file with the QA Manager's, QA Staff's or QA Designee's electronic signature and posted on the network: \\usfs700\ANK_GroupData\Public\DOCUMENT\SOP\~Approved_SOPs~

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Each staff member responsible for this SOP will print & sign this coverpage upon successful review, retaining it as a record in their training manual.

I have reviewed and understand the method reference(s) and this version of the SOP.
I agree to use only this currently approved version of the SOP.

Signature: _____ Printed Name: _____ Date: _____

Summary of Changes from Previous Revision:

- Removed section 7.9 describing commercially purchased Pressure Release Digestion Caps. These are not currently used for this method.
- Section 8.14 updated for clarification.
- Section 8.17 updated to 4 MB for each batch to match corrective action table
- Section 8.18 updated for clarification
- Section 8.19 updated for clarification
- Section 9.1.1 updated to reflect current practice.
- Updated Section 9.1.4
- Section 10.2 updated for clarification
- Sections 11.1, 11.2, 11.3, 11.4, 11.6, and 11.7 had minor updates for clarification
- Section 12.4 updated to clarify that the typical analytical sequence given is just an example, since it varies for each run
- Updated 12.4 to be consistent with 4 MB rule
- Added Section 12.6.1
- Section 17.1 updated to remove requirement for detection limit studies for new analysts
- Minor updates throughout

Table of Contents

1.0. OBJECTIVE:

This Standard Operating Procedure outlines the procedure for determination of trace level mercury (<100 ng/L) in aqueous and soil samples using EPA Method 1631E.

2.0. SCOPE AND APPLICATION:

2.1 EPA method 1631: Mercury in Water and Soils by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (CVAFS), is for determination of Hg within the range of 0.5 – 100 ng/L. Prior to analysis, all Hg is oxidized to Hg (II), reduced to destroy the free halogens, then reduced again to convert HG (II) to volatile Hg (0). The Hg (0) is separated from solution and collected onto a gold trap by purging with argon and is evolved off to a CVAFS cell where the fluorescence emission of Hg (253.7 nm) is determined. The resulting fluorescence (peak height) is directly proportional to the mercury concentration.

2.2 The ease of contaminating samples with mercury and interfering substances cannot be overemphasized. Extreme care must be taken when handling samples, reagent water, and reagents. This method should be performed by analysts experienced in CVAFS techniques and who are trained thoroughly in the sample handling and instrument techniques described in method 1631E.

3.0. DEVIATIONS FROM REFERENCE METHOD:

3.1 The EPA method for 1631E sets the LOQ at 0.5ng/L; however, SGS operates with a standard LOQ of 1.0 ng/L with a DL of 0.31ng/L for waters and a LOQ of 0.25µg/Kg with a DL of 0.08µg/Kg for soils. For client specific cases the LOQ is set at 5.0 ng/L for waters.

3.2 The EPA method requires a reagent blank to be prepared and analyzed whenever new reagents are made. However, a method blank containing all reagents is run with every prep batch, making a separate reagent blank unnecessary.

3.3 The EPA method requires a system blank to be <0.5 ng/L. However, since this method's LOQ was doubled, the system blank criteria is <1.0 ng/L (which is to say, less than the LOQ).

3.4 The EPA method requires a system blank mean result to be <0.50 ng/L with a standard deviation (n-1) of <0.1 ng/l. However, the software SGS uses does not show a concentration value for the system blank until the system is calibrated. Instead, the software uses blank subtraction of the peak heights to give a percent recovery of the lowest standard. The percent recovery range must be between 75-125%.

3.5 The EPA method states that stannous chloride used in this method should be 200 g of $SnCl_2 \cdot 2H_2O$ into 100mL of distilled HCl diluted to 1.0L with reagent water. Due to instrumentation used and its pump settings, the stannous chloride can be reduced to 40 g of $SnCl_2 \cdot 2H_2O$ into 100mL of non-distilled HCl diluted to 1.0 L with reagent water.

3.6 The EPA method states that the stannous chloride should be purged overnight with nitrogen. SGS purges the stannous chloride for an hour with argon. System blanks, method blanks, and DL studies run with stannous purged for an hour meet all QC standards.

3.7 The EPA method requires three method blanks. SGS is inserting an additional method blank after the first MS/MSD pair in order to meet the requirements of three method blanks per batch and adding a fourth method blank for batches of more than ten samples to provide bracketing QC for the first ten.

3.8 The EPA method only requires a CCV at the end of the batch. In order to provide bracketing QC for the first half of the batch, SGS has inserted a CCV after the first MS/MSD pair.

4.0. RESPONSIBILITIES:

4.1. The QA Office maintains a master list of this SOP to ensure review on a timely basis. This system serves as an accounting of SOP distribution and ensures that distributed SOPs are current and complete. The QA Office also maintains a historical file of original cover pages with wet signatures and digitally signed electronic versions of this SOP; including the current revision and any versions archived within the past 5 years.

4.2. The electronic (Word Document) versions of this SOP, both current and any prior versions, are maintained on the computer network in a secure location as a "read only" file.

4.3. It is the responsibility of all personnel to follow this SOP as written, document and gain QA or Technical Director approval for deviations to the SOP and submit needed SOP revisions to the QA Office.

4.4. This SOP is scheduled for review on an annual basis. Any addendum will be incorporated into the SOP and a new revision of the SOP will be distributed by QA. The superseded version will be archived by the QA Office. If there are no addenda to incorporate or updates to make, the SOP is reviewed and given a new revision number. The cover page is signed and dated by the Technical Director and QA then distributed.

4.5. A PDF version of each SOP (generated in Adobe or scanned) is digitally signed by a member of the QA Office as a security measure. The digitally signed PDF, used online, is considered to be a controlled copy of the SOP and is stored on the network.

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All staff have "read" access to these SOPs. Only QAQC has access to "write" on SOPs. Staff is directed to use the controlled electronic versions of SOPs.

5.0. INTERFERENCES:

5.1. Contamination Control – Sample contamination during sample preparation and analysis constitutes one of the greatest difficulties encountered in trace level mercury determination. It is critical that extreme care be taken to avoid contamination. There are two key factors in avoiding/ reducing sample contamination: first, be aware of potential sources of contamination and second, pay strict attention to the work being done.

5.1.1 Ensure that any object or substance that contacts the sample is metal and mercury free. Also, try to minimize the amount of metals you carry into the HgLL clean room (i.e. Keys), times you enter/leave the HgLL clean room, and how often you open and close the storage cabinet in the HgLL clean room. These situations should be especially avoided when you are actively running samples, because of the possibility of dust contamination.

5.1.2 Sample containers – Only fluoropolymer or glass containers with vapor tight lids must be used for sample collection because mercury vapors can diffuse in or out of other materials. Polyethylene and/or polypropylene lab ware may be used for digestion because the sample exposure time to these materials is relatively short.

5.1.3 Sample preparation:

5.1.3.1 Digestions should be performed in a non-metal fume hood equipped with HEPA filtration. The preparation area should be cleaned with a lint-free cloth or wipe soaked in reagent water prior to working in the area.

5.1.3.2 Samples and reagents should only be handled within the digestion area to prevent samples from becoming contaminated. While not being used, the samples and reagents should be capped tightly and stored in a fume hood or in a clean zip-type bag.

5.1.3.3 Care must be taken to prevent substances in samples from contaminating the work station and the instrumentation. Spill prevention should be the first priority, but if a spill does occur the work station should be cleaned before continuing to process additional samples in the area.

5.1.3.4 While processing samples, clean non-talc gloves should be worn during all operations involving handling of apparatus, samples, and blanks. If another substance is touched the gloves must be replaced before continuing.

5.1.4 Sample analysis:

5.1.4.1 Contamination from sample carryover can occur if a sample is processed directly after a sample that contains a relatively high concentration of Hg. If a sample is known or suspected to have a high concentration, a rinse should be put in the position following the high concentration sample on the auto sampler (this process should be repeated until the detection is below LOQ).

5.1.4.2 Significant laboratory or instrument contamination may result when an untreated effluent, in-process waters, landfill leachates, and other undiluted samples containing concentrations above 100 ng/L are processed and analyzed. Samples known or suspected to contain Hg above concentration should be diluted before bringing them into the HgLL clean room.

5.1.4.3 Contamination by indirect contact must be considered at all times. It is imperative that every piece of the apparatus that is directly or indirectly used in collection, processing, and analysis of water samples be thoroughly cleaned.

5.2 Interferences:

5.2.1 Gold and iodide are known interferences.

5.2.2 Fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause “quenching” of the excited atoms. Only pure argon or nitrogen should be used to limit possible interferences.

5.2.3 Water vapor may collect in the gold traps and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to the scattering of the excitation radiation. This condensation is avoided by the Perma Pure Dryer system in the instrument which removes moisture from the sample before it enters the detector.

5.2.4 The use of hydroxylamine hydrochloride to remove free halogens is not needed for solid sample digestates; there is a sufficient amount of $SnCl_2$ in the bubbler to reduce both Hg (II) and free halogens in digestate aliquots smaller than 5 mL.

6.0. SAMPLE HANDLING:

6.1. Aqueous samples must be collected in pre-cleaned fluoropolymer bottles with either fluoropolymer or fluoropolymer –lined caps. The EPA method allows the use of glass bottles if Hg is the only target analyte. Sample bottles must be tested by analyzing at a 5% frequency for each new box received to ensure that they are contaminate-free. **(Note: Bottles for DoD must be contaminate free <1/2 LOQ.)**

6.1.1. To prep sample bottles for contaminate testing, add 2.5 mL of pre-tested 1:1 12 N HCl to a bottle and fill it with reagent water (section 8.2). Add 2.5 mL of BrCl solution to the sample bottle and allow at least 24 hours at room temperature before analyzing. Sample bottles must be less than the LOQ to be considered contaminate free. If the bottles are above LOQ, do not use them and alert your supervisor.

6.1.2. Record the lot number for the sample bottles tested (the ESS lot number on the cleaning certificate, not the Nalgene© lot number), the HCl lot number used, and the date and analyst initials in the black Sample Bottle Tracking logbook.

6.2. To prepare sample bottles for field collection, add 2.5 mL of pre-tested 1:1 12 N HCl to a pre-cleaned 500 mL fluoropolymer bottle or add 1.25 ml of pre tested 1:1 12 N HCl to a pre-cleaned 250ml fluoropolymer bottle, tighten the lid, then secure it in two clean one-gallon polyethylene bags (zip close style Ziploc© bags) and place a blue HCl sticker on the inner bag. **(Note: Nothing is placed inside the polyethylene bags except the unlabeled, preserved sample bottles.)**

6.3. If a trip bank bottle is requested for a kit, prepare the bottle according to section 6.2, but fill the bottle with reagent water. The number of trip blanks requested is per client request but should be 1 per 10 samples.

6.4. For dissolved Hg, a sample is filtered through a 0.45 µm capsule filter (not 0.45 µm hand filters) in a mercury-free clean area prior to preservation. If the sample is filtered, it must be accompanied by a reagent water blank that has been filtered under the same conditions.

6.5. Samples may be shipped to the laboratory unpreserved and un-refrigerated if they are collected in the above containers. However, if a sample is not collected in the above container, they must be preserved within 48 hours of collection. If a sample is preserved, the sample holding time is 90 days. Samples must be sealed in the bags they are received in for all steps of processing and are stored in the HgLL room until analysis is posted. Note: exceptionally high samples should be removed from the room as soon as they are identified to avoid contaminating other samples.

6.6. After posting, hold samples in Low Level room until disposal by current SGS protocol.

6.7. For soil, samples are collected into acid-cleaned glass, polyethylene, or fluoropolymer jars. For all except very low level and high water content samples, polyethylene bags are also acceptable. Dry solids such as coal and ores may be collected and stored in heavy gauge paper pouches commonly used by geologists.

6.8 Sample shipment, storage, preservation, and holding times

6.8.1 Dry samples—Samples such as ores, coal, paper, and wood may be shipped unrefrigerated and stored indefinitely in a cool, dry location known to have an atmosphere that is low in mercury.

6.8.2 Wet sediment samples—Wet sediment samples are chilled and shipped to the laboratory at 0-6°C. Because freezing and thawing may adversely affect homogeneity by causing clumping and separation of the solids from the liquid, wet sediment samples must be aliquoted and weighed at

the laboratory and prior to freezing if they are not analyzed upon receipt. Wet sediment samples may be held for 1 year if aliquoted, weighed, and frozen at < -15°C. Sediment samples may be lyophilized and stored unrefrigerated for 1 year in a low-mercury atmosphere if only total Hg will be determined and no free elemental mercury (Hg0) is expected to be in the samples.

7.0. APPARATUS:

7.1. Instrument: PS Analytical Merlin System (or equivalent) mercury analyzer. This instrument is equipped with a high-intensity mercury lamp, a reference detector, a quartz cell, a 253.7 nm filter, and a transmission detector.

7.2. Pump: Two peristaltic pumps are incorporated in the PS Analytical Merlin Millennium System. It is capable of flow rate settings from 2-15 mL/min.

7.3. Tubing: Viton and Tygon tubing are used for sample injection, sample draining, and the reducing agent.

7.4. Drying system: Perma Pure Dryer System.

7.5. Auto sampler: An auto sampler is also incorporated in the PS Analytical Merlin Millennium System. It uses 50mL polyethylene digestion vessels and plastic sample trays.

7.6. Quality control vessels: 125mL graduated plastic digestion vessels purchased from Environmental Express (or equivalent). Results of MB's must be less than LOQ to be considered contaminant free. These vessels have an error of less than 2%.

7.7. Pipettes: Eppendorf 10-100µL, 100-1000µL, 500-5000µL (or equivalent).

7.8. Laminar flow fume hood with Class 100 clean work station and HEPA filtered air supply.

7.9. Digi Tube 50ml digestion tubes: 50ml vessels used for dilutions are purchased from SCP Science. A C# should be assigned when received and the certificate needs to be attached.

8.0. REAGENTS:

8.1 All chemicals, reagents, and standards must be traceable back to documented written records. The expiration dates of all reagents must be recorded and written on the container. Where applicable, this information must be entered into the LIMS system. Refer to SGS SOP #500 for proper documentation procedures.

8.2 Reagent water – 18 MΩ minimum, ultra pure deionized water starting from a pre-purified (distilled, reverse osmosis, etc.) source. Water should be monitored for Hg, especially after ion exchange beds are changed.

8.3 All glassware must be thoroughly rinsed with reagent water prior to use.

8.4 The Teflon 100 mL volumetric flask must be first rinsed with 1:1 nitric acid and then three more times with reagent water

8.5 Air – HEPA filtered source.

8.6 Reagent grade hydrochloric acid, concentrated

8.7 Reagent grade nitric acid, concentrated

8.8 Auto sampler wash solution –10% HCl solution.

8.9 Blank Solution – 2% v/v HNO_3, dilute 40 mL HNO_3 up to 2000 mL with reagent water.

8.10 Hydroxylamine Hydrochloride certified at 99.9% for mercury analysis– Dissolve 300 g of $NH_2OH \cdot HCl$ in reagent water and bring to 1.0 L. This solution may be purified by the addition of 1.0 mL of $SnCl_2$ solution and purging overnight at 500 mL/min with Hg free Argon (expires 12 months after preparation).

8.11 Stannous chloride ($SnCl_2$) – Dissolve 40 g of $SnCl_2$ into 100 mL of HCl. Bring solution up to 2.0 L with reagent water. Purge for one hour with Hg-free Argon at 500 mL/min to remove all traces of Hg. Make daily.

8.12 Bromine monochloride (BrCl) – In a fume hood, dissolve 27 g of reagent grade KBr in 2.5 L of HCl. Place a clean magnetic stir bar in the bottle and stir for approximately 1 hour in the fume hood. Slowly add 38 g of reagent grade $KBrO_3$ to the acid while stirring. When all of the $KBrO_3$ has been added, the solution color should change from yellow to red to orange. Loosely cap the bottle and allow it to stir another hour before tightening the lid (expires 12 months after preparation).

8.13 Stock Hg standard - 1000 mg/L Mercury commercially purchased. Stock Hg standard is stored outside the HgLL room in the mercury fume hood**.**

8.14 Calibration standard:

8.14.1 **Intermediate Hg standard 1 mg/L**: In a partially filled Teflon 100 mL volumetric flask, add 500 µL BrCl solution (8.12) and 100 µL of 1000 mg/L stock mercury standard (8.13) to a final volume of 100mL with reagent water. Store in a glass bottle for one year or until the NIST expiration date of the original stock, whichever is soonest.

8.14.2 **Working Hg standard 1.0 µg/L**: Working Hg standard is made new everyday. Using a partially filled Teflon 100 mL volumetric flask, add 500 µL BrCl solution and 100 µL of 1 mg/L Intermediate Hg standard (8.14.1) to a final volume of 100 mL with reagent water. Pour into 125 mL digestion container.

8.15 Argon: 99.99% pure is controlled with an internal regulator that can be set between .13 and .50 LPM.

8.16 For each calibration, 3 System Blanks (SB) must be processed. For the SB sample pour 100 mL reagent water (section 8.2) into a 100 mL digestion vessel. Preserve with 0.5 mL of BrCl solution, cap the vessel and homogenize.

8.17 For each batch 4 Method Blanks (MB) must be processed. For the MB sample pour 100 mL reagent water (section 8.2) into a digestion vessel. Add 500 µL of BrCl solution, cap the vessel and vortex. Allow at least 24 hours before analyzing.

8.18 An Initial Calibration Verification (ICV) and Continuing Calibration verification (CCV) must be processed. For the ICV/CCV pour 100 mL of reagent water (section 8.2) into a 100 mL digestion vessel. Add 1 mL of the working standard (section 8.14.2) and 0.5 mL BrCl solution, cap the vessel and homogenize.

8.19 A second source Quality Control Sample (QCS), (LCS in LIMS) must be processed. The QCS Spike is made the same as step (8.14) with a second source of 1000 mg/L Mercury standard. For the QCS, add 0.5

mL BrCl and 2.5 mL of the secondary working standard. Bring up to the final volume of 100 mL with reagent water (section 8.2) into a 100 mL digestion vessel. Cap the vessel and vortex.

9.0. EXTRACTION:

9.1. New sample preservation for water samples.

9.1.1. Before adding BrCl, sample pH must be verified to be pH <2 by the analyst. This is accomplished by using plastic capillary tubes and narrow range pH paper. For samples with pH >2, the PM will be notified, and a sample comment will be made in the HgLL prep book as well as in LIMS.

9.1.2. Samples are preserved by analyst in the Low Level Mercury Clean room by adding 2.5 mL of BrCl solution to each 500mL sample bottle or 1.25ml of BrCl solution to each 250ml sample bottle. **If the sample contains a high amount of organic matter, add additional aliquots of BrCl until a yellow color remains.** Note in log book amount of BrCl used to preserve each sample. Allow 24 hours at room temperature before analysis. Alternatively, pour 100 mL aliquot from a thoroughly shaken, acidified sample, into a 100 mL digestion vessel. Add 0.500 mL of BrCl solution, cap the digestion vessel, and allow a 12-hour minimum at room temperature before analysis.

9.1.2.1. Some highly organic matrices, such a sewage effluent, will require higher levels of BrCl. Add more BrCl to the sample, and allow longer oxidation times, and/or elevated temperatures (placing samples at 50°C for 6 hours). Complete oxidation can be determined by the next step 9.1.3. The sample may be diluted to reduce the amount of BrCl required, provided that the resulting level of mercury is sufficient for reliable determination.

9.1.3. An excess of BrCl should be confirmed visually for presence of a yellow color prior to sample processing or direct analysis to ensure the sample has been properly preserved.

9.1.4. Field blanks and Trip blanks are preserved along with the other samples. Method blanks should be prepared in the cleaned hood (Section 7.8) before samples are preserved.

9.2. Digestion of coal, ores, sediments, soils and other geological media.

9.2.1. Accurately weigh (to the nearest mg) an aliquot of the sample directly into a tared digestion vessel. For wet sediments and soils, weigh 0.5-1.5 grams; for dried materials such as coal, ores, and CRMs (Certified Reference Materials), weigh 0.5-1.0 gram. To better assure homogeneity, sediments and soils should be screened through a 2-mm plastic sieve to remove large rocks and sticks before digestion.

9.2.2. In a fume hood, add 8.0 mL of concentrated HCl, swirl, and add 2.0 mL of concentrated HNO_3 to the sample in the digestion vessel. Cap the vessel with a clean glass marble or inverted fluoropolymer cone. Allow to digest at room temperature for at least 4 hours but preferably overnight.

9.2.3. For coal or other elemental carbon-containing sample, dilute the digestate to the calibration mark (40 ± 0.5 mL) with the 0.07 N BrCl solution and shake the flask to mix thoroughly. The addition of BrCl ensures that Hg will not re-adsorb to the carbon particles, producing low recoveries. After dilution and shaking, allow the sample to settle overnight, or centrifuge prior to analysis. Be sure

that all fine-grained particles are completely settled prior to analysis. This settling can be hastened by centrifuging for 20 minutes at 3000 RPM or by filtering the sample through a 0.45µm filter.

9.2.4. For other than coal or elemental carbon-containing samples, dilute the digestate to volume (40 ± 0.5 mL) with reagent water so that the meniscus is at the calibration line in the neck of the digestion vessel. Shake vigorously and allow settling until the supernatant is clear prior to analysis.

9.2.5. The diluted digestates may be stored up to one year in glass or fluoropolymer containers prior to analysis, or for future re-analysis, if needed.

10.0. CALIBRATION:

10.1 Instrument operating conditions can be found in the low level mercury maintenance log.

10.2 The calibration must contain a minimum of 5 non-zero points and three system blanks, which are used for blank subtraction described in section 10.4 and 10.5. The amount of blank subtraction is determined by the instrument and is located in the calibration tab. The lowest calibration standard is at the minimum level (ML). For waters, calibration points are made by placing 70-80 mL of reagent water (8.2) into a 100 mL digestion vessel. The standards are then preserved with 0.5 mL of BrCl. Concentrations of the calibration standards are prepared by successive dilutions of a 1.0 µg/L Hg working standard (section 8.14.2). The solution in the vessel is then brought up to the 100 ml mark. A summary of the standard preparation volumes is given in the table below.

For Waters

Std ID	Final Conc(ng/L)	Source	Initial vol (mL)	Final Vol (mL)
CB/MB	<LOQ	Sec 8.2	0	100
Std 1	1	Sec 8.14.2	0.1	100
Std 2	5	Sec 8.14.2	0.5	100
Std 3	25	Sec 8.14.2	2.5	100
Std 4	50	Sec 8.14.2	5	100
Std 5	100	Sec 8.14.2	10	100
QCS	25	Sec 8.19	2.5	100
ICV/CCV	10	Sec 8.14.2	1	100
MS/MSD	25	Sec 8.14.2	2.5	100

For soils, calibration points are made by placing 5 mL of HCl into a 50mL digestion vessel, then adding 1.25mL of HNO_3. The vessel is then filled to approximately the 30 mL mark with reagent water (Sec 8.2). The vessels are then spiked according to the following table. The samples are brought up to 50 mL with reagent water and analyzed.

For Soils

Std ID	Final conc (ng/L)	Source	Initial vol (mL)	Final Vol (ml)
CB/MB	<LOQ	Sec 8.2	0	50
Std 1	5	Sec 8.14.2	.25	50
Std2	10	Sec 8.14.2	.5	50
Std3	25	Sec 8.14.2	1.25	50
Std4	50	Sec 8.14.2	2.5	50
Std5	100	Sec 8.14.2	5	50
QCS	25	Sec 8.19	1.25	50
ICV/CCV	10	Sec 8.14.2	1	50
MS/MSD	25	Sec 8.14.2	1.25	50

10.3 Immediately prior to analysis of the standards, the excess BrCl is reduced with 0.250mL of NH_2OH solution (section 8.10). Prepare and analyze a minimum of 3 system blanks prior to analyzing the standards; begin with the lowest concentration and proceed to the highest.

10.4 Tabulate the peak heights. Calculate the mean peak height for the system blanks.

10.5 For each calibration point, subtract the mean peak height of the system blanks from the peak height for each standard. Calculate the calibration factor (CF_x) for Hg in each of the five standards using the mean reagent-blank-subtracted peak height and the following equation:

$$CF_X = ((A_X) - (A_{SB}))/ (C_X) \qquad \text{EQUATION 1}$$

Where:

A_X = Peak height for Hg in standard
A_{SB} = Mean peak height for Hg in calibration blanks
C_X = Concentration of standard analyzed (ng/L)

10.6 Calculate the mean calibration factor (CF_M), the standard deviation of the calibration factor (SD; n-1), and the relative standard deviation (RSD) of the calibration factor, where RSD = 100 x SD/CF_M

10.7 If the RSD $\leq$ 15%, calculate the recovery for the lowest standard (1.0 ng/L) using CF_M. If the RSD $\leq$ 15% and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable, and CF_M may be used to calculate the concentration of Hg in samples, blanks, and standards. If RSD > 15% or if the recovery of the lowest standard is not in the range of 75-125%, recalibrate the analytical system and repeat the test.

10.8 Calculate the concentration of Hg in the system blanks using CF_M. The system blanks must meet the criteria in section; otherwise, mercury in the system must be reduced and the calibration repeated until the system blanks meet the criteria.

10.9 Calculation of solid phase concentrations.

10.9.1 The analytical system in Method 1631E will give analytical results in units of area (or height) for the volume of diluted digestate analyzed. To calculate the solid phase concentration, use the following equation:

$$C_{Hg} = (A_s - A_{BB}) \times V \times d \times 0.1 / (CF_m \times v \times w) \qquad \text{EQUATION 2}$$

where:

C_{Hg} = concentration of mercury in the sample (ng/g wet weight)
A_s = peak area (or height) for mercury in the sample
A_{BB} = peak area (or height) for the average of the bubbler blanks
V = volume of diluted digestate (mL)
d = dilution factor(s); e.g., a factor of 100 in
0.1 = volume in bubbler (L)
CF_m = mean CF from calibration (area (or height))/(ng/L)
v = digestate volume analyzed (mL)
w = sample weight (g)

11.0. ANALYSIS:

11.1 Power up the instrument, the auto sampler, and the computer and allow warming for at least half an hour to obtain stability.

11.2 Place the $SnCl_2$ line into the $SnCl_2$ solution (section 8.11).

11.3 Place the Blank solution line into the blank solution (2% HNO_3) (section 8.9). Check level before beginning and refill if needed.

11.4 Check the level of the auto sampler wash solution (10% HCl) (section 8.8) before beginning and refill if needed.

11.5 Connect the windings and tighten down the cassettes onto the peristaltic pumps.

11.6 Turn on the pumps by going to the analysis tab in the software and clicking the "On" toggle. Check the flow of the sample, $SnCl_2$, and blank lines to ensure proper flow to the instrument. If the flow is not appropriate, adjust tightness on cassettes or replace the winding.

11.7 Place three 50 mL digestion vessels filled with system blanks in the first three positions on the auto sampler (11-13). Load the default calibration. Initiate the rinse sequence by selecting Type: "Sample" and Name: "Rinse." Click the green arrow symbol in the software and save the file as 'HGLL mmddyy **R**.' Be sure to pay close attention to the location samples in auto sampler. Save the sequence, close Millennium, re-open Millennium.

11.8 Create a sequence table by clicking on the calibration icon. Reselect 'Method 1631' and enter the number of blanks being used into the pop-up (3). The software should populate the page with the correct sequence and auto sampler positions (11+). If they are incorrect, correct them before pressing 'OK.'

11.9 Place the reduced system blanks and the calibration into the auto sampler. Initiate the analysis sequence by hitting the green arrow symbol in the software. Name your results file 'HGLL mmddyy.'

11.10 Under the column "Name," type the sample ID. After the calibration has run and passed, you may analyze the entry QC samples followed by paying samples. Samples must be inverted several times to ensure homogeneity.

11.11 For water samples, the initial volume is 50mL which is poured into a 50mL digestion vessel. Then add 0.125ml of NH_2OH into each vessel to neutralize the BrCl (the amount of NH_2OH solution required will be approximately 30 % of the BrCl volume). If extra BrCl has been added to a sample, be sure to add additional aliquots of NH_2OH. Cap and homogenize the sample. The yellow color will disappear, indicating the destruction of the BrCl. Allow the sample to react for 5 minutes with periodic swirling to be sure that no traces of halogens remain. The final volume of the sample is 50mL.

11.12 For every 10 samples a Matrix Spike/ Matrix Spike Duplicate (MS/MSD) must be processed. Pour 100mL from a selected sample. Spike the sample by adding 2.5 mL of working standard (section 8.13.2) into the acidified sample. Process the MS/MSD in the same manner as the original sample. There must be a minimum of 2 MS/MSD pairs for each analytical batch of 20 samples.

11.13 Carryover may occur after analysis of a sample containing a high level of mercury. A rinse of reagent water should be run after samples containing high levels of mercury until the blank result is less than the LOQ.

11.14 If dilution is required, Class A 50ml vials should be used.

12.0. QUALITY CONTROL:

12.1 If this method is to be used, a formal quality assurance program is required. The minimum requirements of this program consist of an initial demonstration of capability, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of two Matrix Spikes (MS) and Matrix Spike Duplicates (MSD) to assess precision and recovery.

12.2 Instrument calibration validation and calibration verification.

12.2.1 Quality Control Sample (QCS) will be analyzed after the calibration. The QCS serves as a Laboratory Control Sample (LCS) also. This standard must be from a source different than the calibration standards. The acceptance range is 77%-123%. For recoveries outside this range, repeat the analysis once. If recovery is still out, recalibration and possibly re-digestion is required.

12.2.2 An Initial Calibration Verification (ICV) standard will be analyzed after the QCS. The ICV standard is also subsequently analyzed after every 10 samples (See section 12.4 for set-up). Recovery must be 77%-123% of the true value

12.3 Preparation and recovery validation.

12.3.1 A Method Blank (MB) will be prepared with each set of samples. Number of MBs is determined by the number of samples in the batch. The acceptance criterion is less than the LOQ. If the measured sample concentration is greater than 10 times the method blank contamination or less than the LOQ, the sample will not require redigestion, but the data must be flagged with a 'B' in LIMS.

12.3.2 A Matrix Spike (MS) and Matrix Spike Duplicate (MSD) will be prepared with each digest batch of 10 samples. The acceptance range is 71%-125%, RPD must be less than or equal to 24. If outside of acceptance criteria reanalyze once. If QCS is within control limits, mark as possible matrix interference. If RPD is outside acceptance criteria, recalibrate and redigest sample.

12.4 Quality of the analyses is controlled by an analytical batch. An analytical batch is a set of samples oxidized with the same batch of reagents and analyzed during the same 12-hour shift. A batch may be from 1 to 20 paying samples. Each batch must be accompanied by 3 system blanks, 1 CCV sample at the beginning and end of the batch, a QCS sample, at least 4 method blanks, and 1 set of MS/MSD at a frequency of 10%. A typical analytical sequence might appear as follows:

A) Three system blanks
B) A minimum of five, non-zero calibration standards
C) Quality control sample (LCS in LIMS)
D) On-going precision and recovery standards (ICV)
E) Method blank
F) Seven samples
G) Method blank
H) Three samples
I) Matrix spike
J) Matrix spike duplicate
K) Method Blank

L) CCV
M) Four Samples
N) Method blank
O) Six samples
P) Matrix spike
Q) Matrix spike duplicate
R) Ongoing precision and recovery standards (CCV)

The above sequence includes calibration and is an example of a typical sequence. Specifics of sample order will vary depending on analyst's judgement, number of samples and sample needs. If system performance is verified at the end of the sequence using the CCV, analysis of samples and blanks may proceed starting at line D, unless more than 12 hours has elapsed since verification of system performance. If more than 12 hours has elapsed, the sequence would be initiated at step C above.

12.5 Trip blanks are used to demonstrate that samples have not been contaminated by the sample collection or transport activities. These should be analyzed immediately before analyzing the samples in the batch (after step E above) to confirm that they are below LOQ. If the Hg concentration is above LOQ, the results for associated samples may not be reported or otherwise used for regulatory compliance purposes or DoD. However, it is up to each individual client as to whether they accept the results or not.

12.6 Any corrective action(s) needed to address a QC outlier or other technical challenges that are not listed in this SOP require the prior approval of the Technical Director or QA Manager.

12.6.1 Reference Attachment A: Corrective Action Table

13.0. CALCULATIONS, REVIEW AND REPORTING:

13.1 ICV/CCV/QCS Recovery: The recoveries for standard solution (both digested standards and the periodic quality control standards) are calculated by dividing the observed value by the expected value. The result is multiplied by 100 to give a percent recovery.

$$\frac{Vo}{Ve} \times 100 = \% \text{ recovery} \qquad \text{EQUATION 3}$$

Vo = observed value
Ve = expected value

13.2 MS/MSD Spike Recovery: The calculation for spike recoveries requires the subtraction of the sample contribution from the response of the spiked sample, and then the division of this result by the expected value of the spike. The result is multiplied by 100 to yield a percent recovery.

$$\frac{Vo - Sc}{Ve} \times 100 = \% \text{ recovery} \qquad \text{EQUATION 4}$$

Vo = observed value of the spiked sample
Ve = expected value for the spike
Sc = observed value of the sample

13.3 MS/MSD Relative Percent Difference (RPD): The relative percent difference between duplicate samples is calculated as the absolute difference between the sample and the duplicate and then divided by the average of the sample and the duplicate. The result is multiplied by 100.

$$\frac{|Sc - Dc|}{\{(Sc + Dc) / 2\}} \times 100 = \text{Duplicate Relative Percent Difference} \qquad \text{EQUATION 5}$$

Sc = observed sample spike concentration
Dc = observed sample spike duplicate concentration

13.4 When posting the prep batch data in LIMS, the posted sequence must exactly match the actual analytical run sequence. This is imperative for establishing the correct QC dependencies needed for accurate reporting.

13.5 Data from the instrument is stored on the computer hard drive and needs to be archived each month. The data is moved from C:\Program Files\P S Analytical to \\Usfs700\ank_instrument_data\MERCURY\DATA in the folder corresponding to the current year. Rename the file AA followed by the date (AALLMMDDYY) update the archive logbook.

14.0. HEALTH AND SAFETY:

14.1. Samples shall be returned to the approved storage location until such time as it is determined that no further analysis will be required.

14.2. Once it has been established that no more analysis of a sample will be required, acid and alkaline preserved samples may be neutralized using the Elementary Neutralization Hood located in GC Prep, unless it is hazardous (i.e. mercury waste, cyanide waste). Refer to the current version of SOP 108 for further instruction.

14.3. All surplus reagent acids shall be neutralized on a daily basis using the Elementary Neutralization Hood located in GC Prep.

14.4. Small volumes of surplus volatile reagents may be allowed to evaporate in a hood at the end of the analytical session.

14.5. Proper Personal Protective Equipment (PPE) must be worn at all times. Proper PPE when handling samples include a lab coat, gloves and safety glasses. In addition, when handling concentrated acid or base preservative a face shield and apron must be worn.

15.0. POLLUTION PREVENTION:

SGS is committed to evaluate all areas of the lab with regard to current and potential pollution prevention. Pollution prevention is described as any technique that reduces or eliminates waste at the point of generation. Further discussion on pollution prevention programs in the laboratory can be found in *SGS Pollution Prevention Plan* (Form F053).

16.0. METHOD PERFORMANCE:

There are no method performance measures to report at this time.

17.0. DETECTION LIMIT (DL) STUDY:

17.1 Detection Limit (DL) studies are performed annually at a minimum, when a significant change in instrument response is observed or when a new instrument is purchased for an analysis. The DL is intended to demonstrate the capability of this method as it is implemented at SGS.

17.2 The statistical DL must be less than or equal to the maximum DL of 0.31 ng/L for waters and 0.08 µg/Kg for soils. An update to the DL does not necessitate an update to this document.

17.3 The suggested DL spiking level is 0.5 ng/L for waters and 0.125 µg/Kg for soil. The maximum DL is 0.078 ug/Kg.

18.0. LIMIT OF DETECTION (LOD):

The LOD is set as 2x the established maximum DL.

19.0. LIMIT OF QUANTITATION (LOQ):

The Limit of Quantitation (LOQ) for mercury in water is currently 1.0 ng/L for waters and 0.25 µg/Kg for soils. This value may change under certain sample conditions (e.g., presence of matrix interferences, sample dilution).

20.0. REFERENCES:

EPA method 1631 (Revision E) Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (August 2002).

Appendix to EPA method 1631 (Revision B) Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (January 2001). Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation.

21.0. ATTACHMENTS:

ATTACHMENT A: Corrective Action Table

ATTACHMENT A: Corrective Action Table

System Blank (SB)	3 at beginning of run.	< 1.0 ng/L	1. Reanalyze once 2. Recalibrate 3. Reanalyze associated samples that are > LOQ and < 10x the CB contamination
Second Source Check (QCS) (LCS in LIMS)	1 per 20 samples or less (25 ng/L).	Recovery 77-123%	1. Reanalyze once 2. Recalibrate, and reanalyze 3. If still outside limits, reprep entire batch
Initial Calibration Verification (ICV)	At beginning of analysis (10 ng/L).	Recovery 77-123%	1. Reanalyze once 2. Recalibrate
Method Blank (MB)	4 method blanks per batch.	< 1.0 ng/L For DoD <0.5 ng/L	1. Reanalyze once 2. Recalibrate 3. Reanalyze associated samples that are > LOQ and < 10x the CB contamination
Matrix Spike /Matrix Spike Duplicate (MS/MSD)	1 per 10 samples (25 ng/L).	Recovery 71-125% RPD ≤ 24%	1. Reanalyze once 2. Check QCS recovery 3. If QCS is in control, note in QC summary as possible matrix interference 4. If RPD out, re-digest and reanalyze 5. If still outside control limits, flag sample as non-homogenous
Continuing Calibration Verification (CCV)	After the first MS/MSD pair and at end of analysis (10 ng/L).	Recovery 77-123 %	NON DOD 1. Reanalyze once, if passing rerun the above samples so all have bracketing passing CCV'S. The run can be continued. 2. Failure, Recalibrate DOD 1. Rerun CCV twice if both are passing continue. Samples above CCV's may still be posted. 2. Failure, Recalibrate

SGS	SGS North America, Inc. - Alaska Division Standard Operating Procedure
NOTE: This document contains CONFIDENTIAL business information and is not intended for distribution.	
S.O.P. Title: Determination of Inorganic Anions by Ion Chromatography	**Revision Date**: February 2020
Method No: EPA 300.0; SW 9056A; SW 5050	**SOP No**: 318r26
Page: 1 of 27	**Supersedes:** 318r25

Signatures below reflect periodic review of Standard Operating Procedures. If the procedure is found adequate with little or no editing necessary, this page is signed and dated. An Addendum may be issued for minor changes that need to be implemented immediately. If it is determined that major edits are required, a new revision will be released with a new signature page.

Technical Director	Date	Quality Assurance (QA) Manager, QA Staff or their Designee	Date
Stephen C. Ede	2/21/20	Samara Pentz	2/21/2020

Original cover pages with wet signatures and the digitally signed electronic SOP versions are available in the Quality Assurance Office.

This document will be converted into a PDF file with the QA Manager's, QA Staff's or QA Designee's electronic signature and posted on the network: \\usfs700\ANK_GroupData\Public\DOCUMENT\SOP\~Approved_SOPs~

This electronically signed PDF will be considered the controlled copy for staff. Any printouts or photocopies are invalid.

Each staff member responsible for this SOP will print & sign this cover page upon successful review, retaining it as a record in their training folder.

I have reviewed and understand the method reference(s) and this version of the SOP.
I agree to use only this currently approved version of the SOP.

Signature: _____ Printed Name: _____ Date: _____

Summary of Changes from Previous Revision:

- Removed section 3.4. (EP300, MB evaluated at the LOQ instead of DL.)
- Edited section 10.6. Linear Calibration Range
- Removed section 13.7. Linear Dynamic Range
- Changed 13.8 to 13.7 and 13.9 to 13.8.
- Removed section 14.3 Archiving. Data files are exported to the network before posting.
- Addenda 1, 2, and 3 are incorporated in this revision.

Table of Contents

1.0. OBJECTIVE:

This document outlines a procedure for analyzing samples for anion concentration by ion chromatography.

2.0. SCOPE AND APPLICATION:

2.1. The matrices applicable to this method/SOP are drinking water, surface water, mixed domestic and industrial wastewaters, ground water, reagent waters, solids (after water extraction), and leachates (e.g., landfill). Note: TCLP leachates cannot be analyzed by this technique.

2.2. Total halogens as chloride can be analyzed by following SW846 Method 5050, and this SOP after the samples are combusted in a Parr bomb calorimeter. (See ASTM D 808-95 for combustion protocols.) Refer to SGS SOP#352 for calorimeter procedure.

2.3. Total sulfur can be analyzed by following SW 846 Method 5050 and this SOP after the samples are combusted in a Parr bomb calorimeter. (See ASTM D 808-95 for combustion protocols.) Refer to SGS SOP#352 for calorimeter procedure.

2.4. A small volume of sample, 20 µL, is introduced into an ion chromatography column. The anions of interest are separated and measured, using a system comprised of a guard disk, analytical column, suppressor device, and conductivity detector.

3.0. DEVIATIONS FROM REFERENCE METHOD:

3.1. Standard viability as referenced in Method 300.1 has been extended to this method/SOP; whereas 300.0 and 9056 indicate 1 month for standards prepared from neat stock. SGS uses multi-anion standard solutions of 1000 mg/L F, Cl, Br, NO3-N, PO4-P and SO4, and allows for a 6 month stock standard viability for them. Working solutions are prepared daily by addition of NO_2-N. The nitrite standards are replaced monthly.

3.2. Method 300.0 requires that duplicate LCS samples be run quarterly. Our normal sample load and batch size meet criteria. If circumstances develop where that is not true, duplicate LCS analysis will be documented for the three month period.

3.3. Method 300.0 requires that all samples analyzed for total nitrate/nitrite with concentration greater than 0.5 mg/L be re-sampled and reanalyzed for Nitrate and Nitrite separately. *Deviation: The laboratory does not require that samples be reanalyzed if the concentration for total nitrate/nitrite is greater than 0.5 mg/L.*

3.4. Method SW9056A states that an ICV/CCV solution should be made from a second source external standard. Deviation: The ICV/CCV solutions are made from the primary source standard. The QCS is made from a second source and is analyzed on a daily basis.

3.5. This method deviates from SW 5050 section 8.4. MS and LCS recoveries are ±30%.

3.6. This SOP deviates from method 300.0 defining residual error as "read back" (section 10). EPA Method Update Rule 2012 understands this method will not have a linear calibration. We adopt the practice from Standard Methods (22nd edition) of checking each calibration point and apply ±50% criteria for the low point and ±10% for all other calibration points.

4.0. RESPONSIBILITIES:

4.1. The QA Office maintains a master list of this SOP to ensure review on a timely basis. This system serves as an accounting of SOP distribution and ensures that distributed SOPs are current and complete. The QA Office also maintains a historical file of original cover pages with wet signatures and digitally signed electronic versions of this SOP; including the current revision and any versions archived within the past 5 years.

4.2. The electronic (Word Document) versions of this SOP, both current and any prior versions, are maintained on the computer network in a secure location as a "read only" file.

4.3. It is the responsibility of all personnel to follow this SOP as written, document and gain QA or Technical Director approval for deviations to the SOP and submit needed SOP revisions to the QA Office.

4.4. This SOP is scheduled for review on an annual basis. Any addendum will be incorporated into the SOP and a new revision of the SOP will be distributed by QA. The superseded version will be returned to the QA Office. If there are no addenda to incorporate or updates to make, the SOP is reviewed and given a new revision number. The cover page is signed and dated by the Technical Director and QA then distributed.

4.5. A PDF version of each SOP (generated in Adobe or scanned) is digitally signed by a member of the QA Office as a security measure. The digitally signed PDF, used online, is considered to be a controlled copy of the SOP and is stored on the network.
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4.6. All staff have "read" access to these SOPs. Only QAQC has access to "write" on SOPs. Staff is directed to use the controlled electronic versions of SOPs.

5.0. INTERFERENCES:

5.1. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion(s) of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

5.2. The water dip or negative peak that elutes near the fluoride peak can usually be eliminated by the addition of the equivalent of 1mL of concentrated eluent (see section 8.2) to 100 mL of each standard and sample. If the water dip is interfering, replacement of the analytical column may be necessary.

5.3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

5.4. Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems. Currently, every injection into the system is filtered through a 0.2 µm membrane filter by the 858 Autosampler.

5.5. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Carbonate and other small organic anions cause known coelution. At concentrations of fluoride above l.5 mg/L, this interference may not be significant. It is the responsibility of the analyst to accurately generate and interpret information in each sample matrix.

5.6. The quantitation of unretained peaks should be avoided. Low molecular weight organic acids (formate, acetate, propionate, etc.) are conductive, coelute with or near fluoride, and will bias the fluoride result in

some drinking and most waste waters. In addition, this method is not recommended for leachates of solid samples (i.e. TCLP extracts) where acetic acid has been used for pH adjustment.

5.7. In the case of an interrupted injection, analytes that have not yet eluted may interfere with an immediately following injection.

6.0. SAMPLE HANDLING:

6.1. Sample Matrix – The matrices applicable to this method/SOP are drinking water, surface water, mixed domestic and industrial wastewaters, ground water, reagent waters, oils, solids (after water extraction), and leachates.

6.2. Sample Collection and Size – Water samples are typically taken and stored in either 60-250 mL HDPE bottles. Documentation of the date and time of collection is important for those analytes that have short hold times.

6.3. Sample Preservation: Samples requiring analysis for Nitrite-N, Nitrate-N, o-Phosphate, and Sulfate need to be cooled to 0-6°C. Those to be analyzed for Bromide, Chloride, and Fluoride do not require refrigeration.

6.4. Holding Times:

6.4.1. For aqueous samples: -Bromide, Chloride, Fluoride, Sulfate 28 days
-Nitrite-N, Nitrate-N, o-Phosphate 48 hours

6.4.2. For soil samples: Soil samples should have the extraction and analysis completed within the 28 day hold time, starting from collection date and time. Following the extraction process described in Section 9, the extract must be analyzed with a 48 hour window for nitrate, nitrite, and o-phosphate; all other analytes are to be analyzed with the 28 day hold time.

6.5. Criterion for Acceptance/Rejection of Samples: No sample will be run on the IC that contains a preservative (e.g. H_2SO_4) or one that may severely damage the instrument and/or column. Samples preserved for Total Nitrate+Nitrite should be scheduled for analysis by Flow Injection.

7.0. APPARATUS:

7.1. Ion Chromatograph: Metrohm Modular Ion Chromatography system (or equivalent) comprised of the following:

7.1.1. IC Detector.

7.1.2. MSM 3 channel suppressor unit, supplied with regenerate by a 2mL Dosino unit and clean water post analysis from the detector

7.1.3. Sample processor capable of intelligent dilution with a 2mL sample Dosino and 10mL dilution Dosino. DI water is drawn from a water vessel.

7.1.4. IC Pump. This pump is able to deliver 0.7 mL of eluent per minute at a pressure between 5.0 and 15.0 MPa. The minimum pressure is set at 1.0 MPa and the maximum pressure is set at 12.0 MPa.

7.1.5. IC Separation Center. This includes an injection valve, a 20 µL sample loop, guard column, separator column (Metrosep A Supp 5), suppressor, temperature-controlled (or temperature compensated) small-volume conductivity cell.

7.1.6. Computer

7.1.7. Column: Metrosep A Supp 5 - 100 mm x 4.0 mm, or 150 mm x 4.0 mm, or equivalent

7.1.8. Metrohm MagIC Net Chromatography Software

7.2. Volumetric flasks of various volumes

7.3. Autopipettors and appropriate tips

7.4. Disposable 10 mL syringes

7.5. 0.45 µm syringe filters

7.6. Sample vials and caps

7.7. Analytical Balance with ±0.1 mg sensitivity to weigh salts for stock standards.

7.8. Analytical Balance with ±10 mg sensitivity to weigh reagents to prepare eluent.

7.9. Conductivity meter.

7.10. Graduated Environmental Express Digestion Vessels with a certified tolerance of ± 0.2 mL.

8.0. REAGENTS:

8.1. Reagent water: Deionized (DI) water directly off the filter line, free of the anions of interest. The DI water should contain particles no larger than 0.20 microns.

8.2. Working Eluent: Using "snips" of concentrated eluent purchased from vendor, add 1 snip per 1L of eluent to be made to volumetric flask and dilute to volume with degassed DI water. Pour eluent slowly from volumetric flask into instrument eluent container to avoid dissolving gasses as this can cause instrumentation issues. Eluent should be made daily.

8.3. If no eluent snips are available, eluent may be prepared using the following steps:

8.3.1. Eluent Concentrate: 3.2mM sodium carbonate and 1.0mM sodium bicarbonate. Let DI water sit in DI container at least overnight to degas before making eluent. Dissolve 33.9163 g sodium carbonate and 8.4022 g sodium bicarbonate in water and bring to a volume of 1 L. Each new lot of concentrate should be checked with a CCV before using for analysis. Eluent concentrate expires 1 year from date made or at the expiration date of either stock standard, whichever is sooner.

8.3.2. Working eluent from concentrate: Add 10 mL of concentrate to 1 L of degassed DI water.

8.4. Regeneration Solution (suppressor): Dilute 5.56 mL of concentrated sulfuric acid to 1 liter with DI water.

8.5. Primary source standard: multi-anion solution of 1000 mg/L F, Cl, Br, NO_3-N, PO_4-P and SO_4 and solution of 1000 mg/L NO_2-N. Purchased commercially prepared from AccuStandard or equivalent.

8.6. Secondary source standard: multi-anion solution of 1000 mg/L F, Cl, Br, NO_3-N, PO_4-P and SO_4 and solution of 1000 mg/L NO_2-N. Purchased commercially prepared from SPEXCertiprep or equivalent.

8.7. Stability of standards: Multi-anion stock standards are stable for at least six months when stored at 0-6°C. The primary and secondary multi-anion stock standard will be replaced six months after open date or manufacturer's expiration date. As NO_2-N is less stable and will oxidize to NO_3 over time, the primary and secondary Nitrite-N stock source standards should be ordered separately and replaced on a monthly basis. The primary stock standards are evaluated daily against the second source to verify continued validity up to the manufacturer's expiration date. Working standards containing nitrite are prepared daily.

8.8. If analyte degradation or contamination is noticed in any standard prior to its assigned date of expiration, it must be replaced immediately.

**NOTE: Pay special attention, when ordering calibration and QC standards, to the units used by the manufacturer. Some standard suppliers express the concentration of nitrate as nitrate-nitrogen and others as simply nitrate. The same is true for nitrite/nitrite-nitrogen. See sections 8.4 and 8.5 for appropriate concentrations.*

8.9. Quality Control Samples: See section 13 for acceptance criteria.

8.9.1. Primary working standard 100mg/L: Dilute 1.0mL of each of the primary stock standards (8.5.) to 10.0 mL with DI water.

8.9.2. Initial and Continuing Calibration Verification (CCV): Dilute 2.0mL of each of the primary stock standards (8.5.) to 200.0mL with DI water in a volumetric flask. This will give a final concentration of 10 mg/L. Place the solution in the bottle in position 150 on the sampler rack.

8.9.3. 2nd source working standard 150mg/L: Dilute 1.5mL of each of the 2nd source stock standards (8.6.) to 10.0 mL with DI water.

8.9.4. The QCS is prepared by diluting 1.0mL of the working secondary source standard (8.9.3) to 10mL with DI water. This will give a final concentration of 15mg/L.

8.9.5. Method Blank (MB) Aqueous: This is an extraction blank that follows all of the steps used in the extraction batch preparation process including filtration through a 0.45 µm filter *if the samples require filtration.*

8.9.6. Laboratory Control Sample 5.0mg/L (LCS) Aqueous: Add 0.5 mL of primary working standards (8.9.1.) to 9.5 mL of DI Water.

8.9.7. Matrix Spike & Matrix Spike Duplicate (MS/MSD) Aqueous: This is prepared by diluting 0.5mL of 100ppm working standard (8.9.1) into 9.5mL of sample.

8.9.8. Method Blank (MB) Solid: This is an extraction blank that follows all of the steps used in the extraction batch preparation process including filtration through a 0.45 µm filter. This is prepared by adding 4.0-4.2 g of pre-rinsed Teflon chips to a 50 mL digestion vessel (7.10.) and following the extraction procedure in section 9.4.

8.9.9. Laboratory Control Sample (LCS) Solid: 50mg/Kg: This is prepared by spiking 4.0–4.2 g of pre-rinsed Teflon chips for soils with 2.0mL of primary working standard (8.9.1) and following the extraction procedure in section 9.4.

8.9.10. Matrix Spike & Matrix Spike Duplicate (MS/MSD) Soil: This is prepared by spiking 4.0–4.2 g of sample with 2.0mL of primary working standard (8.9.1) and following the extraction procedure in section 9.4

8.9.11. MB, LCS, MS/MSD Oil – Total Halogen as Chloride: See SOP#352 for extraction procedure. All bomb batch QC and samples are run on the IC at a 2X dilution.

8.9.12. Calibration Blank (CB): DI water placed in the bottle in position 149 on sampler rack.

8.10. Working Standards and Reagents are made on a daily basis and do not need a logbook entry.

9.0. EXTRACTION:

Total Halogens

9.1. Extraction should be used for solid materials and for oil where the level of analyte resulting from leaching is desired. The extraction of solid waste, oil, and fuel for analysis of Total Halogens as chloride will be performed on the Parr Bomb Calorimeter, via methods D808/SW5050, and SW846/5050 (See ASTM D 808-95 for combustion protocols) per SGS SOP#352. Extracted samples and QC are analyzed at a 2X dilution.

Soil Extractions

9.2. Label plastic digestion vessels (section 7.10) with work order and sample number.

9.3. Weigh out 4.0-4.2 g of a representative portion of the homogenized sample directly into a tared digestion vessel. Record the actual weight in the extraction logbook. Refer to SOP#143 for correct weighing procedure.

9.4. Add 40 mL of DI water to each weighed sample and mix for ten minutes. Filter the resulting slurry with a 0.45 µm membrane filter before loading onto the autosampler. The slurry may be centrifuged at 2200 rpm for 12 minutes before filtration to assist in filtration. If different weights are used, maintain a water to sample ratio of 1 to 10 for solid materials.

9.5. Batch QC for the solid batch (MB, LCS, MS, MSD) must be included with each extraction batch. See section 8.9 for preparation instructions and section 13 for acceptance criteria.

10.0. CALIBRATION:

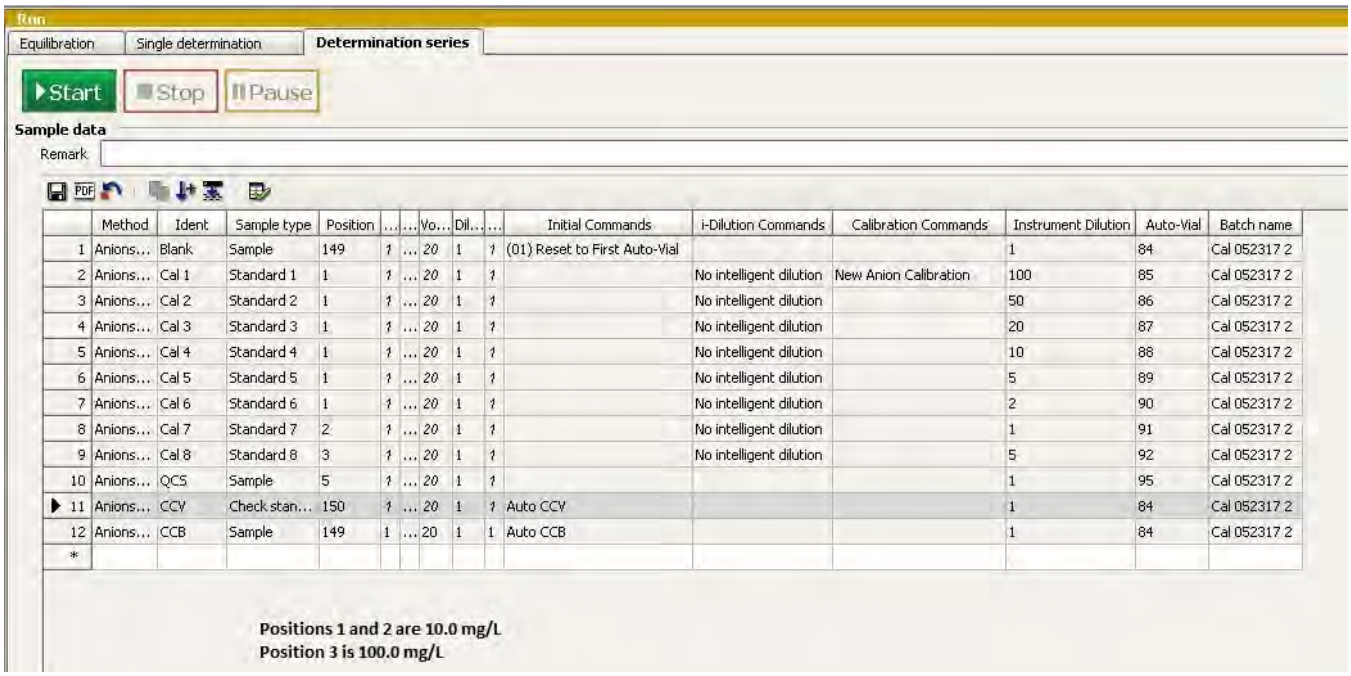
10.1. Recalibration for the instrument does not need to be done daily. It should be done when the QC fails more than once for instrument related reasons. It should also be done following any major maintenance on the instrument, such as changing the column. **Full instructions can be found in the MagIC Net User Guide, which can be found on the IC computer or in the Instrument Manuals folder on the network: \\USFS700\ANK_Groupdata\Public\DOCUMENT\Instrument_Manuals\IC Metrohm**

10.2. To recalibrate the instrument, the following steps should be followed:

10.2.1. For each analyte of interest, prepare calibration standards of two vials of 10.0 mg/L (0.1 mL of primary standards (8.5) diluted to 10.0 mL) and one vial of 100.0 mg/L (1.0 mL of primary standards (8.5) diluted to 10.0 mL) and place into positions as shown in Figure 1. Set up determination series as shown below, paying close attention to the instrument dilutions, to instruct the instrument to perform a calibration of eight concentration levels (0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10

and 20 mg/L). Be sure to select "New Anion Calibration" in the Calibration Commands field for the first sample.

10.2.2. At some specific instances (e.g. Linear Calibration Range failure), additional concentration between 0.1 to 20 mg/L can be included in the calibration.



	Method	Ident	Sample type	Position	...	...	Vo...	Dil...	...	Initial Commands	i-Dilution Commands	Calibration Commands	Instrument Dilution	Auto-Vial	Batch name
1	Anions...	Blank	Sample	149	1	...	20	1	1	(01) Reset to First Auto-Vial			1	84	Cal 052317 2
2	Anions...	Cal 1	Standard 1	1	1	...	20	1	1		No intelligent dilution	New Anion Calibration	100	85	Cal 052317 2
3	Anions...	Cal 2	Standard 2	1	1	...	20	1	1		No intelligent dilution		50	86	Cal 052317 2
4	Anions...	Cal 3	Standard 3	1	1	...	20	1	1		No intelligent dilution		20	87	Cal 052317 2
5	Anions...	Cal 4	Standard 4	1	1	...	20	1	1		No intelligent dilution		10	88	Cal 052317 2
6	Anions...	Cal 5	Standard 5	1	1	...	20	1	1		No intelligent dilution		5	89	Cal 052317 2
7	Anions...	Cal 6	Standard 6	1	1	...	20	1	1		No intelligent dilution		2	90	Cal 052317 2
8	Anions...	Cal 7	Standard 7	2	1	...	20	1	1		No intelligent dilution		1	91	Cal 052317 2
9	Anions...	Cal 8	Standard 8	3	1	...	20	1	1		No intelligent dilution		5	92	Cal 052317 2
10	Anions...	QCS	Sample	5	1	...	20	1	1				1	95	Cal 052317 2
▶ 11	Anions...	CCV	Check stan...	150	1	...	20	1	1	Auto CCV			1	84	Cal 052317 2
12	Anions...	CCB	Sample	149	1	...	20	1	1	Auto CCB			1	84	Cal 052317 2
*															

Figure 1 Standard calibration table

10.2.3. Prepare QCS and CCV samples as outlined in section

10.2.4. Start up instrument as outlined in section 11. After 30 minute equilibration period has passed, begin determination series.

10.2.5. After analysis has completed, highlight all of the standards and select reprocess.

10.2.6. In the reprocess window, select the standard with the lowest concentration. Zoom in on the calibration to verify the integration parameters, listed in the integration tab, are selecting the peaks appropriately. The basic settings are generally effective.

10.2.7. Select the components tab and update the component retention times to match peaks as needed. Press the "Update Retention Times" button, then the "Update" button to apply any changes and verify correct peak labeling.

10.2.8. Once all changes are made and applied to the lowest point, press the "Reprocessing" button and check the "From standards of reprocessing" option. This will build the curve point by point. For instance, the lowest point will have a calibration only containing itself, while point two will have itself and point one, etc.

10.2.9. Select the top point (the highest concentration). The calibration on this standard will contain all points. Press the "Reprocessing" button again, this time choosing the "From selected

determination" option to apply the complete curve to all points. Once the system has completed this, select the "Method" button and choose "Save As" to save the method.

10.2.10. At this point, the calibration is complete. Exit the reprocessing window, then select the blank, QCS, CCV, and CB as well as any calibration point and press the reprocessing button again. With the calibration point selected, press "Reprocessing" and choose the "From selected determination" option to apply the completed curve to the Blank, QCS, CCV, and CB.

10.3. Calibration Verification:

10.3.1. Each calibration point must be evaluated with read back. Validation for the low point is ± 50% of the true value. The criterion for all other points is ± 10% of the true value.

10.3.2. The calibration curve will be verified by the analysis of QCS (second source). QCS data will be submitted (true value of 15mg/L ±10%) with the calibration packet for peer review.

10.3.3. See section 8.9.4 for preparation of the QCS (true value of 15mg/L ±10%).

10.4. Assemble the calibration packet with the following components: 1) IC Calibration Cover Sheet, 2) IC Calibration and Standards Spreadsheet, FW-0102, 3) Calibration Graphs, 4) Handwritten Run Log, 5) Chromatograms (raw data), 6) QCS chromatograms for calibration verification. The calibration packet is to be submitted for review through the peer review process.

10.5. Linear Calibration Range (LCR): Initial verification and verified every 6 months by the analyst.

10.5.1. Calibrate the instrument as described in Sections 10. Verify the linearity of the curve by filling out the Linear Regression Spreadsheet (CW-0013_300.0_9056_Full_LR_Template.xlsx). Input the Area and the expected concentration for each analyte. Once all needed points are entered, enter the slope and intercept value into the corresponding cells. Each calculated value should be within ± 10% of the true value and the regression line should have an $R^2 > 0.995$.

10.5.2. If the calibration fails for linearity using all points, linearity will need to be established for the lower and higher ranges of the calibration. Perform 10.6.1. using the blank and the lowest five calibration points initially and adjust the total number of points, by removing the highest points in the range, until the lower range passes for linearity. Repeat 10.6.1. using the remaining calibration points to determine linearity for the upper range. If the upper range fails for linearity or has fewer than three calibration points, recalibrate with an additional point.

11.0. ANALYSIS:

11.1. Prepare fresh eluent and ensure that the regenerant and water bottles are full. See section 8 for instructions on how to prepare these reagents.

11.2. Check the filter on the Sample Processor and replace if necessary.

11.3. Launch the MagIC Net software and log in with credentials.

**Note: new users will have to be set up by a current user.*

11.4. The instrument will go though self checks. This is complete when the "Status" fields (in the Configuration tab) for both the instrument and sample processor say "ok". **Do not attempt to enter manual mode or**

start the hardware until this completes.

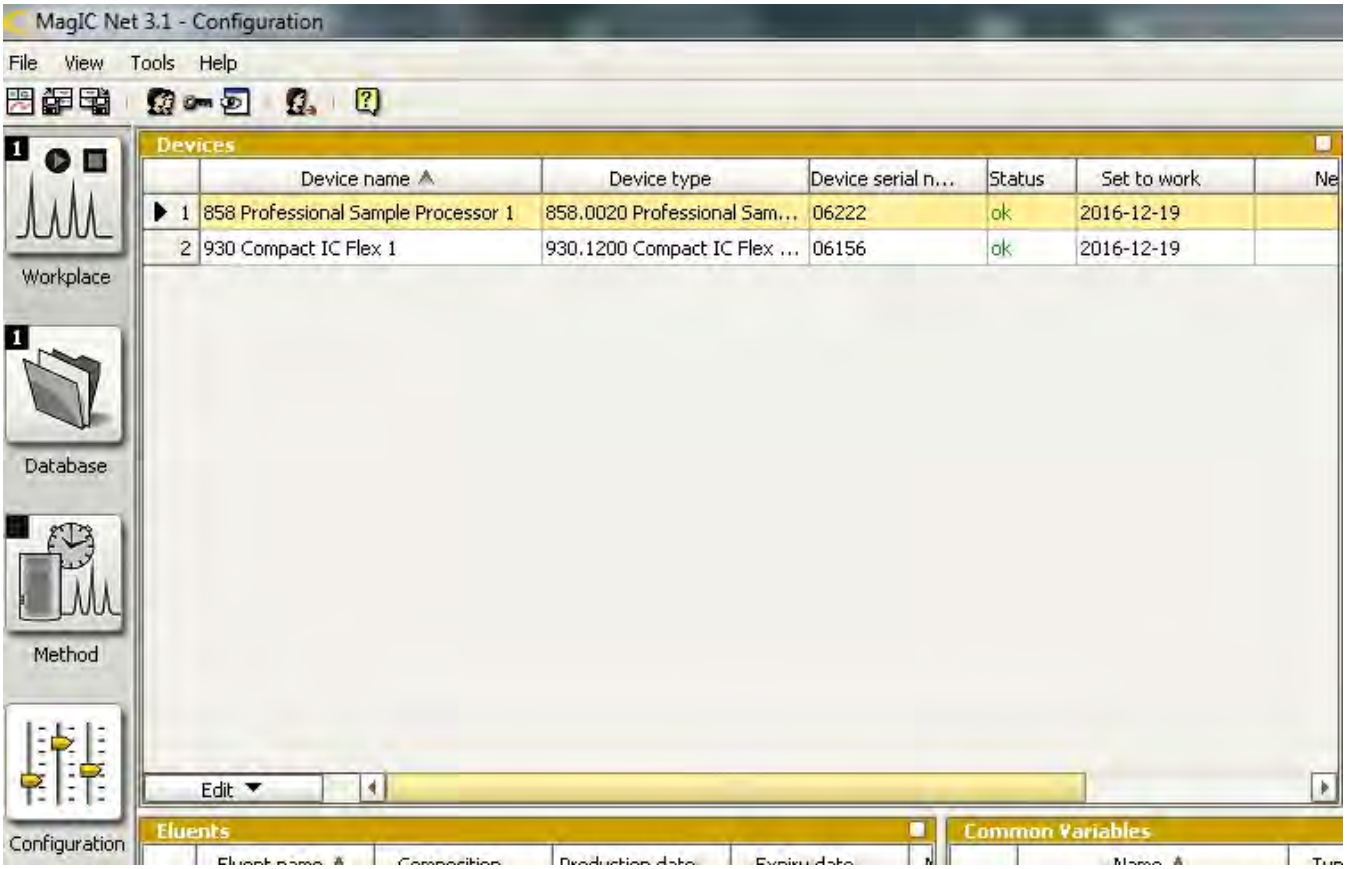


Figure 2 Configuration tab

11.5. Remove all old vials and replace all used vials in the Auto-Vial positions with new vials. The current Auto-Vial is shown in the configuration tab; all used Auto-Vials are from that position back to position 84.

11.6. Once the self checks are complete, purge the eluent line and pump of bubbles by going to the Manual tab on the bottom left of the screen, selecting "All devices" from the drop down menu, the clicking on the 930 Compact IC Flex. Attach a syringe to the outlet tube on the IC pump purge valve and twist the valve counter clockwise to open. Type "2.0" in the flow Input field and hit Start. This will pump eluent at a rate of 2.0 mL/min into the syringe. Continue until about 6 mL has been pumped through, then hit Stop and close the valve.

***NOTE:* DO NOT RUN THE PUMP AT THIS FLOW RATE WITHOUT ENSURING THE VALVE IS OPEN AS THIS CAN DAMAGE THE COLUMN.**

11.7. Next, go to the Workplace tab, then select the Equilibration tab and press "Start HW" to begin equilibration.

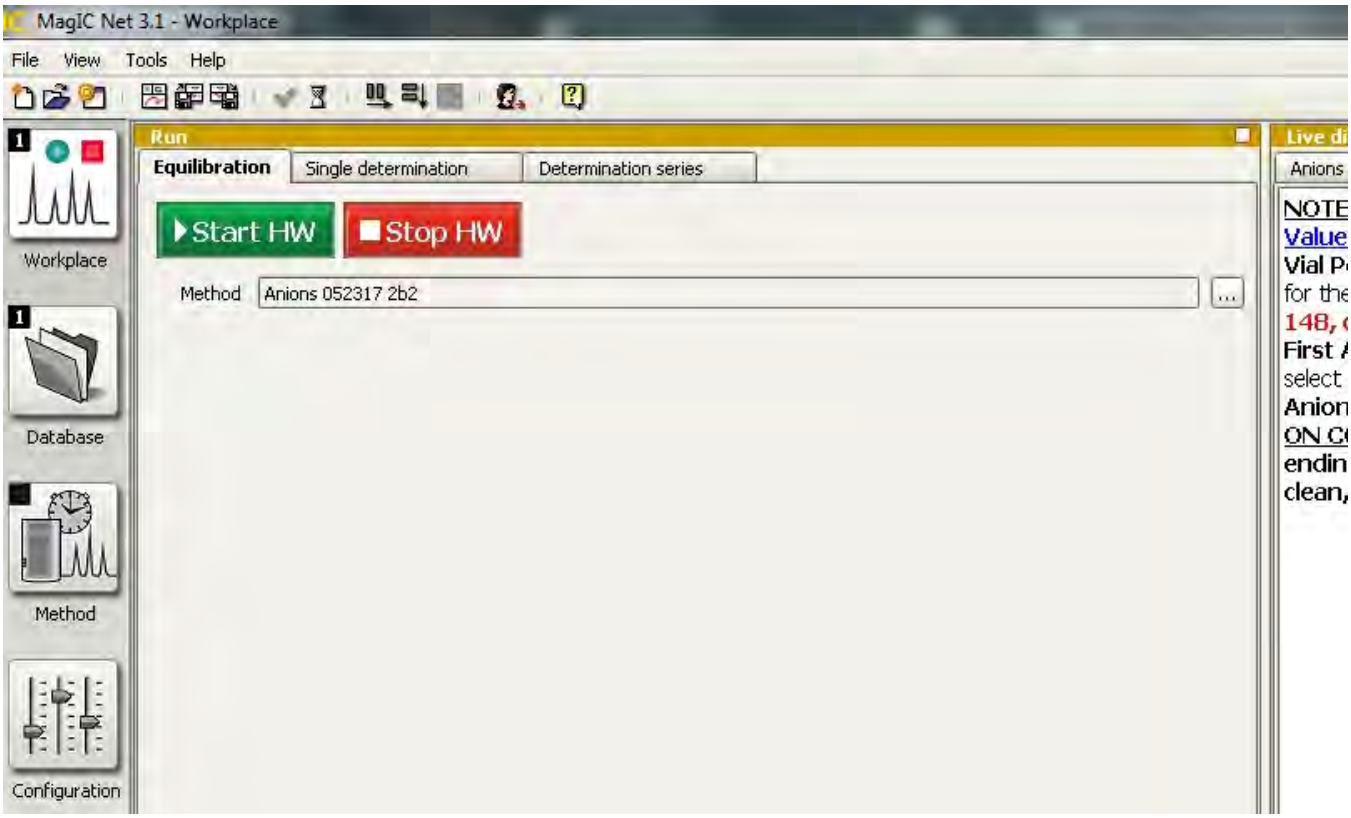


Figure 3 Equilibration tab

11.8. The instrument will begin to equilibrate and will show a graph of the conductivity in the Live display window. It is set up to automatically "step" the suppressor every 10 minutes when not analyzing a sample, therefore the instrument should be allowed to equilibrate for 30 minutes to allow each path to be flushed with regenerant solution and water.

11.9. To ensure the longevity of the instrument, a screening technique has been developed in order to avoid potential harm to the instrument. The conductivity can be taken of each sample, using a portable conductivity meter, prior to analysis in order to determine the most appropriate dilution factor for a sample. The following table can be used to determine the dilution from the conductivity:

Conductivity Reading, µmhos	**Recommended Dilultion**
0 – 300	1X
300 – 800	1X (F, Br, NO_2, NO_3) 5X (Cl, S)
800 – 1000	1X (F, Br, NO_2, NO_3) 10X (Cl, S)
1000 – 1700	2X (F, Br, NO_2, NO_3) 20X (Cl, S)
1700-2000	2X (F, Br, NO_2, NO_3) 25X (Cl, S)

2000-3000	5X (F, Br, NO_2, NO_3) 25X (Cl, S)
3000-4000	10X (F, Br, NO_2, NO_3) 50X (Cl, S)
4000-5000	10X (F, Br, NO_2, NO_3) 100X (Cl, S)
Above 5000	500X to screen

Table 1. Conductivity Screening

**Note – Salinity samples should always be tested by the conductivity screening technique. High salinity samples analyzed at wrong dilution can jeopardize the instrument.*

11.10. Set up the samples to be run. The following standards are required:

11.10.1. A QCS will be run at the beginning of each analytical run preceding the analysis of an ICV and ICB. See section 8 for preparation instructions and section 13 for acceptance criteria.

11.10.2. An ICV and ICB will be run at the beginning of every analytical run. A CCV and CB will automatically be run at a frequency of once every ten injections within the batch. Instrument QC does not count as one of the ten samples in-between CCV/CB. All prep QC, paying samples, MS/MSD, and rinses count towards the number of injections run in-between CCV/CB. See section 8 for preparation instructions and section 13 for acceptance criteria.

11.10.3. A MB will be run at the beginning of each extraction batch at a frequency of one per twenty field samples and one per matrix (water, soil, oil and SW5050). See section 8 for preparation instructions and section 13 for acceptance criteria.

11.10.4. An LCS will be run at the beginning of each extraction batch at a frequency of one per twenty field samples and one per matrix (water, soil, oil and SW5050). See section 8 for preparation instructions and section 13 for acceptance criteria.

11.10.5. A MS/MSD must be run for 5% of field samples for each matrix (1set in each batch of 20 samples or less). See section 8 for preparation instructions. See section 13 acceptance criteria.

11.10.6. For drinking water samples, a low level quantitation (LLQ) needs to be evaluated each analysis day. The calibration point at the LOQ will be used as the LLQ.

11.11. In the Database tab, select Determinations from the top of the screen, hover over Batch, then select New Batch and type in WIC MMDDYY.

11.12. Go back to the Workplace tab and select Determination series. Load the Anions Auto Dilution Template and verify that the method listed in the QCS line is the most current. Double click on the QCS line to open it and select the batch for the new run from the drop down menu.

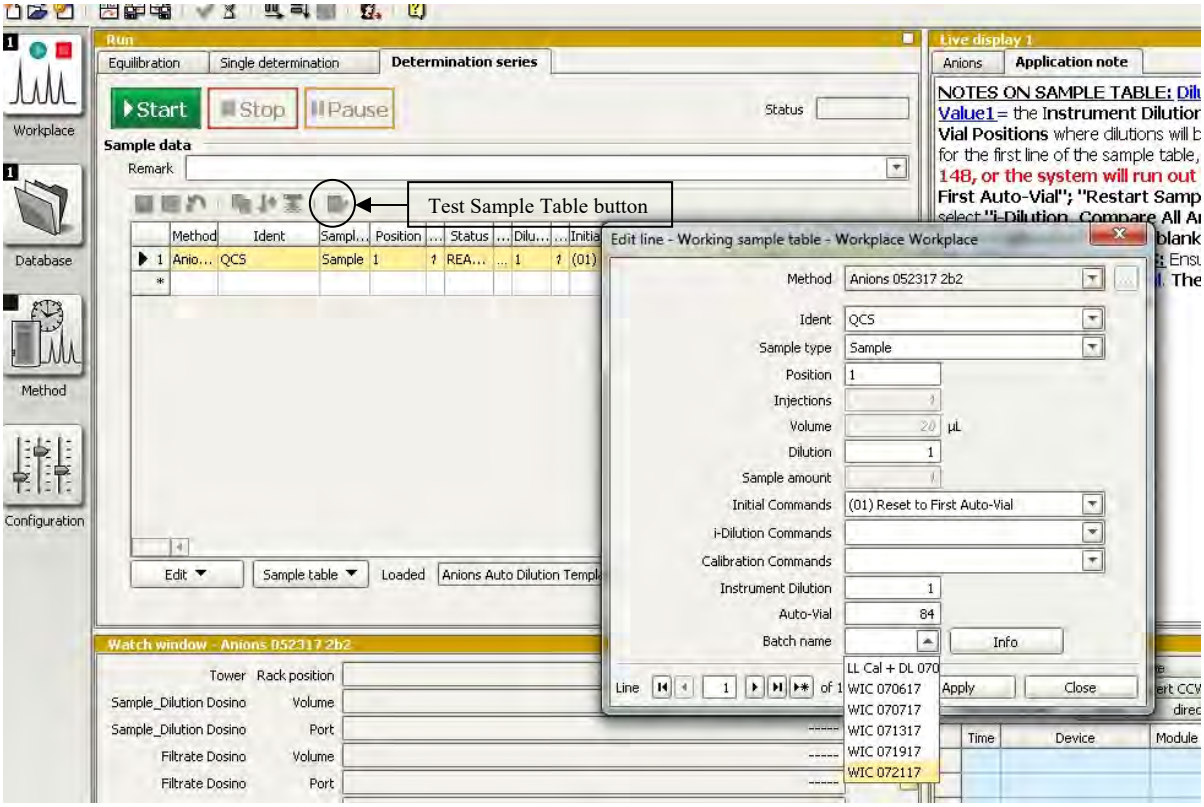


Figure 4 Sample scheduling window

11.13. After the 30 minutes equilibration period has elapsed and the baseline is stable, load the QCS into position 1, fill the bottle in position 149 with DI water, and place 200 mL of CCV solution in the bottle in position 150.

11.14. Press Start to begin the analysis. A CCV/CB pair will automatically be scheduled and correctly begin the counter after the CB so that a CCV/CB pair will be scheduled every 10 samples thereafter.

11.15. Double click on the line beneath the CB to schedule the MB, LCS, and all samples.

11.15.1. Fill out the Ident field with the sample ID (with container ID), ex. 1181234001A.

11.15.2. The Sample type field is Sample for all schedules except for CCV.

11.15.3. The Position field automatically moves to the next position when the next button is pressed, but care should always be taken to ensure the position matches the position on the rack that the sample is in.

11.15.4. The Dilution field is where the manual dilution factor goes if a manual dilution was done on the sample before placing in the rack (see Table 1 for dilution guidelines). If no dilution was done, enter 1.

11.15.5. The Initial Commands field should be left blank for all schedules except for the QCS, which should have "Reset to First Auto-Vial" selected.

11.15.6. The i-Dilution Commands field "No intelligent dilution" should be selected for all schedules.

11.15.7. The Calibration Commands field should be left blank unless a new calibration is being performed.

11.15.8. The Instrument Dilution field should be 1 unless the desired dilution is known. **If this is not 1, causing the instrument to perform an auto dilution for that schedule, and the sample is over range for any analyte, the instrument will not perform further dilutions.** As such, it is better to prepare any necessary dilutions as suggested by Table 1 by hand so the instrument can catch any unknown over range analytes.

11.15.9. The Auto-Vial field should always be 1 higher than the previous schedule.

11.15.10. The batch name should be the batch for that day.

11.16. The "Test Sample Table" button (see Figure 4) should be pressed after all entries are complete to ensure all entries are complete and the program will run through the table without any errors.

11.17. The instrument will run through the sample table, adding CCV/CB pairs every 10 samples and scheduling any auto dilutions at the end of the run, until it hits the end, where it will run a closing CCV/CB pair then shut off as long as the "Stop hardware when sample table is finished" box is checked.

11.18. To retrieve and post a batch, go to the Database tab and select the batch from the drop-down menu. This will allow the user to go through the chromatographs and see the concentrations.

**A note on the results window: the "Concentration_On-Column" field represents the actual result measured by the instrument and should be within the calibrated range or have triggered an intelligent dilution. The "Concentration" field is the Concentration_On-Column field multiplied by the manual dilution, while the "Final Concentration" field is the Concentration_On-Column field multiplied by both the manual and intelligent dilution factors.*

11.19. Reports for any samples requiring manual integration should be printed prior to reprocessing.

11.20. The batch is exported to a folder for posting via LimsBridge. The chromatographs are printed along with a Determination overview (run log).

12.0. LOW LEVEL ANALYSIS

12.1. Some clients may request a very low DL for specific analytes. These requests are handled in a case-by-case manner and are worked closely with the Technical Director and Project Manager. A working Low Level method is described below.

12.2. Working method for low level Nitrate and o-Phosphate

12.2.1. Calibration was built as described in section 10, replacing calibration standards with 10 point calibration: 0.005 mg/L, 0.010 mg/L, 0.020 mg/L 0.050 mg/L, 0.100 mg/L, 0.200 mg/L, 0.500 mg/L, 1.000 gm/L, 2.000 mg/L, 5.000 mg/L.

12.2.2. QC Requirements:

12.2.2.1. QCS is spiked at 4.0 mg/L

12.2.2.2. CCV is spiked at 2.5 mg/L **and is placed in the bottle in position 150.**

12.2.2.3. LCS is spiked at 1.0 mg/L

12.2.2.4. MS/MSD are spiked at 1.0 mg/L

12.2.3. Analysis is performed as described in section 11. It is good practice to replace the filtration membrane on the sample processor and ensure that all other filters are replaced within manufacturer recommended timelines to be sure there is no contamination before analyzing low level samples.

13.0. QUALITY CONTROL:

13.1. Accuracy and Precision Measurements – Aqueous Samples EPA 300:

13.1.1. Laboratory Control Sample (LCS): This must be run at the beginning of every batch of twenty or fewer field samples. The acceptance criteria are ±10% of the true value. Recoveries outside this range will require the identification and repair of the problem and the successful analysis of the LCS before analysis of samples can begin.

13.1.2. Sample matrix spike/duplicate (MS/MSD): A MS/MSD is required for every batch of 20 samples or less. The acceptance criteria are ±10% for the spike recovery. If spike fails to meet control limits and the LCS is within control limits, sample will be flagged for suspected matrix interference.

13.2. Accuracy and Precision Measurements – 9056 water and soil samples

13.2.1. Laboratory Control Sample (LCS): This must be run with every extraction batch. Acceptance criteria is from laboratory based control limits that are generated for each analyte as described in SOP 145.

13.2.2. Sample matrix spike/duplicate (MS): A MS is required every batch of 10 samples or less. The acceptance criteria is from laboratory based control limits that are generated for each analyte as described in SOP 145.

13.2.3. The acceptable relative percent difference (RPD) between the MS/MSD is ≤ ±20%. If spike fails to meet control limits and the LCS is within control limits, sample will be flagged for suspected matrix interference.

13.3. Accuracy and Precision Measurements – Total Halogens, SW5050

13.3.1. Laboratory Control Sample (LCS): This must be run with every extraction batch. The acceptance criteria for the LCS is ± 30% of the true value.

13.3.2. Sample matrix spike/duplicate (MS/MSD): A MS/MSD is required every batch of 20 samples or less. The recovery criteria is ±30%. If spike fails to meet control limits and the LCS is within control limits, sample will be flagged for suspected matrix interference. The relative percent

difference acceptance criteria is ≤ 15 %. If RPD fails to meet criteria, re-extract samples. If RPD still fails to meet criteria, flag samples as suspected matrix interference

13.3.3. The project manager **must** be notified when any total halogen sample extracted and analyzed by the 9056/5050 method reads between 1,000 and 4,000 ppm. This will allow project manager to contact the client and determine if the sample needs to be confirmed by gas chromatography methods.

13.4. Calibration Verification Criteria-

13.4.1. Quality Control Sample (QCS): The QCS is a second source standard run once at the beginning of each run. The acceptance criteria are ±10% of the true value. Recoveries outside this range will require the identification and repair of the problem and the successful analysis of the QCS sample before analysis of samples can begin. This standard must be from a source independent of the calibration standards.

13.4.2. Calibration Verification (ICV/CCV): The acceptance criteria is ±10% of the true value. Recovery outside this range will require the identification and repair of the problem and the successful analysis of a calibration verification sample before the analysis of paying samples can proceed.

13.4.2.1. **For non-DOD samples**: Samples analyzed since the last acceptable calibration verification within the same analysis sequence will need to be reanalyzed once the analysis of another CCV is within acceptable limits. The initial calibration verification (ICV) sample will be analyzed at the beginning of the run; the continuing calibration verification (CCV) after every ten samples and at the end of the run. Additionally, a CCV must be analyzed after the preparation of additional eluent solution. The target analytes' retention times should be within the established retention time windows; however, analyst experience and expertise are vital for proper analyte identification.

13.4.2.2. **For DOD samples:** The analyst may immediately (within 1 hr of the failing CCV and before any other samples have acquired) rerun 2 successive CCVs. If both meet QC criteria for all analytes of interest, then the samples already analyzed may be reported and the run sequence may be continued. Samples following the two passing CCVs are also valid. See SOP 500.

13.4.3. Calibration Blank (ICB/CB): The ICB is analyzed before any samples can be run and must read < LOQ. Thereafter, the calibration blank (CB) is analyzed after every ten samples and at the end of each run. The acceptance criteria for the calibration blank are <LOQ (see section 19 for LOQs). A measured value outside allowable limits may require the reanalysis of some samples. ICB values exceeding the LOQ may be an indication of laboratory reagent contamination. Samples that have an apparent concentration <LOQ will not require reanalysis. Samples having a concentration >10X the ICB contamination will not require reanalysis. All other samples analyzed since the last acceptable blank require reanalysis after appropriate corrective action is performed.

13.5. Blank Criteria-

13.5.1. **Aqueous Samples**: Method Blank (MB): This must be run at the beginning of every batch of twenty or fewer field samples. The MB is analyzed before any samples can be run and must read < LOQ. MB values exceeding the LOQ may be an indication of laboratory reagent contamination. Samples associated with a MB that exceeds this limit must be carefully evaluated; i.e., if the sample is < LOQ or is > 10X the level of contamination exhibited by the MB, it may be reported and flagged. All other samples must be re-extracted and reanalyzed.

13.5.1.1. For DOD clients only, MB recoveries ≥ ½ LOQ require the identification and repair of the problem and the successful analysis of the MB before analysis of samples can begin. Any samples with detectable results (unless they are >10x MB) associated with a MB that exceeds this limit must be reanalyzed.

13.5.1.2. The MB will be evaluated at the DL for drinking water samples.

13.5.2. **Soil Samples (9056):** A method blank (MB) must be prepared with every extraction and analyzed as part of the batch. For soil and oil, the allowable limit is < LOQ. Samples associated with a MB that exceeds this limit must be carefully evaluated; i.e., if the sample is < LOQ or is > 10X the level of contamination exhibited by the MB, it may be reported and flagged. All other samples must be re-extracted and reanalyzed.

**Note: For DOD clients only, MB recoveries ≥ ½ LOQ require the identification and repair of the problem and the successful analysis of the MB before analysis of samples can begin. Any samples with detectable results (unless they are >10x MB) associated with a MB that exceeds this limit must be re-extracted and reanalyzed.*

13.5.3. **Total Halogens, SW9056:** A method blank (MB) must be prepared with every extraction and analyzed as part of the batch. For total halogens, the allowable limit is < LOQ. Samples associated with a MB that exceeds limits must be carefully evaluated; i.e., if the sample is < LOQ or is > 10X the level of contamination exhibited by the MB, it may be reported and flagged. All other samples must be re-extracted and reanalyzed.

Note: DOD criteria are **not applicable total halogens as chloride due to oil matrix.*

13.6. Demonstration of Instrument Operating Specifications:

13.6.1. On a periodic basis it must be shown that the instrument is operating within specifications. The parameters and verification intervals are outlined below.

13.6.1.1. Initial Demonstration of Performance (IDC): Conducted before each new operator can independently operate the instrument, and then annually for each analyst thereafter. This includes the preparation and analysis of four successful laboratory control samples and successful analysis of a blind performance evaluation sample.

13.6.1.2. Detection Limits (DL): Performed every 6 months or when major maintenance occurs (e.g. column change) to determine the acceptance window for identifying the analytes. The DL should also be re-established if there has been a significant change in instrument response.

13.6.1.3. Retention Time Width Study: Performed annually or when major maintenance occurs (e.g. column change) to determine the acceptance window for identifying the analytes. The window used for daily measurements will be three times the standard deviation of the retention times established using three standards measured on analyses performed over a 24 hour period. The minimum setting is 5%.

13.6.2. Analyte Retention Time: If the retention time for any analyte in the daily initial CCV varies from the last set value for the initial CCV by more than +/-3% then the RT will be reset using the RT from the current initial CCV. See Method 300.0, section 11.4 for retention time criteria.

**Note – The retention time window within MagIC Net will be set to 3% of the current retention times. When a peak is not named in the opening QC, this is an indication that the retention time window has shifted and appropriate action should be taken.*

13.6.3. If the response for any analyte in the CCV varies from the calibrated values by more than 10% the test must be repeated using a fresh calibration standard. If the results are still more than ±10%, a new calibration curve must be prepared.

13.6.4. When warranted, manual integration can be done on individual chromatograms. For guidance regarding manual integration, refer to SOP 144.

13.6.5. For all samples or QC requiring any changes to integration, the analyst must provide chromatograms of both before and after the manual integration and initial and date each with a brief comment justifying the integration changes. Each before and after must be included in the Peer Review Report for review.

13.7. Low Level Quantitation (LLQ) will be analyzed at the LOQ for drinking water samples. The LLQ requirement is daily; however, for practical purposes, include the LLQ in every batch.

13.8. Any corrective action needed to address a QC outlier or other technical challenges that are not listed in this SOP require the prior approval of the QA Office or Technical Department.

14.0. CALCULATIONS, REVIEW AND REPORTING:

14.1. Equations:

14.1.1. Sample concentration determination: prepare separate calibration curves for each anion of interest by plotting peak size in area of standards against concentration values. Sample concentration is computed by comparing sample peak response with the standard curve.

14.1.2. Calibration Graphs: Calculate the following parameters: slope (s), intercept (I), and correlation coefficient (r). The slope and intercept define a relationship between the concentration and instrument response:

$$Y = K_2 X_i^2 + K_1 X_i \quad \text{EQUATION 1}$$

Where: Y = predicted instrument response
K_2,K_1 = coefficients
X_i = concentration of standard i

MagIC Net software does these calculations automatically when a new calibration is run.

14.1.3. Relative Percent Difference:

Where: A = Observed sample concentration
B = Observed sample duplicate concentration

$$RPD = \frac{|A-B|}{\left(\frac{A+B}{2}\right)}$$

14.1.4. Spike Recovery:

$$\%\,\mathrm{Recovery} = \frac{(V_0 - S_0)}{V_E} \times 100$$

Where V_0 = observed value of the spike
S_0 = observed value of the sample
V_E = expected value of the spike

14.1.5. Total Halogens are Chloride:

$$H_T = Cl + (0.44369 * Br) + (1.8661 * F)$$

Where: H_T = total halogens as chloride
Cl = observed chloride concentration
Br = observed bromide concentration
F = observed fluoride concentration

14.1.6. Salinity:

$$S = [(Cl*1.65)/(1000)]$$

Where: S = Salinity
Cl = observed chloride concentration

14.2. Review/Peer Review – A peer reviewer must date and initial all chromatograms that have been manually integrated.

14.3. For any drinking water sample that report **Nitrate-N over 10 mg/L, or Nitrite-N over 1.0mg/L.**

14.3.1. **Notify the client immediately** (within 24 hours) of unsatisfactory results by emailing a completed *ALERT: Nitrate-N over 10 mg/L or Nitrite-N over 1.0mg/L report.* See attachment C.

14.3.1.1. Record the date, time, and name of the person contacted in the appropriate area of the form

14.3.2. If **a PWSID number is on the Chain of Custody, notify ADEC.**

14.3.2.1. Email the form, attachment C, to the *correct* ADEC office**. Refer to SOP #109** for details regarding the appropriate ADEC office for the PWSID number. A document of ADEC offices can be found at: \\USFS700\ANK_Groupdata\Public\DOCUMENT\FORMS\Approved\FW\FW-0098_Currentcontacts_ADEC_Divisions_20170830.docx

14.3.2.2. If the Public Water System box is checked, or if the client requests the report be emailed to ADEC, but does not supply a PWSID number, contact the Project Manager so they can request clarification.

14.3.3. **Notify the Project Manager** immediately so the results may be submitted to ADEC via CMDP.

15.0. HEALTH AND SAFETY:

15.1. Samples shall be returned to the approved storage location until such time as it is determined that no further analysis will be required.

15.2. Once it has been established that no more analysis of a sample will be required, acid and alkaline preserved samples may be neutralized using the Elementary Neutralization Hood located in GC Prep, unless it is considered to be hazardous (i.e. mercury waste, cyanide waste). Refer to the current version of SOP 108 for further instruction.

15.3. All surplus reagent acids shall be neutralized on a daily basis using the Elementary Neutralization Hood located in GC Prep.

15.4. Small volumes of surplus volatile reagents may be allowed to evaporate in a hood at the end of the analytical session.

15.5. Proper Personal Protective Equipment (PPE) must be worn at all times. Proper PPE when handling samples include a lab coat, gloves and safety glasses. In addition, when handling concentrated acid or base preservative a face shield and apron must be worn.

16.0. POLLUTION PREVENTION:

SGS is committed to evaluate all areas of the lab with regard to current and potential pollution prevention. Pollution prevention is described as any technique that reduces or eliminates waste at the point of generation. Further discussion on pollution prevention programs in the laboratory can be found in *SGS Pollution Prevention Plan* (Form F053).

17.0. METHOD PERFORMANCE:

There are no method performance measures to report at this time.

18.0. DETECTION LIMIT (DL) STUDY:

Detection Limit (DL) studies are verified annually, and performed when a new operator is trained for drinking water analyses, when a significant change in instrument response is observed, or when a new instrument is purchased for analysis. The DL study is intended to demonstrate the capability of this method as it is implemented at SGS. An update to the DL does not necessitate an update to this document.

The DLs are subject to update for the factors given earlier. The current maximum (MAX) DLs are given below.

	Water	**Soil**	**SW5050**
Anion	**Max DL (mg/L)**	**Max DL (mg/Kg)**	**Max DL (mg/Kg)**
Fluoride	0.05	0.62	1.24
Chloride	0.05	0.62	1.24
Nitrite-N	0.05	0.62	
Bromide	0.05	0.62	1.24
Nitrate-N	0.05	0.62	
Sulfate	0.05	0.62	

19.0. LIMIT OF DETECTION (LOD):

The LOD is defined per SOP 116. LOD verification shall be performed quarterly according to the schedule set by the QA Office.

20.0. LIMIT OF QUANTITATION (LOQ):

The LOQ is defined per SOP 116. LOQ verification shall be performed quarterly according to the schedule set by the QA Office. DLs/LOQs may change at the lab's discretion and need not require an update to this document. Current lab LOQs are listed below.

	Water	**Soil**	**Oil**
Anion	**LOQ (mg/L)**	**LOQ (mg/Kg)**	**LOQ (mg/Kg)**
Fluoride	0.20	2.0	4.0
Chloride	0.20	2.0	4.0
Nitrite-N	0.20	2.0	
Bromide	0.20	2.0	4.0
Nitrate-N	0.20	2.0	
Sulfate	0.20	2.0	

The LOQ for Total Halogens as Chloride is 400 mg/Kg.

21.0. REFERENCES:

21.1. EPA 300.0/4-79-020, Revision 2.1, August 1993
21.2. SW 846 Method SW9056A, Revision 1, February 2007
21.3. DOD QSM (most recent version)
21.4. EPA Method Update Rule 2012
21.5. Standard Methods 22nd Edition
21.6. MagIC Net User Guide v3.2, Metrohm USA Inc., 2014

22.0. ATTACHMENTS:

Attachment A: Quick Reference Guide
Attachment B: Corrective Action Table
Attachment C: Alert Form

Attachment A: QUICK REFERENCE GUIDE

1. Replace eluent, 1 snip per liter
2. Fill water tank and regenerant if needed
3. Remove old vials and replace used auto-vials
4. Purge eluent line and pump for 3 minutes
5. Start hardware and allow to equilibrate for 30 minutes
6. Place fresh DI in bottle in position 149
7. Prepare standards:
   a. Make working 1° solution: 1mL of 1° standards diluted to 10mL
   b. Make working 2° solution: 1.5mL of 2° standards diluted to 10mL
   c. Prepare CCV: 2mL of 1° standards diluted to 200mL, pour into bottle in position 150
   d. Prepare LCS: 0.5mL of working 1° standards diluted to 10mL, mix and pour into vial in position 3
   e. Prepare QCS: 1mL of working 2° solution diluted to 10mL and placed in position 1
8. Low Level standards:
   a. Make LL working 1° solution: 0.1mL of 1° standards diluted to 10mL
   b. Make LL working 2° solution: 0.1mL of 2° standards diluted to 10mL
   c. Prepare CCV: 0.5mL of 1° standards diluted to 200mL, pour into bottle in position 151
   d. Prepare LCS: 1.0mL of LL working 1° solution diluted to 10mL and placed in position 3
   e. Prepare QCS: 4.0mL of LL working 2° solution diluted to 10mL and placed in position 1
9. Filter 10mL of DI and place in position 2
10. Load Anions Auto Dilution template, change batch ID, start sample table
11. Manually measure conductivity of samples to be analyzed and write on lids along with dilution according to table 1
12. Select sample to be MS/MSD
    a. Spike 0.5mL of working 1° solution into 9.5mL of filtered sample for each
    b. Low Level: spike 1.0mL of LL working 1° solution into 9.0mL of sample for each
13. Filter all samples, diluting as needed, place in rack, and fill out sample table
14. Check “Stop hardware when sample table is finished” box
15. Export files to folder, print chromatographs, print Determination overview

Attachment B: CORRECTIVE ACTION TABLE

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
EPA300.0 And SW9056A	Initial Calibration Verification (ICV)	After calibration & at beginning of each analytical batch.	Recovery ±10%	1. Repeat analysis once. 2. Recalibrate
	Calibration Verification Read Back	With each calibration	Low point ± 50% All other calibration points ± 10%	Correct the problem Recalibrate
	Initial Calibration Blank (ICB) Calibration Blank (CB)	Immediately after ICV After each 10 analysis and at the end of the run	Concentration < LOQ	1. Repeat analysis once. 2. Evaluate samples before further analysis. If < LOQ – no reanalysis is required. If >10x concentration in blank – no reanalysis is required. All other samples using the contaminated blank for QC will be reanalyzed.
	QCS (second source check)	After calibration & 1 per analytical batch or daily.	Recovery ±10%	1. Repeat analysis once. 2. Recalibrate
	Continuing Calibration Verification (CCV)	1 per 10 samples and at end of the run.	Recovery ±10%	1. Repeat once and repeat analysis of all associated samples. Recalibrate if second analysis of CCV remains outside criteria. 2. DOD requires 2 successful CCV runs
	Method Blank (MB)	1 per batch of ≤ 20 samples	< LOQ Evaluate at DL for DW ***DOD clients < ½ LOQ (soils and waters)**	1. Evaluate samples before further analysis. If < LOQ – no reanalysis is required. If > 10x concentration in blank – no reanalysis is required. All other samples using the contaminated blank for QC will be reanalyzed. 2. DOD clients – reanalyze MB if > ½ LOQ, and any associated samples.
EPA 300	Laboratory Control Sample (LCS)	1 for each batch of ≤ 20 samples	Aqueous – Recovery ±10%	1. Rerun once. 2. Reanalyze samples.
	Matrix Spike (MS)	1 set per batch of 10 or less	Recovery **±10%**	1. Evaluate LCS if in control, then flag as matrix interference.

Attachment B: CORRECTIVE ACTION TABLE (continued)

SW9056A	Laboratory Control Sample (LCS)	1 for each batch of ≤ 20 samples	Acceptance criteria is from laboratory based control limits that are generated for each analyte as described in SOP 145.	1. Rerun once. 2. Reanalyze samples.
	Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	1 set per batch of 20 or less	Recovery Acceptance criteria is from laboratory based control limits that are generated for each analyte as described in SOP 145. Duplicate RPD ≤ 15%	1. Evaluate LCS if in control, then flag as matrix interference. 1. If RPD is out of control, reanalyze parent & MS/MSD. 2. If RPD is still out of control, flag the parent sample & comment matrix interference.

SW5050/ 9056A (oils for Total Halogens)	Laboratory Control Sample (LCS)	1 for each batch of ≤ 20 samples	Recovery ± 30%	1. Rerun once. 2. Reanalyze samples.
	Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	1 set per batch of 20 or less	Recovery ± 30% Duplicate RPD ≤ 15%	1. Evaluate LCS if in control, then flag as matrix interference. 1. If RPD is out of control, reanalyze parent & MS/MSD. 2. If RPD is still out of control, flag the parent sample & comment matrix interference

Attachment C: ALERT FORM

Use form below: usfs700\ANK-Groupdata\Public\Alert-Nitrate over 10mg/Lor Nitrite-N over 1.0 mg/L

ALERT: Nitrate-N over 10mg/L or Nitrite-N over 1.0mg/L	
Sample # (s)	
PWSID (Yes or No)	
Client/Project	
NOTES	

If a PWSID is associated, the analyst must post the data and e-mail ADEC, and the data must be submitted via CMDP by Data Services

SGS	SGS North America, Inc. - Alaska Division Standard Operating Procedure
NOTE: This document contains CONFIDENTIAL business information and is not intended for distribution.	
S.O.P. Title: Determination of Metals by ICP-MS	**Revision Date**: March 2020
Method No: SW6020A/6020B	**SOP No**: 342r25
Page: 1 of 28	**Supersedes**: 342r24

Signatures below reflect periodic review of Standard Operating Procedures. If the procedure is found adequate with little or no editing necessary, this page is signed and dated. An Addendum may be issued for minor changes that need to be implemented immediately. If it is determined that major edits are required, a new revision will be released with a new signature page.

Technical Director	Date	Quality Assurance (QA) Manager, QA Staff or their Designee	Date
Stephen C. Ede	3/12/20	Jamaica Reuter	3/12/2020

Original cover pages with wet signatures and the digitally signed electronic SOP versions are available in the Quality Assurance Office.

This document will be converted into a PDF file with the QA Manager's, QA Staff's or QA Designee's electronic signature and posted on the network: \\usfs700\ANK_GroupData\Public\DOCUMENT\SOP\~Approved_SOPs~

This electronically signed PDF will be considered the controlled copy for staff. Any printouts or photocopies are invalid.

Each staff member responsible for this SOP will print & sign this cover page upon successful review, retaining it as a record in their training folder.

I have reviewed and understand the method reference(s) and this version of the SOP.
I agree to use only this currently approved version of the SOP.

Signature: _____ Printed Name: _____ Date: _____

Summary of Changes from Previous Revision:

- Updated Section 12.1.1
- Updated section 12.2.1
- Updated Section 12.3.7
- Updated section 12.3.11
- Updated section 12.3.13
- Update Attachment A, BND limits, MB limits and DT limits.

• Table of Contents

1.0. OBJECTIVE:

This Standard Operating Procedure describes the daily operation, tuning, optimization, and analysis procedures for the analysis of samples according to SW846 Method 6020A/6020B for the elements listed as analytes in Attachment D using an Inductively Coupled Plasma-Mass Spectrometer or ICP-MS.

2.0. SCOPE AND APPLICATION:

2.1 This method is applicable to the following sample matrices: ground waters, surface waters, industrial wastes, sludge, oil, and soil samples.

2.2 NexIon 300D:

Software Basics, Trouble Shooting Guide, and Hardware Basics may be found in the Perkin-Elmer Customer Training Course.

2.3 Detailed information regarding requirements by U.S. EPA SW-846 Method 6020A/6020B may be found in Revision 1 of Method 6020A and 6020B Revision 2

2.4 Initial Performance Data: It is the responsibility of the user of this SOP to generate the method specific performance data on the user's specific instrument before the analysis of any samples.

2.5 Aqueous sample, digestates, etc. are nebulized into a spray chamber where a stream of argon carries the sample aerosol through a quartz torch and injects it into an R.F. plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer. The ions are sorted according to their mass-to-charge ratio and measured with a detector.

3.0. DEVIATIONS FROM REFERENCE METHOD:

3.1 Section 11.1 of the reference method indicates that gold should be added to preserve the mercury and to prevent it from plating out in the sample introduction system. Section 11.4 of this SOP outlines the features of the current technology which address this concern.

3.2 EPA 6020A/6020B requires a digested LLQC at the LOQ level with a ± 30% recovery. SGS practice is to perform a quarterly LOQ verification at 1-2x LOQ with ± 50% recovery. As such, LOQ's are digested and analyzed every quarter and will fulfill this requirement.

3.3 EPA 6020B does not require an LLQC throughout the analytical run. An LLIQC and LLIQCS shall be run at the beginning of the run with 20% recovery criteria for DOD and 30% recovery criteria for non-DOD.

4.0. RESPONSIBILITIES:

4.1. The QA Office maintains a master list of this SOP to ensure review on a timely basis. This system serves as an accounting of SOP distribution and ensures that distributed SOPs are current and complete. The QA Office also maintains a historical file of original cover pages with wet signatures and digitally signed electronic versions of this SOP; including the current revision and any versions archived within the past 5 years.

4.2. The electronic (Word Document) versions of this SOP, both current and any prior versions, are maintained on the computer network in a secure location as a "read only" file.

4.3. It is the responsibility of all personnel to follow this SOP as written, document and gain QA or Technical Director approval for deviations to the SOP, and submit needed SOP revisions to the QA Office.

4.4. This SOP is scheduled for review on an annual basis. Any addendum will be incorporated into the SOP and a new revision of the SOP will be distributed by QA. The superseded version will be returned to the QA Office. If there are no addenda to incorporate or updates to make, the SOP is reviewed and given a new revision number. The cover page is signed and dated by the Technical Director and QA then distributed.

4.5. A PDF version of each SOP (generated in Adobe or scanned) is digitally signed by a member of the QA Office as a security measure. The digitally signed PDF, used online, is considered to be a controlled copy of the SOP and is stored on the network.

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All staff has "read" access to these SOPs. Only QAQC has access to "write" on SOPs. Staff is directed to use the controlled electronic versions of SOPs.

5.0. INTERFERENCES:

5.1. Isobaric interferences occur when an isotope of one element is at the same nominal mass as an isotope of another element (e.g., Mo 98 and Ru 98). Corrections for isobaric interferences may be made by measuring the intensity due to the interfering element at another isotope and using its natural abundance ratios to correct for its presence at the analytical mass of interest. Most commonly used corrections for isobaric interferences are already present as default interference equations in the software.

Note: Care should be taken that the isotope measured for correction purposes does not suffer from overlap with other isotopes that may be present in the sample.

5.2. Molecular interferences are caused by molecular species formed in the plasma with plasma or matrix ions (examples of common molecular interferences include ArCl, ClO, Nitrogen dimer, oxygen dimer, oxide species, double charged species, etc.) Predictions about the type of molecular interferences may be made using knowledge about the sample matrix. Molecular interferences can often be corrected for in the same manner as isobaric interferences, i.e., measuring the intensity present at another isotope and using isotope ratios to calculate the amount of the interfering species. For example, corrections for interferences of $Ar^{40}Cl^{35}$ on As at mass 75 may be made by measuring the intensity of ArCl present at mass 77 ($Ar^{40}Cl^{37}$) and converting to the apparent intensity of ArCl at mass 75 by using the isotopic ratio of Cl^{37} to Cl^{35}.

5.3. This instrument method contains correction equations to compensate for the above mentioned interferences. All samples analyzed by this method are subject to correction, the extent of which is based on sample matrix. It is the responsibility of the analyst to identify possible matrix problems and produce data of known quality. All data users should be aware that these corrections are possible without explicit notification.

5.4. Any sample with silver concentrations over calibration range (100 µg/L on actual concentration) at the standard dilution will be re-extracted at a lower sample mass/volume.

5.5. NexIon 300D handles interferences in three ways: Inter-element corrections, reaction cell gas, collision cell gas.

5.5.1. DRC (Dynamic Reaction Cell): Determines interfering molecular ion intensities at an alternative mass (polyatomic correction). A reactive gas (ammonia) selectively targets interferent or isotope of interest.

5.5.2. KED (Kinetic Energy Discrimination) Mode uses He gas and relies on interferent having a larger cross-sectional area. The gas collides more with the interferent, reducing its kinetic energy. The lower kinetic energy ions are then filtered out of the ion stream.

6.0. SAMPLE HANDLING:

6.1 Refer to SOPs 345, 361 and 384 (Digestion of Aqueous Samples (including TCLP leachates), Soil Digests and Digestion of Organic Matrices, respectively) for sample preservation. Digests are stored for one month prior to disposal in accordance with SOP#108.

6.2 Holding Times for all metals in all matrixes, EXCEPT MERCURY are six months. Mercury has a holding time of 28 days.

7.0. APPARATUS:

7.1. NexIon 300D:

7.1.1. Perkin-Elmer NexIon 300D includes the instrument, computer system, software, printer, and autosampler. Instrument capable of scanning the mass range 5-250 amu with a minimum resolution of 1 amu peak width at 5% peak weight.

7.1.2. Recommended peristaltic pump tubing (other sizes may be used to enhance performance or reduce pulsations produced by the pump):

7.1.2.1. Black/Black - 0.76 mm i.d. (for carrier).

7.1.2.2. Orange/Green - 0.38 mm i.d. (for internal standard introduction).

7.1.2.3. Grey/Grey - 1.30 mm i.d. (for drain).

7.1.3. SC- 2DX FAST Autosampler or equivalent.

7.1.4. Argon gas: High purity grade (99.99%).

7.1.5. Helium gas: UHP grade:

7.1.5.1. $H_2O \leq$ 03 ppm
7.1.5.2. $O_2 \leq 0.2$ ppm
7.1.5.3. THC ≤ 0.05 ppm

7.1.6. Ammonia gas, Anhydrous: High purity grade (99.999%).

7.2. Calibrated mechanical pipettes: 20-200 µL, 200-1000 µL, 1000-5000 µL

7.3. Metal-free plastic pipette tips (for the pipettes specified in Section 7.3).

7.4. 14-mL disposable test tubes. (Fisher catalog No: 14-956-6C or equivalent).

7.5. 50-mL Class A vessels for standards (SCP #010-500-263 or equivalent).

7.6. Instrument maintenance logs must be maintained per SGS SOP 111 and 500.

8.0. REAGENTS:

8.1. All stock solutions/chemicals/reagents must be traceable back to documented records. Refer to SGS SOP 112 and 500 and PX-0001 for proper documentation procedures. The expiration dates of all reagents must be recorded and written on the container. Where applicable, this information must be entered into the LIMS.

Note: This SOP requires 50-mL digestion vessels or a class A Teflon volumetric flask to prepare stock standards and working level solutions. All solutions prepared in these vials are made up to volume using the graduations marked on the side of each vial. The accuracy of these markings has been found to be sufficient for the purpose of the analyses described by this SOP.

8.2. Nitric acid, concentrated. (JT Baker "Instra-Analyzed" # 9598-34) or equivalent.

8.3. Hydrochloric acid, (JT Baker "Instra-Analyzed" # 9530-33) or equivalent.

8.4. Reagent water equivalent to ASTM Type I water (ASTM D 1193).

8.5. Single element or multi-element stock solutions of the following elements as needed for Standards, Tuning Solutions, and Performance Solutions.

Li, Be, B, Al, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, Ge, As, Se, Rh, Mo, Ag, Ir, Sr
Cd, In, Sn, Sb, Ba, Tl, Pb, Bi, U, Na, Mg, Si, P, K, Ca, Ti, Fe, Ce, Th, Hg, Au

8.6. NexIon Stock Solutions:

8.6.1. Intermediate Fe Solution: For example, add 2.5 mL of concentrated nitric acid to approximately 20 mL of reagent water in a 50 mL digestion vessel. Pipette the appropriate amount of Fe stock solution. Dilute to 50 mL with reagent water. Refer to **CX-0019** for the current preparation.

8.6.2. NexIon Daily Tuning Stock Solution: Add 5 mL concentrated nitric acid to approximately 30 mL of reagent water in a 100 mL Teflon volumetric flask. Prepare as per **CX-0019**.

8.7. NexIon Daily Tune solution

Prepare by pipetting 50 µL of NexIon Daily Tuning Stock Solution (Section 8.6.2.) into a 50-mL digestion vessel filled with approximately 20 mL of reagent water and 1.0 mL of concentrated nitric acid. Dilute to 50 mL with reagent water and mix well.

8.8. Dual Detector Solution is for normalization between the pulse and analog stages of the detector. Fill a 1-L nalgene bottle with approximately 400 mL of reagent water. Add 20 mL of concentrated HNO_3. Pipette the appropriate single element standards into the bottle and dilute to 1 L with reagent water. Refer to **CX-0009** for the current preparation.

8.9. Internal Standard Solution of Sc, In, Ge, and Ir. Prepare by pipetting the elements at listed volumes into a 4 liter container with approximately 1000 mL of reagent water and 80 mL of nitric acid. Dilute to 4 liters with reagent water. Refer to **CX-0017** for the current preparation.

Note: Internal Standard Solution is added inline through a mixing block, T fitting or equivalent.

8.10. Rinse: containing 4.0% (v/v) hydrochloric acid and 2.0% (v/v) nitric acid and 2 mg/L of Au. Volumes may be made as necessary at a ratio of 80.0 mL of nitric, 160.0 mL of HCL and 0.4 mL of 10,000 mg/L Au per 4000 mL of reagent water.

8.11. Carrier Solution:

8.11.1. For SW 3010/3050: Water containing 2.0% (v/v) nitric acid. Volumes may be made as necessary at a ratio of 20.0 mL nitric acid per 1000 mL of reagent water.

8.12. Stock Calibration Standard Solutions: While this SOP gives directions for making specific concentrations, the analyst may, at times, be directed to prepare alternate concentrations for "fit of purpose." Standards may be prepared from single element solutions or a custom blended solution. All solutions for each stock standard are pippetted into a 100 mL Class A Teflon volumetric flask with about 30 mL of reagent water and 5 mL nitric acid. After all elements for each solution have been added, fill the flask to the mark with reagent water. Refer to **CX-0008** for the current preparations for 6020 Cal 1-4. Refer to **CX-0022** for the current preparation of Hg Cal.

8.13. Stock QCS (Quality Control Sample) solution: The QCS stock must be from a source independent of that used for calibration. The concentrations of the analytes in the QCS are prepared at or near the mid-point of the calibration range and at a concentration not used for calibration. All solutions for each stock standard are pippetted into a 100 mL Class A Teflon volumetric flask with about 30 mL of reagent water and 5 mL nitric acid. After all elements for each solution have been added, fill the flask to the mark with reagent water. Refer to **CX-0008** for the current preparations for 6020 QCS 1-4. Refer to **CX-0022** for the current preparation of Hg QCS.

8.14. Low Level Quantitation Check: The concentrations of the analytes in the LLQC are prepared at the LOQ. A change in the LOQ will require a change in the spike volume. All solutions for each stock standard are pippetted into a 100 mL Class A Teflon volumetric flask with about 30 mL of reagent water and 5 mL nitric acid. After all elements for each solution have been added, fill the flask to the mark with reagent water. Refer to **CX-0013** for the current preparations for Intermediate and Stock LLQC 1-4 and LLQC Hg.

8.15. Low Level Quantitation Check 3050: The concentrations of the analytes in the LLQCS are prepared at the LOQ. A change in the LOQ will require a change in the spike volume. All solutions for each stock standard are pippetted into a 100 mL Class A Teflon volumetric flask with about 30 mL of reagent water and 5 mL nitric acid. After all elements for each solution have been added, fill the flask to the mark with reagent water. Refer to **CX-0029** for the current preparations for Intermediate and Stock LLQCS 1-4 and LLQCS Hg.

8.16. Post Digestion Spike (BND): Pipette 50 µL of QCS (1-4) + Hg QCS Standard (Section 8.13) into a 14 mL test tube, match the analytical dilution and pipette enough diluent for a final volume of 5 mL. Mix.

8.17. Interference Check Solution Stocks

8.17.1. Interference Check Solution A Stock (ICSA 1): 10,000 µg/mL of Cl^-; 2000 µg/mL of C; 1000 µg/mL each of Al, Ca, Fe, K, Mg, Na, P, and S; and 20 µg/mL each of Mo and Ti. **Note**: Inorganic Ventures Cat #6020ICS-0A (or equivalent).

8.17.2. Interference Check Solution AB 1 (ICSAB 1)

Prepare by adding 5 mL of concentrated nitric acid to a 100 mL Class A Teflon volumetric flask with about 30 mL of reagent water. After all elements have been added, fill the flask to the mark with reagent water. Refer to **CX-0012** for the current preparation.

8.17.3. Interference Check Solution AB 2 (ICSAB 2)

Prepare by adding 5 mL of concentrated nitric acid to a 100 mL Class A Teflon volumetric flask with about 30 mL of reagent water. After Sb has been added, fill the flask to the mark with reagent water. Refer to **CX-0012** for the current preparation.

8.18. ICSA (QC STD 7): Prepare by adding acids at volumes noted below to a 50-mL digestion vessel containing about 30 mL of reagent water. Add 1 mL of ICSA 1 Stock (Section 8.17.1) and dilute to 50 mL with reagent water. Prepare this solution as needed.

8.18.1. For soil/water matrices (SW 3050/3010): 1.0 mL HNO_3 and 80 µL of HCl.

8.19. ICSAB (QC STD 6): Prepare by adding acids at volumes noted below to a 50-mL digestion vessel containing about 30 mL of reagent water. Add 1 mL of ICSA 1 stock (Section 8.17.1), 2 mL of ICSAB 1 (Section 8.17.2) and 2 mL of ICSAB 2 (Section 8.17.3) and dilute to 50 mL with reagent water. Prepare this solution as needed.

8.19.1. For soil/water matrices (SW 3050/3010): 1.0 mL HNO_3 and 80 µL of HCl.

8.20. Working calibration scheme: Prepare fresh calibration standards daily in Class A volumetric labware. Prepare the calibration standards according to the charts below. Be sure to fill the vessel with about 20 mL of reagent water. Then add the acids followed by the appropriate spikes and/or dilutions found in attachment E.

8.21. Diluent:

8.21.1. Standard Water and Soil Matrices (SW 3010 / 3050): 1.25% (v/v) nitric acid

Fill a 1-L container with approximately 500 mL of reagent water. Add 12.5 mL of concentrated nitric acid to the container and dilute to the 1-L mark with reagent water.

8.21.2. HCl Diluent: 2% nitric acid, 0.2% hydrochloric acid.

This diluent should be used for dilutions equal to or greater than 25X, including the standard dilution for 3010 TCLP.

Fill a 1-L container with approximately 500 mL of reagent water. Add 20 mL of concentrated nitric acid and 2 mL of concentrated hydrochloric acid. Dilute to the 1-L mark with reagent water.

9.0. DIGESTION:

Refer to SOPs 345, 361 and 384 (Digestion of Aqueous Samples (including TCLP leachates), Soil Digests and Digestion of Organic Matrices, respectively) for sample preparation.

10.0. CALIBRATION:

10.1. The instrument must be calibrated before analysis of any samples with a blank and five calibration standards. If less than five calibration standards are used, refer to the SGS SOP 500 for the criteria used in dropping calibration points. **Note:** Perkin-Elmer's software documentation refers to "blank subtraction;" however, this is actually a zeroing of the instrument to the blank response before calibration is initiated. No blank subtraction is performed following calibration. The manufacturer describes the calibration technique as "force through zero." This technique has been shown to be linear at the blank response.

10.2. The concentrations of the standards used should be entered into the calibration page of the analytical method in the ICP/MS software according to the values of the standards prepared in Section 8.20.

10.3. The first standard run should be the lowest level standard containing analyte and be equal to or less than the LOQ, followed by standards of increasing concentration in order to minimize cross-contamination and carryover.

10.4. Software will label the calibration as follows: Blank, Standard 1, Standard 2, Standard 3, Standard 4, and Standard 5.

10.5. The R-value (linear regression correlation coefficient) for each element must be greater than or equal to 0.998.

10.6. The average of three replicates for all standards, QC, and samples will be used to determine concentrations.

11.0. ANALYSIS:

11.1. Initiate the plasma and allow a warm-up of at least 30-60 minutes. The tuning procedures may be carried out during warm-up

11.2. Before calibration and analysis of samples, the instrument must undergo a series of performance checks to ensure that the instrument is operating properly.

11.2.1. For the NexIon 300D:

11.2.1.1. While using the Dual Detector Solution (Section 8.10), select the "Dual Detector Calibration" tab, right click and select "Quick Optimize". When calibration is complete, open the interactive window, review the graph and print it to archive with the tune package. Run the dual detector calibration twice. It is a good practice to do the dual detector calibration every day, but it only needs to be done once a week or whenever detector voltages are changed.

11.2.1.2. Switch to the Daily Tune Solution (Section 8.9) after rinsing the lines.

11.2.1.3. Torch Alignment: Select "Torch Alignment," right click and select "Quick Optimize". There is no printout.

11.2.1.4. Mass Calibration and Resolution: Select "Mass Calibration and Resolution," right click and select "Quick Optimize". The software will automatically check the limits, make adjustments and rerun if there is a failure. After each run the results will print out.

11.2.1.4.1. The measured mass for each analyte must be +/- .05 AMU of the exact mass.

11.2.1.4.2. The measured peak width must be 0.7 amu, +/- 0.1 amu at 10% peak height.

11.2.1.5. Autolens STD/DRC: Select "AutoLens STD/DRC" right click and select "Quick Optimize". Print the graph to archive with the tune package and label it as "STD/DRC."

11.2.1.6. KED Mode Autolens: Select "KED Mode Autolens" right click and select "Quick Optimize". Print the graph to archive with the tune package and label it as "KED." Only needed if collision gasses are used.

11.2.1.7. Daily Performance: Select "Daily Performance Check," right click and select "Quick Optimize". The software will automatically check the limits except for the RSDs, make adjustments and rerun if there is a failure. After each run the results will print out.

11.2.1.7.1. The RSDs for the five replicates of Be, Mg, In and U need to be less than or equal to 5%.

11.2.1.7.2. Monitor daily performance measures for Be sensitivity, Mg sensitivity, In sensitivity background, U sensitivity, % double charged and % oxide levels.

Background at mass 220	≤ 5 cps
Ce++	≤ 3%
CeO	≤ 2.5%
Be intensity	> 2,000 CPS
Mg intensity	> 15,000 CPS
In intensity	> 40,000 CPS
U intensity	> 30,000 CPS

11.2.1.8. After tuning, aspirate rinse for about 5 minutes before beginning the calibration to avoid carry-over contamination.

NOTE: These performance requirements must be achieved before any analysis is performed. Oxides and double charged levels can be adjusted by slightly varying the nebulizer flow rate. **The Daily Performance Report must be printed and submitted with each analytical batch.

11.3. Open the "6020A" workspace

11.3.1. Calibration standards and QC solutions prepared in Section 8.21 are to be placed into their assigned autosampler (A/S) positions.

11.3.2. Edit the Sample window under the batch analysis to update the schedule with new sample information and autosampler locations. The default page will have rinse times and pump speeds already entered. Ensure that the proper dilution factor is entered for each sample. Save the sample window with the date of analysis.

11.3.3. Typical Sample Dilutions: Dilute all samples and digested QC with the appropriate amount of diluent in the 14 mL disposable test tubes. Refer to Section 8.22 for the diluent preparations.

3010 (5X): 1.0 mL of sample into 4.0 mL of diluent for a final volume of 5 mL.

3050B (10X): 0.5 mL of sample into 4.5 mL of diluent for a final volume of 5 mL.

3010T (25X): 200 µL of sample into 4.8 mL of HCl Diluent for a final volume of 5 mL.

Note: The LB for TCLP extraction is diluted by prep. Check to ensure the final dilution of the LB matches that of the most concentrated sample in the batch.

11.3.4. The choice can be made to automate CCV/CB rates at every 10 samples analyzed or specify CCV/CB analysis at particular times during the run (not to exceed an interval of 10 samples) within the method under the QC tab / QC Frequency sub-tab. The default is automated at 10 samples.

11.3.5. Just prior to analysis, press the Restart QC button (this resets QC to run every ten samples) under the 'Analysis' drop-down menu. Then select the samples to be analyzed under the Batch tab in the sample window by highlighting the rows to be analyzed. Make sure that row 1 containing the calibration command is highlighted or that calibration is performed prior to the analysis of any samples.

11.3.6. Select "Analyze Batch".

11.3.7. All samples containing target analytes above linear range shall be diluted and re-analyzed.

11.4. Each analysis consists of an injection followed by a rinse of the sample probe. Then, after acquisition of data, the sample introduction system is rinsed a second time before the next injection.

11.4.1. To ensure mercury is cleared from the system, the sample probe moves to the 1st rinse station where it is rinsed in a rinse solution containing 1 mg/L gold, then moves to rinse station 2 where it is rinsed a 2nd time with the same rinse solution. Following data acquisition, the valve switches back to the load position and the probe and sample loop are rinsed with the gold solution. After the probe and sample loop rinse, the valve switches to the inject position so that the nebulizer and spray chamber can be rinsed with the gold solution as well.

11.4.2. Analysis of mercury by method 6020A/6020B is accomplished by the addition of gold to both the rinse (Method 6020A/6020B 7.6.3), and the calibration standards. Gold acts as an oxidizing agent for mercury, preventing volatilization of elemental mercury, thus retaining it in solution and preventing plating out in the sample introduction system.

11.4.3. Analysis of mercury by ICP-MS is possible with the SC-FAST sample introduction system even without adding gold to the rinse. Addition of gold to the rinse improves on ESI's already superb mercury washout times. Testing done by ESI has shown complete washout times for 1 ppb of Hg was 23 seconds and 5 ppb of Hg was 30 seconds even without using gold in the rinse.

11.5. At the end of the analytical run, print out the following and include them with the raw data.

11.5.1. Open the "report option window."

11.5.2. Open "CAL REPORT.rop" file.

11.5.3. Print the report view.

11.5.4. Open "RUN-COVER.rop" file.

11.5.5. Print the report view.

11.5.6. Open "SGS1.rop" file to reset.

12.0. QUALITY CONTROL:

12.1. Initial Demonstration of Laboratory Performance - The following items must be completed before the analysis of any samples is performed by each laboratory using this method.

12.1.1. Instrument Detection Limits (IDLs) - IDLs must be determined at least once using new equipment, after major instrument maintenance such as changing the detector, and or/ at a frequency designated by the project. IDLs are useful means to evaluate the instrument noise level and

response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. This procedure states that the IDLs be estimated by calculating the sum of the standard deviations of the three runs on three nonconsecutive days from the analysis of a reagent blank solution with seven consecutive measurements. Each measurement must be performed as though it was a separate sample (i.e., with rinsing in between). The IDL must be less than or equal to the DL. Refer to SOP 500 for further guidance.

12.1.2. Detection Limit Study (DLs) - In order to determine the DL in a matrix, the analytes should be spiked into the matrix of interest (e.g., ground water matrix, or other sample preparation procedure matrix) at a level that is three to five times the estimated DL. The spiked matrix is then carried through the entire sample preparation procedure. Each replicate result must be calculated the same as if it were a final client sample result. The DL is calculated by multiplying the standard deviation obtained from a minimum of seven replicates by the one-sided 99% confidence level t-statistic. See Section 17 for specific conditions for performing DL studies. Refer to SOP 116 for further guidance.

12.2. Linear Dynamic Ranges

12.2.1. The linear range establishes the highest concentration that may be reported without diluting the sample. Following calibration, the laboratory may choose to analyze a standard at a higher concentration than the high standard in the calibration. The standard must recover with 10% of its true value, and if successful, establishes the linear range. The Linear range standards must be analyzed in the same instrument run as the calibration they are associated with (i.e., on a daily basis) but may be analyzed anywhere within that run. If a linear range standard is not analyzed for any specific element, the highest standard in the calibration becomes the linear range.

12.2.2. Calibrate the instrument as described in Sections 10 and 11 and run a series of standards that increase in concentration until the measured value deviates 10% from the expected value. The upper limit is determined to be the value of the highest standard that is within 10% of the expected value.

Note: the Linear Dynamic Range should be re-evaluated on the following basis:

- Semi-annually
- Whenever new PA tube is installed in the RF generator
- Upon any significant change to the instrument (i.e. new detector or alternate sample introduction system)

Refer to SOP 500 for further guidance.

12.3. Analyses of Quality Control (QC) samples – QC samples are analyzed at periodic intervals to evaluate method and instrument performance. Each QC type is described below along with relevant evaluation criteria. All analyses for analytes of interest must be bracketed by acceptable QC to avoid performing corrective action

12.3.1. Quality Control Sample – *Note: SGS terms this the **QCS** while Method 6020A/6020B uses another identification for this second source standard.* Analysis of the QCS occurs immediately following the ICV to verify the accuracy of the calibration curve. The results of the target analytes must be within ±10% of the true value. If the 10% criteria is not met, the QCS may be analyzed a second time. If the QCS is still outside of acceptance criteria, the cause of the error must be determined and a recalibration must be performed.

12.3.2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV) Analysis (standards are from the same source as the calibration curve):

12.3.2.1. The ICV is required at the beginning of the analytical sequence.
12.3.2.2. The CCV is analyzed after every 10 samples and at the end of the analytical sequence.

12.3.2.3. The limits are ±10% of the true value.

12.3.2.4. If the ICV criteria is not met, the ICV may be analyzed a second time. If the ICV is still outside of acceptance criteria, the cause of the error must be determined and a recalibration must be performed

12.3.2.5. If the CCV criteria is not met:

12.3.2.5.1. For non-DOD samples: the CCV may be analyzed a second time. If the CCV is still outside of acceptance criteria, the cause of the error must be determined and a recalibration must be performed. Samples run between CCV's not within limits must be reanalyzed. If the rerun meets QC criteria, then the run sequence may be continued. Samples following the passing CCV are valid.

12.3.2.5.2. For DOD samples: The analyst may immediately (within 1 hr of the failing CCV and before any other samples have acquired) rerun 2 successive CCVs. If both meet QC criteria for all analytes of interest, then the samples already analyzed may be reported and the run sequence may be continued. Samples following the two passing CCVs are also valid.

12.3.3. Continuing Calibration Blank (CB) analysis. The CB is required at the beginning of the analytical sequence, after every 10 samples and at the end of the analytical sequence.

12.3.3.1. The limits are < LOQ for each element.
Note: For DoD clients, the limits are < LOD (< ½ the LOQ).

12.3.3.2. If the CB criteria are not met, the CB may be analyzed a second time. If the CB is still outside acceptance criteria, the cause of the error must be determined and a recalibration must be performed. Samples run between CB's not within criteria must be evaluated and possibly reanalyzed. If the analyte concentration is less than the LOQ or 10X the level of that seen in the CB, the analyte data can be reported with an appropriate comment. All samples outside of these criteria must be reanalyzed. If failure occurs consistently, the IDL and DL must be re-evaluated.

12.3.4. Low Level Initial Quantitation Check (LLIQC/LLIQCS) is spiked at the LOQ. This is analyzed at the beginning of the analytical sequence. The LLIQC limits are ± 20% for DOD and ± 30% for non-DOD. If an analyte is greater than +20% for DOD or +30% for non-DOD on the LLIQC or LLIQCS but the analyte is non-detect (<LOQ) in the sample it can be reported with a comment on the LLIQC or LLIQCS.

12.3.5. ICSA (QC Std 6) and ICSAB (QC Std 7) solutions - Required at the beginning of analytical run or every 12 hours, whichever is more frequent. Per client request, ICSA and ICSAB may be analyzed at the end of the run. The Internal Standard recoveries in the ICSA and ICSAB solutions must be in the range of 70-130%.

12.3.5.1. ICSA criteria for DoD clients evaluates the absolute values of all non-spiked analytes and limits them to < LOD (unless they are a verified trace impurity from one of the spiked analytes). Corrective action: Flag any analytes that exceed limits. This criterion is in exceedance of the method.

12.3.5.2. ICSAB criteria for DoD clients are ± 20% of expected values. Corrective action: Flag any analytes that exceed limits. This criterion is in exceedance of the method.

12.3.6. Internal Standards: Intensities must be monitored in all solutions. The ICP/MS software will report the % recovery for each internal standard being used.

12.3.6.1. The RSD of the internal standards in the Calibration Standards must be within 10%. If the internal standards do not meet these criteria, re-run once. If they are still outside acceptance criteria, recalibrate.

12.3.6.2. Intensities of the internal standards in CCV and CB solutions must be within ± 30% of the levels in the original calibration blank. If the internal standards do not meet criteria, terminate the analysis, correct the problem, re-calibrate, and reanalyze all affected samples.

12.3.6.3. Intensities of internal standards in samples must be within 70-130% of that in the original calibration blank. If the internal standards do not meet criteria, dilute the sample five-fold and reanalyze. This procedure is followed until the internal standard intensities fall within the prescribed window.

12.3.7. Method Blank (MB): the MB is analyte-free reagent water that has been processed and analyzed identically to an unknown sample to assess systematic contamination. One MB will be prepared and analyzed for each sample batch of 20 samples or less. Results for analytes of interest in the MB must be less than half the LOQ OR are less than project specific requirements. **Note:** For DoD clients, the MB must be less than half the LOQ. Samples containing detectable amounts of contamination may require re-digestion. If the measured sample concentration is greater than 10 times the MB contamination or less than the LOQ, the samples will not require re-digestion, but detect DoD data must be flagged with a 'B' in LIMS. All other samples will require re-digestion and reanalysis.

12.3.8. Leachate Blank (LB): The LB is the leachate used for TCLP samples. The LB is brought through the TCLP process as if it were a sample. It is evaluated in the same manner as an MB.

12.3.9. Laboratory Control Sample (LCS): the LCS is reagent water that has been spiked with known concentrations of analyte that is processed and analyzed identically to an unknown sample to assess system accuracy. One LCS will be prepared and analyzed for each sample batch of 20 samples or less. See Attachment C for the acceptance criteria for the LCS. If an analyte of interest has a %recovery that is greater than the acceptance criteria and the associated sample results for that analyte are below the LOQ, then those samples may be reported with appropriate qualifiers. If an analyte of interest has a %recovery less than the acceptance criteria, then those samples affected will require re-digestion.

12.3.10. Matrix Spike (MS) and Matrix Spike Duplicate (MSD): the MS/MSD is prepared and analyzed to determine the accuracy and precision of the analytical system and are prepared for each set of 20 samples or less of a similar matrix. Samples are spiked at a level equal to that of the LCS. See Attachment C for recovery and RPD acceptance criteria. If the recovery for an analyte of interest does not meet criteria, perform a bench spike (BND). If the RPD is outside of criteria, and there is a sample DUP, evaluate the RPD for the DUP. If the DUP RPD passes, then post with comment.

If the DUP RPD fails, then it is confirmed that the sample is non-homogenous. Post the data with a comment. If there is not a sample DUP and the analyte of interest is detected in the sample, the sample/MS/MSD must be re-extracted.

Note: If an LCSD was analyzed with the batch and is within RPD limits, then analytical precision is shown to be in control and all data can be posted with comment.

12.3.11. Post Digestion Spike (BND): the BND is performed only on spiked samples that do not meet MS recovery evaluation criteria. An aliquot of digested sample at standard or inflated dilution is spiked with a known concentration of analyte. Recoveries calculated on the BND for 3010/3050 should be between 75% and 125% of the expected values. The BND recoveries for 3050O (matrix 3) should be between 70-130% of expected values.

12.3.11.1. If the spike is not recovered within the acceptance limits and the LCS for that analyte is in control, then the recovery problem is judged matrix related and the sample will be diluted and re-spiked.

12.3.11.2. Analytes that do not meet acceptance limits will be commented on in the parent sample, or all associated samples in the prep batch should be run by method of standard additions (MSA).

12.3.12. Sample Duplicate (DUP): Analyze one DUP sample for every matrix in a batch of twenty samples or less. The RPD of the DUP should be ≤ 20%. These limits should not be exceeded for analyte values greater than 100 times the IDL. Preferentially, the RPD requirement is fulfilled by the MS/MSD RPD. However, in some complex matrices, when the MS/MSD RPD is outside limits, the sample/sample DUP can be utilized as a separate evaluation for sample homogeneity.

12.3.13. Dilution Test (DT): A 5-fold further dilution on top of the standard dilution. If the analyte concentration in the selected sample is sufficiently high (50x above the LOQ), the DT must agree within ±20% of the original determination. If not, interference must be suspected and the sample flagged. One dilution test must be performed for each digestion batch of twenty samples or less of each matrix.

12.4. See Attachment A for specific corrective actions. Any corrective action needed to address a QC outlier that is not listed in this SOP requires the approval of the QA Manager or Technical Director.

13.0. CALCULATIONS, REVIEW AND REPORTING:

13.1 The NexIon software performs all calculations necessary to convert raw data (ion counts/second) to concentration (µg/L). The calculated quantities are selected by choosing the desired options in the Report Options screen. The default report option for the NexIon 6020 Method is EPA6020 SGS1.rop. If the user desires, this format can be edited and saved under a new name.

13.2 All calculations performed in the software are based on the ratio of the analyte intensity (cps) to the internal standard intensity (cps). In all calculations where internal standards are used the ratio of the analyte intensity to internal standard intensity is taken before any other calculation is performed.

13.3 Quality Control Sample results may be checked using the QC Checking features in the ICP/MS software. All values entered in the default 6020 method should be checked and edited to match the true values used by the laboratory.

13.4 The recoveries for standard solutions (both digested standards and the periodic quality control standards) are calculated by dividing the observed value by the expected value. The result is multiplied by 100 to give a percent recovery.

$$\frac{Vo}{Ve} \times 100 = \% \text{ recovery}$$

Vo = observed value
Ve = expected value

13.5 The calculation for spike recoveries requires the subtraction of the sample contribution from the response of the spiked sample, the division of this result by the expected value of the spike, and the multiplication by 100 yields percent recovery.

$$\frac{Vo-Sc}{Ve} \times 100 = \% \text{ recovery}$$

Vo = observed value of the spiked sample
Sc = observed value of the sample
Ve = expected value of the spike

13.6 The RPD between duplicate samples is calculated as the absolute difference between the sample and the duplicate, divided by the average of the sample and the duplicate, all multiplied by 100.

$$\frac{|Sc - Dc|}{\{(Sc + Dc) / 2\}} \times 100 = \text{Duplicate Relative Percent Difference (Dup RPD)}$$

Sc = observed sample concentration
Dc = observed duplicate sample concentration

13.7 The post digestion spike (BND) recovery is calculated as the difference of the BND concentration minus the sample concentration all divided by the expected concentration of the BND. The resultant value is multiplied by 100 to give percent recovery.

$$\frac{BSc - Sc}{BSe} \times 100 = \% \text{ recovery}$$

BSc = observed value of post-digestion spike
Sc = observed value of sample
BSe = expected value of post-digestion spike

13.8 Samples that have been digested using concentration procedures must have the concentrations of the elements multiplied by the appropriate factor.

13.9 Data Archiving: The raw data files produced by the ICP/MS software are moved over to the network on a monthly basis. The archive location is: \\usfs700\ANK_Instrument_Data\METALS\ICPMS\DATA.

14.0. HEALTH AND SAFETY:

14.1. Samples shall be returned to the approved storage location until such time as it is determined that no further analysis will be required.

14.2. Once it has been established that no more analysis of a sample will be required, acid and alkaline preserved samples may be neutralized using the Elementary Neutralization Hood located in GC Prep, unless it is

considered to be hazardous (i.e. mercury waste, cyanide waste). Refer to the current version of SOP 108 for further instruction.

14.3. All surplus reagent acids shall be neutralized on a daily basis using the Elementary Neutralization Hood located in GC Prep.

14.4. Small volumes of surplus volatile reagents may be allowed to evaporate in a hood at the end of the analytical session.

14.5. Proper Personal Protective Equipment (PPE) must be worn at all times. Proper PPE when handling samples include a lab coat, gloves and safety glasses. In addition, when handling concentrated acid or base preservative, a face shield and apron must be worn.

14.6. Liquid argon represents a potential cryogenic hazard and safe handling procedures should be used when handling liquid argon tanks at all times.

14.7. Anhydrous Ammonia is an irritant and corrosive to the skin, eyes, respiratory tract and mucous membranes. Exposure to rapidly expanding gases may cause severe chemical burns and frostbite to the eyes, lungs, and skin.

14.8. The ICP/MS instruments are fully interlocked to protect the user from dangers such as high voltages, radio frequency generators, and intense ultra-violet light. At no time should the operator attempt to disable these interlocks or operate the instruments if any safety interlock is known to be disabled or malfunctioning.

14.9. Spilled samples, reagents, and water should be cleaned up from instrument and autosampler surfaces immediately. In the case of acid spills the acid should be neutralized with sodium bicarbonate solution before cleanup.

15.0. POLLUTION PREVENTION:

SGS is committed to evaluate all areas of the lab with regard to current and potential pollution prevention. Pollution prevention is described as any technique that reduces or eliminates waste at the point of generation. Further discussion on pollution prevention programs in the laboratory can be found in *SGS Pollution Prevention Plan* (Form F053).

16.0. METHOD PERFORMANCE:

There are no method performance measures to report at this time.

17.0. DETECTION LIMIT (DL) STUDY:

DL studies are performed when a significant change in instrument response is observed, when a new instrument is purchased for analysis. The DL is intended to demonstrate the capability of this method as it is implemented at SGS. An update to the DL does not necessitate an update to this document. Further guidance on performing a DL study can be found in SOP 116.

18.0. LIMIT OF DETECTION (LOD):

The LOD is defined per SOP 116; LOD verification shall be performed quarterly according to the schedule set by the QA Office.

19.0. LIMIT OF QUANTITATION (LOQ):

LOQs may be adjusted for sample dilution or the presence of matrix interferences. LOQs are established based on experimental DL studies and comparison to program and project-specific reporting limit requirements**.** LOQ information is only provided to give the reader an idea of the reporting capabilities of the method as it is implemented at SGS. LOQs may change at the laboratory's discretion.

Element	LOQ - Oil (µg/Kg)	LOQ - Soil (µg/Kg)	LOQ - Water (µg/L)
Ag	250	20	0.4
Al	NA	2000	40
As	1250	100	1.0
B	NA	2000	40
Ba	500	30	0.6
Be	500	10	0.2
Bi	NA	20	0.4
Ca	NA	5000	100
Cd	500	20	0.4
Co	NA	50	0.2
Cr	2000	40	0.8
Cu	500	60	1.2
Fe	NA	5000	100
K	NA	10000	200
Mg	NA	5000	100
Mn	NA	20	0.4
Mo	500	100	1.0
Na	NA	10000	200
Ni	500	20	0.4
P	NA	2000	100
Pb	500	20	0.2
Sb	500	100	0.6
Se	500	100	4.0
Si	NA	NA	NA
Sn	NA	100	1.0
Sr	NA	100	NA
Ti	NA	100	2.0
Tl	250	20	0.4
V	2500	300	4.0
Zn	4000	250	5.0
Hg	20	4.0	0.04

20.0. REFERENCES:

20.1. "Inductively Coupled Plasma-Mass Spectrometry", U.S. EPA SW-846 Method 6020A rev. 1.

20.2. NexIon 300D ICP-MS Customer Training Course, 2000, Perkin-Elmer Corporation.

20.3. "Inductively Coupled Plasma-Mass Spectrometry", U.S. EPA SW-846 Method 6020B rev. 2.

21.0. ATTACHMENTS:

Attachment A: Corrective Action Table
Attachment B: Method Nomenclature
Attachment C: Limits for LCS, MS, MSD and RPD
Attachment D: ICP-MS Isotopes

Attachment A: CORRECTIVE ACTION TABLE

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW6020A/ 6020B	Tune	Daily.	See Sections 11.2.1.7.1 and 11.2.1.7.2	1. Find source of problem and correct. 2. Repeat Tune.
SW6020A/ 6020B	Daily Instrument Performance	Daily.	See Section 11.2.1.	1. Find source of problem and correct. 2. Repeat Daily Instrument Performance Check.
SW6020A/ 6020B	Calibration	Daily before each method.	Correlation coefficient ≥ 0.998.	1. Find source of problem and correct. 2. Repeat calibration
SW6020A/ 6020B	Calibration Blank (CB)	After calibration & 1 per 10 sample readings & at the end.	Concentration < LOQ **For DoD:** < ½ LOQ or <1/10th the amount measured in any sample	1. Initial CB: Correct problem and repeat once. If that fails, recalibrate. 2. CB: For DOD: All samples following the last acceptable calibration blank must be reanalyzed. For non-DOD. Repeat analysis once. 3. Fix problem 4. Recalibrate. CB failures due to carryover may not require a new calibration. 5. Samples that are non-detect may be reported. Comment on the CB. For level 2 DOD clients, report on the sample. 6. Samples that are >10x the LOQ may be reported. Comment on the CB. For level 2 DOD clients, report on the sample.
	Initial Calibration Verification (ICV)	After Calibration	±10%	1. Repeat analysis once. 2. Fix problem. 3. Recalibrate.
SW6020A/ 6020B	Continuous Calibration Verification (CCV)	1 per 10 sample readings & at end.	±10%	1. Refer to SOP 500 Attachment D
SW6020A/ 6020B	Quality Control Std. (QCS)	After Calibration	±10%	1. Repeat analysis once. 2. Fix problem. 3. Recalibrate.
SW6020A/ 6020B	Lower Limit Initial Quantitation Check (LLIQC/LLIQCS)	After Calibration	±20% for DOD ±30% for non-DOD	1. Repeat analysis once. 2. Fix problem. 3. Recalibrate

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW6020A /6020B	Method Blank (MB)	1 per batch of 20 samples or less	Concentration < ½ LOQ OR project specific. **For DoD:** < ½ LOQ	1. Repeat analysis once. 2. Evaluate samples; if N.D. or >10X MB, OK to report. Apply B flag for DoD if detect results reported without compliant blank. 3. Re-digest and reanalyze samples with concentration of contaminant > LOQ & <10X MB value.
SW6020A/ 6020B	Leachate Blank (LB)	1 per 3010 TCLP batch of 20 samples or less	Concentration < LOQ For DoD: < LOD	1. Same as for the MB. See above.
SW6020A/ 6020B	Laboratory Control Sample (LCS)	1 per batch of 20 or less	See Attachment C	1. Repeat analysis once. 2. Evaluate samples; if LCS is high but samples are ND for that analyte, ok to report, but comment on sample. Re-digest and reanalyze samples with concentration of contaminant > LOQ. 3. If LCS is low, re-digest and reanalyze samples.
SW6020A/ 6020B	Matrix Spike (MS) /Matrix Spike Duplicate (MSD)	1 per batch of 20 or less.	See Attachment C for recovery criteria. %RPD criteria for: 3010/3050 is 20 3050O is 30	1. If recovery is outside of control, perform a bench spike (BND) 2. If RPD is outside of control, and there is a sample DUP: 2.1. If DUP RPD is outside of control, comment on sample homogeneity. 2.2. If DUP RPD is in control, post with comment. 3. If RPD is outside of control, and there is not a sample DUP: 3.1. Evaluate parent sample. If the target analyte is ND, report with comment. 3.2. If target analyte is detect, re-digest and reanalyze. 3.3. If still outside of limits, flag sample as non-homogeneous.
SW6020A/ 6020B	Post Digest Spike (BND)	When required.	For 3010/3050: 75-125% For 3050O: 70-130%	1. Dilute and re-spike. 2. Run all associated samples by MSA. 3. Flag data as suspected matrix interference. Or, J-flag affected analytes in parent sample

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SW6020A/ 6020B	Duplicate (DUP)	Once for every sample matrix in a batch of ≤ 20 samples. Can be derived from MS/MSD.	≤ 20% RPD for analytes greater than 100 times the IDL.	1. If RPD outside of control, evaluate the MS/MSD RPD. 2. If it is out as well, flag sample as non-homogenous.
SW6020A/ 6020B	Dilution Test (DT)	1 per batch of 20 or less.	1. Evaluate analytes greater than 50X LOQ in sample. 2. The 5X dilution must agree within ±20% of original.	Flag data as suspected matrix interference.
SW6020A/ 6020B	ICSA	After calibration, or every 12 hours, whichever is more frequent.	Internal Standards: 70 – 130% (For DoD: Absolute values of non-spiked analytes < LOD)	1. If internal standards fail to meet criteria, recalibrate. 2. Flag any analytes that fail DoD criteria
SW6020A/ 6020B	ICSAB	After calibration, or every 12 hours, whichever is more frequent.	Internal Standards: 70-130%. (For DoD: spiked analytes ±20 % of expected values)	1. If internal standards fail to meet criteria, recalibrate. 2. Flag any analytes that fail DoD criteria
SW6020A/ 6020B	Internal Standards	In Calibration Standards	RSD is established at 10%.	1. Rerun once 2. Recalibrate
		In all solutions.	In CCV/CB: ±30% original cal blank intensity.	1. Terminate analysis. 2. Correct problem. 3. Re-calibrate.
			In Samples: 70-130% original calibration blank intensity.	1. Dilute the sample fivefold and reanalyze. 2. Continue until criteria are met.

Attachment B: METHOD NOMENCLATURE

METHOD SYMBOL	SGS SYMBOL	METHOD NAME	SGS NAME
CCV	ICV,CCV	Calibration Verification Solution	Continuing Calibration Verification
DUP	DUP	Duplicates	Duplicates
LCS	LCS	Laboratory Control Sample	Laboratory Control Sample
CCB	CB	Calibration Blank	Calibration Blank
MB	MB	Preparation Blank	Method Blank
DT	DT	Dilution Test	Dilution Test
LLQC	LLQC	Low Level Quantitation Check	Low Level Quantitation Check
BND	BND	Bench Spike	Bench Spike
ICV	QCS	Initial Calibration Verification (second source)	Quality Control Sample (second source)

Attachment C: ACCURACY LIMITS FOR LCS, MS, and MSD

	3010 Water/ 3010 TCLP		3050 Soils		3050O Oils
Analyte	Lower (%)	Upper (%)	Lower (%)	Upper (%)	Range (%)
Aluminum (Al)	84	117	78	124	
Antimony (Sb)	85	117	72	124	70-130
Arsenic (As)	84	116	82	118	70-130
Barium (Ba)	86	114	86	116	70-130
Beryllium (Be)	83	121	80	120	70-130
Bismuth (Bi)	-	-	80	120	
Boron (B)	73	130	74	128	
Cadmium (Cd)	87	115	84	116	70-130
Calcium (Ca)	87	118	86	118	
Chromium (Cr)	85	116	83	119	70-130
Cobalt (Co)	86	115	84	115	
Copper (Cu)	85	118	84	119	70-130
Iron (Fe)	87	118	81	124	
Lead (Pb)	88	115	84	118	70-130
Lithium (Li)	78	126	75	120	
Magnesium (Mg)	83	118	80	123	
Manganese (Mn)	87	115	85	116	
Mercury (Hg)	70	124	74	126	
Molybdenum (Mo)	83	115	83	114	70-130
Nickel (Ni)	85	117	84	119	70-130
Phosphorus (P)	80	120	80	120	
Potassium (K)	87	115	85	119	
Selenium (Se)	80	120	80	119	70-130
Silver (Ag)	85	116	83	118	70-130
Sodium (Na)	85	117	79	125	
Strontium (Sr)	82	118	75	129	
Thallium (Tl)	82	116	83	118	70-130
Thorium (Th)	87	121	81	116	
Tin (Sn)	86	115	82	121	
Titanium (Ti)	83	115	83	117	
Uranium (U)	87	120	83	120	
Vanadium (V)	86	115	82	116	70-130
Zinc (Zn)	83	119	82	119	70-130

Attachment D: ICP/MS Isotopes

The following isotopes should be monitored for ICP/MS analyses.
Determination of the primary isotope will be based on user knowledge and matrix. The tables below are to be used only as a general guideline. Interferences generally result in a biased high isotope. In most cases, an attempt should be made to report the lowest recovering isotope if there is a significant difference between isotopes.

Reportable Element Isotopes

Analyte		Preferred	Alternate	Notes
Lithium	**Li**	**7**		
Beryllium	**Be**	**9**		
Boron	**B**	**11**		
Aluminum	**Al**	**27**		
Vanadium	**V**	**51**		
Chromium	**Cr**	**52**		
Manganese	**Mn**	**55**		
Cobalt	**Co**	**59**		
Nickel	**Ni**	**60**		
Copper	**Cu**	**65**	63	Use 63 with high Ca
Zinc	**Zn**	**66**	68	
Arsenic	**As**	**75**		
Selenium	**Se**	**82**	78	
Strontium	**Sr**	**88**		
Molybdenum	**Mo**	**95**	98	Isotopes are essentially equal
Silver	**Ag**	**107**	109	Isotopes are essentially equal
Cadmium	**Cd**	**114**	111	Use 111 with high Mo
Tin	**Sn**	**118**		
Antimony	**Sb**	**121**	123	Isotopes are essentially equal
Barium	**Ba**	**135**	137	Isotopes are essentially equal
Mercury	**Hg**	**202**	201	If W is present; use lowest recovering isotope
Thallium	**Tl**	**203**	205	Isotopes are essentially equal
Lead	**Pb**	**206, 207, 208**		The reported value for lead is the sum of the three isotopes.
Bismuth	**Bi**	**209**		
Uranium	**U**	**238**		
Sodium	**Na**	**23**		
Magnesium	**Mg**	**24**	25	
Silicon	**Si**	**28**	29	
Phosphorus	**P**	**31**		
Potassium	**K**	**39**		
Calcium	**Ca**	**43**		
Titanium	**Ti**	**47**		
Iron	**Fe**	**54**	57	

Element Isotopes for Monitoring Only

Analyte		Isotope	Notes
Tungsten	**W**	**184, 186**	
Chlorine	**Cl**	**37**	
Carbon	**C**	**13**	
Scandium	**Sc**	**45**	Internal Standard
Chromium	**Cr**	**53**	
Nickel	**Ni**	**58, 62**	
Zinc	**Zn**	**67**	
Germanium	**Ge**	**74**	Internal Standard
Selenium	**Se**	**77**	
Krypton	**Kr**	**8**	
Molybdenum	**Mo**	**97**	
Cadmium	**Cd**	**106, 108**	
Gold	**Au**	**197**	
Indium	**In**	**115**	Internal Standard
Iridium	**Ir**	**193**	Internal Standard
Lead	**Pb**	**204**	
Titanium	**Ti**	**48**	
Iron	**Fe**	**56**	

Attachment E: 6020 Calibration Setup for NexIon

NexIon 3010/3050 - 6020 Calibration					
A/S		**6020 (SW 3010/3050)**			
		Standards	**Acids/Au**	**Final Vol**	
2	LLIQC	0.5 mL LLQC (1 – 4) + Hg LLQC	1.000 mL HNO3 0.100 mL dHCl	50 mL	QC Std 9
1	Blank/CB		1.000 mL HNO3 0.100 mL dHCl	50 mL	QC Std 8
2	Std 1	10 mL of Std 2	0.800 mL HNO3 0.080 mL dHCl	50 mL	
3	Std 2	5 mL of Std 3	0.900 mL HNO3 0.090 mL dHCl	50 mL	
4	Std 3	5 mL of Std 4	0.900 mL HNO3 0.090 mL dHCl	50 mL	
5	Std 4	10 mL of Std 5	0.800 mL HNO3 0.080 mL dHCl	50 mL	
6	Std 5	0.250 mL Cal (1 – 4) + Hg Cal	1.000 mL HNO3 0.100 mL dHCl	50 mL	
7	ICV/CCV	0.100 mL Cal (1 – 4) + Hg Cal	1.000 mL HNO3 0.100 mL dHCl	50 mL	QC Std 1/5
8	QCS	0.5 mL QCS (1 – 4) + Hg QCS	1.000 mL HNO3 0.100 mL dHCl	50 mL	QC Std 2