PLAN OF OPERATIONS
Integrated Waste Management

MONITORING PLAN

Donlin Gold Project

May 2022 Update

Prepared By:

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Anchorage, Alaska 99503

TABLE OF CONTENTS

FIGURES

TABLES

APPENDICES

ACRONYMS

AAC	Alaska Administrative Code
ABA	Acid-Base Accounting
ADEC	Alaska Department of Environmental Conservation
ADF&G	Alaska Department of Fish & Game
ADNR	Alaska Department of Natural Resources
ANDA	Anaconda Creek (surface water monitoring station)
AP	acid generating potential
APDES	Alaska Pollutant Discharge Elimination System
ARD	acid rock drainage
AS	Alaska Statute
ASTM	American Society for Testing and Materials
CCBC	Crooked Creek below Crevice Creek (surface water monitoring station)
CCBO	Crooked Creek below Omega Creek (surface water monitoring station)
CCBW	Crooked Creek upgradient of the pit (surface water monitoring station)
CWD	contact water dam
FEIS	Final Environmental Impact Statement
MIW	monitoring/interceptor well
MW	monitoring well
MWMP	meteoric water mobility procedure
NP_{CO3}	neutralization potential from carbonate material
Plan	Integrated Waste Management Monitoring Plan
QAPP	Quality Assurance Project Plan
QAQC	Quality Assurance Quality Control
SOB	south overburden
SRS	seepage recovery system
TSF	tailings storage facility
TSS	total suspended solids
USFWS	U.S. Fish & Wildlife Service
WAD	weak acid dissociable
WQS	water quality standards
WRF	waste rock facility
WTP	water treatment plant
USACE	U.S. Army Corps of Engineers

UNITS OF MEASURE

°F	Fahrenheit
ft	feet/foot
km	kilometer
m	meter
ppm	parts per million

ELEMENTS AND COMPOUNDS

$CaCO_3$	calcium carbonate
NP_{CO3}/AP	ratio of neutralizing potential from carbonate minerals to acid generating potential
WAD	weak acid dissociable

1.0 INTRODUCTION

Donlin Gold LLC[1] (Donlin Gold) is proposing the development of an open pit, hardrock gold mine in southwestern Alaska, about 277 miles (446 km) west of Anchorage, 145 miles (233 km) northeast of Bethel, and approximately 10 miles (16 km) north of the village of Crooked Creek (Figure 1-1). This integrated waste management monitoring plan (Plan) was prepared for the proposed project by Donlin Gold in accordance with state regulations governing the management of solid wastes and is submitted to the Alaska Department of Environmental Conservation (ADEC) in accordance with Alaska Statute (AS) 46.03.010 et. seq. and Title 18 Alaska Administrative Code (AAC) 60.005 et. seq.

This Plan may be revised periodically (Table 1-1) during operations based on regulatory changes, periodic reviews, facility changes, and review of monitoring results which indicate that further attention is warranted.

Table 1-1: Record of Changes and Amendments

Date	Section (s) Revised or Amended
June 2019	Updated to reflect requirements contained in original permit issued January 18, 2019
May 2022	Updated; new section 2.2 added

1.1 Purpose

This Plan presents the elements of Donlin Gold's proposed monitoring and sampling program that was initiated for baseline data collection and that will be refined and continued during the construction, operations, closure, and post-closure phases of the project. The project area is the location of much of the proposed project's infrastructure, including the processing facilities and mining locations. The monitoring and sampling described in this Plan includes only the monitoring activities that will be reported to ADEC as part of the Waste Management Permit[2] (Permit) requirements. Monitoring for other resources, such as aquatic resources, dam safety, and permitted air and water discharges are addressed under specific permit requirements and/or other monitoring plans, for example water treatment plant (WTP) discharges authorized under Alaska Pollutant Discharge Elimination System (APDES) permit AK55867.

1.2 Sampling Protocol and Quality Assurance/Quality Control

The list of monitoring parameters, required sample bottles, sampling procedures, and quality assurance/quality control for surface water and groundwater samples are described in the Quality Monitoring and Quality Assurance Program Plan (QAPP) contained in Appendix A.[3] The protocol for analysis of overburden, waste rock, and tailings samples for acid base accounting analysis is also contained in Appendix A.

[1] Donlin Gold LLC is a limited liability company equally owned by Barrick Gold U.S. Inc. and NovaGold Resources Alaska, Inc.

[2] ADEC issued Waste Management Permit 2017B001 on January 18, 2019

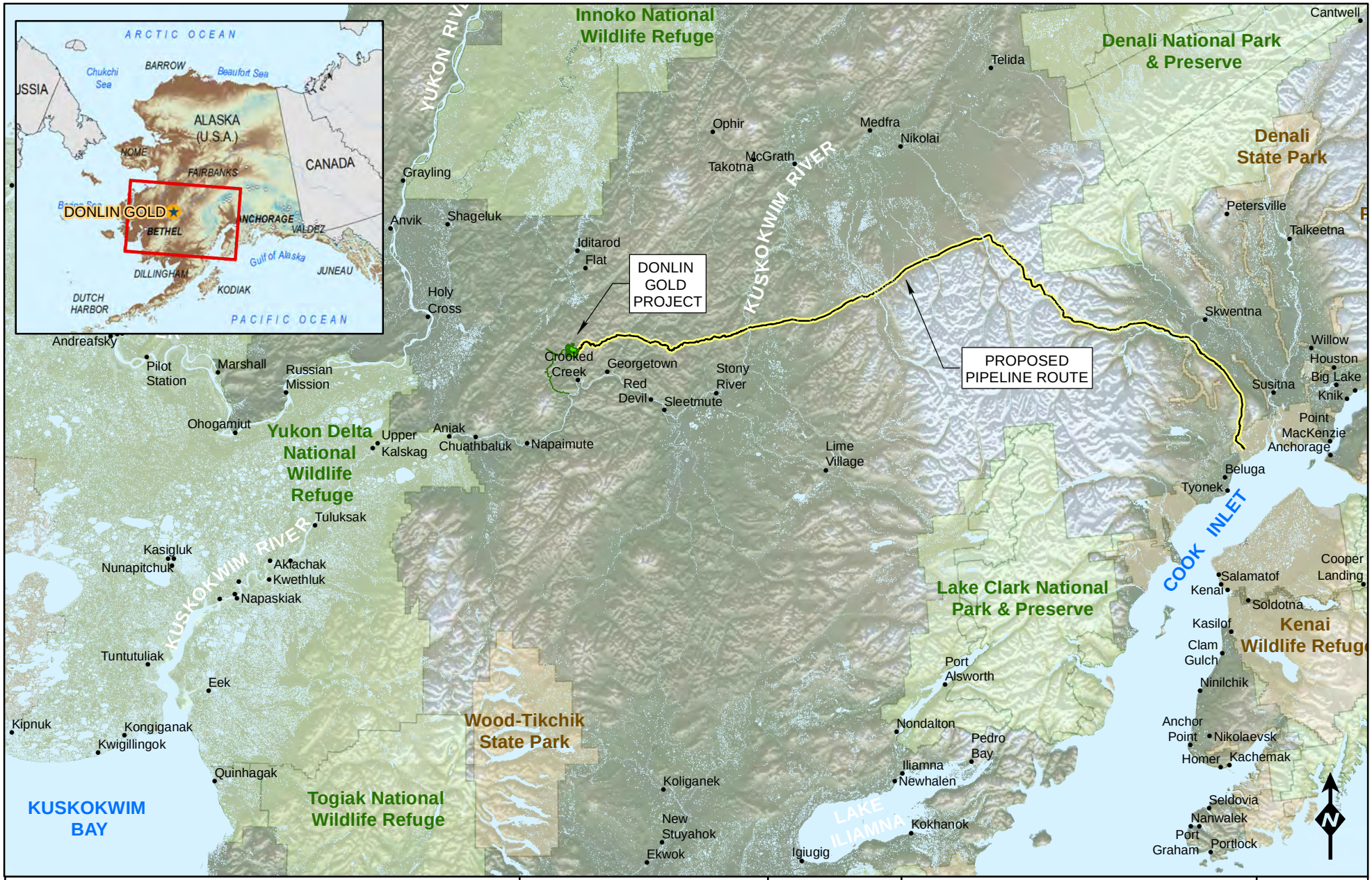
[3] Section 2.5.14 of the Permit requires the QAPP to be updated no later than 90 days prior to commencing facility construction

1.3 Administrative Information

Name of Facility:	Donlin Gold LLC
Type of Facility:	Proposed Gold Mine and Process Plant Operation
Location:	Latitude 62º01’36” North, Longitude 158º13'15” West
Corporate Information:	A Delaware Limited Liability Company jointly held by NovaGold Resources Alaska, Inc. and Barrick Gold U.S. Inc.
Business Name:	Donlin Gold LLC
Address:	2525 C Street, Suite 450
	Anchorage, Alaska 99503
Telephone:	(907) 273-0200
General Manager:	Dan Graham
Operations Manager:	_____

Designated Contact Person for Regulatory Issues:

Enrique Fernandez, Environmental Manager
Donlin Gold LLC
2525 C Street, Suite 450
Anchorage, AK 99503
Telephone: (907) 273-0200



- Populated Place
- Proposed Natural Gas Pipeline Alignment
- Proposed Infrastructure Layout
- Federal Administrative Boundaries
- State Administrative Boundaries

Seward Meridian, UTM Zone 5, NAD83

SCALE:

0 12.5 25 50 mi

0 20 40 80 km

DONLIN GOLD

PROJECT LOCATION MAP

DONLIN GOLD PROJECT

FIGURE:

1-1

DG: PER540.mxd, 10/05/16, R01

1.4 Project Description

The proposed Donlin Gold project would require approximately three to four years to construct, with the active mine life currently projected to be approximately 27 years. The mine is proposed to be a year-round, conventional “truck and shovel” operation using both bulk and selective mining methods.

The *Project Description,* SRK 2016a provides a detailed description of the overall project area and infrastructure necessary to support the development, operation, and closure of the project. The *Tailings Management Plan, Volume IIIA,* SRK 2016c and *Waste Rock Management Plan, Volume IIIB,* SRK 2016b provide detailed information on management of tailings and waste rock.

1.5 Objectives

The objective of monitoring will be to verify the project operates within Permit limitations and other Permit requirements, thereby minimizing impact to the environment during construction, operations, and post-closure. Compliance monitoring data would also be compared to baseline data which characterized the pre-development surface water and groundwater systems in the project area. This comparison would be used to identify and evaluate the potential changes caused by development and operation of the project.

2.0 COMPLIANCE MONITORING AND SAMPLING – CONSTRUCTION AND OPERATIONS

Monitoring surface water and groundwater resources is an integral part of the environmental protection measures at the proposed project. Pre-mining studies have established baseline conditions against which changes can be compared over time. Figure 2-1 depicts the locations of compliance monitoring and sampling locations for construction activities and Figure 2-2 shows monitoring and sampling locations during operations.

During construction and operations, there is ongoing disturbance of the land surface, excavation of borrow material sites, stripping of the mine site, movement of development rock, and placement of waste rock and tailings that could, if not managed properly, affect water quality. Overburden and waste rock will be sampled and analyzed in order to classify and manage this material appropriately. Tailings will be sampled and analyzed to evaluate filtrate and solids characteristic. Tailings solids characterization will include acid rock drainage (ARD) generating potential.

Monitoring and sampling will be initiated with the start of mine site construction and continue into operations as reagents are introduced into the beneficiation process and more sites become relevant to the overall compliance of the project.

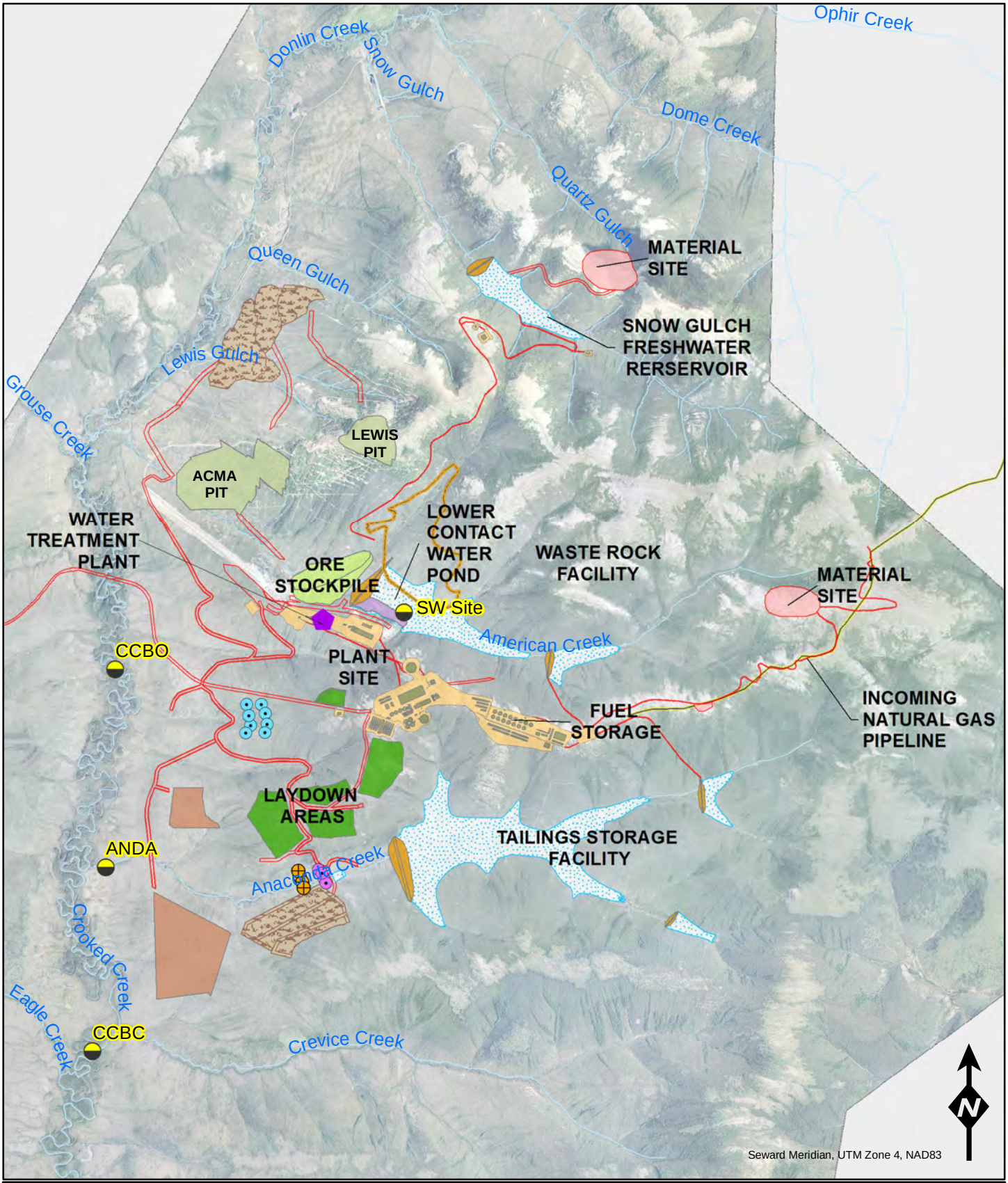
2.1 Solution (Process Water) Monitoring

Solution management at the project encompasses all aspects of water management for the proposed Donlin Gold project. The *Plan of Operations: Water Resources Management Plan* SRK 2017 provides a description of the solution management of the different water categories during construction, operations, closure, and post-closure. Monitoring requirements are described below.

All process solutions would be controlled under the fluid management system, which consists of the following components:

- Lower and Upper Contact Water Dams (CWDs), containing surface and seepage water from the Waste Rock Facility (WRF), pit dewatering water, surface water from the south overburden (SOB) stockpile, and pit surface water.
- Process plant, including but not limited to, all tanks, basins, sumps, pumps, and piping necessary to interconnect the components that contain process fluid within this plant.
- Tailings storage facility (TSF) impoundment, tailings discharge lines, reclaim barge and return lines, and seepage recovery system (SRS).

Monitoring requirements for the process fluid management system are shown in Table 2-1.



- Compliance Monitoring Well
- Monitoring/Interceptor Well
- Surface Water (SW) Site
- Water Supply Well
- Water Treatment Plant

DONLIN GOLD

MONITORING/SAMPLING LOCATIONS CONSTRUCTION

DONLIN GOLD PROJECT

SCALE:
0 0.25 0.5 1 mi
0 0.4 0.8 1.6 km

FIGURE:
2-1

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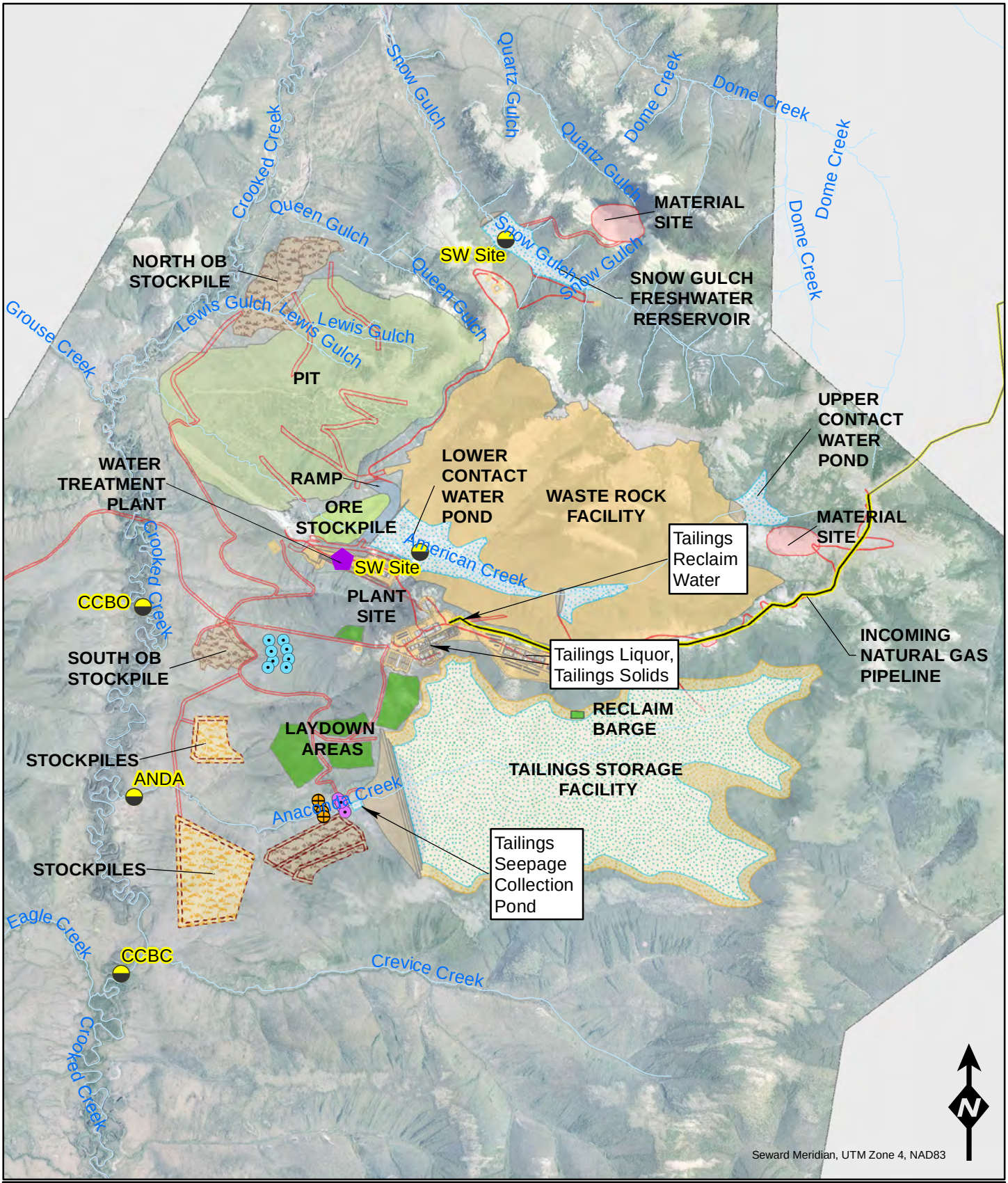


- Compliance Monitoring Well
- Monitoring/Interceptor Well
- Surface Water (SW) Site
- Water Supply Well
- Water Treatment Plant

DONLIN GOLD

MONITORING/SAMPLING LOCATIONS OPERATIONS

DONLIN GOLD PROJECT

SCALE:
0 0.25 0.5 1 mi
0 0.4 0.8 1.6 km

FIGURE: **2-2**

DG: PER0090.mxd, 06/10/16, R12

Table 2-1: Process Fluid Management System Monitoring Requirements

Identification	Parameter (Appendix A)	Frequency
Lower CWD	Long List-1*	Quarterly
Tailings at process plant (post cyanide detoxification)	pH, Weak Acid Dissociable (WAD) cyanide	2 samples per day
Tailings liquor (filtrate)	Long List-1*	Quarterly
Tailings solids (residue)	Long List-1* Static Acid Based Accounting (ABA) analysis**	Quarterly composite
Tailings reclaim water	Long List-1*	Quarterly

* After two years of monitoring and sampling, the analytical profiles for three of the quarters may be reduced to the following: pH, conductivity, alkalinity (as calcium carbonate [$CaCO_3$]) bicarbonate, and total and WAD cyanide. Any results of analysis from the reduced sample parameters inconsistent with previous water quality analyses would require re-sampling and Long List-1 analysis. The annual full parameter analysis would provide a database for comparison and enable the water quality trends to be tracked over the life of the operation.
** Material for which static Acid Base Accounting (ABA) analysis results indicate less than 1.4 to 1 ratio of neutralization potential as carbonate to acid generating potential (NP_{CO3}/AP) would require kinetic testing using laboratory humidity cells. A meteoric water mobility procedure (MWMP) extraction (ASTM International 2013) would also be performed on a composite sample of tailings solids collected over the quarter, and would be analyzed for the parameters in Long List-1.

Individual parameters may be proposed to ADEC for reduction after additional sampling. The criteria for reducing parameters would be based on the potential for changes that could result in water quality concerns.

2.2 Surface Water Monitoring/Sampling

Surface water samples include those locations with the potential to be affected by process, dewatering, or transportation and storage activities. Figure 2-1 shows the locations of upgradient and downgradient surface water monitoring/sampling stations. Table 2-2 lists monitoring locations, parameters, and frequency of monitoring/sampling.

Table 2-2: Surface Water Sampling Locations

Identification	Parameter (Appendix A)	Frequency
American Creek Freshwater Diversion	Long List 1	Quarterly during the first year of operations
Snow Gulch Fresh Water Reservoir	Long List-1	Quarterly*
CCBW	Long List-1	Quarterly*
CCBO	Long List-1	Quarterly*
ANDA	Long List-1	Quarterly*
CCBC	Long List-1	Quarterly*

* Sampling would be attempted seasonally during high- and low-runoff conditions

2.2.1 Mercury Monitoring

Along with the surface water monitoring strategy for the long list of water quality parameters (section 2.2), Donlin Gold will conduct focused monitoring for total mercury. The objective of the mercury monitoring will be to ensure that the project does not cause or contribute to

exceedances of water quality standards for mercury beyond background levels in streams near the project area.

The FEIS reported that atmospheric deposition of total mercury in the vicinity of the project could increase by approximately 40 percent due to the project and that this could lead to a corresponding 40 percent increase in the total mercury concentrations in surface water near the project (USACE 2018). This estimate is conservative as it did not account for important environmental dynamics. Ramboll (2021) completed a more refined estimate of the project's potential mercury-related impacts to the surface water of nearby streams by using a mass balance approach. This refined analysis accounted for the fact that current mercury concentrations in the streams near the mine site are primarily due to the weathering and erosion of mercury-enriched surface and subsurface geologic features and, secondly and to a lesser extent, from atmospheric deposition. The revised analysis also accounted for the 93 percent retention of mercury in the terrestrial environment, and for stream diversion and runoff management and treatment planned by the project. In summary, the mercury study indicated that the project would likely result in negligible impacts (<1%) on mercury mass loading in streams near the project area and, in most cases, result in reductions from baseline mercury mass loadings.

The total mercury monitoring strategy specifically addresses the water quality of Crooked Creek and its tributaries near the project site that are the most likely to be affected by deposition of mercury associated with project air emissions. A monthly monitoring frequency will be adequate to properly characterize total mercury at different flow rates. Because most of the mercury originates from the weathering and erosion of mercury-enriched surface and subsurface geologic features, it is appropriate to conduct the monthly monitoring during the ice-free period when these events occur. This is also when deposition-related impacts from the project are likely to be seen. Monitoring will include measurements for total mercury, TSS, and flow. Total mercury will also be measured in the regular surface water sampling (Section 2.2). At least three years of baseline data will be collected prior to the start of operations. The rationale for the monitoring sites is included in Table 2-3 along with the frequency of sampling. Locations are shown on Figure 2-3.

Table 2-3: Mercury Monitoring Sites

Monitoring Site ID	Description	Rationale	Parameter	Frequency*
OPHR	Crooked Creek tributary; mouth of Ophir Creek	Ophir is a large tributary upstream of DCBO.	Total mercury; TSS; Flow	Monthly during open water
DOME	Crooked Creek tributary; mouth of Dome Creek	Large watershed north of the project.	Total mercury; TSS; Flow	Monthly during open water
AMER	Crooked Creek tributary; mouth of American Creek	0.3% of American watershed will remain after construction of facilities. Stormwater from undisturbed areas may contribute to Crooked Creek mercury loading	Total mercury; TSS; Flow	Monthly during open water, flow may not be present due to very small area not associated with mine site facilities and water management systems
ANDA	Crooked Creek tributary; mouth	Large watershed in the project area	Total mercury; TSS; Flow	Monthly during open water

Monitoring Site ID	Description	Rationale	Parameter	Frequency*
	of Anaconda Creek			
GRSE	Crooked Creek tributary; mouth of Grouse Creek	Tributary to Crooked Creek which is a naturally significant contributor of mercury mass loadings to Crooked Creek	Total mercury; TSS; Flow	Monthly during open water
EAGL	Crooked Creek tributary; mouth of Eagle Creek	Tributary to Crooked Creek which is a naturally significant contributor of mercury mass loadings to Crooked Creek	Total mercury; TSS; Flow	Monthly during open water
CV1	Crooked Creek tributary; mouth of Crevice Creek	Tributary to Crooked Creek which is a naturally significant contributor of mercury mass loadings to Crooked Creek	Total mercury; TSS; Flow	Monthly during open water
DCBO DCBD CCBW CCBC	Crooked Creek mainstream location	Crooked Creek mainstem locations	Total mercury; TSS; Flow	Monthly during open water
CR0.3	Crooked Creek mainstream downstream location	Data already collected for other programs (i.e., ARMP, and Section 2.2)	Total mercury; TSS; Flow	Quarterly

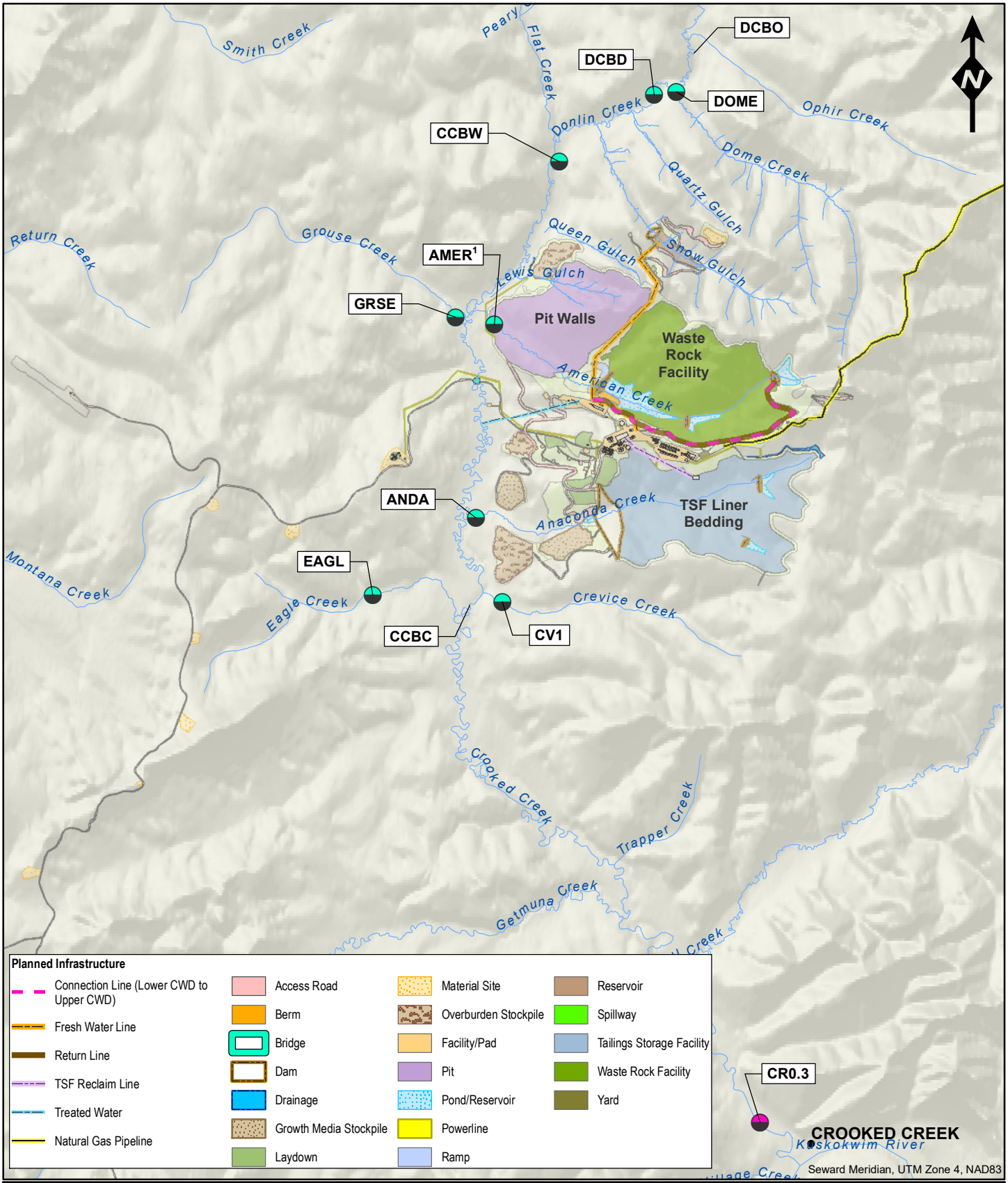
* Open Water = Typically May through October

Donlin Gold will analyze water quality for total mercury, TSS, and flow and provide the ADEC with quarterly and annual reports summarizing monitoring results. The requirements for quarterly and annual monitoring reports are discussed in the Waste Management Permit (2017DB0001) section 2.6.2 and 2.6.3 respectively.

If a statistically significant increase in the concentration of total mercury above the water quality standard is discovered at one of the total mercury surface water monitoring stations, Donlin Gold will notify the ADEC and conduct corrective actions. The requirements of corrective actions are discussed in the Waste Management Permit (2017DB0001) section 2.7, including the requirement to implement a plan to determine the cause of the exceedance and restore compliance.

Ramboll (2021) determined that the total mercury in the water quality of the streams near the project is primarily from geologic sources, rather than from air deposition. Most of the mercury enters the water because of stream erosion and the ensuing suspension/resuspension of sediments, which are then transported downstream. Therefore, if an unanticipated, statistically significant increase in total mercury above the water quality standard occurs, this could be addressed though the implementation of engineering control methods that focus on reducing stream erosion and sediment loads in water, including:

- Methods for reducing stream erosion include bank stabilization projects that reduce the erodibility of the stream banks (e.g., rip rap installation, placement of woody debris, or the reestablishment or enhancement of vegetation on the banks). The Alaska Department of Fish and Game has developed a Streambank Revegetation and Protection (ADF&G 2005) for Alaska that includes detailed examples of proven techniques.



Hg Monitoring Interval

- Monthly during open water
- Quarterly

[1]Flow may not be present due to very small area not associated with mine site facilities and water management systems

DONLIN GOLD

MERCURY MONITORING STATIONS

DONLIN GOLD PROJECT

SCALE:

0 0.5 1 2 mi

0 1 2 4 km

FIGURE:

2-3

DG: PER0640, 3/29/2022, R01

- Methods for reducing suspension and sedimentation of sediments include stormwater management techniques such as the installation of check dams, sediment basins, etc. The ADEC has developed the Alaska Stormwater Guide (ADEC 2009) which includes proven examples of engineering controls to use for reducing sediment load in streams.

- Water management techniques, such as diverting surface flows for use in project operations, may be practical in some circumstances.

In any event, the development of a corrective action plan would depend on the site-specific conditions that are observed at the time and may require an adaptive management approach.

The American Creek watershed will be reduced to 0.3 percent of its original size during the mine operation phase; the remaining drainage will be contained in the mine process water collection systems. It is possible this drainage could see higher levels of increased mercury concentrations than other areas of the watershed. However, stream flow in American Creek could be non-existent due to the small size of the catchment area and open pit dewatering. As noted above, Donlin Gold would monitor this location and if flow is remains, sample the water. If a statistically significant increase of total mercury is detected, Donlin Gold would work to address the exceedance and prevent reoccurrence. For American Creek, potential actions would be determined based on-site conditions at the time, but could include:

- Installation of a sediment pond to collect the remaining flow and allow stream solids to settle in the pond.

- Installation of check dams to collect and slow down water velocity and reduce stream erosion.

- Installation of other controls (e.g., designed to maintain bank stability) to limit sediment loadings to the drainage.

- Collection of the remaining water for use in mine operations; any discharges flow through the wastewater treatment plant.

2.2.2 Temperature Monitoring

Donlin Gold will conduct temperature monitoring of Crooked Creek surface waters. The objective of the temperature monitoring is to ensure that the project does not cause or contribute to exceedances of water quality standards for temperature beyond background levels near the mine site.

The capacity of a stream to buffer against temperature increase is directly influenced by water volume and the size of the surface area that is exposed to the energy source (i.e., ambient temperature, or solar radiation). Therefore, the Donlin Gold project's predicted streamflow changes, including potential loss of cool groundwater inflows in Crooked Creek, can affect the water temperature in Crooked Creek. BGC (2021) studied potential surface water temperature changes for Crooked Creek, taking into consideration the predicted streamflow losses, and using the warmest year in the available record of continuous flow and temperature monitoring (i.e., 2005). The results projected increases in Crooked Creek stream temperatures, but these would remain below the State of Alaska's water quality temperature standards of 55.4°F for egg/fry incubation and spawning areas and 59.0°F for migration routes and rearing areas (Alaska Department of Environmental Conservation, March 5, 2020). Of note, even during the warmest period of the year (i.e., July and August), for most of the time during 2005 the stream water temperature would have been well below the most restrictive standard (55.4°F). BGC

(2021) also considered the discharge of treated effluent at a temperature of 40°F and determined it would increase the temperature buffering capacity of Crooked Creek. Though 2005 was the warmest temperature record available for the study, it is conceivable that future stream temperatures could potentially exceed the 2005 record, including recognizing the possible effects of global warming. Stream temperatures are associated with ambient air temperatures.

The Crooked Creek temperature monitoring strategy will focus on Crooked Creek water near the mine site, which is the area where significant streamflow reductions could occur. Surface water temperatures and flow measurements will be taken during July and August each year, at two monitoring stations, DCBO and CCBC (See Figure 2-4). The DCBO monitoring station is located upstream of the mine site and above the area of predicted streamflow reductions. This station will serve as a baseline or reference point. CCBC is located downstream of the mine area and near the downstream limit of the significant streamflow reductions in the creek. CCBC will serve as the monitoring station representative of the surface water temperature in Crooked Creek near the mine site where streamflow reductions are predicted. Each station will have a stream gauge equipped with a pressure transducer to measure flow and temperature sensor to collect data. Ambient temperature readings will be taken at the Donlin Gold camp or mine site meteorological station.

Prior to the start of construction activities that could result in streamflow reductions, Donlin Gold will collect at least 3 years of baseline data for both monitoring stations and ambient temperature. The flow and temperature data for each station will be compared on a daily basis to calculate the range of Relative Percent Difference (RPD) and temperature difference (DT) between the two stations under baseline conditions.

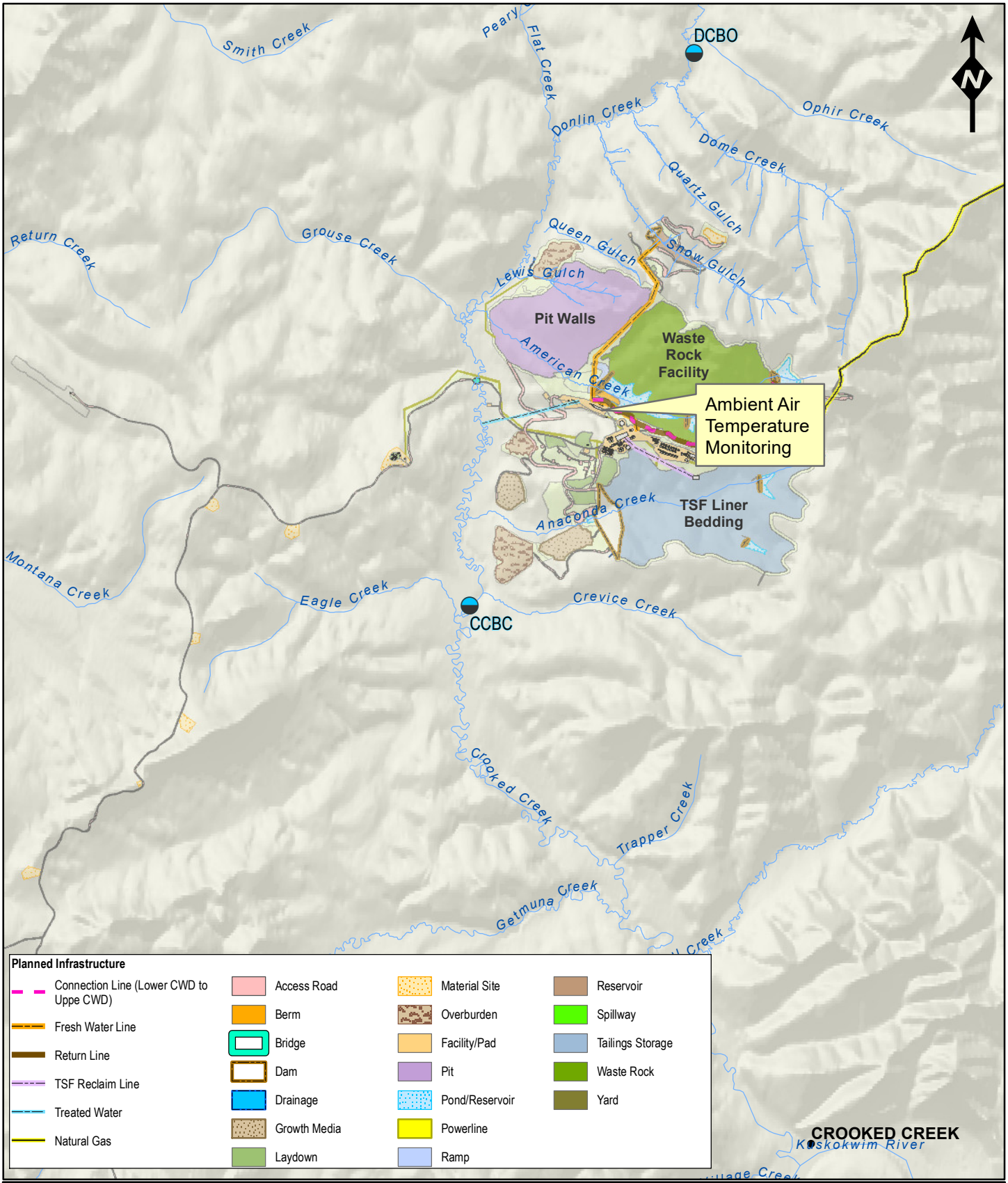
Donlin Gold will analyze water quality for temperature and flow and provide the ADEC with 3rd Quarter and annual reports summarizing monitoring results. The requirements for quarterly (i.e., 3rd Quarter as data would only be available for one quarter) and annual monitoring reports are discussed in the Waste Management Permit (2017DB0001) sections 2.6.2 and 2.6.3 respectively.

If a statistically significant increase of surface water temperature above the water quality standard is discovered at CCBC, Donlin Gold will notify the ADEC and conduct corrective actions. The requirements of corrective actions are discussed in the Waste Management Permit (2017DB0001) section 2.7, including the requirement to implement a plan to determine the cause of the exceedance and restore compliance.

If an unanticipated, statistically significant increase in stream temperature above the water quality standard occurs, this could be addressed though the implementation of engineering control methods or water management techniques that focus on increasing flow and/or reducing stream water temperature during critical ambient temperature periods, including:

Increase discharge of water from the Snow Gulch freshwater dam into Crooked Creek.

- Cool treated effluent to a target temperature prior to release to Crooked Creek.
- Store treated effluent for increased discharge to Crooked Creek during low flow/high temperature periods.
- Adding groundwater from newly developed wells outside the mine area.



Stream flow and Temperature Monitoring Station

Seward Meridian, UTM Zone 4, NAD83

DONLIN GOLD

STREAM FLOW AND TEMPERATURE MONITORING STATIONS

DONLIN GOLD PROJECT

SCALE:

0 0.5 1 2 mi

0 1 2 4 km

FIGURE:

2-4

DG: PER0641, 4/20/2022, R01

In any event, the development of a corrective action plan would depend on the site-specific conditions that are observed at the time and may require an adaptive management approach.

2.3 Waste Rock Facility Monitoring

Waste rock management and operational monitoring and sampling of the WRF are described in the *Waste Rock Management Plan, Volume IIIB,* SRK 2016b. Based on monitoring described in the Waste Rock Management Plan, the ratio of neutralizing potential from carbonate minerals to acid generating potential (NP_{CO3}/AP) would be calculated and used to classify waste rock as described in SRK (2016b). Laboratory analyses for total sulfur and NP_{CO3} and ABA calculations would be maintained on site. This geochemical data would be processed on a monthly basis to calculate the average NP_{CO3}/AP for placed waste rock, and to record final destinations.

2.4 Solid Waste Landfill

Inert waste materials generated during construction and operations would be disposed of in solid waste landfill trenches. These inert landfills would be operated as described in the *Integrated Waste Management Plan, Volume III,* SRK 2019.

Because materials disposed of within the landfill trenches are inert, the potential for leachate is minimal. Furthermore, as required by Section 2.2.6.13 of the Permit designated landfill trenches would be a minimum of 50 ft (15 m) from any surface water feature. They would also be greater than 200 ft (61 m) from drinking water sources. Surface water runoff would be diverted away or around landfill trenches to minimize infiltration. Additionally, trench bottoms would be located a minimum of 10 ft (3 m) above the existing or expected future groundwater table, or at least two feet above the natural ground surface. Consequently, no special groundwater or surface water monitoring is currently planned. Operational visual monitoring and reporting will be done in accordance with the requirements of the Permit and as described in Donlin Gold and SRK 2019.

2.5 Tailings Storage Facility Monitoring

Operational monitoring and reporting for the Tailings Storage Facility (TSF) will be in accordance with the Alaska Department of Natural Resources (ADNR) Dam Safety Operating Permit and as described in the *Tailings Management Plan, Volume IIIA,* SRK 2016c. Environmental monitoring is summarized below.

2.5.1 TSF Water Monitoring

Water monitoring at the TSF is summarized in Table 2-4.

Table 2-4: TSF Water Monitoring

Identification	Parameter (Appendix A)	Frequency
TSF Starter Dam Pond	Long List-1	Quarterly
SRS Collection Pond	Long List-1	Quarterly
TSF monitoring and interceptor wells (MIWs) MIW-1, MIW-2, MIW-3, MIW-4	Long List-1	Quarterly
	Static Water Depth	Weekly
	Record instantaneous and totalizer flow for monitoring/interceptor wells (if operation is required)	Weekly

Identification	Parameter (Appendix A)	Frequency
TSF Compliance monitoring wells (MWs) MW-1, MW-2, MW-3, MW-4[4]	Long List-1	Quarterly
	Static Water Depth	Weekly

[4] These wells would only be monitored if an exceedance of background and Water Quality Standard is observed in the MIWs.

3.0 AVIAN AND TERRESTRIAL WILDLIFE MONITORING

Visual inspection of the tailings impoundment surface would occur during each shift and would focus on the tailings decant pool and unconsolidated tailings depositional areas. Employees would be directed to report to security any unusual circumstances involving wildlife. In addition, all site personnel would have specific responsibility to thoroughly inspect and report any wildlife mortalities or animals mired in unconsolidated tailings.

Operational standards require the tailings discharge from the process plant and the resultant reclaim pool to be non-toxic to avian and terrestrial wildlife species. Some natural mortality would occur within the boundaries of the mine site; however, occurrences within specific process component areas, such as the tailings impoundment, would require special collection and sampling. All wildlife mortalities would be reported to the security officer on duty as soon as possible, and the species would be noted.

Any onsite wildlife mortalities associated with facility activities would be reported to the U.S. Fish & Wildlife Service (USFWS), the Alaska Department of Fish & Game (ADF&G), and ADEC within one working day of discovery. A written follow-up report (Appendix B) would be submitted to USFWS and ADF&G with the date the mortality was discovered and identification of species. The follow-up report would be submitted within seven days of the initial verbal notification to allow verification of analytical results. A semi-annual summary (Appendix B) would review mortality occurrences during the ice-free period (generally April through September) and during the ice cover (October through March). In the event of wildlife mortality, the semi-annual report would be submitted to the following agencies, as appropriate, within 30 days of the end of the reporting period:

U.S. Fish & Wildlife Service
Ecological Service
101 12th Avenue
Fairbanks, Alaska 99701
Telephone (907) 456-0388

Alaska Department of Environmental Conservation
Northern Regional Office
610 University Avenue
Fairbanks, Alaska 99709
Telephone (907) 451-2101

Alaska Department of Fish & Game
Habitat Division
1300 College Road
Fairbanks, Alaska 99701-1599
Telephone (907) 459-7289

All carcasses would be collected and preserved using appropriate protocols[5] and made available for final collection by USFWS or ADF&G, depending on species (i.e., migratory bird or game species).

Animals mired in unconsolidated tailings material would be extracted and moved or herded to a safe area. All attempts to extract mired animals would be based on evaluation as to the health and safety of people and that of the animal.

[5] For example, USGS, USFWS and NPS, “Wildlife Specimen Collection, Preservation and Shipment”, Techniques and Methods 15-C4

4.0 COMPLIANCE MONITORING AND SAMPLING – CLOSURE

The *approved Plan of Operations: Reclamation and Closure Plan,* SRK 2018 describes reclamation and closure activities for the Project. Table 4-1 provides a summary of anticipated post-closure monitoring. Figure 4-1 shows the monitoring and sampling locations during and after closure.

Table 4-1: Summary of Closure and Post-Closure Monitoring

Monitoring Location	Monitoring Parameters	Frequency	Approximate Duration of Monitoring
Pit Lake	Water level	Annual	Until pit fills to operating level (estimated as 50-55 years after mine closure)
	Water quality by depth (Long List-1)	Every 5 years after closure	Until analyses indicate a stable condition
	Water quality of discharge - per APDES permit	Per APDES permit	While WTP is operational, and until analyses indicate a stable condition that meets WQS if WTP operation is discontinued; as accepted by ADEC
TSF[6]	Erosion stability	Quarterly	Until observations indicate a stable condition
	Pond location and level, Pond surface water quality at spillway (Long List-1)	Quarterly	Until pond surface water consistently meets WQS, also per any APDES permit requirements
	SRS water quality (Long List-1) and flow	Quarterly	Until analyses indicate a stable condition
	MIW and compliance MW water quality (Long List-1) and water level[7]	Quarterly for first 5 years, annually for next 5 years and then every 5 years thereafter	Until analyses indicate a stable condition
WRF	Seepage water quality (Long List-1) and flow	Quarterly	Until analyses indicate a stable condition
	Erosional stability		Until observations indicate a stable condition
Surface Water (CCBC and CV1)	Water quality (Long List-1) and flow	Quarterly, CV1 monitored for three years after closure and then only after discharge to Crevice Creek is initiated	Until flows and water quality are stabilized; also, per any APDES permit requirements.

[6] This facility will have additional requirements for compliance through the ADNR-Dam Safety Program certificates

[7] MWs would be monitored if background water quality and WQS are exceeded in the MIWs.

Surface water and groundwater monitoring of the TSF, SRS, Pit Lake, and WRF would continue during closure and post-closure. The monitoring would remain depending on compliance history up to or beyond 30 years until each specific facility has been stabilized, physically and chemically, to the satisfaction of the applicable regulatory agencies.

4.1 Tailings Storage Facility

Several years before the end of operations, tailings deposition would be modified to direct the operating pond toward the southeast corner of the TSF. This would be done in anticipation of final closure of the TSF, when the tailings surface runoff would be directed to the closure spillway into Crevice Creek. At cessation of processing operations, the TSF water would be pumped from a small, lined impoundment located on the southeast corner of the TSF to the pit through a reclaim pipeline. Prior to discharge over the spillway, the pond water will be monitored and be required to meet the applicable Alaska Water Quality Standards (WQS). Until that time, pumping of the water to the pit would continue.

The SRS, consisting of the pond and monitoring/interceptor wells would remain immediately downstream of the closure footprint of the main tailings dam. During operations, water from the SRS would be pumped back to the TSF pond, process plant or WTP. During the closure and post-closure periods, the SRS collection pond would be used to monitor water quality in the TSF underdrain. The SRS pond water would be pumped to the pit lake for as long as needed to show compliance with WQS. The SRS collection pond would be decommissioned when it can be demonstrated the water quality of water from the TSF underdrain meets applicable WQS to be discharged into Anaconda Creek. Stormwater runoff from the reclaimed downstream face of the dam would flow to the collection pond until WQS are met and then the runoff would flow to Anaconda Creek. The *Plan of Operations: Reclamation and Closure Plan* SRK 2018 describes in detail the long-term management of the TSF underdrain water.

4.2 Pit Lake

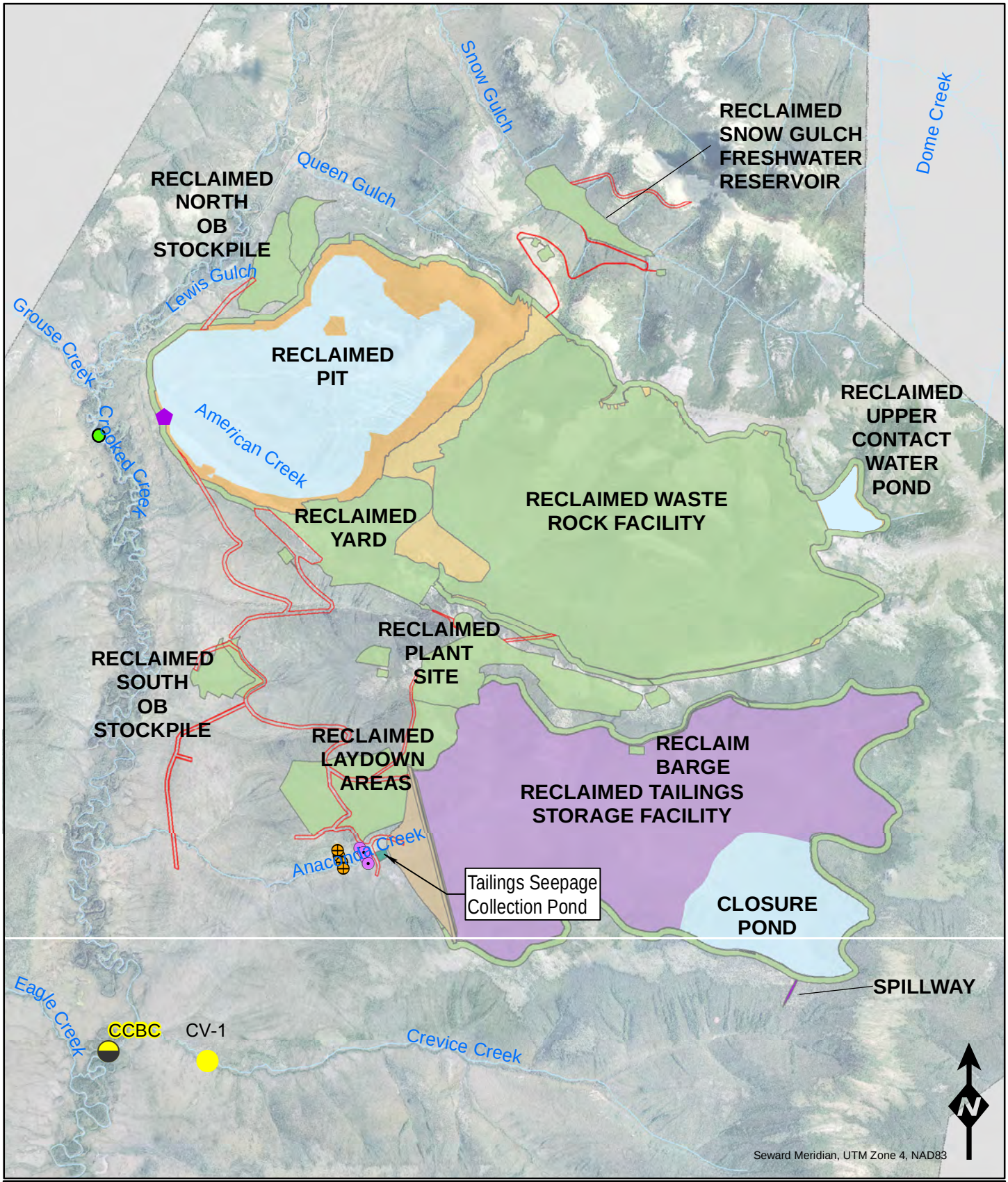
The mined-out open pit would begin to form a pit lake prior to cessation of processing operations and is the central feature of proposed post-closure water management. As the pit fills over approximately 55 years, water level and quality (at different depths) would be monitored, and the pit lake model would be re-calibrated as data become available. Approximately five years before pit water would need to be discharged, a WTP would be built at the site as described in the *Plan of Operations: Water Resources Management Plan, Volume IIIA,* SRK 2017. Monitoring of the pit lake water quality and discharge from the WTP would continue over the long-term.

4.3 WRF Stability Monitoring

Post-closure stability monitoring of the WRF would consist of visual inspection including, but not limited to covered areas, areas of potential stormwater concentration, storage facility base areas where seepage would have the highest potential to occur, and stormwater control structures. Inspections would be carried out for a period of not less than five years. The frequency of inspections would be at least once annually in the spring and following storms that equal or exceed the 25-year, 24-hour storm event. The purpose of the inspections would be to observe and document the following:

- Physical integrity of the soil cover including areas of erosion, ponding, differential settling, etc.
- Extent of vegetation establishment and density.
- Evidence of any staining, discoloration, streaking or moisture conditions indicating significant geochemical reactivity of disposal facility surfaces.
- Condition of stormwater control structures.
- Location and extent of any ponded stormwater.

Conditions that require repair, maintenance, or further evaluation would be documented, with appropriate follow up scheduled for completion. Documentation of inspections, repairs, and evaluations would be submitted to ADEC on an annual basis.



Compliance Monitoring Well

Monitoring/Interceptor Well

Post Closure Water Treatment Plant Outfall

Reclaimed Water Treatment Plant

Surface Water Site

DONLIN GOLD

MONITORING/SAMPLING LOCATIONS CLOSURE AND POST-CLOSURE

DONLIN GOLD PROJECT

SCALE:

0 0.25 0.5 1 mi

0 0.4 0.8 1.6 km

FIGURE: **4-1**

DG: PER0091.mxd, 06/10/16, R15

5.0 MONITORING RECORDS AND REPORTING

5.1 Documentation of Measurements, Monitoring, and Quality Assurance Program Plan

Sampling and documentation will be conducted in accordance with the Donlin Gold 2019 QAPP (Appendix A), which includes detailed procedures on collecting site measurements and samples, sample handling, data management, and QA/QC.

5.2 Monitoring, Reporting, and Records Retention

Donlin Gold will submit quarterly monitoring reports to ADEC. Quarterly reports will be submitted within 60 days of the end of the first three quarters of each calendar year. The quarterly reports will include, at a minimum, all information described in Section 2.6.2 of the Permit. Donlin Gold will submit annual reports to ADEC by March 1st of the following year. The annual reports will serve as the fourth quarter monitoring report and include, at a minimum, all information described in Section 2.6.3 of the Permit.

As required by Section 2.6.5 of the Permit, all records, information, and reports resulting from monitoring activities will be retained in Alaska for a minimum of five years and made available to ADEC for review upon request. This includes providing certified copies to ADEC if requested.

5.3 Permit Exceedance Notification

For each groundwater and surface water monitoring location, Donlin Gold will establish baseline conditions and submit to ADEC a baseline conditions report prior to the start of facility construction. In accordance with Section 2.6.1 of the Permit, when there is a statistically significant increase in the concentration of a constituent above the baseline conditions and the concentration is above a WQS, Donlin Gold will verbally notify ADEC no later than 5:00 pm of the next regular work day from the time the exceedance has been identified.

5.4 Corrective Action

If the visual monitoring described in this Plan and required by Section 2.5.2 of the Permit shows damage or potential damage to the waste disposal facilities that could lead to water quality violations, Donlin Gold will comply with the requirements of 18 AAC 60.815.

When a statistically significant increase in a constituent concentration is detected above baseline conditions and above a WQS at any groundwater or surface water monitoring location, Donlin Gold will comply with the requirements in 18 AAC 60.820-860.where applicable. Statistical significance shall be determined using one of the methods outlined in 18 AAC 60.830(h) or another method approved in writing by ADEC. Beyond the notification requirements described in Section 5.3 above, Donlin Gold will comply with the applicable notification requirements in 18 AAC 60.850(c).

After Donlin Gold notifies ADEC that there is an exceedance of baseline conditions and the concentration is above a WQS at a groundwater or surface water monitoring location, or there is non-compliance with another permit condition, Donlin Gold will:

- Determine the extent of the exceedance or non-compliance,

- In consultation with ADEC and as documented in writing, implement a plan to restore compliance and determine the cause of the exceedance or non-compliance,

- Submit to ADEC within seven working days after verifying the exceedance or non-compliance, a plan for corrective actions to prevent adverse environmental impacts and avoid future exceedance or non-compliance of a similar nature, and

- Implement the corrective actions as approved by ADEC.

6.0 REFERENCES

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Appendix A
Quality Assurance Project Plan (QAPP) Water Quality Monitoring, Sampling and Analysis Activities

(This QAPP was prepared for environmental baseline studies and will be updated once permits are issued.)

and

Acid Based Accounting Analysis Protocol

Quality Assurance Project Plan (QAPP)

Sediment and Water Quality Monitoring, Sampling and Analysis Activities

June 2021

4720 Business Park Blvd. Suite G-25
Anchorage, Alaska 99503

Based on the Generic Tier 2 Quality Assurance Project Plan for Sediment and Water Quality Monitoring Sampling and Analysis Activities (Revision 2) as directed by the Alaska Department of Environmental Conservation

TABLE OF CONTENTS

APPENDICES

FIGURES

TABLES

ACRONYMS

AAC	Alaska Administrative Code
ADEC	Alaska Department of Environmental Conservation
APDES	Alaska Pollutant Discharge Elimination System
ARMP	Aquatic Resources Monitoring Plan
ASTM	ASTM International
COC	chain of custody
CFR	Code of Federal Regulations
CSV	comma-separated value
DL	detection limit
DO	dissolved oxygen
Donlin Gold	Donlin Gold LLC
DOW	Division of Water
DQO	data quality objective
EC	electrical conductivity
EDD	electronic data deliverable
EDGE	EQuIS Data Gathering Engine
EDP	electronic data processor
GAI	Golder Associates, Inc
HDPE	high-density polyethylene
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IDL	instrument detection limit
LCS/LCSD	laboratory control sample/laboratory control sample duplicate
LOD	limit of detection
LOQ	limit of quantitation
MDL	method detection limit
MS/MSD	matrix spike/matrix spike duplicate
NAD 83	North American Datum of 1983
ND	non-detect
NFG	National Functional Guidelines
NIST	National Institute of Standards Technology
ORP/Eh	oxidation/reduction potential
PPE	personal protective equipment
PQL	practical quantitation limit
QA	quality assurance
QAP	quality assurance plan
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
QC	quality control
%R	percent recovery
RL	reporting limit
RPD	relative percent difference

SD	sediment
SOPs	Standard Operating Procedures
SRM	standard reference material
SW	surface water
TDS	total dissolved solids
TSS	total suspended solids
USEPA	United States Environmental Protection Agency
UTM	Universal Transverse Mercator
WMP	Waste Management Permit
WQBELs	water quality-based effluent limitations
WQS	water quality standards

UNITS OF MEASURE

±	plus or minus
≤	less than or equal to
≥	greater than or equal to
µmhos/cm	micromhos per centimeter
µS/cm	microsiemens per centimeter
°C	degrees Celsius
°F	degrees Fahrenheit
km	kilometers
L	liter
mg/L	milligrams per liter
ml	milliliter
ng/L	nanograms per liter
ntu	nephelometric turbidity unit
s.u.	standard units

ELEMENTS AND COMPOUNDS

Ag	silver
Al	aluminum
As	arsenic
Ba	barium
Be	beryllium
Ca	calcium
Cd	cadmium
Cl	chloride
Co	cobalt
CO_3	carbonate
COC	chain of custody
Cr	chromium
Cu	copper
F	fluoride
Fe	iron
H_2SO_4	sulfuric acid
HCl	hydrochloric acid
HCO_3	bicarbonate
Hg	mercury
HNO_3	nitric acid
K	potassium
Li	lithium
Mg	magnesium
Mn	manganese
Mo	molybdenum
Na	sodium
NaOH	sodium hydroxide
Ni	nickel
OH	hydroxide
Pb	lead
Sb	antimony
Se	selenium
SO_4	sulfate
Tl	thallium
V	vanadium
Zn	zinc

1.0 PROJECT MANAGEMENT ELEMENTS

1.1 Title and Approvals

Title: Tier 2 Quality Assurance Project Plan (QAPP) for Sediment and Water Quality Monitoring Sampling and Analysis Activities for the Donlin Gold Project.

Name: Enrique Fernandez, Project Manager Phone: 907-273-0200

Donlin Gold LLC email: efernandez@DonlinGold.com

Signature: _____ Date: _____

Name: Rachelle Borne, Quality Assurance (QA) Phone: 504-400-3476
Arcadis U.S., Inc. email: Rachelle.Borne@arcadis.com

Signature: _____ Date: _____

Name: Ted Wall, Data Manager Phone: 720-409-3112
Arcadis U.S., Inc. email: ted.wall@arcadis.com

Signature: _____ Date: _____

Name: , Project Manager Phone:

ADEC DOW Program email:

Signature: _____ Date: _____

Name: , QA Officer Phone:

ADEC DOW WQSAR Program email:

Signature: _____ Date: _____

Name(s): Lloyd (Danny) Twitchell, Field Specialists and Technicians Phone:
Donlin Gold LLC email: dtwitchell@donlingold.com

Signature(s): _____ Date: _____

1.2 Distribution List

The QAPP distribution list is summarized in Table 1.

Table 1: Distribution List

Name	Position	Agency/ Company	Division/ Branch/Section	Contact Information
Dan Graham	General Manager	Donlin Gold LLC	Not applicable	Phone: 907-273-0200 Email: dgraham@DonlinGold.com
Enric Fernandez	Environmental and Permitting Manager	Donlin Gold LLC	Not applicable	Phone: 907-273-0200 Email: efernandez@DonlinGold.com
Ted Wall	Data Manager	Arcadis U.S., Inc	Not applicable	Phone: 720-409-3112 Email: ted.wall@arcadis.com
Rachelle Borne	Quality Assurance (QA)	Arcadis U.S., Inc	Not applicable	Phone: 504-400-3476 Email: Rachelle.Borne@arcadis.com
Charles Homestead	Lab Manager	SGS North America Inc.	Not applicable	Phone: 907-562-2343 Email: Charles.Homestead@sgs.com
Mary McDonald	Lab QA Manager	SGS North America Inc.	Not applicable	Phone:907-562-2343 Email: Mary.McDonald@sgs.com
Stephen Ede	Technical Director	SGS North America Inc.	Not applicable	Phone:907-562-2343 Email: Stephen.Ede@sgs.com
to be determined	Project Manager	Alaska Department of Environmental Conservation (ADEC)	Division of Water	Phone: Email:
to be determined	QA Officer	ADEC	Division of Water, Water Quality Standards, Assessment, and Restoration/QA	Phone: Email:

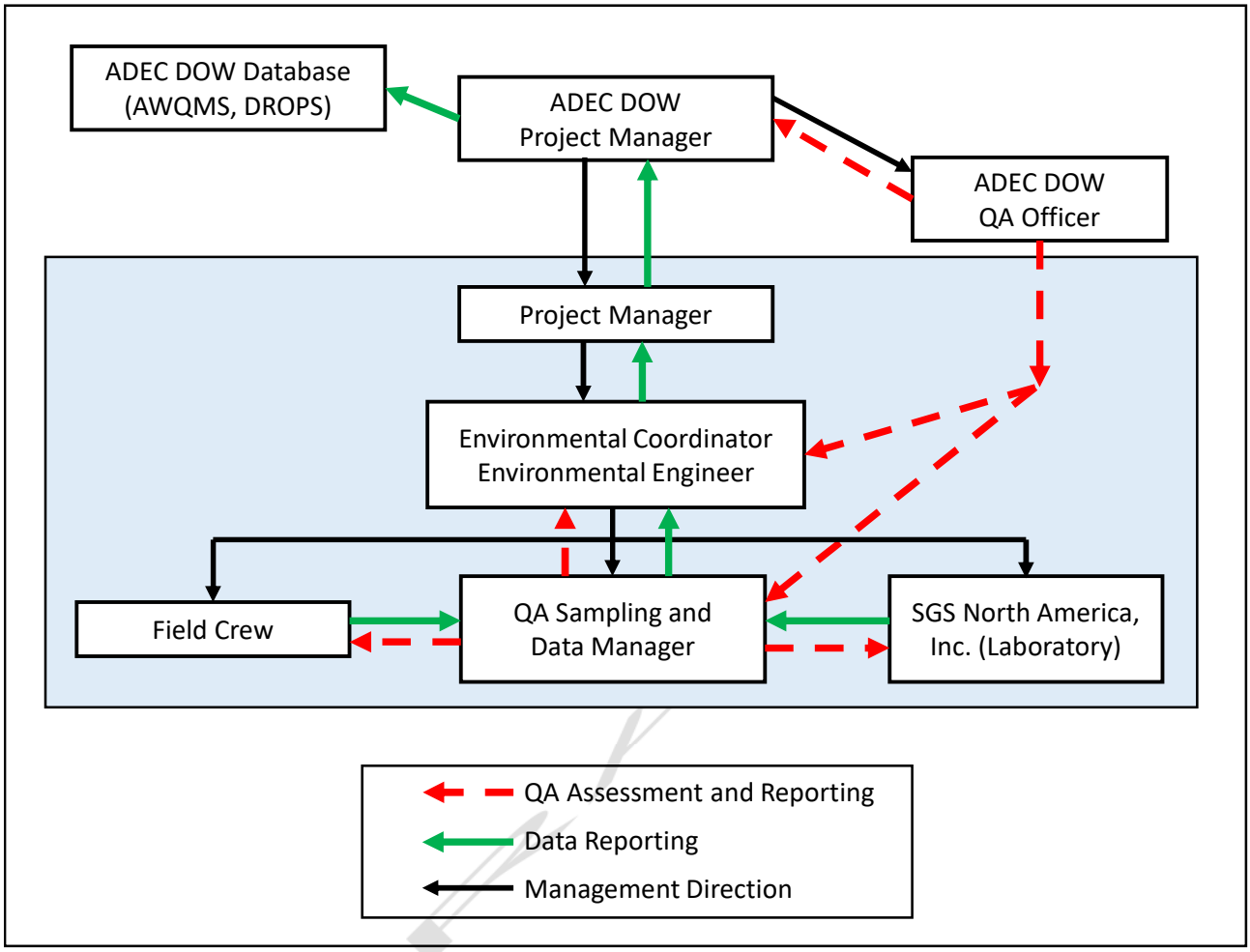
1.3 Project Task/Organization

The project organizational responsibilities for this project are summarized in Table 2, and the water quality sampling program organizational chart for reporting to ADEC when permits are submitted is presented as Figure 1.

Table 2: Project Organizational Responsibilities

Position Title	Agency or Company	Division Branch/Section	Responsibilities
Project/ Environmental/ Permitting Manager	Donlin Gold LLC	Not applicable	Responsible for overall technical, financial, and contractual management of the project. Responsible for the environmental sector of the project, overseeing technical, financial, and contractual management of the project and subsequent reporting of QA reviewed (validated and verified) data to ADEC. Responsible for the permitting sector of the project, overseeing technical, financial, and contractual management of the permitting program.
QA, Sampling and Data Manager	Arcadis U.S., Inc.	Not applicable	Responsible for QA review to verify 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 blind lab performance evaluation samples, and lab audits. These assessments are performed independent of overall project management.
Field Sampling staff	Donlin Gold LLC	Not applicable	Responsible for the collection, data transcription, and delivery of data to the QA, Sampling and Data Manager.
Laboratory Manager	SGS North America, Inc.	Not applicable	Responsible for overall review and approval of contracted laboratory analytical work, responding to sample result inquiries, and method-specific details. Responsible for quality assurance/quality control (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 U.S. Environmental Protection Agency (USEPA)-approved analytical methods.
Laboratory Quality Assurance Manager/Officer	SGS North America, Inc.	Not applicable	Responsible for QA/QC of water quality laboratory analyses as specified in the QAPP. Along with Laboratory Manager, the Lab QA Officer reviews and verifies the validity of sample data results as specified in the QAPP and appropriate USEPA-approved analytical methods.
Project Manager	ADEC	Division of Water	Responsible for overall technical and contractual management of the project. For permit-related monitoring projects, responsible for ensuring that permittee complies with permit-required water quality monitoring as specified in the approved QAPP.
Water Quality Assurance Officer	ADEC	Division of Water	Responsible for QA review and approval of plan and oversight of QA activities, ensuring that collected data meets project's stated data quality goals.

Figure 1: Donlin Gold Organizational Chart



1.4 Background and Project Objectives

1.4.1 Introduction

Donlin Gold LLC[1] (Donlin Gold) has proposed the development of an open pit, hardrock gold mine in southwestern Alaska, about 277 miles (446 km) west of Anchorage, 145 miles (233 km) northeast of Bethel, and 10 miles (16 km) north of the Village of Crooked Creek as shown on Figure 2.

The proposed Donlin Gold project's sediment and water quality monitoring program was established with the overall purpose of collecting baseline data of known and sufficient quality to provide defensible documentation of naturally occurring levels and variability of trace elements in surface water and groundwater. The data collected by this program will provide the basis for the evaluation of potential environmental impacts and form the basis for the long-term monitoring necessary to successfully plan and execute final site closure and post-closure monitoring.

1.4.2 Project Background

Surface water sample collection at the Donlin Gold project area was initiated in 1996. Groundwater monitoring began in 2003. The project site monitoring locations routinely sampled for part or all of the period during which the site monitoring program was active are shown on Figure 3. The site monitoring locations were selected to characterize conditions in areas of proposed infrastructure and previously disturbed ground as shown on Figure 4.

Monitoring and annual summary reporting have been typically performed by contractors (1996-1999, 2002-2006) and by Placer Dome, Barrick, or Donlin Creek/Donlin Gold employees (2000, 2007-2015). No monitoring or water quality data collection was performed in 2001. Groundwater and surface water quality monitoring was discontinued at the Donlin Gold project area in December 2013 and June 2015, respectively, as sufficient data existed to characterize current conditions. Surface water quality sampling and biomonitoring resumed in October 2019 and continues to the present.

Exhibit 1 below summarizes water quality monitoring performed to date.

[1] Donlin Gold LLC is a limited liability company, jointly owned by Barrick Gold U.S. Inc. and NovaGold Resources Alaska, Inc. on a 50/50 basis.

Exhibit 1: Water Quality Monitoring Performed to Date – Donlin Gold Project

Date	Consultant	Activity
1996	CH2M Hill, Inc.	surface water only
1997	CH2M Hill, Inc.	surface water only
1998	Agra Earth & Environ. Inc.	surface water only
1999	AMEC Earth & Environ. Inc.	surface water only
2000	Placer Dome U.S., Inc.	surface water and groundwater
2001	No monitoring performed	
2002	HMH consulting Ltd/Gates & Co.	surface water only
2002	Water Management Consultants	groundwater only
2003	HMH Consulting	surface water only
2004	HMH Consulting	first and second quarters, surface water only
2004	Golder Associates, Inc. (GAI)/Lynx	third quarter, surface water only
2004	Water Management Consultants	first and second quarters, groundwater only
2004	Lynx	third and fourth quarters, groundwater only
2005 through third quarter 2007	Lynx for Placer Dome U.S., Inc.	surface and groundwater first quarter 2005
	Barrick Gold of North America	second quarter 2005 through third quarter 2007
Fourth quarter 2007	Barrick Gold of North America	surface and groundwater
2008 through 2013	Donlin Creek LLC/Donlin Gold	surface and groundwater
2014 through second quarter 2015	Donlin Gold	surface water only
Fourth quarter 2019 through present	Donlin Gold	surface water and biological monitoring

Figure 2: Project Location Map

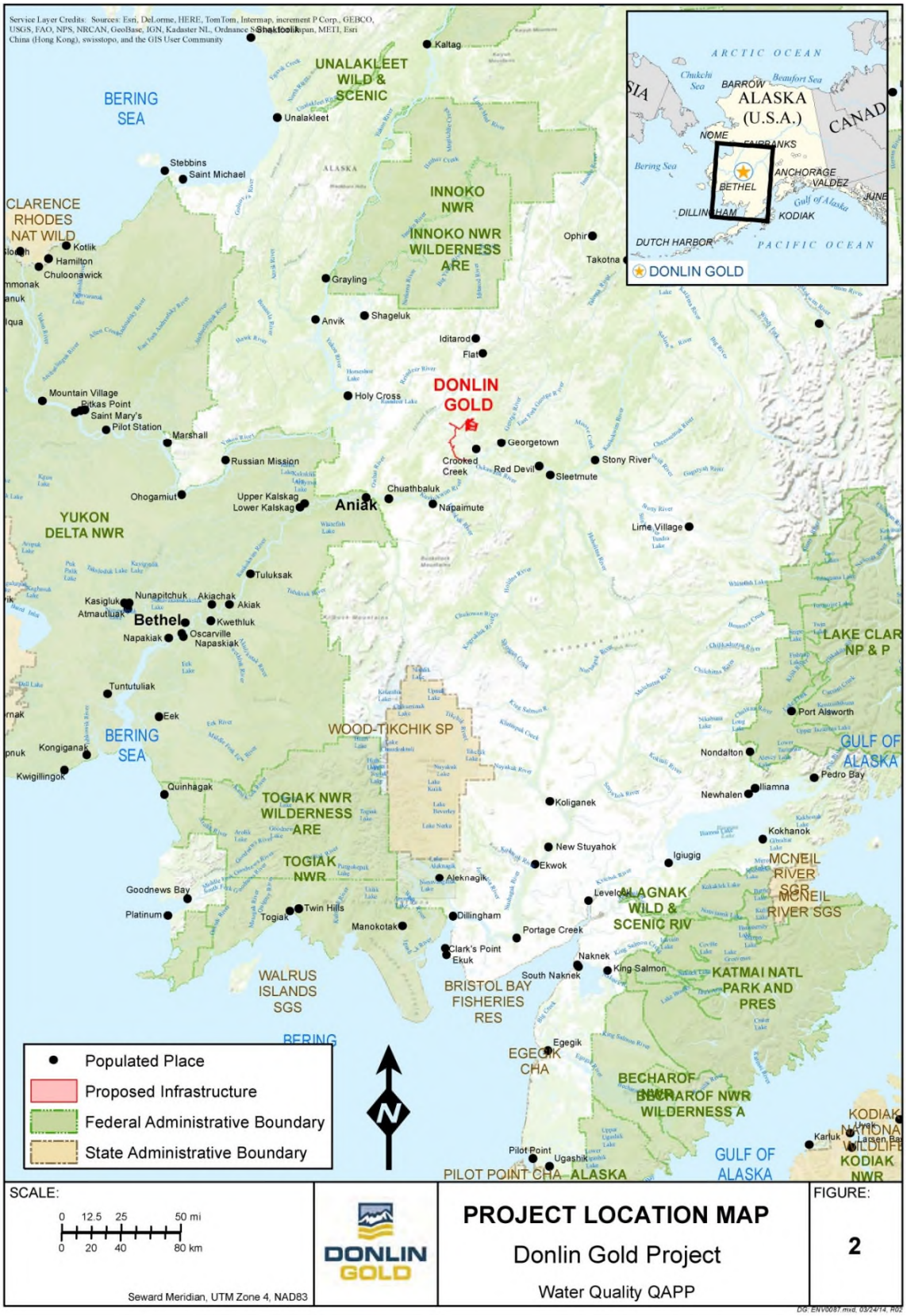
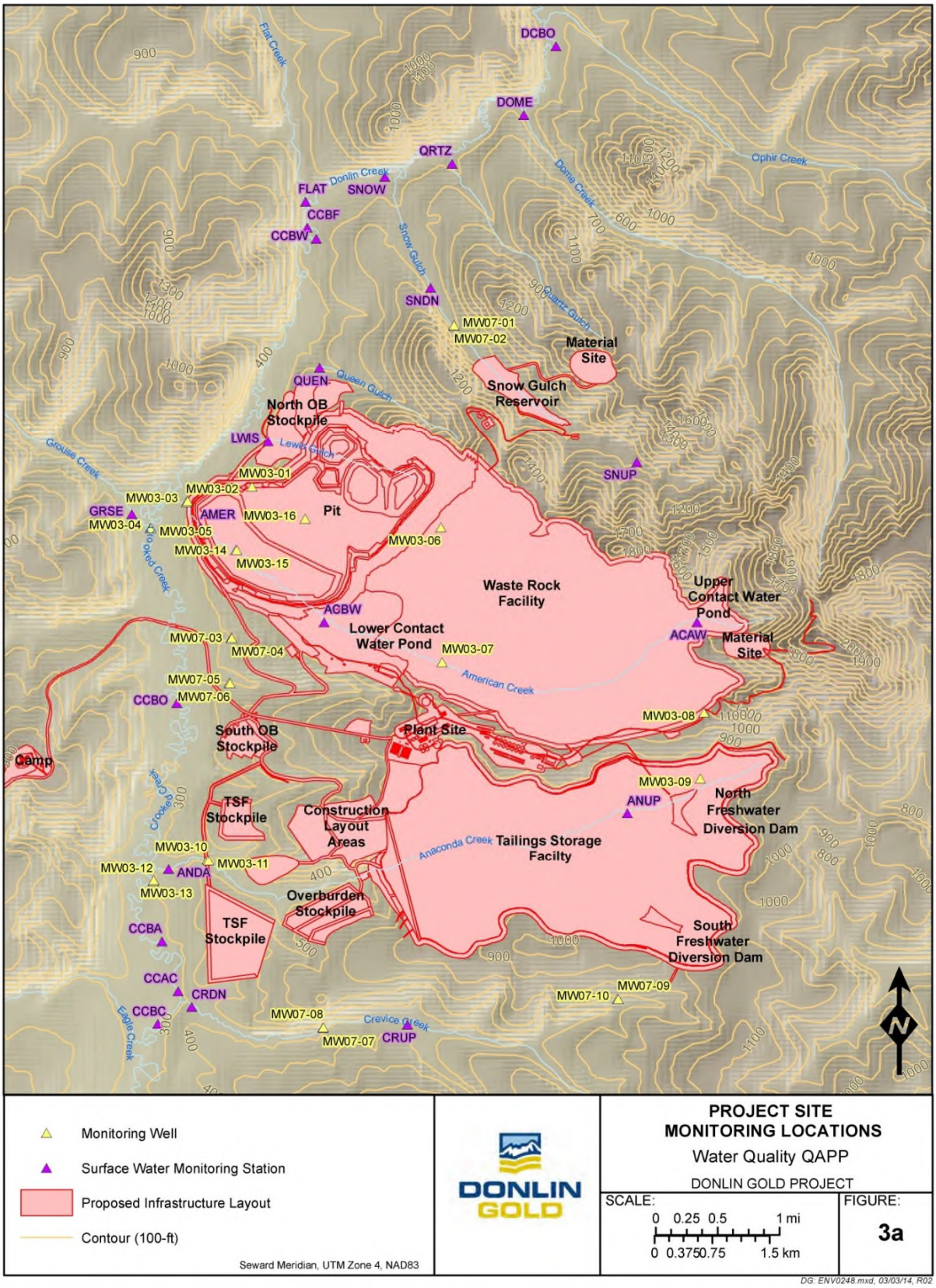


Figure 3: Historic Project Site Monitoring Locations



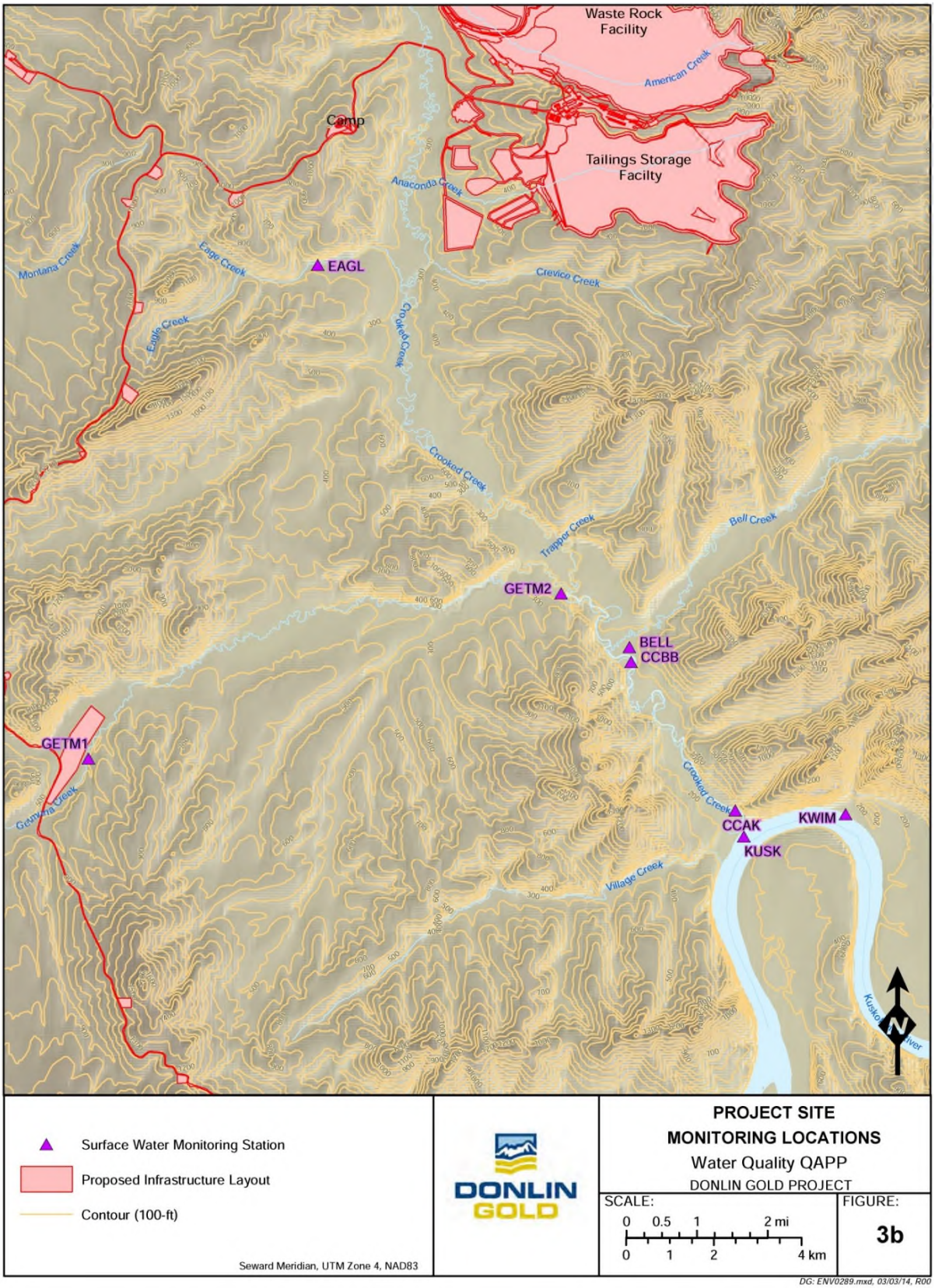

Waste Rock Facility
American Creek
Camp
Tailings Storage Facilty
Anaconda Creek
Montana Creek
Eagle Creek
EAGL
Crevico Creek
Crooked Creek
Trapper Creek
Bell Creek
GETM2
BELL
CCBB
GETM1
Gemuna Creek
CCAK
KWIM
KUSK
Village Creek
Kuskokwim River
N
Surface Water Monitoring Station
Proposed Infrastructure Layout
Contour (100-ft)
Seward Meridian, UTM Zone 4, NAD83
DONLIN GOLD
PROJECT SITE
MONITORING LOCATIONS
Water Quality QAPP
DONLIN GOLD PROJECT
SCALE:
0 0.5 1 2 mi
0 1 2 4 km
FIGURE:
3b
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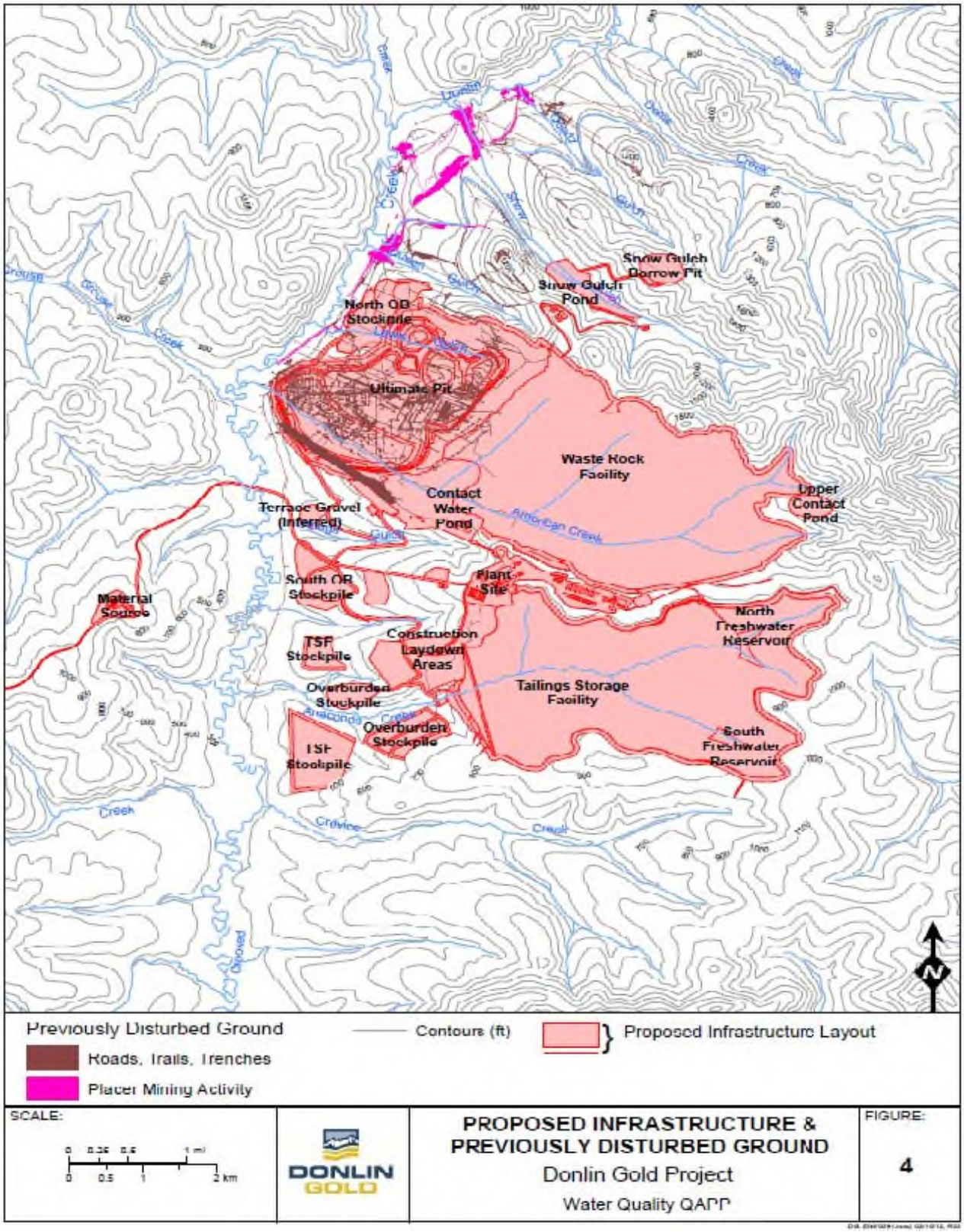
Figure 4: Proposed Infrastructure and Previously Disturbed Ground



During 2004, GAI compiled, reviewed, and assessed water quality electronic data files previously generated for the Donlin Gold project. As part of this task, a single EQWin electronic database file of water quality data (1996–2003, surface water only) was prepared and delivered to Placer Dome (now Barrick). Since 2009, data were migrated to the EQuIS Professional database (Current version 7), developed by EarthSoft Inc., which has streamlined workflow for data field entry, QA, and reporting.

1.4.3 Surface Water Sampling Plan

The surface water sampling plan was first established in 1996. It included 13 water quality monitoring stations located throughout the project area but concentrated along Crooked Creek (and Donlin Creek above the confluence with Flat) and on its tributaries (American, Anaconda, Dome, Flat, Grouse, Quartz, Lewis, Queen, and Snow Creeks) immediately upstream of their confluence with Crooked Creek. These original 13 monitoring stations were located to gather water quality and surface flow data for entire drainage basins.

As the project progressed, understanding of both flow and metals loading from the respective basins increased. In 2005, the sampling plan was redesigned to include the addition of new surface water quality sampling stations and to discontinue monitoring at others. The network was expanded to further define Snow Gulch (upstream), American Creek (mid and upstream), and Upper Anaconda Creek, and to encompass the Crevice Creek drainage (to the south of the proposed facilities).

In 2019, the list of sampling station was further revised to address the post EIS needs of the project. The revised monitoring site selection is presented below with discussion on the rationale for the changes. The water quality sample stations were determined to be the best sites in terms of both location and access based on an aerial reconnaissance review and past experience. These monitoring station locations are presented on Figure 5. It is anticipated that these locations will be sampled going forward. A summary of the monitoring history for all of the historical surface water monitoring location is provided on Figure 6.

Figure 5: Active Surface Water Quality Monitoring Stations

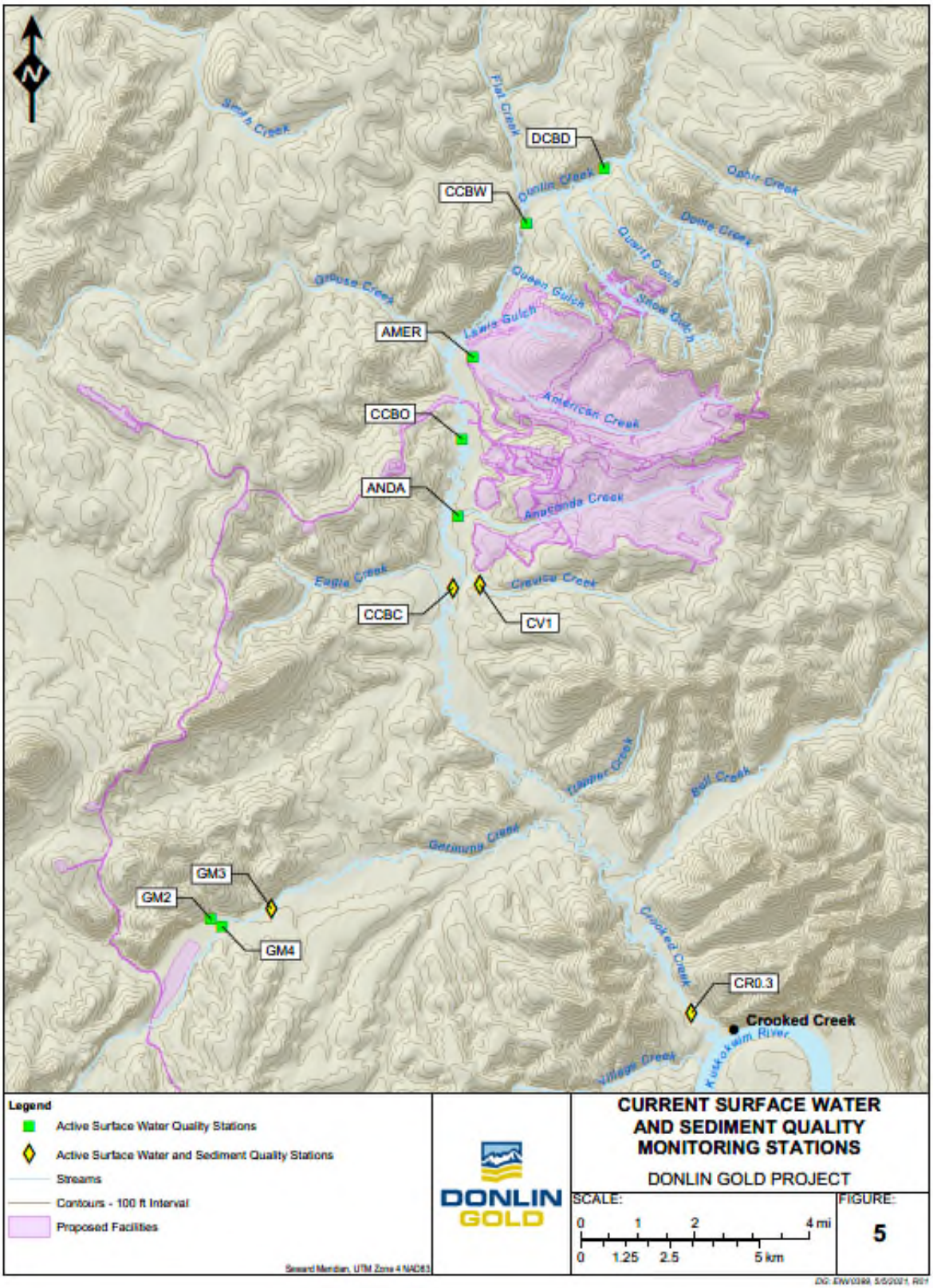


Figure 6: Surface Water Location Monitoring History

	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016-2018	2019	2020	2021
ACAW										X	X	X	X	X	X	X	X	X	X	X				
ACBW										X	X	X	X	X	X	X	X							
AMER	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X
ANDA	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X
ANUP										X	X	X	X	X	X	X	X	X	X	X				
BELL																		X	X	X				
CCAC										X	X	X	X	X	X	X	X	X	X	X				
CCAK	X	X	X	X	X		X	X	X			X	X	X	X			X	X	X				
CCBA							X	X	X															
CCBB																		X	X	X				
CCBC										X	X	X	X	X	X	X	X	X				X	X	X
CCBC										X	X	X	X	X	X	X	X	X				X	X	X
CCBF	X	X	X	X	X																			
CCBO	X	X	X	X	X		X			X	X	X	X	X	X	X	X	X	X	X		X	X	X
CCBW										X	X	X	X	X	X	X	X	X	X	X		X	X	X
CR0.3												X	X	X	X							X	X	X
CRDN										X	X	X	X	X	X	X	X	X	X	X			X	
CRUP										X	X	X	X	X	X	X	X							
CV1												X	X	X								X	X	X
DCBD												X	X	X	X							X	X	X
DCBO	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X
DOME	X	X	X	X	X		X	X	X				X	X	X									
EAGL														X	X	X								
FLAT	X	X	X	X	X		X	X	X															
GETM1																	X		X	X				
GETM2																		X	X					
GM3																	X					X	X	X
GRSE	X	X	X	X	X		X	X	X				X	X										
KUSK	X	X	X	X	X		X	X	X															
KWIM			X		X		X	X	X															
LWIS	X	X	X	X	X		X	X	X															
QRTZ	X	X	X	X	X		X	X	X				X	X	X									
QUEN	X	X	X	X	X		X	X	X															
SNDN										X	X	X	X	X	X	X	X							
SNOW	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X		X				
SNUP										X	X	X	X	X	X	X	X	X	X	X				

Surface water quality within the project area can be segregated into three basic categories of influence:

- **Category 1:** waters draining undisturbed and non-mineralized areas;
- **Category 2:** waters draining area of defined mineralized zone only with no placer mining activities;
- **Category 3:** waters draining from areas of both placer mining and the mineralized zone.

The surface water sampling plan is designed to characterize these three area categories as well as to establish upstream and downstream controls. The surface water hydrologic data collection sites vary from the surface water quality monitoring stations because they are intended to achieve different goals. Additional grab samples and field parameters are collected when practical.

Water quality monitoring stations sites not included in the 2015 revised sampling program are listed below, along with the rationale for their exclusion. The locations of these stations are shown on Figure 3:

- **ACBW (Category 2):** American Creek site, below proposed waste rock and seepage collection pond facilities, was previously designed as a long-term monitoring station through reclamation and closure. Monitoring was conducted from the first quarter of 2005 to the third quarter of 2012.
- **ANUP (Category 1):** Upper Anaconda Creek site is above any potential influence from proposed diversions or other physical disturbance. Monitoring was conducted from second quarter 2005 to third quarter 2013.
- **CCBA (Category 3):** Crooked Creek below Anaconda Creek site was replaced by CCAC. The channel and banks are better defined at CCAC, and the location will support a cable crossing for use in long-term stream flow monitoring. Monitoring was conducted at this station from second quarter 2002 to third quarter 2004.
- **CCBC (Category 3):** Crooked Creek below Crevice Creek site is below all proposed facilities and potential impacts at Crevice Creek. Additional lower sites were reinstated to compensate for discontinuing this site. Monitoring was conducted from third quarter 2005 to second quarter 2013.
- **CCBF (Category 1)**: Crooked Creek downstream of Flat Creek site is replaced by Station CCBW, which is now being used to characterize this area. Monitoring was conducted from second quarter 1996 to third quarter 2000.
- **CRUP (Category 1):** Upper Crevice Creek site is above any potential influence from proposed Anaconda facilities. Monitoring was conducted from third quarter 2005 to third quarter 2012.
- **DOME (Category 1):** Dome Creek site is upstream of all current and proposed activities and provides no critical data for long-term monitoring. Data collection started during second quarter 1996 and was discontinued after third quarter 2004. This location was added back into the sampling program and monitored from third quarter 2008 to third quarter 2010 in support of proposed exploration.

- **EAGL (Category 3):** Data from CCBO will be used to characterize this area. Eagle Creek site was initially established at upper Eagle Creek during second quarter 2009 and phased out after first quarter 2011.
- **FLAT (Category 1):** Sufficient data exist to characterize Flat Creek from areas upstream of proposed activities. Monitoring was conducted from second quarter 1996 to third quarter 2004.
- **GRSE (Category 3):** Sufficient data exist to characterize Grouse Creek from areas upstream of proposed activities. Monitoring was conducted from second quarter 1996 to first quarter 2009.
- **GETM1 (Category 1)** Getmuna Creek temporary location, downstream of proposed port road and adjacent to proposed material site. One sample was collected during first quarter 2012.
- **KWIM (Category 1):** Adequate data exist to characterize the Kuskokwim River water quality at this site (Kuskokwim above Crooked Creek confluence). Discontinued after third quarter 2004.
- **KUSK (Category 1):** Adequate data exist to characterize the Kuskokwim River water quality at this site (Kuskokwim below Crooked Creek confluence). Discontinued after third quarter 2004.
- **LWIS (Category 3):** Lewis Gulch drains a mineralized area and will be disturbed by proposed operations. Discontinued after third quarter 2004.
- **QRTZ (Category 1):** Quartz Creek site is upstream of all proposed activities and provides no critical data for long-term monitoring. Monitoring was resumed in third quarter 2008 in support of proposed exploration, then discontinued after third quarter 2010.
- **QUEN (Category 1):** Queen Gulch is upstream of all activities and provides no critical data for long-term monitoring. Sampling was discontinued after third quarter 2004.
- **SNDN (Category 2):** Lower Snow Gulch crosses both the mineralized trend and historical placer mining. This site is above both the mineralization trend and placer mining areas. Discontinued after third quarter 2012.

The surface water quality monitoring station network and rationale as of 2015 are presented in Table 3, with monitoring stations retained for sampling from 2020 onward highlighted in bold. The water quality monitoring stations were optimized in terms of location and access based on an aerial reconnaissance review and past experience. The locations of these water quality monitoring stations are presented on Figures 3 and 5.

Table 3: Surface Water and Sediment Monitoring Stations and Site Representativeness

Station Description	Station ID	Rationale and Purpose	Category	Sample Type	Geographic Coordinates (meters) UTM Zone 4 NAD 83	
					Easting	Northing
American Gold above confluence with Crooked Creek	**AMER**	**American Creek below all planned facilities and disturbance and above confluence with Crooked Creek**	**2**	**SW**	**539333**	**6878839**
American Creek above waste rock	ACAW	American Creek upstream of proposed waste rock placement near proposed upstream diversion of water around all facilities. Also upstream of mineralization in American Creek. Placed to determine quality of diversion water that would be directed to Crooked Creek as non-mine water	1	SW	545787	6877604
Anaconda Creek above confluence with Crooked Creek	**ANDA**	**Below all proposed facilities at Anaconda Creek and above Crooked Creek**	**1**	**SW**	**539055**	**6874441**
Snow Gulch upstream of activity and mineralization trend	SNUP	Snow Gulch crosses both the mineralized trend and historical placer mining. This site is above both the mineralization trend and placer mining	1	SW	545024	6879725
Snow Gulch above confluence with Crooked Creek	SNOW	Snow Gulch below mineralization and historical placer tails and above confluence with Crooked Creek	3	SW	541729	6883397
Crooked Creek above Crevice Creek.	CCAC	Below all proposed facilities and potential impacts to Crooked Creek. This site replaces CCBA	3	SW	538972	6872889
Bell Creek above confluence with Crooked Creek	BELL	Below all proposed facilities and potential impacts to Crooked Creek	1	SW	543636	6863886
Crooked Creek above confluence with Kuskokwim River	CCAK	Below all proposed facilities and potential impacts to Crooked Creek	3	SW	546040	6860167
Crooked Creek below Bell Creek	CCBB	Below all proposed facilities and potential impacts to Crooked Creek, below both Bell Creek and Getmuna Creek	3	SW	543667	6863547

Table 3 (Continued): Surface Water and Sediment Monitoring Stations and Site Representativeness

Station Description	Station ID	Rationale and Purpose	Category	Sample Type	Geographic Coordinates (meters) UTM Zone 4 NAD 83	
					Easting	Northing
Crooked Creek below the confluence of Crevice Creek	**CCBC**	**Monitoring downstream from mine site and Crevice Creek confluence**	**3**	**SD SW**	**538757**	**6872355**
Crooked Gold below Ophir Creek	**CCBO**	**Downstream of Ophir Creek, which drains from the camp area and airstrip**	**3**	**SW**	**539021**	**6876552**
Crooked Creek directly below Lyman Wash Plant	**CCBW**	**Crooked Creek below influence of historical placer mining operation**	**3**	**SW**	**540832**	**6882598**
Lower Crooked Creek above the Village of Crooked Creek	**CR0.3**	**Located at a section of river where flows were split into three distinct channels by a gravel bar**	**3**	**SD SW**	**544826**	**6861571**
Lower Crevice Creek above confluence with Crooked Creek	CRDN	Crevice Creek below any potential influence from Anaconda facilities	1	SW	539215	6872587
Lower Crevice Creek	**CV1**	**Downstream from tailings pond discharge post-reclamation**	**3**	**SD SW**	**539223**	**6872458**
Donlin Creek below Ophir Creek	DCBO	Upstream of all proposed activity and above any disturbance from historical placer mining. Project Control	1	SW	543948	6885105
Donlin Creek below Dome	**DCBD**	**Upstream of all proposed activity and above any disturbance from historical placer mining. Project Control**	**1**	**SW**	**543948**	**6885105**
Getmuna Creek above confluence with Crooked Creek.	GETM2	Getmuna Creek below any potential influence from Port Road and associated materials sites	1	SW	542076	6865101
Upper Crevice Creek	CRUP	Crevice Creek above any potential influence from Anaconda facilities	1	SW	542022	6872357

Table 3 (Continued): Surface Water and Sediment Monitoring Stations and Site Representativeness

Station Description	Station ID	Rationale and Purpose	Category	Sample Type	Geographic Coordinates (meters) UTM Zone 4 NAD 83	
					Easting	Northing
Anaconda Creek upstream	ANUP	Anaconda Creek above any potential influence from diversions or other physical disturbance	1	SW	539055	6874441
American Creek below proposed waste rock storage	ACBW	American Creek below waste rock and downstream of seepage collection pond. Designed as long-term monitoring station through reclamation and closure	2	SW	540937	6877606
Snow Gulch downstream of mineralization trend	SNDN	Snow Gulch below the mineralized trend and above historical placer tails	2	SW	542329	6881964
Getmuna Creek below where the north and south forks come together	**GM3**	Upstream from all mining activity, but downstream from two Donlin-Jungjuk Road crossings, and a material source.	**3**	**SD SW**	**533008**	**6862976**

Notes:
Stations IDs in **bold** were included in the 2020 sampling program.
NAD 83 = North American Datum of 1983
SD = Sediment
SW = Surface Water
UTM = Universal Transverse Mercator

1.4.4 Groundwater Sampling Plan

A total of 26 wells have been installed for the groundwater monitoring network (Figure 7). Monitoring well locations were established to characterize the groundwater system both upgradient and downgradient of each major facility. Two of the 26 wells have been decommissioned and plugged (MW03-04 and MW03-05). Table 4 summarizes groundwater monitoring well location, monitoring target, and current status; the wells are located as shown on Figure 7.

In many of these locations, near the lower reaches of a creek where groundwater is likely discharging to the surface water system, two pairs of wells were installed to evaluate vertical gradients. One well was screened in the shallow groundwater system and the other in the deep groundwater systems. These were installed to evaluate vertical gradients near the lower reaches of the creek, where groundwater is likely discharging to the surface water system.

1.4.5 Sediment Sampling Plan

Sediment sampling will be initiated in 2021 and will be conducted annually from four locations: CR0.3, GM3, CCBC, and DCBD (Figure 5). Analytical results from these samples would be used in conjunction with the collocated fish tissue sampling to identify changes in element concentrations and to aid in understanding of how they could be affecting aquatic resources. Sediment sampling will be performed immediately following fish whole body element concentration sample collection. Biological monitoring, including fish tissue sampling, is outside the scope of this document.

Composite sampling will be completed during the second quarter of each year using Lexan tubes with end caps. The composite samples will be collected in three increments along a 20-foot transect at each location to account for the inherent heterogeneity of sediment analyte concentrations. Each increment will be collected from 0 to 6 inches below ground surface.

1.4.6 Project Objectives of the QAPP

The purpose of the QAPP is to formalize the procedures and associated quality control for all related activities including sample collection, sample handling and shipping, contracted laboratory services, review of laboratory results, and data management.

The objectives of the QAPP are to:

- Describe the various components of the sediment and water quality monitoring program.
- Provide a foundation and structure to administer water management planning.
- Implement standardized procedures for program components.
- Provide an overview of the overall project goals and the rationale for sediment and water quality monitoring locations and frequency.

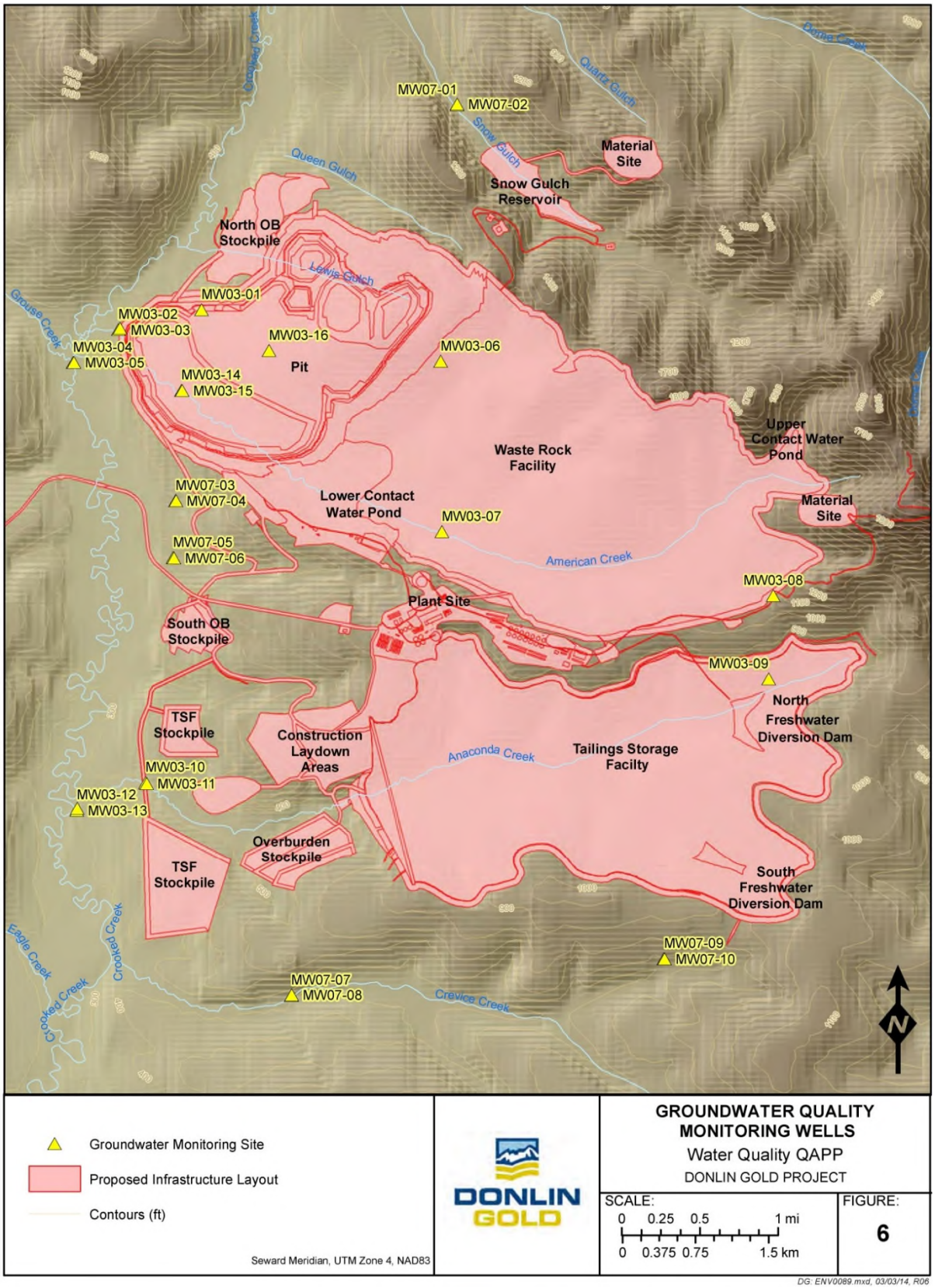
Table 4: Groundwater Monitoring Stations and Site Representativeness

Well ID	Geographic Coordinates (meters) UTM Zone 4 NAD 83		Monitoring Target	Notes
	Easting	Northing		
MW03-01	539999	6879366	Downgradient from mineralized zone	Sampling discontinued after 4Q2013
MW03-02	539144	6879164	Bedrock downgradient from pit/upstream from American Creek	Sampling discontinued after 4Q2013
MW03-03	539163	6879178	Alluvium downgradient from pit/upstream from American Creek	Sampling discontinued after 4Q2012
MW03-04	538680	6878830	Bedrock downgradient from pit/downstream from American Creek	Sampling discontinued after 4Q2013, well decommissioned and plugged with grout in 2014.
MW03-05	538685	6878841	Alluvium downgradient from pit/downstream from American Creek	Sampling discontinued after 4Q2012, well decommissioned and plugged with grout in 2014.
MW03-06	542457	6877089	Shallow groundwater downgradient of waste rock facilities	Not part of program, Completed below permafrost
MW03-07	542470	6877084	Downgradient from the proposed waste rock facilities	Sampling discontinued after 4Q2013
MW03-08	545875	6876430	Upgradient from the proposed waste rock facilities	Sampling discontinued after 4Q2013
MW03-09	545829	6875574	Upgradient from the proposed tailings facility	Sampling discontinued after 4Q2013
MW03-10	539423	6874503	Deep groundwater downgradient from proposed tailings facility	Sampling discontinued after 4Q2013
MW03-11	539433	6874500	Shallow groundwater downgradient from proposed tailings	Well is dry
MW03-12	538714	6874223	Bedrock downgradient from proposed tailings/downstream from Anaconda Creek	Sampling discontinued after 4Q2012
MW03-13	538719	6874245	Alluvium downgradient from proposed tailings/downstream from Anaconda Creek	Sampling discontinued after 4Q2012
MW03-14	539782	6878537	Existing groundwater quality in the mineralized zone	Sampling discontinued after 4Q2013
MW03-15	539797	6878539	Existing shallow groundwater quality in the mineralized zone	Sampling discontinued after 4Q2012
MW03-16	540692	6878952	Groundwater upgradient from the proposed pit	Sampling discontinued after 4Q2013
MW07-01	542627	6881469	Shallow groundwater - Snow Gulch	Sampling discontinued after 4Q2013
MW07-02	542627	6881477	Deep groundwater - Snow Gulch	Sampling discontinued after 4Q2013
MW07-03	539729	6877401	Shallow groundwater - downgradient from mill facility – Omega North	Sampling discontinued after 4Q2012

Table 4 (Continued): Groundwater Monitoring Stations and Site Representativeness

Well ID	Geographic Coordinates (meters) UTM Zone 4 NAD 83		Monitoring Target	Notes
	Easting	Northing		
MW07-04	539734	6877400	Deep groundwater - downgradient from mill facility – Omega North	Sampling discontinued after 4Q2013
MW07-05	539703	6876817	Shallow groundwater - downgradient from mill facility – Omega Gulch	Not sampled quarterly as of December 2012
MW07-06	539714	6876812	Deep groundwater - downgradient from mill facility – Omega Gulch	Sampling discontinued after 4Q2013
MW07-07	540910	6872313	Deep groundwater - downgradient of potential water diversion from Anaconda Creek to Crevice Creek.	Sampling discontinued after 4Q2013
MW07-08	540912	6872313	Shallow groundwater - downgradient of potential water diversion from Anaconda Creek to Crevice Creek.	Ice Cap @ 25 feet (7.62 meters)
MW07-09	544752	6872692	Deep groundwater - upgradient of potential water diversion from Anaconda Creek to Crevice Creek.	Sampling discontinued after 4Q2013
MW07-10	544752	6872692	Shallow groundwater - upgradient of potential water diversion from Anaconda Creek to Crevice Creek.	Sampling discontinued after 4Q2013

Figure 7: Groundwater Quality Monitoring Wells



1.5 Project Description and Schedule

1.5.1 Project Description

Surface Water Monitoring Program

The purpose of the surface water monitoring program is to collect data that establish the baseline conditions of surface water systems in the area potentially affected by development as depicted on Figure 4. These data may be used during mine planning and permitting and for water quality monitoring throughout mine construction, operations, reclamation, closure, and post-closure.

The primary objectives for the surface water monitoring program are to:

- Continue to monitor the loading from key drainage basins.
- Determine and document the effects of the mineralized zone and historical placer mining on the surface water quality in the region.
- Provide data to support water balance modeling.
- Establish long-term monitoring stations for the life of the project mine from exploration from construction, through operations, and into closure and reclamation.

Groundwater Monitoring Program

The purpose of the groundwater monitoring program is to document the existing baseline, baseline groundwater chemistry, and piezometric surface within the areas where mine development is proposed (Figures 4 and 7).

The general objectives of the groundwater monitoring program are to:

- Collect data that can be used to establish the background condition of the bedrock and alluvial groundwater systems in the area. Data will be collected for groundwater quality and groundwater elevations.
- Collect aquifer characteristic data that can aid in facility design and site-wide water management.
- Develop an overall conceptual model of baseline groundwater conditions at the site to support the permitting process.

Sediment Monitoring Program

The purpose of the sediment quality monitoring program is to document the existing baseline and any changes in element concentrations where mine development is proposed.

The general objectives of the groundwater monitoring program are to:

- Collect data that can be used to establish background element concentrations.
- Collect data, along with collocated fish tissue samples, to identify changes in element concentrations and aid in understanding how they could be affecting aquatic resources.

- Develop an overall conceptual model of baseline sediment conditions at the site to support the permitting process.

1.5.2 Project Implementation Schedule

Water quality monitoring, sampling, and analysis were initiated in 1995. In December 2013, groundwater quality monitoring at the Donlin Gold project area was discontinued. The wells have been placed in caretaker mode and have not been decommissioned. The surface water monitoring program was discontinued after the June 2015 second quarter sampling event but was restarted in the fourth quarter of 2019. Although sufficient surface and groundwater data exist to characterize current conditions for the proposed Donlin Gold project, surface water sampling was reinitiated in 2019 and 2020 according to the Aquatic Resources Monitoring Plan, Plan of Operations – Volume VI C[2] (ARMP) due to potential changes to the baseline condition resulting from wildfires in the area.

The historical and current sampling schedule is described in Section 1.4.2.

1.6 Data Quality Objectives and Criteria for Measurement Data

1.6.1 Data Quality Objectives

The Donlin Gold project is not currently under a permit by the ADEC; however, a baseline QAPP was developed in support of baseline data collection. The Laboratory Procedures Program establishes protocols and minimum QA/QC requirements for contracted laboratory services to obtain analytical data that meet project requirements. The components described in this section should be reflected in the contractual agreement between Donlin Gold and the analytical testing laboratory providing services to the Donlin Gold project. Requirements and protocols specified in this section are to be reviewed in detail with the testing lab and agreed upon in writing.

Known and documented data quality is an essential component of accurate environmental site assessments and effective decision-making associated with any water quality monitoring program. Achieving defined data quality objectives requires clear, concise, and detailed communications with contracted analytical laboratories. The purpose of this section is to establish specific analytical parameter lists for sediment and water quality monitoring at the proposed Donlin Gold project site.

The parameter lists include the names, units, basis, analytical method, maximum reporting limit, and the allowable holding time for each parameter to be analyzed (Table 5, Water Short List-1; Table 6, Water Long List-1; and Table 7, Sediment List-1). The bottle sets required for each analytical list and reporting instructions for the testing labs are provided in Tables 8 and 9, respectively. The specifications in these tables are used in establishing contractual agreements with contract laboratories before the initiation of analytical services. It is recommended that laboratory contract agreements periodically be reviewed and updated as required.

[2] Donlin Gold, LLC. 2020. Aquatic Resources Management Plan, Plan of Operations – Volume VII C Donlin Gold Project. DNG020-18-001F1. March. Available online at: http://dnr.alaska.gov/mlw/mining/largemine/donlin/pdf/poo-armp2020.pdf.

Table 5: Short List-1, Water Quality Parameters for Analysis of Water Samples

Parameter	Basis	Units	Method[1]	Reporting Limit	Holding Time
GENERAL					
pH	Laboratory	s.u.	SM20 4500-H B	0.01	as soon as possible (ASAP)
Electrical Conductivity	Laboratory	µmhos/cm	SM20 2510B	1	28 days
Total Dissolved Solids (TDS)	Dissolved	mg/L	SM20 2540C	10	7 days
Total Suspended Solids (TSS)	Total Recoverable	mg/L	SM20 2540D	1	7 days
MAJOR CATIONS					
Calcium (Ca)	Dissolved	mg/L	USEPA 200.8	0.5	6 months
Magnesium (Mg)					
Sodium (Na)					
Potassium (K)					
MAJOR ANIONS					
Alkalinity, total*	Dissolved	mg/L	SM20 2320B	5	14 days
Bicarbonate *					
Carbonate*					
Hydroxide*					
Sulfate (SO_4)	Dissolved	mg/L	USEPA 300.0	1	28 days
Chloride (Cl)				1	
Fluoride (F)				0.1	
METALS					
Aluminum (Al)	Total/Dissolved	mg/L	USEPA 200.8	0.02	6 Months
Arsenic (As)				0.005	
Barium (Ba)				0.003	
Cadmium (Cd)				0.0005	
Iron (Fe)				0.04	
Lithium (Li)				0.01	
Manganese (Mn)				0.001	
Nickel (Ni)				0.002	
Zinc (Zn)				0.005	
Mercury (Hg)	Total Recoverable	ng/L	USEPA 1631 E	1	90 days
Methyl Mercury	Total Recoverable	ng/L	USEPA 1630	0.5	6 Months
CALCULATIONS					
Hardness (as $CaCO_3$)	Dissolved	mg/L	USEPA 200.8	2	6 months

* As $CaCO_3$ s.u. = Standard Units mg/L = milligrams per liter ng/L = nanograms per liter
µmhos/cm = micromhos per centimeter

Required Sample Preparation Procedures: For total recoverable metals by Inductively Coupled Plasma Mass Spectrometry (ICPMS) 200.8: Digestion – USEPA 200.2[2]

Method References:

[1]USEPA (200.8): USEPA Method 200.8, Trace Elements by ICP-MS, Revision 5.4, 1994

[1]USEPA (300.0): USEPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.2, October 1993

[1]USEPA (1631 E): USEPA Method 1631, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, Revision E, August 2002

[1]USEPA (1630): Method 1630, Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS, 2nd revision, January 2001

[1]SM20: Standard Methods for the Examination of Water and Wastes, 20th Edition (1998)

[2]USEPA 200.2: Sample Preparation Procedure for Determination of Total Rec. Elements, Rev. 2.8, October 1994

Table 6: Long List-1, Water Quality Field and Lab Parameters for Analysis of Water Samples

Parameter	Basis	Units	Method[1]	Reporting Limit	Holding Time
FIELD PARAMETERS (COLLECTED BY FIELD CREW)					
pH	Field	s.u.	YSI 556 Probe	0.01	ASAP
Electrical Conductivity		µS/cm or µmhos/cm	YSI 556 Probe	1	ASAP
Water Temperature		Degree C	YSI 556 Probe	0.01	ASAP
Air Temperature		Degree C	Digital Thermometer	0.01	ASAP
Oxidation/Reduction Potential		millivolts	YSI 556 Probe	0.1	ASAP
Dissolved Oxygen (DO)		mg/L	YSI 556 Probe	0.01	ASAP
Turbidity (surface water only)		ntu	YSI 556 Probe	0.1	ASAP
GENERAL					
pH	Laboratory	s.u.	SM20 4500-HB	0.01	ASAP
Electrical Conductivity	Laboratory	µmhos/cm	SM20 2510B	1	28 days
Total Dissolved Solids (TDS)	Dissolved	mg/L	SM20 2540C	10	7 days
Total Suspended Solids (TSS)	Total Recoverable	mg/L	SM20 2540D	1	7 days
MAJOR CATIONS					
Calcium (Ca)	Dissolved	mg/L	USEPA 200.8	0.5	6 months
Magnesium (Mg)					
Sodium (Na)					
Potassium (K)					
MAJOR ANIONS					
Alkalinity, total*	Dissolved	mg/L	SM20 2320B	5	14 days
Bicarbonate*					
Carbonate*					
Hydroxide*					
Sulfate (SO_4)	Dissolved	mg/L	USEPA 300.0	1	28 days
Chloride (Cl)				1	
Fluoride (F)				0.1	
NUTRIENTS					
Nitrate+Nitrite (N)	Total Recoverable	mg/L	SM20 4500NO_3-F	0.1	28 days
Ammonia (as N)		mg/L	SM20 4500NH_3-F	0.1	28 days
CYANIDE					
Cyanide, total	Total	mg/L	SM20 4500CN C,E	0.005	14 days
Cyanide, WAD (weak acid dissociable)	Total Recoverable	mg/L	SM20 4500-CN I	0.005	14 days

Table 6 (continued): Long List-1, Water Quality Field and Lab Parameters for Analysis of Water Samples

Parameter	Basis	Units	Method[1]	Reporting Limit	Holding Time
METALS					
Aluminum (Al)	Total Recoverable/ Dissolved	mg/L	USEPA 200.8	0.02	6 months
Antimony (Sb)				0.001	
Arsenic (As)				0.005	
Barium (Ba)				0.003	
Beryllium (Be)				0.0004	
Boron (B)				0.02	
Cadmium (Cd)				0.0005	
Chromium (Cr)				0.001	
Cobalt (Co)				0.004	
Copper (Cu)				0.001	
Iron (Fe)				0.04	
Lead (Pb)				0.0002	
Lithium (Li)				0.01	
Manganese (Mn)				0.001	
Molybdenum (Mo)				0.01	
Nickel (Ni)				0.002	
Selenium (Se)				0.005	
Silver (Ag)				0.001	
Thallium (Tl)				0.001	
Vanadium (V)				0.02	
Zinc (Zn)				0.005	
Mercury (Hg)	Total Recoverable	ng/L	USEPA 1631 E	1	90 Days
Methyl Mercury	Total Recoverable	ng/L	USEPA 1630	0.5	90 days
CALCULATIONS					
Hardness (as CaCO3)	Dissolved	mg/L	USEPA 200.8	2	6 months

* As $CaCO_3$ s.u., Standard Units mg/L, milligrams per liter ng/L, nanograms per liter µmhos/cm, micromhos per centimeter µS/cm, microSiemens per centimeter

Required Sample Preparation Procedures: For total recoverable metals by ICPMS 200.8: Digestion – USEPA 200.2[2]

Method References:

[1]USEPA (200.8): USEPA Method 200.8, Trace Elements by ICP-MS, Revision 5.4, 1994

[1]USEPA (300.0): USEPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.2, October 1993

[1]USEPA (1631 E): USEPA Method 1631, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, Revision E, August 2002

[1]USEPA (1630): Method 1630:, Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS, 2nd revision, January 2001

[1]SM20: Standard Methods for the Examination of Water and Wastes, 20th Edition (1998).

[2]USEPA 200.2: Sample Preparation Procedure for Determination of Total Rec. Elements, Rev. 2.8, October 1994

Table 7: Sediment List-1, Quality Parameters for Analysis of Sediment Samples

Parameter	Basis	Method[1]	Reporting Limit	Holding Time
GENERAL				
Cyanide	Total Recoverable	SM21 4500-CN C,E	0.06	14 days
MAJOR CATIONS				
Calcium (Ca)	Total Recoverable	SW-846 6020B	50	180 days
Magnesium (Mg)			50	
Sodium (Na)			100	
Potassium (K)			100	
METALS				
Aluminum (Al)	Total Recoverable	SW-846 6020B	20	180 days
Antimony (Sb)			1	
Arsenic (As)			1	
Barium (Ba)			0.3	
Beryllium (Be)			0.1	
Boron (B)			20	
Cadmium (Cd)			0.2	
Chromium (Cr)			1	
Cobalt (Co)			0.5	
Copper (Cu)			0.6	
Iron (Fe)			50	
Lead (Pb)			0.2	
Manganese (Mn)			0.2	
Mercury (Hg)	Total	USEPA Method 1631E	0.0003	90 days
Methyl Mercury	Total	USEPA Method 1630	0.05	90 days
Molybdenum (Mo)	Total Recoverable	SW-846 6020B	1	180 days
Nickel (Ni)			0.2	
Selenium (Se)			2	
Silver (Ag)			0.5	
Sodium (Na)			0.2	
Thallium (Tl)			0.1	
Uranium (U)			0.1	
Vanadium (V)			5	
Zinc (Zn)			2.5	
Lithium (Li)	Total Recoverable	SW-846 6010D	5.0	180 days

Notes:
All values given in milligrams per kilogram (mg/kg).

Required Sample Preparation Procedures: For total recoverable metals by ICPMS 6020B: Digestion – SW-846 3050B

Method References:
[1]SW-846 6020B: ICPMS
[1]SW-846 6010 Inductively Coupled Plasma-Atomic Emission Spectrometry
[1]SM21 4500-CN C: Total Cyanide in Water Distillation

Table 8: Bottle Set List for Short List -1 and Long List-1

List Type	Bottle Count	Parameters	Sample Bottle Specification
Short List-1 (Total of 6 bottles per set)	1	pH, alkalinity, carbonate (CO_3), bicarbonate (HCO_3), OH, electrical conductivity (EC), total dissolved solids (TDS)	500 milliliter (ml) high-density polyethylene (HDPE), unpreserved, 0.45 micron membrane filtered
	1	SO_4, Cl, F	60 ml HDPE, unpreserved, 0.45 membrane filtered
	1	Total suspended solids (TSS)	1 liter (L) HDPE, unpreserved, unfiltered
	1	Ca, Mg, Na, K, dissolved basis (other metals, dissolved basis: only if requested)	250 ml HDPE, nitric acid (HNO_3) preserved, 0.45 membrane filtered
	1	Metals, total basis	250 ml HDPE, HNO_3 preserved, unfiltered
	1	Mercury, total basis – USEPA 1631E	500 ml HDPE, hydrochloric acid (HCl) preserved, unfiltered
	1	Methyl mercury, total basis – USEPA 1630 (Brooks Rand Laboratory)	500 ml Teflon (fluropolymer), HCL preserved, unfiltered
Long List-1 (Total of 7 bottles per set)	1	pH, alkalinity (CO_3, HCO_3, OH), EC, TDS, SO_4, Cl, F	500 ml HDPE, unpreserved, 0.45 membrane filtered
	1	TSS	1 L HDPE, unpreserved, unfiltered
	1	Nitrate/Nitrite-N, ammonia-N – total basis	250 ml HDPE, sulfuric acid (H_2SO_4) preserved, unfiltered
	1	total cyanide, WAD cyanide – total basis	125 ml HDPE, sodium hydroxide (NaOH) preserved, unfiltered
	1	Ca, Mg, Na, K, (dissolved basis); and dissolved metals	250 ml HDPE, HNO_3 preserved, 0.45 membrane filtered
	1	Metals, total basis	250 ml HDPE, HNO_3 preserved, unfiltered
	1	Mercury, total basis – USEPA 1631E	500 ml HDPE, HCl preserved, unfiltered
	1	Methyl Mercury, total basis – USEPA 1630 (Brooks Rand Laboratory)	500 ml Teflon (fluropolymer), HCL preserved, unfiltered

Table 9: Measurement Quality Objectives - Water (Method-Specific Minimum QA/QC Acceptance Criteria Requirements)

Parameter	Method	Initial Calibration (Linearity or R^2)	Calibration Verification Standard. (% Recovery)	Laboratory Control Standard (% Recovery)	Matrix Spike (% Recovery)	Method Duplicate (% Recovery)	Field Duplicate (RPD)	Method Blank
pH	USEPA 150.1	pH meter per manufacturer	±0.05 pH units	±0.05 pH units	Not applicable	±0.1 pH units	30%	Not applicable
Specific Conductance	SM20 2510B	conductivity meter per manufacturer	90-110	90-110	Not applicable	≤ 20	30%	≤ reporting limit
TDS	SM20 2540C	Not applicable	Not applicable	75-125	Not applicable	≤ 25	30%	≤ reporting limit
TSS	USEPA 160.2	Not applicable	Not applicable	75-125	Not applicable	≤ 25	30%	≤ reporting limit
Alkalinity*	SM20 2320B	pH meter per manufacturer	Not applicable	85-115	Not applicable	≤ 20	30%	≤ reporting limit
Chloride	USEPA 300.0, rev 2.2	≥ 0.995	90-110	85-115	75-125	≤ 20	30%	≤ reporting limit
Sulfate	USEPA 300.0, rev 2.2	≥ 0.995	90-110	85-115	75-125	≤ 20	30%	≤ reporting limit
Fluoride	USEPA 300.0, rev 2.2	≥ 0.995	90-110	85-115	75-125	≤ 20	30%	≤ reporting limit
Ammonia (as N)	SM20 4500NH_3-F	≥ 0.995	90-110	75-125	75-125	≤ 25	30%	≤ reporting limit
Nitrate+Nitrite (as N)	USEPA 300.0, rev 2.2	≥ 0.995	90-110	90-110	90-110	≤ 20	30%	≤ reporting limit
Cyanide, total	SM20 4500-CN C,E	≥ 0.995	90-110	75-125	75-125	≤ 25	30%	≤ reporting limit
Cyanide, WAD	SM20 4500-CN C,E	≥ 0.995	90-110	75-125	75-125	≤ 25	30%	≤ reporting limit

Parameter	Method	Initial Calibration (Linearity or R^2)	Calibration Verification Standard. (% Recovery)	Laboratory Control Standard (% Recovery)	Matrix Spike (% Recovery)	Method Duplicate (% Recovery)	Field Duplicate (RPD)	Method Blank
Metals by ICPMS	USEPA 200.8, rev 5.4	Not applicable	85-115	85-115	70-130	≤ 20	30%	≤ reporting limit
Mercury	USEPA 1631, rev E	≥ 0.995	77-123	77-123	71-125	≤ 24	30%	≤ reporting limit
Methyl Mercury	USEPA 1630	CF ≤ 15%	80-120	67-133	65-135	≤ 35	30%	≤ reporting limit

Note:
* Alkalinity to also include bicarbonate, carbonate, and hydroxide (all as $CaCO_3$).
RPD = relative percent difference

Table 10: Measurement Quality Objectives - Sediment (Method-Specific Minimum QA/QC Acceptance Criteria Requirements)

Parameter	Method	Initial Calibration (Linearity or R^2)	Calibration Verification Standard. (% Recovery)	Laboratory Control Standard (% Recovery)	Matrix Spike (% Recovery)	Method Duplicate (% Recovery)	Field Duplicate (RPD)	Method Blank
Cyanide, total	SM21 4500-CN C,E	0.995	90-110	75-125	75-125	≤ 20	50%	≤reporting limit
Methyl Mercury	USEPA 1630	CF ≤ 15%	80-120	67-133	65-135	≤35	50%	≤reporting limit
Total Mercury	USEPA 1631E	0.995	77-123	77-123	71-125	≤24	50%	≤reporting limit
Metals by ICPMS	SW-846 6020B	0.998	90-110	85-115	72-128	≤ 20	50%	≤reporting limit
Lithium by ICP	SW-846 6010D	--	90-110	80-120	75-125	<20	<50	<reporting limit

The parameter lists were developed to meet the objectives and strategies of an effective sediment and water quality monitoring program for the proposed Donlin Gold project to:

- Define existing water quality (both surface water and groundwater) within the vicinity of the proposed project site location.
- Identify changes in element concentrations in water and sediment and aid in understanding how they could be affecting aquatic resources.
- Provide a means for comparing area water quality (past, current, and future) to Alaska regulatory criteria.
- Provide a cost-effective means of assessing various project site features with respect to water quality including past, current, and future influences, as well as long-term and short-term trends.
- Establish an accurate and technically defensible sediment and water quality monitoring database to use for a variety of water quality assessments and tasks such as predicting the water quality at various project facilities and developing future water quality-based effluent limitations (WQBELs) associated with the water discharge permitting process defined by the APDES.

The parameter lists are intended to be working documents. Modifications and revisions to existing lists may be necessary when and if deficiencies are identified or when lab practices or procedures change. At a minimum, existing lists should be reviewed annually and be revised and updated as needed. Additional parameter lists can be developed and implemented when additional or different water quality data needs are identified.

1.6.2 Measurement Quality Objectives

The relative quality of field measurements, field sampling, and laboratory data can be measured by the precision, accuracy, representativeness, comparability, and completeness of the data. Section 4.2 defines these quality parameters, the procedures commonly used for their measurement, and typical parameter acceptance criteria, where applicable.

It should be noted that data quality measurements can originate at many different levels such as in the field versus in the lab (i.e., field duplicate versus lab method duplicate). The point of origin and type of measurement are both important when evaluating data quality measurements.

Typical acceptance criteria for water are included in Table 9. Acceptance criteria for sediment are included in Table 10.

Detectability is the ability of the method to reliably measure an analyte concentration above background. ADEC Division of Water (DOW) uses two components to define detectability: 1) method detection limit (MDL) or detection limit (DL), and 2) practical quantification limit (PQL), reporting limit (RL), or limit of quantitation (LOQ).

- The MDL or DL is the minimum value the instrument can discern above background but without certainty of the accuracy of the measured value. For field

measurements, the manufacturer's listed instrument detection limit (IDL) can be used.

- The PQL, RL, or LOQ is the minimum value that can be reported with certainty and is usually some multiple of the MDL.

Note: The measurement method of choice should, at a minimum, have a PQL or RL three times more sensitive than the respective ADEC water quality standard (WQS) and/or permitted pollutant level (for permitted facilities).

Sample data measured below the MDL are reported as non-detect (ND). An ND value is flagged with a "U" flag, along with a number to indicate that the ND value is reported to the limit of detection (LOD), which is generally either 2 or 3.18 times the MDL, depending on analyte and analysis method. Detections as concentrations greater than or equal to (≥) the MDL but less than or equal to (≤) the PQL, RL, or LOQ are reported as estimated data with a "J" flag within all electronic files. Sample data measured above the PQL, RL, or LOQ are reported as reliable data per the specific sample analysis unless otherwise qualified by the analytical laboratory.

1.7 Special Training Requirements/Certification

Training at the Donlin Gold project site is accomplished by reviewing the QAPP and previous Donlin Gold procedures manuals for historical purposes along with training by experienced and/or senior staff. Additional laboratory sample collection/handling suggestions/directions are relayed by the Technical Director at SGS North America Inc.

Contracted laboratory staff and the Lab Supervisor are responsible for appropriate certification and training within the lab facility. Additional information is provided in the SGS North America Inc. Quality Assurance Plan (QAP) included in Appendix C.

Specialized training required for the proposed Donlin Gold project sediment and water quality monitoring program is summarized in Table 11.

Table 11: Specialized Training Requirements for the Donlin Gold Project

Specialized Training	Field Staff	Lab Staff	QA, Sampling and Data Manager	Lab Supervisor
Safety training	X	X	X	X
Water sampling techniques	X		X	
Instrument calibration and QC activities for field measurements	X		X	
Instrument calibration and QC activities for laboratory measurements		X		X
QA principles	X		X	X
QA for water monitoring systems			X	
Chain-of-custody (COC) procedures for samples and data	X	X	X	X
Handling and Shipping of Hazardous Goods	X	X	X	X
Specific USEPA-Approved Field Measurement Method Training	X		X	
Specific USEPA-Approved Lab Analytical Method Training		X		X
ADEC Microbiological Drinking Water Certification	Certification for microbiological analysis is limited to the individually certified analyst.			
Lab Analytical Methods Training		X		X

2.0 DATA GENERATION AND ACQUISITION

2.1 Sampling Process Design

The sampling process was designed to produce sufficient data of appropriate quality in the Donlin Gold project area for the intended program purpose and objectives. The sampling process design included:

- Defining the roles and responsibilities of persons involved in the sampling program (Section 1.3, Table 2);
- Specifying the required sample analyses and data quality objectives;
- Defining the location, type, and frequency of samples to be collected;
- Adopting appropriate sampling and data management protocols;
- Developing a QA program to verify that sampling program requirements are being met.

The roles and responsibilities of persons involved in the sampling program are described in Section 1. The remainder of the sampling program design is described in the following subsections.

2.1.1 Surface Water Quality Objectives and Site Representativeness

The purpose of the surface water monitoring program is to collect data that establish the baseline conditions of surface water systems in the area potentially affected by development. These data may be used during mine planning and permitting, and for water quality monitoring throughout mine construction, operations, reclamation, closure, and post-closure.

The objectives for the surface water monitoring program are to:

- Continue to monitor the loading from key drainage basins.
- Determine and document the effects of the mineralized zone and historical placer mining on the surface water quality in the region.
- Aid in modeling water balance requirements.
- Establish long-term monitoring stations for the life of the mine from construction through operations, and ultimately closure and reclamation.

Table 3 includes a summary of the surface water monitoring stations in the most recent monitoring program, and the rationale and purpose of each station.

2.1.2 Groundwater Quality Objectives and Site Representativeness

The purpose of the groundwater monitoring program is to document the existing groundwater chemistry and piezometric surface where mine development is proposed.

The objectives of the groundwater monitoring program are to:

- Collect data that can be used to establish the background condition of the bedrock and alluvial groundwater systems in the area. Data will be collected for groundwater quality and groundwater elevations.
- Collect aquifer characteristic data that can be used to aid in facility design and site-wide water management.
- Develop an overall conceptual model of baseline groundwater conditions at the site to support permitting.

A summary of the wells in the most recent groundwater monitoring program, the target zone for each well, and the number of samples collected through the end of 2011 are included in Table 4. Completion details for the monitoring wells are included in Table 12.

2.1.3 Sediment Quality Objectives and Site Representativeness

The purpose of the sediment monitoring program is to document the existing sediment chemistry where mine development is proposed.

The objectives of the sediment monitoring program are to:

- Collect data that can be used to establish background element concentrations.
- Collect data, along with collocated fish tissue sampling, to identify changes in element concentrations and aid in understanding how they could be affecting aquatic resources.
- Develop an overall conceptual model of baseline sediment conditions at the site to support the permitting process.

Surface Water vs. Groundwater

Alaska WQS (18 Alaska Administrative Code [AAC] 70) stipulate that “fresh waters” (surface waters) in the State of Alaska are protected for all designated use classifications. These use classifications are as follow:

- Water supply – drinking, culinary, and food processing;
- Water supply – agriculture, including irrigation and stock watering;
- Water supply – aquaculture;
- Water supply – industrial;
- Water recreation – contact recreation;
- Water recreation – secondary recreation;
- Growth and propagation of fish, shellfish, other aquatic life, and wildlife.

Although established to protect surface water uses, Alaska WQS also apply to groundwater, and regulations stipulate that groundwater is protected for all use classifications, including “aquaculture,” to which “aquatic life” criteria apply. Aquatic life criteria are frequently more stringent than drinking, culinary, and food processing water supply standards.

Because Alaska WQS apply to surface water and groundwater (except turbidity), a single “full suite” parameter list (Long List-1) is used for both surface water and groundwater monitoring.

Table 12: Monitoring Well Completion Summary (Metric Units of Measurement)

Well ID	Geographic Coordinates (meters) UTM Zone 4 NAD 83		Surface Casing	Total Depth	Top of Screen	Bottom of Screen	Top of Sand	Bottom of Sand	Casing Diameter	Depth to Water
	Easting	Northing	(meters)	(meters)	(meters)	(meters)	(meters)	(meters)	(centimeters)	(meters)
MW03-01	539999	6879366	6.1	22.9	16.4	22.5	14.9	22.9	10.2	9.8
MW03-02	539144	6879164	6.1	24.4	17.8	19.5	16.4	21.3	5.1	1.6
MW03-03	539163	6879178	6.1	6.4	4.9	6.4	3.0	6.4	5.1	2.1
MW03-04	538680	6878830	9.1	27.4	13.6	16.6	12.7	18.1	5.1	2.4
MW03-05	538685	6878841	6.1	11.3	7.9	11.0	6.7	11.3	10.2	2.5
MW03-06	542457	6877089	9.1	24.1	17.7	23.8	19.8	24.1	5.1	1.4
MW03-07	542470	6877084	6.1	6.1	4.3	5.8	3.2	6.1	5.1	1.7
MW03-08	545875	6876430	9.1	27.4	20.4	26.5	18.3	27.4	5.1	20.1
MW03-09	545829	6875574	9.1	19.2	12.5	18.6	11.0	19.2	5.1	8.7
MW03-10	539423	6874503	9.1	27.7	24.1	27.1	22.6	27.7	5.1	4.8
MW03-11	539433	6874500	4.9	9.5	6.4	9.5	5.5	9.5	5.1	9.1
MW03-12	538714	6874223	12.2	48.9	45.9	48.9	44.1	48.9	5.1	4.7
MW03-13	538719	6874245	5.5	11.9	7.9	11.0	6.7	11.6	10.2	4.9
MW03-14	539782	6878537	12.2	182.0	160.1	177.1	160.1	177.1	2.5	0.0
MW03-15	539797	6878539	9.1	24.4	17.7	23.8	16.2	24.4	5.8	1.9
MW03-16	540692	6878952	33.5	186.0	173.8	186.0	173.8	186.0	2.5	45.7
MW07-01	542627	6881469	12.2	25.5	19.3	25.5	18.4	25.5	15.2	18.7
MW07-02	542627	6881477	12.2	47.9	41.7	47.9	40.9	47.9	15.2	4.5
MW07-03	539729	6877401	7.6	17.9	11.7	17.9	11.0	17.9	15.2	5.5
MW07-04	539734	6877400	9.1	48.0	41.7	48.0	39.7	48.0	15.2	5.8
MW07-05	539703	6876817	7.2	23.8	17.6	23.8	16.6	23.8	15.2	2.4
MW07-06	539714	6876812	7.0	47.9	33.7	39.9	32.7	39.9	15.2	3.2
MW07-07	540910	6872313	9.0	45.1	38.6	44.7	37.5	45.1	15.2	2.6
MW07-08	540912	6872313	6.0	18.0	11.6	17.8	10.6	18.0	15.2	Ice plug @ 7.6
MW07-09	544752	6872692	11.7	47.6	41.6	47.6	40.2	47.6	15.2	12.8
MW07-10	544752	6872692	5.9	20.5	14.3	20.4	13.5	20.5	15.2	13.2

2.1.4 Sample Collection Locations, Parameters, and Schedule

Surface water sample station and sediment monitoring well locations are listed in Table 3 and shown on Figure 5. Groundwater monitoring well locations are listed in Table 4 and shown on Figure 7.

Two water quality sample parameter lists have been generated for flexibility. Long List-1 (Table 6) has been used for the baseline water quality monitoring and sampling at the Donlin Gold project. Short List-1 (Table 5) has been prepared in anticipation of a reduced data requirement during permitting but has not been used for baseline water quality characterization. The lists are as follow:

- Short List-1 (Table 5) includes the general chemistry, major cations, major anions, and metals identified as key indicators of water quality. The specific metals were selected based on historical knowledge of existing mineralogy, geochemistry, and previous water quality monitoring performed on and in the vicinity of the project site. This list is optional if, during permitting, a definitive parameters list is required, then fewer analyses may be requested from the laboratory.
- Long List-1 (Table 6) includes all parameters on Short List-1 (Table 5), plus the majority of inorganic parameters for which there are regulatory criteria established under Alaska WQS (18 AAC 70). Parameters not contained on Long List-1, for which regulatory criteria exist, include color, fecal coliform bacteria, oil and grease, petroleum hydrocarbons, radioactivity, settleable solids, temperature, turbidity, asbestos, organic chemicals, disinfection byproducts, chlorine/total residual chlorine, and sulfide.

Additionally, a sediment sampling list (Table 7) has been generated for sediment analysis. This list includes metals analyzed by method SW 6020B as well as cyanide (SM4500-CNC,E) and lithium (SW-846-6010D).

The sampling frequencies for each surface water monitoring station, groundwater monitoring well, and sediment location are listed in Table 13. Surface water locations marked with a “1” footnote indicate that these sites have the potential of no collection during the winter months due to creek bed freezing. Winter months can also delay or eliminate site visits and sample collection due to harsh weather climates and can affect any one of the sites in the baseline list.

Table 13: Sampling Schedule

Location ID	Parameter List	Sample Type	Sample Frequency
SURFACE WATER LOCATIONS			
AMER	Long List-1	I, G	Quarterly
ANDA	Long List-1	I, G	Quarterly
DCBD	Long List-1	I, G	Quarterly
CCBC	Long List-1	I, G	Quarterly
CCBO	Long List-1	I, G	Quarterly
CCBW	Long List-1	I, G	Quarterly
CR0.3	Long List-1	I, G	Quarterly
CV1	Long List-1	I, G	Quarterly
GM3	Long List-1	I, G	Quarterly
GROUNDWATER LOCATIONS			
MW03-01	Long List-1	I, G	Quarterly
MW03-02	Long List-1	I, G	Quarterly
MW03-03	Long List-1	I, G	Quarterly
MW03-04	Long List-1	I, G	Quarterly
MW03-05	Long List-1	I, G	Quarterly
MW03-07	Long List-1	I, G	Quarterly
MW03-08	Long List-1	I, G	Quarterly
MW03-09	Long List-1	I, G	Quarterly
MW03-10	Long List-1	I, G	Quarterly
MW03-12	Long List-1	I, G	Quarterly
MW03-13	Long List-1	I, G	Quarterly
SEDIMENT LOCATIONS			
CRO.3	Sediment	G	Annual (Q2)
GM3	Sediment	G	Annual (Q2)
CCBC	Sediment	G	Annual (Q2)
DCBO	Sediment	G	Annual (Q2)
I = In Situ Measurements	*G = Grab Sample*		*Q2 = Second Quarter*

2.1.5 Water Quality Analytical Basis

The bases for water quality sample analysis at the proposed Donlin Gold project are as follows:

- Dissolved – the concentration determined on a sample after filtration through a 0.45-micron membrane filter. Filtration is performed in the field, or very soon after sampling, and before sample preservation.
- Total – the concentration determined on an unfiltered sample after vigorous digestion, or the sum of the concentrations of both the dissolved and suspended fractions.
- Total Recoverable – the concentration determined on an unfiltered sample after moderately vigorous digestion.

Water quality is assessed compared to regulatory criteria using “Total Recoverable” concentrations, as specified in Long List-1 (Table 6) and Short List-1 (Table 5). For all practical purposes, total and total recoverable are identical. The rationale is based on the premise that consumers of drinking water typically do not filter water before ingestion and are therefore exposed to both the dissolved and suspended components. A similar premise applies to aquatic life criteria because aquatic organisms are exposed to both the dissolved and suspended components of the water they inhabit. Analysis requirements for effluent limitation parameters associated with discharge permits issued under the APDES are most frequently required on a “total recoverable” basis.

Although laboratory analyses for pH, electrical conductivity, major ion chemistry (calcium, magnesium, sodium, potassium, alkalinity, bicarbonate, carbonate, hydroxide, fluoride, chloride, and sulfate) were previously conducted on filtered samples, these analyses are now and will continue to be run on unfiltered samples, per common practice. Total dissolved solids are analyzed on a “dissolved” basis using filtered samples.

When a comparison of “dissolved” versus “total recoverable” metals is required (as listed in Table 6), this option can be arranged before the initiation of sample collection by marking bottles that require field filtration. Analysis for dissolved metals requires the collection of one additional sample bottle of filtered water that is also field-preserved with nitric acid. If filtering is required at the lab, the sample cannot be collected with preservative and instead must be collected in a non-preserved bottle.

2.2 Surface Water, Groundwater, and Sediment Sampling Method Requirements

Producing data of known quality that are considered representative of the sampling environment at an appropriate level of detail can only be achieved by establishing and adhering to a quality-oriented field procedures program. The sampling procedures, described below, provide specific protocols for performing field measurements, sample collection, and handling, along with an appropriate level of associated QA/QC.

In general, the field specialists collecting the samples will wear disposable gloves, personal protective equipment (PPE), flotation devices (if needed), and observe precautions (field level risk assessment) before and during the collection of samples. Sampling staff must be aware of the potential chemical, physical, and biological hazards associated with the sampling environment.

2.2.1 Sample Types

In-situ field measurements and grab samples are collected from each of the active sediment, surface water, and groundwater monitoring stations. Field measurements are collected and recorded before sample collection. Samples collected within the Donlin Gold project area for laboratory analyses are characterized as "Grab Samples." Composite samples are not required to meet Donlin Gold's baseline sediment water quality monitoring objectives; however, composite sediment samples will be collected as described in Appendix A.

Historically and currently, samples have not been described as either composite or grab samples on sampling field documentation. These descriptions are added when entered into electronic records compiled by field personnel and are specified on the COC form before sample submission. Samples are assigned appropriate codes "SW-Grab" or "GW-Grab" by the field personnel during data entry and must be transcribed correctly to the COC.

Surface water and sediment analytical laboratory sample suites are described in Section 2.1.1 and those for groundwater are described in Section 2.1.2. Surface water and groundwater field measurements are described below.

Sampling Equipment

Field instruments used for field measurements require a program of control, calibration, adjustment, and maintenance. Portable water quality instruments in good working order are used for the field measurement of a standard set of field parameters. The field instruments and the parameters measured are summarized in Table 14. The makes and models of these instruments may vary over time.

Field crews use field instrumentation maintained at the project site and/or brought in from off site. Field equipment handling, including pumps and other equipment used in sampling, is discussed separately in the surface water, sediment, and groundwater field sampling procedures described in Section 2.3.1.

2.2.2 Sample Bottle Sets

Bottle sets to allow for analysis of parameters listed in Short List-1 (Table 5) and Long List-1 (Table 6) are provided by SGS North America Inc. and consist of the bottles listed in Table 8. Sediment samples will be collected using Lexan tubes and submitted to the laboratory in triple-bagged Ziploc freezer bags or similar for analysis of parameters listed in Sediment List-1 (Table 7); these sample

containers are not provided by the lab. Preservation and holding times for aqueous samples are included in Tables 5 and 6 by individual method and parameter.

Table 14: Field Instruments and Parameters

Equipment	Parameter
Geotech/Keck 100 m Portable Water Level Meter	Water Level (groundwater wells)
Swoffer Metric Model 2100 C-140 Current Velocity Meter	Stream Flow Velocity
YSI 556 Multi-Probe System	pH Water temperature Dissolved oxygen (DO) Oxidation/reduction potential (ORP/Eh) Conductivity
Hach 2100P Portable Turbidimeter	Turbidity
Digital Thermometer	Air temperature

2.2.3 Sampling Methods

Field Measurements Methods

Surface water, sediment, and groundwater field measurements are performed as a component of the surface water quality sample collection process. Parameters routinely measured in the field immediately before sampling include:

- Stream flow (as conditions allow, surface water sampling stations only);
- Air temperature (surface water sampling stations only);
- Water temperature;
- pH;
- Conductivity;
- ORP/Eh;
- DO;
- Turbidity.

Field measurements made during surface water monitoring are performed in situ whenever possible. In-situ measurements are particularly advantageous for more time-sensitive parameters such as DO and ORP/Eh. Under very cold conditions, it may be necessary to collect a sample in the field and conduct field measurements in the field office. In this case, a sample specifically for field measurements is collected in a clean, unpreserved sample bottle, and all measurements are performed as soon as possible after sample collection.

Surface Water Sampling Methods

General surface water monitoring tasks are described in this section. Detailed procedures for groundwater monitoring and sampling are described in Appendix A.

Surface water monitoring begins with an inspection of the designated reach of the stream, followed by collecting qualitative data, quantitative parameters, and sample collection.

The following is a general description of the surface water monitoring process undertaken at each station. All field observations and measurements are recorded on a surface water monitoring field form:

- Observations are made for conditions within the reach of the stream that may impact data collection, such as ice/overflow thickness, weather, and stream flow conditions, and the information is recorded on the sampling sheet.
- If the station is equipped with a staff gage, the water level height is measured and recorded (summer/fall quarters).
- Before entering water for stream velocity measurements, field water quality parameters are measured. Water quality measurements are allowed to stabilize before being recorded.
- For stream flow velocity, conditions observed at the site (e.g., if holes were drilled in the ice for general velocity, or if stream velocity is too high for measurements on stream flow sheet; second page of Surface Water Monitoring Field Form) are recorded.
- Water quality samples are collected for laboratory analysis.
- All pertinent data and information are recorded on the Surface Water Monitoring Field Form. The original sheet is copied and scanned at the end of each day, and the electronic copy is transmitted to the QA, Sampling and Data Manager.

Groundwater Sampling Methods

General groundwater monitoring tasks are described in this section. Detailed procedures for groundwater monitoring and sampling are described in Appendix A.

The groundwater monitoring process begins with an inspection of all monitoring wells to determine which ones will need to be thawed before initiating the monitoring tasks. Ideally, this inspection is performed 1 week before the scheduled monitoring event, as it may take 24 hours or more to thaw some wells.

Three monitoring well and sampling pump configurations are in place at the Donlin Gold project site for well purging and water quality sampling: 1) conventional standpipe wells requiring a portable submersible pump, 2) conventional wells with an installed dedicated pump, and 3) wells equipped with dedicated nitrogen-driven displacement pumps manufactured by BarCad© (BarCad pump). The use of bailers for groundwater quality sampling at the Donlin Gold project site is not necessary and will be avoided. Table 12 provides the well construction and completion details for each well. Monitoring procedures vary according to the type of well.

Each groundwater well sampling round includes the following tasks:

- Observe conditions in the vicinity of the well, weather, and any other conditions that may impact water quality.
- Thaw the well using heat trace or other means (if necessary).
- Measure the water level in the well.
- Purge the well to collect water quality samples representative of groundwater conditions.
- Measure field parameters during the well purging to verify that the well has been adequately purged. Establish that water quality has stabilized and record data.
- Before collection of the water quality sample, measure field parameters and record data.
- Collect water quality samples for lab analysis.
- Record all pertinent data and information on the Groundwater Field Form (Appendix B). Copy and scan the original sheet at the end of each day, and transmit the electronic copy to the QA, Sampling and Data Manager.

Sediment Sampling Methods

General sediment quality monitoring tasks are described in this section. Detailed procedures for sediment sampling are described in Appendix A.

The following is a general description of the sediment collection process undertaken at each station:

- Identify the proposed sample location.
- Don personal protective equipment, as required by the HASP.
- Set up equipment needed to collect samples and extend measuring tape to establish a 20ft transect parallel to stream/creek/drainage. The transect may be adjusted to account for significant obstacles. The midpoint of the transect should be the pre-determined sample location.
- Sediment samples will be collected from 0 to 0.6 ft below ground surface at the center and each end of the transect (3 locations total) using Lexan tubes. Sediment is to be collected from inundated areas with fine sediment accumulation (typically the inside of stream bends), from underneath a water column between a few inches to approximately one foot.
- Composite the three Lexan tube samples into one container for analysis.

2.3 Sample Handling and Custody Requirements

2.3.1 Sampling Procedures

The following sampling procedures are used at the Donlin Gold project site.

Surface Water Sampling

- Surface water sampling procedure;
- Field measurement of stream flow;
- Field measurement of surface water pH, temperature, DO, ORP/EH, and conductivity;
- Field measurement of turbidity.

Groundwater Sampling

- Groundwater sampling procedure;
- Thawing wells with a submersible heat trace;
- Water level measurement in a monitoring well;
- Well purging with submersible pumps;
- Groundwater field measurements.

Sediment Sampling

- Sediment sampling procedure.

General Sampling Procedures

- Clean hands/dirty hands procedure;
- Sample bottle labeling procedure;
- Cooler shipping procedure;
- Field instrument handling procedure;
- Field equipment and instrument decontamination procedure.

These procedures are included in Appendix A.

2.3.2 Chain of Custody

Original COC forms must accompany all samples submitted for laboratory analysis and must be legible (see Appendix B for reproducible forms). Minimum information requirements on COC forms include the following:

- Project name;
- Name of sampler and/or name of primary contacts;
- Phone and email address of sampler and/or primary contact;
- Reporting and invoicing instructions;

- Sample point identifications;
- Date and time collected;
- Depth of sediment sample, if applicable;
- Analyses requested;
- Method of shipment.

Parameter lists, including parameter name, basis, units, and required methodology, reporting limits, and reporting instructions for all requested analyses, are also included with each sample submittal.

Once collected, all samples remain in the custody of the sampler or are secured until the samples are prepared for shipment. The field manager reviews and verifies the completeness of all COC forms before sample shipment. Copies are made of all sample submittal paperwork and mailed under separate cover to the Donlin Gold QA, Sampling and Data Manager.

2.3.3 Shipping Requirements

For the testing laboratory to generate valid test results, the integrity of field samples must be intact upon receipt at the laboratory. Protocols ensuring proper integrity of field samples from the time of collection to the time of receipt at the testing lab include:

- Packing samples to prevent breakage or leakage;
- Immediately cooling and maintaining unpreserved samples at 39 degrees Fahrenheit (°F) ± 3.6°F (4 degrees Celsius [°C] ± 2°C)
- Delivering samples to the lab in a timeframe that allows analysis within the parameters' recommended holding times;
- Confirming the receipt and integrity of field samples with documentation generated by the shipper and the testing lab.

2.4 Analytical Methods and Requirements

Monitoring is conducted in accordance with USEPA-approved analytical procedures in compliance with 40 Code of Federal Regulations (CFR) Part 136, "Guidelines Establishing Test Procedures for Analysis of Pollutants," and SW-846 methods. SGS North America Inc.'s standard operating procedures (SOPs) comply with guidelines set by ADEC. The SOPs are reviewed and updated as necessary every 3 years and distributed to ADEC. SGS North America Inc.'s SOP and QAP are held electronically on the Donlin Gold network for data review.

The Donlin Gold project's field personnel and QA, Sampling and Data Manager are responsible for verifying that all equipment and field sampling bottle sets and associated methods comply with the specifications referenced above. Clear communication with the laboratory on any changes in methods and sample bottle sets will be documented in any future updated QAPPs and the field procedures manual.

2.5 Quality Control Requirements

Quality control activities undertaken to verify the defensibility of the data are discussed generally in Section 2.2.3. This section further details the QA performed during sample collection. Detailed sample collection procedures for both groundwater and surface water (included in Appendix A) will be followed closely.

2.5.1 Field-Generated QA/QC Samples

To monitor the quality of certain field activities, and to aid in evaluating the quality of the analytical data generated from the field and in the lab, field blank, equipment rinse blank, field duplicate, and reference material samples are periodically collected and submitted to the laboratory for analyses, along with other field samples. One set containing one field blank, one equipment rinse blank, and one field duplicate per 10 samples will be submitted for analyses for each sampling event.

Field blanks are collected by processing deionized water through applicable sample collection equipment and filtration apparatus (if used) and into the appropriate sample bottles. Field duplicate samples are generated by collecting and preparing two complete sets of appropriate sample containers at the same time from the same sample station. In addition to a field blank and a field duplicate sample, an equipment rinse blank sample is required if multi-use sampling equipment is used for several sampling stations (e.g., non-dedicated pumps, hoses, re-usable filter vessels, or intermediate sample transfer containers). No equipment rinse blanks are required if all sampling equipment is single-use (disposable) and/or dedicated to a single site. A field-generated standard reference material (SRM) sample is prepared and submitted once per year to evaluate lab proficiency for selected parameters.

The field manager assigns unique sample point identifications to the QA/QC samples so that their identity as field-generated QA/QC samples is not easily discernible by the analytical testing lab. A field form is completed for each field QA/QC sample, clearly identifying pertinent information about the sample including sample type (i.e., field duplicate, field blank, SRM), sample point (if a field duplicate), preparation technique, and analytes and known concentrations if an SRM (attach certified values and other accompanying information).

The following sections provide additional details regarding field-generated QA/QC samples. Specific procedures for collecting these samples are included in Appendix A.

Field Blank Samples

One field blank sample is required for every 10 samples. Two field blanks are required, at a minimum, for both Donlin Gold groundwater location lists and surface water location lists for all parameters listed in Long List-1 (Table 6). Field blank samples are required for every quarterly sampling event.

Field Duplicate Samples

One duplicate sample is required per 10 samples. Two duplicates are required, at a minimum, for Donlin Gold groundwater, sediment, and surface water locations for all parameters listed in Long List-1 (Table 6). Duplicate samples are required for every quarterly sampling event.

Equipment Rinse Blank Samples

Equipment rinse blank samples are collected to monitor effects of sampling equipment used at multiple monitoring stations and the effectiveness of equipment decontamination. Equipment rinse blank samples are required once per groundwater, sediment, and surface water event for the Long List-1 (Table 6) parameters.

Field-Generated SRM Samples

At a minimum, a field-generated sample containing known concentrations of all or a selected sub-set of parameters listed on Short List-1 (Table 5) or Long List-1 (Table 6) will be prepared and submitted once per calendar year. The SRM may be prepared by the field manager following the supplier's instructions, or directly by the supplier. Typically, the supplier is responsible for the controlled concentrations of parameters in the list. It is then transferred into an appropriate sample bottle set (supplied by the analytical lab) and included with a standard shipment of field samples to the testing laboratory.

2.5.2 Laboratory Quality Control Measures

Lab-Generated Trip Blank

A trip blank, filled with laboratory reagent water, should travel with all of the samples during shipping to and from the field with empty and full sample kits in the cooler. Its purpose is to identify contaminants introduced from the environment during sampling and shipping to the laboratory. If a particular parameter of interest is selected for possible contamination, samples are to be collected for analysis as normal, and it is suggested that the trip blank travels with the sample bottles of that particular analysis. For example, methyl mercury samples are easily contaminated during sample collection, and tracking of contamination should be captured by the trip blank for all methyl mercury samples collected. Because this trip blank can also be contaminated, the trip blank is compared to a laboratory blank (consisting of the same reagent produced by the lab). This lab-provided trip blank should be included on the COC, which is filled out by the field team, and marked for the appropriate parameters. A trip blank that remains unopened during sampling and sample handling can be evaluated for discrepancies between total and dissolved metals, as it documents the concentration of metals in the lab water. Lab-provided trip blanks for methyl mercury and low-level mercury samples will have to be ordered separately for each analytical method. If a trip blank is to be used for methyl mercury, the methyl mercury samples must be separated out with the methyl mercury trip blank and packaged in separate coolers.

Lab-Generated Blank Water Analyses

Lab-provided blank water, known as lab-produced deionized water, is recommended for analysis before each 5 gallon (19 L) batch is provided to Donlin Gold LLC for field QA/QC sample analysis. Analysis of the provided water should be reported in the relevant data packages.

Known and documented data quality is an essential component of accurate environmental site assessments and effective decision-making associated with any sediment and water quality monitoring program. Achieving defined data quality objectives requires clear, concise, and detailed communications with contracted analytical laboratories. Consistency in the use of fundamental laboratory techniques and practices over time is essential for creating a useful, reliable, and technically defensible database of analytical test results. The laboratory QAP and SOPs (Appendix C) establish protocols and minimum QA/QC requirements for their contracted services appropriate to produce analytical data that meet project requirements.

The laboratory's instrumentation and maintenance, calibrations per analytic method, and specific quality control activities are verified by the laboratory quality assurance manager. Within these measures, the lab is to provide all relevant quality control information in the case narratives of each report as well as a summary of the data. This allows review and validation of data for the QA, Sampling and Data Manager of these reports.

The parameter lists include the names, units, basis, analytical method, maximum reporting limit, and the allowable holding time for each parameter, as seen in Table 5 (Short List-1) and Table 6 (Long List-1). The specifications in these tables are used in establishing contract agreements with contract laboratories before initiation of analytical services. "Hard copies" of Tables 5 and 6 should be on file in the Anchorage office with the most recent contract before sample submittal for laboratory testing. It is recommended that laboratory contract agreements periodically be reviewed and updated as required. Laboratory minimum requirements are discussed in Section 1.6.

2.6 Instrument Testing, Inspection, Calibration and Maintenance

Before any sampling event at the Donlin Gold project site, all equipment and instruments must be tested through an operational check, inspected for damage and wear, calibrated, and maintained in accordance with manufacturer specifications. Before use during sampling, appropriate maintenance must be conducted on field instruments found to have a significant defect or failing to meet acceptable operating specifications during calibration and calibration verification procedures.

Documentation for maintenance of any instrument, typically conducted off site, must be maintained on the Instrumentation Check Out/In List at the Donlin Gold camp, which is used to track any equipment leaving the project site. A blank Instrumentation Check Out/In List is included in Appendix B. The Instrumentation Check Out/In List will be maintained to record a field instrument's make(s)/model(s), status of parts needed, working status, deficiencies (if any), instrument maintenance records, and any additional pertinent information. Manufacturer's manuals for the multiprobe meter and turbidity meter are kept with the field sampling equipment.

Typically, and most often, the YSI 556 multiprobe meters are sent off site for calibration, updates, and maintenance after each quarterly sampling event. These meters will be tracked at every shipping event.

Field instrument preparation, calibration, and/or operational checks typically are performed at the beginning of each day's sampling. These tasks are performed following instrument manufacturer's recommended procedures or the procedures contained in this QAPP. Field instrument calibration is checked initially (before sampling locations), at the completion of the day's field measurements, and as needed throughout the day (if readings are skewing or otherwise suspected to be off) to establish and document that instruments are operated within specified tolerances.

Calibration measurements for field instruments will be documented on the Instrument Calibration Form (Appendix B). Standards used for instrument calibration, operational checks, and calibration verification must be in accordance with applicable criteria such as the National Institute of Standards and Technology (NIST), ASTM International (ASTM) standards, or other accepted procedures outlined in the instrument manufacturer's specifications. Copies of the instrument calibration form will be readily available at the Donlin Gold project site.

The Donlin Gold project site is subject to varying climatic conditions during a typical calendar year. During the fall, winter, and spring months, air temperatures may be below freezing for extended periods of time. Electrodes used for measuring pH, ORP/Eh, DO, and specific conductance may be ruined or rendered inoperable if allowed to freeze. Procedures must be followed to protect field instrumentation from freezing in the field during sediment and water quality monitoring events as described in Appendix A.

2.6.1 Field Equipment and Instrument Decontamination

All sample collection equipment and field instrumentation that comes into contact with a sample must be decontaminated following sampling. The field equipment and instrument decontamination procedure is included in Appendix A.

2.7 Inspection/Acceptance of Supplies and Consumables

Standard solutions and materials used for instrumentation calibration and troubleshooting according to the manufacturer's specifications will be inspected often for expiration dates. If a medium is expired, it will not be used. The Donlin Gold field crew will routinely check the dates of expiration of standards before any sampling event.

Detailed instrumentation directions are included in procedures listed in Section 2.3.1. All calibration sessions, completed before and at the end of the day (after a full day of sampling), will be documented. Likewise, equipment and products used during the sampling event(s) will be cleaned often using the methods described in the field equipment and instrument decontamination procedure.

Laboratory calibrations and inspections are explained in each SOP and QAP, and are provided in Appendix C.

2.8 Data Acquisition Requirements (Non-Direct Measurements)

Donlin Gold is currently only collecting defensible and reliable water quality data for water baseline studies. There currently are no permits that guide this QAPP.

2.9 Data Management

The Donlin Gold project QA, Sampling and Data Manager has overall responsibility for the implementation and execution of the data management program. Program policies and procedures include the following:

- All original field forms and lab reports are organized, compiled, managed, and maintained as discreet records for each calendar year using binders or other suitable means of organization. One complete set of copies is prepared for archival purposes.
- All original hard copy data review and validation paperwork is added to field form and lab report records for each calendar year.
- A single water quality electronic database file is managed and maintained for the project at the Anchorage, Alaska, Donlin Gold facility.
- All outside requests for water quality data will be administered by the QA, Sampling and Data Manager using the data reporting features of the EQuIS database management software.

2.9.1 Sampling Documentation

Analytical data may be technically acceptable but not defensible as a result of poor documentation and recordkeeping. Without adequate and accurate records, data subpoenaed for litigation purposes may be disqualified, and any decisions based on the data may be dismissed or rendered inaccurate. It is therefore critical that all information related to environmental sampling be accurately and adequately documented to allow reconstruction and verification by a third party at a future time.

All pertinent field measurement and water quality sampling information is recorded on standardized field forms (see Appendix B, Surface Water, Groundwater, and Sediment Monitoring Field Forms) during each day of field activities at each water quality monitoring station. The field manager is responsible for verifying that sufficient detail is recorded on the forms. No general rules can specify the extent of information that must be entered on the forms; however, they should contain sufficient information so that all field activities can be reconstructed without relying on the memory of the field personnel. All entries must be made in indelible ink. All corrections will consist of single-line-out deletions that are initialed and dated.

Field Documentation

The sampling team is responsible for field observations, field equipment calibration and maintenance information, field measurements, and sample documentation including monitoring station identification and other pertinent information. Field forms (Appendix B) are to be completed and maintained for each monitoring event.

Proper documentation of sample custody includes keeping records of all materials and procedures involved in sampling. Standardized field forms are used to record field measurement data. All information on the monitoring station and associated water quality samples, including the locations of each monitoring station, are recorded by field personnel. The field manager reviews all data before leaving the monitoring station. Copies of completed field forms and field notebooks (if any) are maintained at the project site office for periodic review and future reference. Original, completed field forms are delivered to Donlin Gold's designated manager of the water quality database for key information data entry.

Corrections to Documentation

All original data are recorded with indelible ink. No accountable documents are destroyed, even if they are illegible or contain inaccuracies that require a replacement document. If an error is made on an accountable original document assigned to an individual, that individual must make corrections by drawing a line through the error, initialing and dating the lined-out item, and entering the correct information. The erroneous information is not to be obliterated and must remain legible (single-line strikethrough). Errors discovered on documents must be corrected by the individual who made the entry. All such subsequent corrections are initialed and dated.

Field Forms

A standardized field form (Appendix B, Surface Water, Groundwater, and Sediment Field Forms) is to be filled out each time a water quality sample is collected. At a minimum, entries on the field form will include the following:

- Proper monitoring station identification (See Table 13 for the most recent active monitoring station identifications);
- Date and time of sample collection (Note date and time on form MUST match bottle label);
- Weather conditions and temperature at the time the sample was taken;
- Name(s) of sampler(s);
- Sample type;
- Sampling method, particularly if methods deviate from standardized field procedures;
- Sample depth, when applicable;
- Data generated from all field measurements;

- Details of actual work effort, particularly any deviations from the field operations plan or SOPs.

Strict custody procedures are maintained for field forms. While used in the field, forms remain with the field personnel at all times. Upon completion of the field effort, the original field forms are transferred to the QA, Sampling and Data Manager. Photocopies of the original forms are used as working documents.

Field Corrective Action

Field monitoring corrective actions are conducted when field measurement results are not within the acceptable error tolerance range and may include the following:

- Comparison of parameter measurements with readings previously recorded;
- Comparison of DO readings with the saturation value for water at the temperatures recorded (In the absence of gross pollution, DO in flowing surface water should typically be at or near saturation. DO in groundwater can vary depending on source water conditions but typically is below saturation.);
- Recalibration of equipment (YSI multi-meter);
- Repair or replacement of faulty equipment;
- Re-sampling when feasible.

The field manager is responsible for implementing appropriate field corrective actions when they are deemed necessary. Field crew members must send electronic copies of the original field forms completed during the day of sample collection so that field corrective action (if needed) can be applied in a timely manner and before shipping samples off site. All field corrective actions are to be recorded during review of field sheets (See Appendix D). Field data are managed as described in Section 2.9.2.

2.9.2 Electronic Data Management

Electronic data for the Donlin Gold project are managed using the EQuIS 7 Professional environmental data management system and associated database. EQuIS is a comprehensive application specifically developed for managing environmental data. The software was designed to meet all requirements for the collection, storage, analysis, and reporting of data. EQuIS and the associated database is the primary resource for the management of all sediment and water quality monitoring data generated at the Donlin Gold project.

Some of the specific features and capabilities that EQuIS provides include:

- Integration with Microsoft® Excel for all data importing, exporting (reporting), and analysis;
- Capacity for comparing data to user-defined regulatory criteria and qualifying reported data with user-defined flagging;

- Flexible reporting features with customized, user-defined report formats that can be modified to meet data end-user needs;
- An effective utility for querying databases.

This section is not intended to provide a "how-to" guide on the specific use and maintenance of a database file using EQuIS software. Rather, it is intended to provide a basic description of the EQuIS database file structure developed for the project and provide an overview of some of the features and capabilities of the EQuIS data management software.

A project-specific EQuIS database file structure was developed for the Donlin Gold project during the second quarter of 2009. This database file structure includes the following components:

- Sample stations (both surface water and groundwater);
- Analytical parameters;
- Various database code tables of reference values, which include parameter class, preparation methods, result codes, result quality, sample class, sample matrix, sampling frequency, sampling method, station type, units, analytical methods, testing laboratories, reporting limits, and water quality standards (inclusive of all applicable Alaska numeric criteria).

Currently, a single EQuIS water quality data base facility (EQuIS_Donlin) is managed and maintained for the project.

Electronic Management of Field Data

Field data are entered into EQuIS using Excel import file templates developed for this purpose. The contents of the Excel files are uploaded to the EQuIS Data Gathering Engine (EDGE), where the field data may be organized before being imported into the single EQuIS water quality database. Many of the code features used to associate information with each individual measurement "result" data point are components of the import file structure. These components include information such as database sample number, date and time of collection, all necessary field parameter results, and comments. The Excel import files then generated from EDGE are sent to the QA, Sampling and Data Manager for QC reviews then imported into EQuIS via the Electronic Data Processor (EDP).

Electronic Management of Laboratory Analytical Data

EQuIS makes extensive use of flat file formats, which provides robust delivery of analytical data, lab QC data, and other pertinent information requested by Donlin Gold. As previously mentioned, reference values are standard in EQuIS and have been submitted to the laboratory for their generation of electronic document deliverables. Once the file has been populated with the results and QC information from the lab, the file is uploaded separately into the EDP, an interface in EQuIS, which allows the review and import of analytical results. Any errors, by means of order, size, code type, mapping, and other reference values are automatically highlighted in EDP so that issues can be resolved by the lab before importing. The intent of EDP is to hold laboratories responsible for their

sample delivery groups, which include lab sample number, laboratory ID, sampling method, parameter, units, analytical test method, sample preparation method, result, qualifiers, result quality and laboratory quality control results.

2.9.3 Data Storage and Retention

Because the data currently collected are in support of the Donlin Gold project's water quality baseline studies, the retention time is indefinite. All original sheets and reports are held within a library on site and placed on the Donlin Gold internal network for archival purposes.

3.0 ASSESSMENTS

Procedures for collecting site data and for executing a comprehensive review and validation process of both field and laboratory data are provided to verify that these data meet defined quality requirements.

Each component of the sediment and water quality monitoring program has a specific QA/QC protocol. Discussion of QA/QC protocols and procedures for each of the following program components are integrated throughout this QAPP. The following summarizes the program's major components:

- **Field QA/QC** identifies the procedures to be used in the field to verify that samples and field monitoring data are collected according to the requirements of the project. The objective of field QA/QC is to produce data, both field measurements and samples collected for laboratory analyses, that are representative of the environment sampled and that are of known and acceptable quality.
- **Laboratory QA/QC** identifies the minimum acceptable requirements that contract laboratories must observe in order to demonstrate that samples are analyzed according to methodologies acceptable to the USEPA and that reported results are of acceptable quality. The objective of the laboratory QA/QC program is to produce data that will meet state and federal analytical requirements, including project permit requirements, and that meet all project objectives for data uses.
- **Data QA/QC** identifies the protocols to be used as part of the data review and validation program to assess if laboratory and field data are of acceptable quality. The objective of the data review and validation program is to demonstrate and document that data reported meet project-specified requirements. If data fail to meet pre-determined acceptance criteria, results are flagged using the following qualifiers:

  J – The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.

  UB – The sample result (organic parameter) is less than five times the associated blank contamination and is considered a high estimated value due to contamination present in an associated blank sample.

  R – The data are unusable. The sample results are rejected due to serious deficiencies in meeting QC criteria. The analyte may or may not be present in the sample.

  Corrective action procedures are provided to identify, investigate, and correct any deficiencies or anomalies.

3.1 Assessment and Response Actions

Collection of analytical data for the parameters listed in Tables 5, 6, and 7 is verified by thorough, independent validation of the monitoring project preparation. Data validation measures include the following:

- Blind sample reviews (standard reference material samples), one per year per matrix, for critical parameters;
- Thorough review of all laboratory results, including method blank and control sample results, in the analytical reports to verify that they meet the measurement quality objectives specified in Tables 9 and 10;
- Sample splits – Five to six sample splits sent per year of water quality sampling to another lab (optional);
- QA review of the field measurement data through completion of the Field Data Review and Validation Checklist (Appendix D).

3.2 Revisions to QAPP

The QAPP will be reviewed annually by the QA, Sampling and Data Manager. Minor changes to the QAPP are permissible without formal comment and may include changes to Donlin Gold project staff, the QAPP distribution list, updates to the table contents, and minor editorial changes.

Major changes to the QAPP, though not anticipated until the project is under permit, require approval by the ADEC DOW QA Officer or ADEC Project Manager before implementation. Major changes include lead project staff changes (Project Manager; Environmental Manager; QA, Sampling and Data Manager; and contracted laboratories), critical criteria and method-specific data validation, new monitoring methods, and contents of Table 9, Measurement Quality Objectives.

3.3 QA Reports to Management

The contract laboratory final reports are submitted to the Donlin Gold QA, Sampling, and Data Manager, who will review these reports as described in Section 4.2. In addition, an annual data quality assessment is conducted by a contractor, and a report of the findings is submitted to Donlin Gold for review by the Environmental Manager; Environmental Coordinator; and QA, Sampling, and Data Manager.

If significant discrepancies from the requirements of this QAPP are identified during these reviews and assessments, corrective actions to correct the discrepancies will be evaluated and implemented by Donlin Gold.

4.0 DATA VALIDATION AND USABILITY

4.1 Data Review, Verification, and Validation Requirements

Data validation is the process of determining the compliance of analytical field and laboratory data with established method criteria and project specifications. It is a systematic process consisting of data comparison, screening, checking, auditing, verification, training/certification, and review. The process typically involves the use of method criteria summaries and data review and validation checklists.

It is important that the data reviewers be familiar with the specific methods and QA/QC requirements associated with the Donlin Gold project in order to properly review and validate associated analytical data. Water quality monitoring data are used for establishing baseline conditions, predicting water quality at various project facilities, and developing water quality discharge limitations. For these reasons, and because the data may also be the basis for future closure and reclamation decisions and strategies, it is critical that sample analyses and associated data meet method requirements and project specifications.

4.1.1 Field Data Validation Methods

Field data are first reviewed by field personnel performing the field measurements. As with laboratory data, the field personnel have primary responsibility for the technical quality of field data and for ensuring that field methods are properly performed and that instrumentation is in good working order.

Surface water, groundwater, and sediment sample field forms generated by the Donlin Gold field personnel are reviewed by the QA, Sampling and Data Manager using the Field Data Review and Validation Checklist. As with the laboratory data, if the field data fail to meet acceptance criteria or are deemed invalid for other reasons, results are flagged with qualifiers (see Section 3.0), and corrective action is required. The Corrective Action Form is used to document the issue, and a resolution and corrective action will be clearly defined and implemented. This form, along with a reproducible Field Data Review form and Field Data Review and Validation Checklist are, is included in Appendix D.

4.1.2 Laboratory Data Validation Methods

Analytical data generated by the laboratory for the Donlin Gold project baseline data are first reviewed by the testing laboratory. The laboratory has primary responsibility for correctly identifying and quantifying analytes of interest, identifying matrix interferences, and for identifying and correcting instrument anomalies when possible. The laboratory is also responsible for the technical quality of the data and for meeting all quality control parameters by correctly following the analytical methods and using instrumentation that is in proper working order for the given method.

Evaluation of total and dissolved metals will involve comparison of results where dissolved concentrations are greater than total concentrations. Sample results are acceptable if the following criteria are met:

1. Where both results are greater than five times the LOQ, and the RPD between results is less than or equal to 20 percent;
2. Where the total metals result is less than or equal to five times the LOQ, and the absolute value of the difference between the results is less than or equal to the LOQ. If the total metals result is not detected at the LOD, then the value of the LOD will be used for the comparison.
3. Where both total and dissolved results are below the LOQ.

For an individual sample where criteria are not met for up to 30 percent of the parameters, then the associated QC data (including method blanks and field blanks) will be evaluated for bias. If the results for more than 30 percent of the parameters fail to meet the criteria, then both total and dissolved samples will be reanalyzed. If reanalysis does not eliminate the problem, then results will be qualified by the laboratory. This is only applicable to SGS, as other labs do not have this criterion for reporting samples outside of 20 percent RPDs.

4.2 Final Data Review and Validation

4.2.1 Laboratory Deliverables

The laboratory is responsible for laboratory data deliverables for all samples. Analytical results will be provided by the laboratory in a digital format (i.e., PDF), as well as an electronic data deliverable (EDD) in either an ASCII comma-separated value (CSV) format or in a Microsoft Excel worksheet.

Upon receipt, the data packages will be examined to ensure that the correct analyses requested on the COC were performed for each sample submitted. If discrepancies were noted, the QA Manager will be notified and will promptly follow up with the laboratory to resolve any issues. Each data package will be validated in accordance with the procedures presented in this QAPP. Data that do not meet the specified standards will be flagged. However, it should be noted that the use of flagged data may not necessarily be restricted.

Data reports for all parameters will include, at a minimum, the following items:

General Requirements:

- The data deliverable package will be paginated and of reproduction quality such that all pages are legible.
- Title/Cover Page, main laboratory phone number, signature of laboratory director, facility name and address, date of report preparation, date of sampling and receipt, and a summary table that cross-references the field identification numbers to the laboratory identification number for each sample;

- Table of contents;
- Chain of custody;
- Methodology review including method numbers and revision with a detailed discussion of any method modification;
- Laboratory chronicle including sample holding times and sample condition upon receipt at the laboratory (including sample temperature and pH when a pH adjustment is required).

Requirements for Metals and General Chemistry Analysis:

- Analytical results summary form including sample identification numbers, sample matrix, date sample collected, date sample received, date sample analyzed, dilution factor, list of analytes, detected analyte concentrations, and method detection limits;
- Blank results summary;
- Spike sample results summary;
- Duplicate sample results summary;
- Laboratory control sample results summary.

Sample results on the report forms will be corrected for dilutions. Unless otherwise specified, all results will be reported uncorrected for blank contamination.

4.2.2 Data Verification and Usability

A procedure for data verification and usability will be followed throughout the implementation of the scope of work. The purpose of this procedure is to continuously monitor and confirm that all data generated comply with the project-specific data quality objectives (DQOs). The decision on whether data can be used will be based on the validation results. The data validator will use the USEPA National Functional Guidelines (NFG) for Inorganic Data Review, October 2004; this QAPP; and laboratory-specific QC samples recovery limits as guidance where appropriate.

Validation will be performed as a Tier II and will include verification of the following items:

- COC appropriately completed;
- Requested analyses performed;
- Sample preparation and analysis within holding times;
- Blank results [field blank and method blank];
- Duplicate results (laboratory duplicates, matrix spike [MS]/matrix spike duplicate [MSD], laboratory control sample [LCS]/laboratory control sample duplicate [LCSD], and field duplicates);
- Spike recovery results (LCS/LCSD and MS/MSD);

- Achievement of target RLs;
- Completeness (field completeness and laboratory completeness);
- Validity and usability of data.

Following validation, the data will be flagged, as appropriate, and any use restrictions noted. It should be noted that qualification of results does not automatically invalidate data. This point is repeatedly emphasized in the USEPA NFG for data validation and is inherently acknowledged by the very existence of the data validation/flagging guidelines. The goal to produce the best possible data does not necessarily mean producing data without QC qualifiers. Qualified data provide useful information.

The field sampling has been devised so that the loss of any single data point will not hinder description of the distribution of potential constituents of concern. Subsequently, a reasonable decision rule would be that 90 percent of the data points are not rejected and deemed unusable.

Data Precision Assessment Procedures

Field precision is difficult to measure because of temporal variations in field parameters. However, precision will be controlled and quantified using experienced field personnel, properly calibrated meters, and duplicate field measurements. Field duplicates will be used to assess precision for the entire measurement system including sampling, handling, shipping, storage, preparation, and analysis.

Analytical precision will be evaluated by calculating the RPD for field duplicates, laboratory duplicates, and MS/MSD samples as follows:

$$RPD = \{(abs [D1 - D2]) / [(D1 + D2)/2]\} * 100$$

Where: abs = absolute value

RPD = relative percent difference

D1 = sample value

D2 = duplicate sample value

Data Accuracy Assessment Procedures

The accuracy of field measurements will be controlled by employing experienced field personnel, using properly calibrated field meters, and adhering to established protocols. The accuracy of field meters will be assessed by review of calibration and maintenance logs.

Laboratory accuracy will be assessed by evaluating the results of spiked samples (e.g., LCS, surrogates, and MS) for percent recovery (%R). %R will be calculated as follows:

$$\%R = [(A - X) / B] * 100$$

Where: A = value measured in spiked sample or standard

X = value measured in original sample

B = amount added to sample or true value of the standard

Data Representativeness Assessment Procedures

Representativeness will be assessed by examining sample preservation, results of the precision and accuracy evaluation, and adherence to method holding time. Failure of field or laboratory personnel to properly handle samples may result in qualification of the data as estimated or unusable. The use of laboratory data from a sample with a failed holding time could render the data unusable. The representativeness review will qualitatively consider whether precision and/or accuracy are sufficient to characterize the representativeness of the samples.

Blank Sample Assessment Procedures

Blank samples will be used to determine the existence and magnitude of contamination resulting from laboratory or field activities. The method blank is used as a check on laboratory procedures as well as possible contamination from laboratory equipment (e.g., reagents, glassware). Equipment blanks are collected in the field from the sampling equipment to check for possible residual contamination and assess potential cross-contamination during sampling. Trip blanks determine the integrity of the sample container for loss or addition of analytes due to handling and transport. Detections in any blank samples will be used to qualify similar detections in associated field samples.

Data Completeness Assessment Procedures

Completeness of a field or laboratory data set will be calculated by comparing the number of usable measurements (all measurements except rejected data) obtained to the total number of usable measurements planned. Completeness will be calculated as follows:

Completeness = (usable data points obtained/total data points planned) * 100

As a general guideline, overall project completeness is expected to be at least 90 percent. The assessment of completeness will require professional judgment to determine data usability for the intended purposes.

Data Comparability Assessment Procedures

Comparability will be assessed by evaluating whether samples were collected in a manner similar to that of previous sampling events and analyzed using analytical methodology similar to that of previous events.

Sensitivity Assessment Procedures

Sensitivity is related to the PQL, RL, or LOQ. In general, PQLs/RLs/LOQs should be less than the applicable standard. Analytical results for samples reported as non-detected for an analyte that have PQLs/RLs/LOQs greater than the applicable standard cannot be used to demonstrate compliance with the applicable standard. Samples contaminated with sufficient quantity of material, such that dilutions are performed, are a leading cause of PQLs/RLs/LOQs exceeding applicable criteria. However, there may be instances where such exceedances are insignificant relative to the site-specific DQOs. The sensitivity review will qualitatively consider whether the PQLs/RLs/LOQs are sufficiently low to compare analytical results to the applicable standards while considering the project DQOs.

4.3 Reconciliation with User Requirements

Data verification methods are reviewed by the QA, Sampling and Data Manager and the Environmental Manager in accordance with baseline water quality data requirements to verify that the methods are appropriate to meet the program objectives. Modifications to the monitoring program are reviewed annually and will be updated as necessary. The current QAPP is designed to guide collection of baseline data for the Donlin Gold project.

Appendix A
Field Procedures Program

	STANDARD OPERATING PROCEDURE	
DONLIN GOLD	GENERAL ENVIRONMENTAL SAMPLING PROCEDURES	
	EFFECTIVE DATE	**DOCUMENT NUMBER**
	10/28/2021	ENV-SOP-0036

PURPOSE

To set procedures for general tasks related to environmental sampling as required for surface water, groundwater, and other environmental sampling programs for Donlin Gold employees or contractors in support of environmental studies and monitoring.

SCOPE

This SOP describes procedures for clean hands/dirty hands sampling, sample bottle labeling, sample packaging and shipping, field instrument handling, field equipment decontamination, portable sampling pump decontamination, and Grundfos RediFlo2 pump lubricating fluid replacement.

RESPONSIBILITY

- It is the responsibility of Field Environmental Coordinators to conduct environmental monitoring tasks following accepted procedures.

HEALTH AND SAFETY

Safety of people is the first priority when conducting any task. Personnel must be well-trained (per the procedures below) with standard routines, safety procedures, personal protection equipment, and emergency response actions.

ENVIRONMENTAL

Potential consequences of departing from standard:

- Departure from this Standard could result in injury to people, damage to facilities and/or the Environment resulting in pollution to the land or water, and obtaining erroneous field or laboratory water quality data.

REFERENCES

- Quality Assurance Project Plan for the Donlin Gold Project Water Quality Monitoring, Sampling, and Analysis Activities.
- Field Forms (Water Quality Monitoring, Sampling and Analysis Activities QAPP)

PROCESS

CLEAN HANDS/DIRTY HANDS PROCEDURE

The purpose of the clean hands/dirty hands procedure is to prevent cross-contamination during mercury/methylmercury sampling from container handling. All operations involving contact with the mercury/methylmercury sample bottle and transfer of the mercury/methylmercury sample from the sample collection device to the mercury/methylmercury sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the mercury/methylmercury sample.

Additional sample bottles that are not being analyzed for mercury/methylmercury do not require that gloves be changed between bottle sets and do not require the specific “clean hands/dirty hands” procedure described herein; however, clean, fresh gloves must still be donned by all individuals handling sample bottles and operating the peristaltic pump at the start of sampling and whenever gloves become contaminated.

Procedure:

1. Designate one member of the team as “clean hands” and the other as “dirty hands.”
2. “Dirty hands” opens a bag containing non-talc gloves.
3. “Clean hands” removes a pair of clean gloves from “dirty hands” and puts them on.
   IMPORTANT: “Clean hands” will only be allowed to touch the inner bags and sample bottles from this point on (making sure not to touch anything in the surrounding environment).
4. “Dirty hands” removes a pair of clean gloves and puts them on (after all equipment is set up, new gloves are needed).
5. “Dirty hands” removes an empty bagged sample bottle set from the container/cooler, closes container/cooler, and opens the bag for “clean hands.”
6. “Clean hands” reaches into the bag and takes out the inner bag from “dirty hands” who is holding the outer bag of the double bagged mercury bottle.
7. “Dirty hands” seals the outer bag and places it back into the cooler.
8. “Clean hands” removes the bottle cap and holds the cap in one hand. With the other hand, “clean hands” fills the sample bottle from the pump tube (**groundwater**) or by dipping into the flowing water stream, taking precaution to keep their hand downstream of the opening of the bottle (**surface water**). Fill the bottle until there is a little room for closure, then seal the bottle tightly. Take precautions to not touch the insides of the bottles and their appropriate lids and caps during sampling collection. **Note:** If dissolved constituents are to be determined, “dirty hands” must perform field-filtration using an appropriate filtration apparatus equipped with 0.45µm membrane filtration media, the bottle should be marked with an “F” prior to sampling.

There are two alternate methods for steps 1 through 8 accepted for collecting **surface water samples** that involve “dirty hands” to temporarily be a second set of “clean hands”:

Method 1 (open water):

a) “Dirty hands” puts new nitrile gloves on
b) “Dirty hands” collects the sample in a non-preserved, clean or sterile, intermediate container to transfer into the appropriate sample bottle held by “clean hands.” The intermediate container is rinsed several times with sample water before the sample is collected.
c) Submerge the intermediate sample container at the sampling point such that the mouth of the container is under the water surface 2 to 3 inches (5-8 cm), if possible.
d) “Dirty hands” fills all bottles held by “clean hands” at that location, careful not to cause splashing while bottles are being filled, as some bottles contain preservative, leaving no headspace.
e) “Clean hands” seals sample bottle tightly.

Method 2 (during times when sampling from auger holes in ice):

a) “Dirty hands” puts new nitrile gloves on
b) “Dirty hands” prepares the peristaltic pump, places a new and cleaned (Alconox washed and dried) silicon tube in the pump, places one end of the tube into the stream water, and turn pump on.
c) Allow the pump to run for a couple of minutes, with stream water running through the tubing
d) The sample may now be collected directly into the sample bottles from the peristaltic pump at a low flow rate. “Clean hands” holds the water bottle, assuring that the hose does not touch the walls of the bottle and that the flow rate from the pump is low enough to not cause splashing while bottles are being filled, as some bottles contain preservatives, leaving no headspace.
e) “Clean hands” seals sample bottle tightly.

9. “Dirty hands” retrieves the outer mercury bottle bag from cooler and opens the bag.
10. “Clean hands” reaches inside the outer bag, held by “dirty hands,” to place the bottle inside.
    For mercury sample only: “clean hands” reaches inside the outer bag for the inner bag and places the bottle inside the inner bag and seals, then places the inner bag in the outer bag. **For methyl mercury sample only (if sampled):** “clean hands” reaches inside the outer bag for the inner bag and places the bottle inside the inner bag and seals, then places the inner bag in the outer bag and into a clean black garbage bag.
11. “Dirty hands” seals the outer bag and labels the sample set bag with the site location code and time and places the bagged sample into the cooler.

FILTERING PROCEDURE

When required, filtration is done in the field as soon as possible after sample collection. During very cold conditions it may be necessary to filter samples at the field office. When filtration at the field office is necessary, bulk samples are collected in clean, unpreserved intermediate sample containers such as 1-gallon plastic jugs to provide sufficient water volume to fill all sample bottles in the required sample bottle set.

Samples collected for dissolved analyses will be filtered using the following procedure:

1. Collect sample water into a decontaminated and triple rinsed plastic container (transfer vessel) and filter from the container.
2. Install new or deconned tubing in the peristaltic pump and a new 0.45-micron disposable filter on the discharge side of the line.
3. Pump water from the transfer vessel through the filter and into the appropriate bottles (normal, field blank, and rinse blank samples) as specified in the QAPP. Use clean gloves when filling and handling sample bottles, with hands/dirty hands procedure used for mercury/methylmercury sample bottle filling and handling.
4. Use a peristaltic pump with clean tubing equipped with a 0.45-micron disposable filter for each sample. Note: If extremely turbid sample water is obtained, it may be necessary to use a pre-filter (usually 3.0 micron) followed by 0.45-micron filtration.
5. Fill sample container with filtered sample; ensure appropriate preservative is added or already present in sample bottles requiring preservative.

SAMPLE BOTTLE LABELING PROCEDURE

Each sample container requires a label large enough to record the information needed to readily identify the sample. The information recorded on each label will include the project name, sample point, date/time collected, filtered or unfiltered, preservation, and sampler's initials. Permanent waterproof ink or permanent marker should be used for all labeling purposes.

Labeling procedure:

1. Carry the cooler containing the bottle sets to a clean location, where cross contamination can be avoided.
2. Put on a pair of clean nitrile gloves.
3. Pull the sample set out of the cooler, dry it off with a new paper towel for every sample, and set aside on clean paper towels.
4. Record the information from the original field forms onto each label, double checking the date and time, and place them on the correct sample bottles for analysis.
5. Place all the collected bottles back into a new bag, clearly labeling the bag with the site location and sample date/time.

Side note: If a mercury or methylmercury sample is to be collected, the sample label is to be placed on the outside of the second clear double bag and not directly on the bottle. For methylmercury, the two bagged bottle with the label on the outside of the bag, will need to be stored in a dark trash bag with a mercury trip blank and closed up.

To maintain consistent record keeping and to aid in maintaining electronic database records, it is important to record the sample station identification on the sample label exactly as it is listed in the Quality Assurance Project Plan.

SAMPLE PACKAGING AND SHIPPING PROCEDURE

Samples are packed and shipped using the following procedure:

1. Remove old shipping labels from the outside of the cooler, verify the inside of the cooler is clean (clean if necessary), then line the cooler with a plastic garbage bag.
2. Check the caps on the sample bottles are secure then place each sample bottle set in a plastic bag, such as a 13-gallon trash bag.

3. Place the sample bottle sets upright in the cooler, leaving room for ice and surround the samples with sufficient packing material, such as "bubble wrap" to prevent breakage and direct contact from sample to ice packs. Plastic sample containers may be used to separate glass containers from each other.
4. Include the "temperature blank" sample bottle and the trip blank, provided by the lab.
5. Fill the remaining cooler volume with ice packs or ice that has been placed in plastic bags.
6. Check the COC form(s) to ensure that all samples in the cooler have been properly recorded. Sign the COC form(s) to relinquish custody. If more than one cooler comprises the sample submittal, include copies of COC form(s) and all other pertinent paperwork in each cooler. Make electronic copies of all COC forms for record, and forward pertinent information to the QA, Sampling and Data Manager, while also holding a copy of the files on hand.
7. Place the completed COC form(s) and other submittal paperwork in a zipper-locking plastic bag and place it inside the cooler.
8. Seal the cooler using nylon strapping tape or other suitable tape at both ends. It is recommended that at least three wraps of tape around the cooler body be used.
9. Place a signed, dated custody seal across the opening of the cooler and secure with clear tape.
10. Secure the shipping label to the top of the cooler.
11. Transport the cooler to a secure storage area or to the shipping agent.

Hard copy air way bills are not distributed to Donlin Camp and instead issued a waybill number when checked in at the carrier. At this point, it is sufficient that once the cooler(s) have made it to the carrier office and is issued a way bill number, the way bill number must be retrieved by the field technician and filled out on the copy Chain of Custody. Once filled, the COC must be scanned and emailed to the QA, Sampling and Data Manager, the Lab Project Manager, and Donlin Gold's Shipping and Receiving Clerk. The shipping carrier is not responsible for training on sample Chain of Custody carriers.

If there are samples that are shipped to a secondary lab, all parties must be notified above and the cooler(s) of interest MUST contain the Donlin Gold Warehouse address, attention to the QA, Sampling and Data Manager, and Warehouse clerks. These coolers will be held overnight (if needed) at the Donlin Gold Warehouse and checked in and relinquished by the QA, Sampling, and Data Manager for the next FedEx flight.

For coolers that are carried on as personal luggage by the field crew and not shipped as freight, it is the field crew member's responsibility to notify the QA, Sampling and Data Manager, the Lab Project Manager and the DGLLC's Shipping and Receiving Clerk, that these samples will be "hand carried in" from camp. It is also the field crew member's responsibility to verify that these coolers make it to the Laboratory.

FIELD INSTRUMENT HANDLING PROCEDURE

Prior to beginning field activities:

- Select a cooler/insulating box of adequate size to hold all of the field instruments and associated equipment needed (as well as temperature and trip blanks) for performing field measurements.
- Equip the inside of a cooler with padding such as "bubble wrap" (sample protection)

When freezing conditions occur, add an adequate heat source to the cooler (heat packs, hand warmers, or other source) to maintain the temperatures inside the cooler above freezing while in the field.

FIELD EQUIPMENT AND INSTRUMENT DECONTAMINATION PROCEDURE

Decontamination procedures differ depending on the instrument or equipment, as described below:

For the water level meter and peristaltic pump, the following procedure should be followed prior to quarterly sampling (not in the field):

1. Rinse in water
2. Wash with Alconox or equivalent anionic detergent
3. Rinse in deionized water
4. Air dry

5. Dispose of Alconox cleaning agent at the proper waste facility.

The purpose of the water and Alconox wash is to remove particulate matter and other potential contaminants. The purpose of the final deionized water rinse is to remove detergent and any residual contaminants.

For the YSI Multi-Probe system, the following procedure should be followed (also refer to the YSI Operations Manual):

1. Thoroughly rinse all probes three times with tap water
2. Place the probe in the storage/transport cup, which should have ¼ inch of tap water or pH 4 buffer (if preferred) before traveling to the new site or for short-term storage

   If continuing to another site for sampling:

3. Rinse the probe with deionized water at the new location to remove residual tap water
4. After the deionized rinse, rinse with the sample water at new location. The probe is now ready for measurements at the new location.
5. After the sample bottles are filled, repeat steps 1 and 2 above.

Tap water is preferred and advised for the rinse solution between site locations, but deionized water may be used as an alternative if tap water is unavailable. It is recommended that pH 4 calibration solutions be placed in the probe cap as a buffer solution to keeps the probes primed between sampling locations. ***Note: deionized water should never be used in the probe cap for probe storage as it will cause the pH probe to malfunction and require immediate replacement.***

It is important to field check the YSI with a known and certified solution often in the field, as often as between sites, allowing the YSI to register readings to the nearest environmental conditions. Certificate of Analyses for the calibration solution should be stored on site.

To retrieve these documents:

1. Record all lot numbers of the calibration solutions that are currently in use
2. Go to: www.coleparmer.com
3. Enter the lot number of the solution
4. A downloadable PDF certificate is available and should be stored as a copy on the network.

If the YSI multi-purpose probes appear to contain deposits or contaminants that cannot be removed by the rinse steps described above, and a "drift" in parameter readings is observed, the YSI meter should be sent into the nearest vendor for repair, or the simple cleaning methods described below can be done weekly or as needed to remove stubborn deposits:

1. Spray probes with the over-the-counter cleaning agent, "Scrubbing Bubbles," making sure that the lenses are sprayed over well, OR use Alconox solution.
2. Allow bubbles to sit for a couple of minutes.
3. Using the small tube brush included in the maintenance kit; carefully scrub around all the probes to remove debris and build-up.
4. Rinse well with tap water, making sure to remove all the suds.
5. Dispose of any diluted cleaning agents and water at the proper waste facility

PORTABLE SAMPLING PUMP DECONTAMINATION PROCEDURE

Field Rinse Procedure:

This procedure is used between wells during the same quarterly sampling event. See "**Camp Procedure**" below for procedure for pump decontamination prior to quarterly sampling events. This field rinse procedure is for only for baseline sampling of wells, and not to be used for decontamination after sampling of a well in which there is a history of or indication of contamination.

The following procedure is followed:

1. After sampling at a well is complete, disconnect power and remove dedicated tubing.

2. Drain all well water from the pump and move to the next well.
3. Prior to connecting the tubing and power at the next well, rinse the exterior of pump and wetted portion of the power lead with DI water.
4. Connect tubing and power supply, place pump in well in accordance with sampling procedure.
5. The purge water at the following well is used to rinse the internal portion of the pump prior to a sample being collected.

Camp Procedure:
This procedure is used prior to each quarterly sampling event and is conducted at Donlin Camp. Decontamination between wells during quarterly sampling is done following the "**Field Equipment and Instrument Decontamination Procedure"**
Decontamination Equipment and Supplies:

- 2-inch (5-cm) diameter PVC well casing, capped on one end, 5 ft (1.5 m) in length
- hand-held sprayer with Alconox solution
- hand-held sprayer with deionized/distilled water
- Minimum of 3 gallons (11L) of deionized water provided by the lab
- paper towels

Decontaminate the pump after each use by performing the following procedure:

1. Decontaminate the exterior of the pump, support cable, and discharge hose:
2. Spray the pump and the hose with Alconox solution.
3. Rinse with deionized/distilled water and dry with paper towels.
4. Decontaminate the interior of the pump and discharge hose:
    - Install the pump into the 2-inch (5-cm) casing and vertically position the assembly.
    - Fill the 2-inch (5-cm) casing with deionized/distilled water.
    - Start the pump and continuously pour deionized/distilled water into the casing until 3 gallons (11 L) have been pumped through the complete assembly.
5. Collect an equipment rinse blank sample, if required (refer to Section 3.6.3).
6. Remove the pump from the 2-inch (5-cm) casing.

GRUNDFOS REDIFLO2 PUMP LUBRICATING FLUID (DEIONIZED WATER) REPLACEMENT PROCEDURE

The Grundfos RediFlo2 pump lubricating fluid, which is deionized water, should be replaced annually using steps 1 through 6 below. The lubricating fluid level should be checked prior to groundwater sampling events each quarter using steps 5 and 6 below to verify the fluid level is full and no air is present

Equipment and Supplies:

- motor filling syringe (Grundfos Part # 3P107)
- flat-bladed screwdriver
- lab produced deionized water

Replace the Grundfos RediFlo2 pump lubricating fluid following the procedure described below.

1. Make sure the pump is de-energized by turning the start/stop switch to the STOP position, turn off the generator, and unplug the pump.
2. Turn the pump and motor upside down and remove the screw on the bottom of the pump.
3. Empty the water from the motor and, using the syringe, refill the motor with deionized/distilled water to the bottom edge of the screw hole.
4. Replace the filling screw and turn the pump over several times.
5. Remove the filling screw to let any air trapped inside escape.
6. If necessary, top off again with deionized/distilled water and replace the screw.
   Note: severe motor damage will occur if the motor is operated without lubricating deionized water.

REVISION HISTORY

Revision #	Description of Change	Prepared By	Date
1	Drafted Document	Mike Rieser	3/13/2012

2	Change portable pump field decontamination procedure	Mike Rieser	4/2/2012
3	Add field filtering procedure	Mike Rieser	6/19/2012
4	Clarification of new gloves for every bottle of “Clean Hands/Dirty Hands” procedure, sample packing procedure changes, secondary lab shipping.	Tisha Woolley	8/29/2013
5	Clarification on temperature and trip blanks	Tisha Woolley	11/21/2014
6	Adjustments to “clean hand/dirty hands” procedure	Arcadis	10/28/2021

	STANDARD OPERATING PROCEDURE	
DONLIN GOLD	GROUNDWATER MONITORING PROCEDURES	
	EFFECTIVE DATE	**DOCUMENT NUMBER**
	11/21/2014	ENV-SOP-0037

PURPOSE

To set procedures for groundwater sampling by Donlin Gold employees or contractors in support of environmental studies and monitoring.

SCOPE

This procedure describes groundwater monitoring and sampling from Donlin Gold monitoring wells and related tasks.

RESPONSIBILITY

It is the responsibility of Field Environmental Coordinators to conduct environmental monitoring tasks following accepted procedures.

HEALTH AND SAFETY

Safety of people is the first priority when conducting any task. Personnel must be well-trained (per the procedures below) with standard routines, safety procedures, personal protection equipment, and emergency response actions.

ENVIRONMENTAL

Potential consequences of departing from standard:

- Departure from this Standard could result in injury to people, damage to facilities and/or the Environment resulting in pollution to the land or water, and obtaining erroneous field or laboratory water quality data.

REFERENCES

- *Quality Assurance Project Plan (QAPP); Water Quality Monitoring, Sampling, and Analysis Activities Donlin Gold Project*
- "Groundwater Monitoring Field Form", "General Environmental Sampling Procedures", and "Quality Control Sample Collection Procedures"

PROCESS

Groundwater Monitoring Procedure

1. Observe conditions in the vicinity of the well, weather, and any other aspects that may impact water quality.
2. Thaw the well using heat trace or other means (if necessary). See **Thawing Wells with a Submersible Heat Trace** procedure below.
3. Measure water level in the well. See **Water Level Measurement** procedure below. If the well is flowing or showing artesian conditions, a Margo plug should be installed. **Margo Plug Installation** procedures are in the **Water Level Measurement** section below.
4. Measure the depth of well. See **Well Depth Measurement** procedure below.
5. Purge the well to insure that the collected water quality sample is representative of groundwater conditions. See **Groundwater Well Purging Procedure** below.
6. Measure field parameters during the well purging process to verify that the well has been adequate purged. Establish that water quality has stabilized. See **Groundwater Field Measurements** procedure below.
7. Prior to collection of the water quality sample, perform final measurements of field parameters including pH, specific conductance, temperature, oxidation/reduction potential, and dissolved oxygen.
8. Collect water quality samples for lab analysis. Record all pertinent data and information on the Groundwater Monitoring Field Form (see *Quality Assurance Project Plan*), making sure to copy, scan and send the information at the end of the sampling day. See **Groundwater Quality Sample Collection** procedure below.

Thawing Wells with a Submersible Heat Trace Procedure

The following is equipment required for thawing wells using a submersible heat trace:

- Portable generators;
- Fuel for generators;
- Motor oil for generators;
- Fuel and oil spill containment pan to place under the portable generator;
- Oil absorbents;
- Long extension cords (with LED light connectors if available); and
- Clean plastic bag or tarp (to place tubing and heat trace on).

It may take more than a day to thaw some wells, depending on the thickness of ice and the borehole diameter. After determining which wells are frozen, and noting how difficult those wells have historically been to thaw, integrate well thawing with other well monitoring tasks to efficiently use time in the field. Some wells will partially refreeze overnight and will need to be re-thawed if not sampled immediately. Record any thawing information that may help with future thawing at each well. Have as many generators as practical running in the same vicinity to complete an area more easily and facilitate overnight refueling. The following are other important procedures to follow:

- Do not pull the heat trace out of the well until the well has thawed sufficiently. If the heat trace is removed too early it may be difficult to re-install.
- After completing water quality sampling tasks, be sure to re-install the heat trace before the well refreezes.
- Use caution around the heat trace plug; do not pull on the plug directly; replace or fix it if needed.

The following describes the procedure used for thawing wells using a submersible heat trace:

1. Inspect the wellhead for damage and/or vandalism, and record observations on the groundwater monitoring field form.
2. Plug the heat trace into the generator.
3. Connect both the deep and shallow well trace at the same time when they are in close proximity.
4. Place the generator in the sled, containment pan, or on spill rags. In addition to protecting the environment from spills it will also help to keep it level as snow melts around the exhaust.
5. Top off the fuel and check the oil.
6. Start the generator.
7. Check the switches and LEDs on the cords to confirm that they are energized.
8. Check the progress of the well thawing periodically by gently tugging the heat trace. However, do not pull the heat trace out of the well if ice is still present.
9. Run the generators overnight if needed. Refuel as needed and check the oil periodically.
10. Verify that the ice is adequately melted before pulling out the heat trace and dedicated tubing. (A small amount of ice may be floating at the surface but should not pose any problems).
11. Place the tubing/heat trace in a clean plastic bag or clean tarp.
12. Measure and record the water level before installing the sampling pump.
13. After completing the water quality sampling, secure the dedicated tubing to the heat trace and re-install it in the well.

Water Level Measurement Procedure

Water level data are measured in all groundwater monitoring wells during each monitoring event. Water level measurements are performed prior to quarterly water quality monitoring. Results are recorded on the Groundwater Monitoring Field Form (see *Quality Assurance Project Plan*).

Two separate procedures for performing water level measurements are described below:

#1 – An electronic water level indicator is used to measure depth to water surface in all monitoring wells to the nearest 0.01 ft., or 0.01 m if using a metric meter. Water levels measured in monitoring wells are measured after the well is thawed with heat trace (if frozen) and before any water has been purged in the water quality sample collection process.

#2 – Water levels are measured in monitoring wells equipped with BarCad system pumps (MW03-14, MW03-16) by temporarily removing the valve manifold before using the electronic water level meter. It is not necessary to perform a water level measurement in monitoring well MW03-14 if artesian conditions are present, which has historically been the case.

The equipment and supplies required and instrument preparation procedure for performing water level measurements for the quarter, is as follows:

Equipment and Supplies:

- GeoTech/Keck portable electronic water level meter, or equivalent;
- Alconox solution;
- Deionized water provided by SGS; and
- Paper towels.

Instrument preparation procedure:

1. Soak the paper towels with Alconox solution, and wipe down the stainless steel probe and about the first 30 ft (9 m) of the measuring tape.
2. Rinse the wetted parts with deionized water provided by the lab and roll the tape and probe back onto the reel.
3. Discard any Alconox solution used at proper waste water facility (must be carried out of field in a container).

<u>#1 - Water Level Measurement in Wells Not Equipped with BarCad System Pumps</u>

Procedure:

1. Turn the sensitivity knob to the highest setting.
2. Press the battery test button; the buzzer should sound and the red light will come on if the battery is in good condition. If the battery is defective, refer to the equipment operating manual for battery changing procedures.
3. Lower the probe and tape into the well. Stop lowering the probe when the buzzer sounds and the red light comes on.
4. Turn the sensitivity knob to the lowest setting at which the buzzer sounds and the light stays lit.
5. Slowly lift the cable until the light and buzzer go off. Lower the cable to the point where the light and buzzer just come on. It may be necessary to do this several times to find this point accurately.
6. Read the depth to water off the cable at the designated reference point (at the top of the inner PVC casing, north side of the well) to the nearest 0.01 ft. or 0.01 m. Record the following data on the Groundwater Monitoring Field Form (see *Quality Assurance Project Plan*): “depth to water,” “total well depth”, and “depth of water column” (note: “depth of water column” equals “total well depth” minus “depth to water”). If available, also record the reference point elevation, and calculate and record the water level elevation in feet above mean sea level (ft amsl).
7. Reel the probe back up out of the well and turn the sensitivity knob to the off position.

<u>#2 Water Level Measurement in Wells Equipped with BarCad System Pumps</u>

Procedure:

1. Wells equipped with BarCad system pumps will require the use of two crowfoot wrenches to loosen the middle and lower nuts from each other. The middle nut should turn easily by hand once it has been loosened.
2. Lift the “W” manifold (WM) up about 4 inches (10 cm) until the compression union that is connected to the Teflon drop tube has cleared the top of the BarCad riser pipe. The compression union is located at the bottom of the WM’s stainless ¼-inch (0.6-cm) tube. While taking water levels, leave the center valve in the position (open or closed) it was in at the start of this procedure.
3. Stop and hold the WM so that the bottom of the stainless union is resting on the lip of the riser pipe, and secure it in that position. This can be done by either having a second person hold the manifold or by tying it securely to a brace, such as a piece of wood, placed vertically next to the riser pipe. Keep the manifold vertical at all times during this operation. At no time should the Teflon tube be allowed to become kinked or bent over the top of the riser pipe.

4. Lower the water level indicator probe to the surface of the water inside the riser pipe. Note that the water level will drop slightly when the 4 inches (10 cm) of Teflon drop tube are lifted out of the water.
5. Note: water level meters with probes 5/8 inch (1.6-cm) diameter and larger will not fit. If a smaller probe is not available, do not perform the water level measurement.
6. Read the water level depth off the cable at the designated reference point (at the top of the riser pipe on the north side of the well) to the nearest 0.01 ft or 0.01 m. Take several measurements to verify that the water level has reached equilibrium prior to recording the final water level measurement result. Record the following data on the Groundwater Monitoring Field Form (see *Quality Assurance Project Plan*): "depth to water," "total well depth", and "depth of water column" (note: "depth of water column" equals "total well depth" minus "depth to water"). If available, also record the reference point elevation, and calculate and record the water level elevation in feet above mean sea level (ft amsl).
7. Reel the probe back up out of the well and turn the sensitivity knob to the OFF position. Re-attach the WM. The middle and lower nuts should be slightly tightened together with crowfoot wrenches.

Margo Plug Installation

If the well is observed to be artesian (flowing), a temporary Margo plug should be installed to control the water. There should be a few plugs of various sizes at the Donlin camp if needed.

1. Ensure the Margo plugs to be used will fit the PVC well casing.
2. Fit the top of the plug with an oversize washer below the top nut so that the plug cannot fall down the well.
3. Lower the Margo plug in the well so that the top is just above the PVC casing.
4. Tighten the Margo plug so a seal is created, but do not over tighten as this can break the casing.
5. Check the well pipe to ensure the seal is not leaking.
6. Document date, time, and type of plug used to plug the well.

Well Depth Measurement

Well depth is pertinent information on the condition of the well, and identifies problems that may develop over time such as silting-in of the well or frost-jacking of the casing. Well depth is essential during the annual non-sampling inspections. Weighted graduated steel tape (or similar instrument) is used to determine the total well depth, allowing a smaller weight to avoid damage and/or tangling the tape to the pump wires.

The following describes the well depth procedure using the pull-over method:

1. Open the well cap.
2. Note the Measuring Point at the top of the well casing. (This is typically the north side of the well, marked with a black tick mark).
3. Drop the weighted steel measuring tape slowly into the inner casing of the well while paying attention to the feel of the pull (or give) of the tape to be sure it is not snagging onto the pump wires.
4. Once the weight has hit the bottom of the well, use the top of the measuring point of the outer steel casing and measure the depth to the nearest 0.01 meter. This is the well depth from Top of Casing (TOC).
5. Keep the thumb and index finger on the TOC measurement on the tape. Mark on the tape and record that number.
6. If the well is not too high, continue to hold the position on the tape with your index finger, pull-over the tape on the outer casing all the way to the ground so that the mark with the index and thumb just touch the ground. Record the tape measurement at the top of the casing at the measurement point. This measurement is the well depth below ground surface (BGS). If the well steel casing is high above the ground follow steps 8 and 9 below.
7. The difference between the well depth below top of casing (TOC) and below ground surface (BGS) is the well stickup height.
8. If the well casing is high above the ground: Measure the distance from the ground surface to the top of the PVC (stickup height). This may require measuring the protective cover height, then subtracting the distance from the top of the protective cover to the top of the PVC well casing.
9. The well depth BGS is the well depth from TOC minus the stickup height.

Notes: If the well depth from TOC has decreased over time, the well may be silting-in or the casing may have separated. If the well depth from TOC stays constant but the depth BGS changes, the well may either be frost jacking or subsiding. If the well depth BGS is constant but the stickup height decreases, the PVC stickup may have been cut.

Groundwater Well Purging Procedure

After the water level measurement procedure is completed, purge the monitoring well prior to collecting a water quality sample. The following sections provide detailed procedures for well purging, using three different techniques: a portable pump or a dedicated pump (either an electric or BarCad pump).

Well Purging Procedure Using a Portable Submersible Pump (Grundfos RediFlo2 or equivalent)

1. The minimum volume to be purged is equal to three casing volumes. Determine the minimum volume and record it on the Groundwater Monitoring Field Form (see *Quality Assurance Project Plan*). For a 4-inch (10-cm) diameter well, this volume is roughly equivalent to 2 gal/ft (25 L/m) of water column. For a 2-inch (5-cm) diameter well, this volume is roughly equivalent to 0.5 gal/ft (6.2 L/m) of water column. For a listing of well casing diameters, see the *Quality Assurance Project Plan.*
2. Connect the bottom end of the tubing to the pump and carefully lower the pump into the well to the desired depth for purging/sampling. Lower the pump as slowly as possible into the well in order to minimize turbidity. Do not allow the pump to reach the bottom of the well.
3. Connect the power leads of the controller to the Reel EZ assembly. Then plug the controller power cord into to the generator.
4. Fill the generator with unleaded gasoline and check the oil. Add oil if necessary.
5. Set the generator's automatic (eco) throttle control switch to the manual position.
6. Start the generator with the circuit breaker switched off. Allow the generator to warm up until a constant voltage output is obtained.
7. Switch the circuit breaker ON.
8. Check the frequency display on the front of the controller. It should read zero. If it does not, refer to the "Troubleshooting" section of the manufacturer's manual.
9. If the controller has not been used for more than six months, leave the controller on for at least 15 minutes before proceeding.
10. Start the pump by pressing the Start/Stop switch into the START position.
11. Slowly advance the frequency rate by pressing the "up" arrow on the controller.
12. Adjust the discharge rate of the pump by adjusting the "up" and "down" arrows on the controller. If the pump stops inadvertently during normal operation, do not restart it until all the water in the discharge line has drained back through the pump and into the well.
    Note: **DO NOT PUMP TOO FAST!** The well purging rate should not be great enough to produce excessive turbulence, typically no greater than 1 gallon/minute (3.8 L/minute).
13. Begin measuring field parameters when 1/2 of the minimum purge volume has been removed from the well (see **"Groundwater Field Measurements Procedure"**). Record field parameter results and associated well purge volumes at consecutive intervals. The well purging process is deemed complete when a minimum of three casing volumes have been removed and consecutive field measurements are stabilized as described in the **"Groundwater Field Measurements Procedure"**.
14. For wells that can be pumped dry with the sampling equipment being used, the well should be evacuated to just above the well screen and allowed to recover prior to sample withdrawal. Allow the well to recover to within 85% of the original water level prior to resuming pumping. It is important not to completely dewater the zone being sampled. If the recovery rate is fairly rapid and time allows, evacuation of more than one volume of water is preferred. However, if the minimum volume of water has not been purged after successive periods of recovery, note the collection details on the groundwater monitoring field form and collect the sample.
15. When well purging is complete, record final field measurements.
16. Use the "down" arrow on the controller to reduce the amount of flow from the pump to a suitable flow rate prior to performing the water quality sample collection procedure.
17. After purging and sampling are completed, stop the pump by pressing the start/stop switch into the STOP position.
18. Switch the breaker on the generator to the OFF position and turn the generator off.

19. Disconnect and store all power cables.
20. Reel the pump back out of the well and secure the well cap. Decontaminate the pump as described in the "General Environmental Sampling Procedures" SOP.
21. Store the pump where it will be protected from freezing temperatures.
    Note: the controller has a limited temperature operating range. The lid of the protective case for the controller must be left open while the pump is operating to provide cooling. In very cold temperatures, it may be necessary to put heat packs on the converter.

Well Purging Procedure Using a Dedicated Electric Pump

Equipment needed:

- Discharge and valve assembly for dedicated pump system;
- Generator; and
- Extension cord.

Procedure:

1. The minimum volume to be purged is equal to three casing volumes. Determine the minimum volume and record it on the Groundwater Monitoring Field Form (see "Appendix C, Form II"). For a 4-inch (0.10-cm) diameter well, this volume is equivalent to 2 gal/ft (25 L/m) of water column. For a 2-inch (5-cm) diameter well, this volume is equivalent to 0.5 gal/ft (6.2 L/m) of water column. For a listing of well casing diameters, see the *Quality Assurance Project Plan*.
2. Attach the PVC discharge and valve assembly to the dedicated pump head.
3. Connect an extension power cord between the dedicated pump electrical plug and the generator.
4. Fill the generator with unleaded gasoline and check the oil. Add oil if necessary.
5. Set the generator automatic (eco) throttle control switch to the manual position.
6. Start the generator with the circuit breaker switched off.
7. Switch the circuit breaker on.
8. Control the discharge rate by adjusting the plastic valve.

Well Purging Procedure Using the BarCad System Pump

These well purging procedures apply to monitoring wells equipped with the BarCad pump system, currently MW03-14 and MW03-16. Additional procedural requirements are provided for MW03-14 only at the end of this section.

Procedure:

1. There are 2 hoses coming out of the BarCad. One has a piece of black tape which goes to the Blatypus. The other has a piece of blue tape, indicating that this is the point of entry from the well. The regulator that hooks into the tank is already default set to 300psi. No adjustments need to be made to this.
2. The Blatypus controller has an ON switch (the upper switch, which is always ON). It also has a heater switch (the lower switch).
3. There are two dials. The green dial (counter intuitively) is the "STOP" time and the red dial is the "GO" time. There are lights showing which is in operation at any given time. The STOP dial is set to "10 Seconds" (meaning that if the STOP dial is on 3, it will stop for 30 seconds.) The GO dial is on "Minutes" (meaning that if it is set on 3, it will go for 3 minutes).
   Note: To find the correct flow, different settings of STOP and GO may be adjusted, where it pumps just enough water that it doesn't cycle itself and pump air continuously. You will know when this happens because it will pump out all of its water, and then make a hissing and sputtering sound. If it does pump air, restart back at 1 minute STOP, 30 seconds GO, and slowly increase the GO time until you are getting water again. For example: A good general STOP/GO suggestion is a 1 minute STOP, 3 minutes GO, though may prove unsuccessful. It might be able to only handle 1min STOP and 1min GO (but might not pump much or any water), or it might handle 1min STOP and 7min GO (unlikely). Work with it until you are getting water, but not pumping so much it cycles and you get air and sputtering.

4. After set-up and pumping, go check periodically and see how much water is being pumped out of the well. Collect parameters when reaching the correct purge.

   Note: If you wish to use the regulator to cycle the other well during this refill phase, disconnect the gas inline from the BarCad manifold and use the valve on the manifold to regulate the refill.

5. Repeat the initial purge steps for all subsequent purge cycles. After the initial purge, you should begin measuring field parameters in the purge water. Record field parameter results and associated well purge volumes at intervals as well purging proceeds toward completion. The well purging process is deemed complete when consecutive field measurements for pH, specific conductance, and temperature are stabilize within 10%.
6. If the well dries up prior to removing the minimum purge volume, allow the well to recover to within 85% of the original water level prior to resuming purging. If the minimum volume of water has not been purged after the third period of recovery, proceed to step 14, noting well purging and water quality sample collection details on the "Groundwater Monitoring Field Form".
7. When the well purging procedure is complete, record final field measurements results and proceed with water quality sample collection procedure.
8. Backflow procedure: After the sample has been collected, allow the system to finish purging. When the spray rate from the sample return line drops off, indicating that water is starting to enter the riser pipe, shut off both valves at the top of the manifold and then turn the valve attached to the regulator outlet so that it points away from the regulator and toward the gold colored muffler to vent off the small volume of pressurized gas trapped between the regulator and the manifold.
9. Attach the gas in-line to the center port (sample return port) and open the valve attached to the regulator and the valve on the manifold's center port. The side port valve should be cracked slightly open. Allow gas to run into the sample return line for 20 or 30 seconds, pushing any water droplets clinging to the inside of the sample return line back down the line and below any potential zones of permafrost.
10. Close the center valve on the manifold, and vent off the remaining pressure in the line from the regulator.
11. Disconnect the gas in-line from the manifold.
12. Slightly open the center valve on the manifold and allow the gas in the sample return line to vent very slowly to the air. (The low flow rate is to prevent water droplets from being lifted back up to levels of possible permafrost.) Allow the gas to continue venting slowly from the side port until system is at equilibrium.
13. Place the protective brass cap loosely over both manifold valve fittings so that the water levels inside the riser pipe may be in equilibrium with the atmosphere.

Modified Procedure for Purging/Sampling Well (MW03-14)

Procedures for purging and sampling well MW03-14 are the same as for the MW03-16, except for the following modifications:

1. MW03-14 is typically the last well to be purged and sampled during groundwater monitoring field activities due to the long thawing period.
2. The heat trace should be energized as quickly as possible at the MW03-14 well after the field crew arrives at the Donlin Gold Project site.
3. At the end of the backflow procedure described in Step 14 above, both manifold valves should be closed. This will allow water to refill into the riser pipe only until the gas pressure in the trapped nitrogen gas pocket reaches equilibrium with the water pressure of the formation. This should occur before the water level reaches the possible permafrost zones.

Groundwater Field Measurements Procedure

Field measurements are performed as a component of the well purging process and prior to collecting the water quality sampling for analytical laboratory analysis. Parameters that are measured in the field include the following:

- Air temperature;
- Water temperature;
- pH;
- Conductivity;
- ORP/Eh; and

- Dissolved oxygen.

All field parameters are measured during the well purging process in order to verify that the well has been adequately purged, and to establish that water quality parameters have stabilized prior to collecting water quality samples. These measurements should be taken and recorded after ½ of the minimum purge volume (or 1½ of well volume) has been removed from the well. Measurements are then recorded at least twice more until the minimum purge volume has been achieved.

Procedure:

1. Rinse the YSI 556 multi-meter probe, or equivalent, with tap water.
2. Check the meter using the standard field checks in the YSI probe cups (pH of 7, ORP and Conductivity solution) that is nearest to expected field conditions. Recalibrate the probe using appropriate standards if necessary. Rinse probe.
3. Initiate the well purging procedure using a dedicated or portable pump, and continue until at least one half of the minimum purge volume has been removed from the well (for wells with BarCad system pumps, complete one full purge cycle before proceeding to step 4).
4. Direct the well purge flow into a clean beaker or other suitable container, allowing the container to fill and overflow. Alternatively, a flow-through cell specifically designed for field measurements can be used.
5. Immerse multi-probe in beaker, or installed in flow-through cell, and turn on meter. Read the temperature, pH, DO, ORP/Eh, and EC and record the results after the readings have stabilized.
6. At appropriate intervals during the well purging process, conduct the field measurements using the YSI meter. Note and record the date/time, purge volume, and associated field measurement results on the "Groundwater Monitoring Field Form" (see *Quality Assurance Project Plan*). Continue until well purging process is complete and water quality parameters have stabilized. Water quality parameters are considered stable when three successive readings, collected 3-5 minutes apart, are within:
    - ± 3% for temperature (minimum of ± 0.2° C);
    - ± 0.1 for pH;
    - ± 3% for conductivity;
    - ± 10 mv for redox potential;
    - ± 10% for dissolved oxygen (DO); and
    - ± 10% for turbidity.
7. If applicable, note any problems such as erratic readings. Very cold ambient air conditions may cause freezing of water on the sensors, leading to erratic readings.
8. Decontaminate the multi-probe between wells in accordance with pump as described in the General Environmental Sampling Procedures SOP.

Groundwater Quality Sample Collection Procedure

After well purging and collection of field parameters is complete, collect groundwater samples using the following procedure:

1. Put on a pair of clean gloves—sampling personnel must wear clean, "non-powdered", polyethylene, PVC, or nitrile gloves from the box or if the gloves are stored in a clean bag.
2. Collect samples following "Clean Hands/Dirty Hands Procedure", as described in "ENV-SOP-0036, General Environmental Sampling Procedures".
3. Field Filtration is performed prior to any sample preservation using the "Field Filtering Procedure" described in "ENV-SOP-0036, General Environmental Sampling Procedures". A minimum of 1 L of water will be pumped through the filter prior to sample collection.
4. Carefully note the sample station, sample date/time, and any other pertinent information on the sample bottles.
5. Fill out the "Groundwater Monitoring Field Form" (see *Quality Assurance Project Plan*), documenting the sample station, sampling location, date/time of water quality sample collection, site conditions, all field measurement data, and any other pertinent information before leaving the site.

REVISION HISTORY

Revision #	Description of Change	Prepared By	Date
1	Drafted Document	Mike Rieser	3/13/2012
2	Added reference to field filtering procedure	Mike Rieser	6/19/2012
3	Revised decontamination prior to water quality sampling/ New BarCad well purge instructions/filter sample order change	Tisha Woolley	4/23/2013
4	Clarification of type of standards for YSI Field checks	Tisha Woolley	8/29/2013
5	Well Depth Measurement and Margo Plug Procedure	Tisha Woolley	3/20/2014
6	Source of nitrile gloves; word clarification.	Tisha Woolley	11/24/2014

	STANDARD OPERATING PROCEDURE	
DONLIN GOLD	SURFACE WATER MONITORING PROCEDURES	
	EFFECTIVE DATE	**DOCUMENT NUMBER**
	6/11/2021	ENV-SOP-0038

PURPOSE

To set procedures for surface water monitoring and sampling by Donlin Gold employees or contractors in support of environmental studies and monitoring.

SCOPE

- This procedure describes surface water sampling from Donlin Gold monitoring wells and related tasks.

RESPONSIBILITY

- It is the responsibility of Field Environmental Coordinators to conduct environmental monitoring tasks following accepted procedures.

HEALTH AND SAFETY

Safety of people is the first priority when conducting any task. Personnel must be well-trained (per the procedures below) with standard routines, safety procedures, personal protection equipment, and emergency response actions.

ENVIRONMENTAL

Potential consequences of departing from standard:

- Departure from this Standard could result in injury to people, damage to facilities and/or the Environment resulting in pollution to the land or water, and obtaining erroneous field or laboratory water quality data.

REFERENCES

- Quality Assurance Project Plan for the Donlin Gold Project Water Quality Monitoring, Sampling, and Analysis Activities.
- Surface Water Monitoring Field Form, General Environmental Sampling Procedures, Quality Control Sample Collection Procedures

PROCESS

Surface Water Sampling Procedure

In addition to the procedures below, sampling personnel must wear clean, non-powdered, polyethylene, PVC, or nitrile gloves, and must follow the clean hands/dirty hands, filtering, sample bottle labeling, sample packaging and shipping, field instrument handling, and field equipment and instrument decontamination procedures as described in SOP-0036, General Environmental Sampling Procedures.

Procedure:

1. Carry equipment to the sampling location.
2. Set up equipment needed to collect samples and mark the bag of sample bottles with that location name.
3. Locate a sampling site at a point in the stream that exhibits the greatest flow and/or highest velocity.
4. Put on a pair of clean gloves—sampling personnel must wear clean, “non-powdered”, polyethylene, PVC, or nitrile gloves.
5. Collect samples following “clean hands/dirty hands” procedures, as detailed in the General Environmental Sampling Procedures.
6. Collect Quality Control samples as specified in the Quality Assurance Project Plan, using the methods described in the Quality Control Sample Collection Procedures.

7. Fill out the appropriate field form (see Quality Assurance Project Plan), documenting the sample station, sampling location, date/time of water quality sample collection, site conditions, all field measurement data, Field filter Lot #, and any other pertinent information should be noted before leaving the site.

Field Measurement of Stream Flow

Using the Swoffer Current Velocity Meter (Model 2100 C) and Swoffer "Top-Set" Wading Rod (Model 1518), or equivalent:

1. Visually check wading rod and velocity meter for damage. Repair damage to equipment as necessary.
2. Evaluate each reach of stream to determine if the site is suitable, and safe, for an adequate flow measurement. The criteria for determining if the site conditions are ideal for a flow measurement are as follows:
    a. The channel is straight within the reach
    b. The flow in the reach is confined to a single channel
    c. The flow lines of the reach are distributed proportionately across the channel
    d. The reach has a uniform slope, and the measurement is done midway between the slope controls
    e. There are few, if any, in-stream obstructions within reach to disrupt flow lines, such as fallen logs, boulders, or sand/gravel bars
    f. There are no downstream obstructions that may cause backwater at the measurement section, such as beaver dams or road culverts
    g. There is good access to the gauging site under all flow conditions, including flooding conditions.
3. Working in pairs, designate one individual to perform the measurements, and one to record data on Surface Water Monitoring Field Form (see Quality Assurance Project Plan).
4. Anchor a surveyor's tape tautly across the stream perpendicular to the direction of stream flow, and attach it on either side of the stream. Provide at least a foot of clearance between the water surface and surveyor's tape.
5. Note the time and gage height, if a staff gage is present, at the beginning of the measurement.
6. Divide the stream width into 10 or more, but no more than 20, equal intervals, or "verticals."
7. Attach the velocity sensor to the wading rod.
8. The person taking measurements in the stream informs the recorder of the location of the first surveyor's tape measuring interval, measuring the total stream depth at that vertical using a wading rod or tape measure. Record total depth measurements to the nearest ⅛ inch (0.3 cm).
   Note: If the stream is frozen, an ice auger will be used to create a series of holes so that measurements can be taken.
9. Velocity measurements will be taken at 60% of the total depth. This is done by measuring the depth on the larger sliding rod (actual depth), then setting the smaller rod (60% depth) to the equivalent number. For example, if the depth is 0.5 meters, slide the probe down until the smaller parallel rod reads 0.5 meters, this will pace the velocity sensor at 60% (0.3 meters) of total depth.
10. The person measuring stream-flow should stand downstream of the surveyor's tape, facing upstream, holding the wading rod vertical in the water column with the velocity sensor facing directly into the current, standing to one side of the sensor to avoid influencing the velocity sensor readings.
11. Repeat the stream velocity measurement procedure at each interval, or "vertical". The data recorder records all measurement data and other appropriate information on the Surface Water Monitoring Field Form (see Quality Assurance Project Plan).

Field Measurement of Surface Water pH, Temperature, Dissolved Oxygen (DO), ORP/Eh, and Conductivity

Using the YSI model 556 multi-meter, or equivalent:

1. Rinse the probe with tap water.
2. Periodically check the meter using the standard (pH 7 solution, ORP solution or Conductivity solution) in the YSI probe check cups, that is nearest to expected field conditions. Recalibrate the probe using appropriate standards if necessary (see Quality Assurance Project Plan).
3. Perform measurements in-situ if conditions allow. If a measurement is performed ex-situ, use a clean beaker of sample water.
4. Immerse multi-probe in stream, or beaker, and turn on the meter. For in-situ measurements, the probe should be equipped with a weighted probe-guard to protect the sensors from damage. For ex-situ measurements, swirl the sample in the beaker to provide thorough mixing. Read the temperature, pH, DO, ORP/Eh, and EC, and record the measurements after the readings have stabilized.
5. If applicable, note any problems such as erratic readings. Very cold ambient air conditions may cause freezing of water on the sensors, leading to erratic readings.
6. Rinse the multi-probe with tap water and store it according to the manufacturer's directions, (see Manufacturer's Equipment Manual).

Field Measurement of Turbidity

Using the Hach 2100P turbidimeter, or equivalent:

1. Calibrate the turbidimeter before each sampling event, using pre-manufactured formazin gel calibrating blanks. For reference, refer to the manufacturer Instrument and Procedure Manual.
2. Collect a sample in an appropriate container cell.
3. Wipe the cell with a soft, lint-free cloth to remove water spots and fingerprints.
4. Apply a thin film of silicone oil and wipe with a soft cloth to obtain an even film over the entire surface.
5. Place the instrument on a flat, sturdy surface. Do not hold the instrument while making measurements.
6. Insert the sample cell in the instrument cell compartment so the diamond or orientation mark aligns with the raised orientation mark in front of the cell compartment.
7. Close the lid.
8. Press READ.
9. The display will show "- - - - NTU", then the turbidity in Nepholometric Turbidity Units (NTUs).
10. Record the turbidity after the lamp symbol turns off.
11. Dump the container contents and rinse with deionized water. Before storing, clean the instrument with a clean, dry cloth while avoiding the photocell on the inside of the meter.

REVISION HISTORY

Revision #	Description of Change	Prepared By	Date
1	Drafted Document	Mike Rieser	3/13/2012
2	Added references to applicable General Environmental Sampling Procedures	Mike Rieser	6/19/2012
3	Clarified YSI standards to use for YSI field checks between sites	Tisha Woolley	8/29/2013
4	Minor typographical and formatting changes	Michael Hay	6/11/2021

	STANDARD OPERATING PROCEDURE	
DONLIN GOLD	QUALITY CONTROL SAMPLE COLLECTION	
	EFFECTIVE DATE	**DOCUMENT NUMBER**
	06/11/2021	ENV-SOP-0039

PURPOSE

To set procedures for collecting quality control samples as required for surface water, groundwater, sediment, and soil sampling programs for Donlin Gold employees or contractors in support of environmental studies and monitoring.

SCOPE

- This procedure describes collecting field blank, field duplicate, and equipment rinse blank samples and related tasks.

RESPONSIBILITY

- It is the responsibility of Field Environmental Coordinators to conduct environmental monitoring tasks following accepted procedures.

HEALTH AND SAFETY

Safety of people is the first priority when conducting any task. Personnel must be well-trained (per the procedures below) with standard routines, safety procedures, personal protection equipment, and emergency response actions.

ENVIRONMENTAL

Potential consequences of departing from standard:

- Departure from this Standard could result in injury to people and damage to facilities and/or the Environment, resulting in pollution to the land or water and obtaining erroneous field or laboratory water quality data.

REFERENCES

- *Quality Assurance Project Plan (QAPP); Water Quality Monitoring, Sampling, and Analysis Activities Donlin Gold Project*
- Surface Water Monitoring Field Form or Groundwater Monitoring Field Form, as applicable

PROCESS

Field Blank Sample Procedure

Collection of field blanks will be conducted during water quality sampling according to the procedure below.

1. Prepare the field blank at the project site using deionized water provided by the laboratory and a complete set of sample bottles corresponding to the parameter list for lab analysis.
2. Label the field blank sample bottles with a code that will not alert laboratory personnel that this is a blank sample.
3. Fill the appropriate set of sample containers with lab produced deionized water. Use exactly the same procedures as are being used for environmental samples. Use the same preservatives, as provided by the lab. Perform field filtering for dissolved parameters, using the Field Filtering procedure described in "ENV-SOP-0036, General Environmental Sampling Procedures". Filter lot numbers should be recorded in the notes section. Filtering blank water can indicate a filter contamination.
4. Measure field parameters in the field blank deionized water using a clean intermediate container, having rinsed the container and instruments beforehand with the same deionized water.
5. Record all information on a field form, in the same manner as for normal water quality monitoring activities. Indicate this as a field blank sample on the field form, but do not transfer this information to the laboratory.

6. Place the field blank sample bottle set in the same cooler as the normal samples marking the bag with the site name and time, and deliver all samples to the laboratory in the same manner and at the same time. If a methyl mercury bottle set is to be collected, ensure the sample is double bagged and labeled on the outside of the double bag. Once this is completed, place this double bagged sample and a trip blank into a dark black bag, seal and place with the other bottles for this sample.

Field Duplicate Sample Procedure

Field duplicates will be collected for water quality, sediment, and soil samples according to the procedure below.

1. Take an extra set of sample bottles into the field.
2. Label the field duplicate sample bottles with a code that will not alert laboratory personnel that this is a field duplicate sample.
3. Take the primary sample in the normal manner, after purging the well (if applicable) and measuring field parameters.
4. Collect the field duplicate sample in exactly the same manner as the primary sample. Filter any bottles and record the filter lot number in the notes section.
5. Generate a separate field form for the field duplicate sample and record all information in the same manner as for the primary water quality sample. Indicate this as a field duplicate sample on the field form and to which primary sample the duplicate corresponds, but do not transfer this information to the laboratory.
6. Place the field duplicate sample bottle set in the same cooler as the normal samples, marking the bag with the site name, date and time, and delivers all the samples to the laboratory in the same manner and at the same time. If a methyl mercury bottle set is to be collected, ensure the sample is double bagged and labeled on the outside of the double bag. Once this is completed, place this double bagged sample and a trip blank into a dark black bag, seal and place with the other bottles for this sample.

Equipment Rinse Blank Sample Procedure

Collection of equipment rinse blanks will be conducted during water quality sampling according to the procedure below.

1. Take a large container of deionized water provided by the laboratory and an extra set of sample bottles into the field.
2. Label the equipment rinse blank sample bottles with a code that will not alert laboratory personnel that this is a rinse blank sample.
3. Collect the equipment rinse blank sample immediately after collecting the normal water quality sample, and after decontaminating the sampling equipment in the normal manner.
4. Details of collecting the equipment rinse blank sample may differ according to the specific sampling equipment being used. The equipment rinse blank sample is intended to represent deionized water that has been processed in the same manner as a water quality sample collected from the field. This may be as simple as placing deionized water in an intermediate sample container and then transferring to the sample bottles; or may involve pumping deionized water through a pump hose. Filter bottles, as if collecting a normal sample. Record lot number on the notes section. Collect field parameters are measured using a procedure similar to that used during normal field monitoring activities.
5. Generate a separate field form for the equipment rinse blank sample, and record all information in the same manner as for primary water quality sample. Indicate this as an equipment rinse-blank sample on the field form but do not transfer this information to the laboratory.
6. Place the equipment rinse blank sample bottle set in the same cooler as the normal samples, mark the bag with site name, date/time, and deliver all samples to the laboratory in the same manner and at the same time. If a methyl mercury bottle set is to be collected, ensure the sample is double bagged and labeled on the outside of the double bag. Once this is completed, place this double bagged sample and a trip blank into a dark black bag, seal and place with the other bottles for this sample.

REVISION HISTORY

Revision #	Description of Change	Prepared By	Date
1	Drafted Document	Mike Rieser	3/13/2012

2	Revised to reference applicable General Environmental Sampling Procedures	Mike Rieser	6/19/2012
3	Filter lot numbers to be recorded in the notes section and site name, date/time on every bag clarification	Tisha Woolley	06/26/2013
4	Methyl Mercury sample packaging instructions and laboratory provided deionized water	Tisha Woolley	07/23/2014
5	Field Filtering blank water clarification	Tisha Woolley	11/24/2014
6	Expansion of scope to include sediment and soil collection	Michael Hay	6/11/2021

	STANDARD OPERATING PROCEDURE	
DONLIN GOLD	SEDIMENT SAMPLE COLLECTION PROCEDURES	
	EFFECTIVE DATE	**DOCUMENT NUMBER**
	4/30/2021	ENV-SOP-0040

PURPOSE

To set procedures for sediment sampling by Donlin Gold employees or contractors in support of environmental studies and monitoring.

SCOPE

This procedure describes sediment sampling from creeks at Donlin Gold and related tasks. Low-level mercury sampling protocols apply when collecting samples for mercury analysis.

RESPONSIBILITY

It is the responsibility of Field Environmental Coordinators to conduct environmental monitoring tasks following accepted procedures.

HEALTH AND SAFETY

Safety of people is the first priority when conducting any task. All field personnel must be familiar with and must have the appropriate training required by Donlin Gold as described in the project Health and Safety Plan (HASP). Personnel must be well-trained (per the procedures below) with standard routines, safety procedures, personal protective equipment (PPE), and emergency response actions. PPE necessary for this task is outlined below, in addition to other standard PPE required for field work:

- Chest waders with good traction soles
- Personal flotation device (PFD)
- Safety vest
- Full-arm nitrile (or similar) gloves
- Safety glasses
- Throw ring for onshore personnel

The following additional Health and Safety protocols should be followed:

- Walk established paths whenever possible to avoid slip/trip hazards. Take your time and watch your footing.
- Always wear a PFD within 10 feet of water and always have three points of contact when entering and exiting the stream channel.
- One member of the sampling team should act as a Shore Watch, positioned out of the water (downstream of the sediment sampler), overseeing the sample collection and in possession of the throw ring.
- Take breaks as needed to avoid repetitive use injury or muscle strain and take turns with co-workers as needed.
- Do not touch sediments with bare hands or detect odors by placing sediments close to your nose.
- STOP WORK when conditions change or become unsafe and discuss if/how to proceed safely before resuming work.

ENVIRONMENTAL

Potential consequences of departing from standard:

- Departure from this Standard could result in injury to people and damage to facilities and/or the Environment, resulting in pollution to the land or water and obtaining erroneous field or laboratory water quality data.

PROCESS

Sediment Sampling Procedure

In addition to the procedures below, sampling personnel must wear clean, non-powdered, polyethylene, PVC, or nitrile gloves, and must follow the clean hands/dirty hands, filtering, sample bottle labeling, sample packaging and shipping, field instrument handling, and field equipment and instrument decontamination procedures as described in SOP-0036, General Environmental Sampling Procedures.

Equipment List:
The following list identifies materials that may be required:

- Health and Safety equipment/PPE as outlined above
- Global Positioning System (GPS) unit
- Plastic mixing spoon
- Plastic or stainless steel scoop/trowel
- Disposable plastic sheeting
- Steel rod or sediment probe (e.g., rebar), approximately 4 feet
- Lexan tubing (2-inch diameter), 1-ft long sections, minimum of three, with end caps; cleaned and placed in plastic bags
- Tape measure (at least 20 feet)
- Waterproof survey rod or meter stick
- Turkey baster (minimum 6-inch length) or plastic syringe barrel with plastic tubing (greater than 6-inch tubing length)
- Sample containers (1-gallon Ziploc freezer bags, 1-liter plastic HDPE bottles, or 1-liter glass jars, and/or other laboratory-supplied containers), labels, and forms
- Cleaning equipment – Distilled water, non-phosphate soap (Alconox or similar), spray bottles, brushes
- Transport container with ice
- Erasable whiteboard
- Digital camera
- Field notebook

Procedure:

The procedure below outlines sediment collection using Lexan tubes. Sediments may alternatively be collected using a scoop or trowel; however, use of a scoop or trowel runs a significant risk of losing fine grained sediment as the scoop or trowel is raised through the sediment column. Scoops or trowels should only be used when a push core is unsuccessful at retrieving an acceptable sample, or when water depth is less than 2 inches and sediment contains gravel or larger grain size. Use of plastic scoops/trowels are preferred. If a metal trowel is required, care must be taken to collect sample that did not directly contact the trowel.

1. Don PPE, as required by the HASP.
2. Identify the proposed sample location in the field notebook and/or field forms along with other appropriate information (location, date, time, personnel, weather, etc.). Field staff will target areas of sediment accumulation (typically the inside of stream beds) and avoid areas where sediment sample collection is not possible (e.g., areas of cobbles). The steel rod/sediment probe can be used to verify a 6-inch thickness of sediment can be obtained without hitting refusal.
3. Verify all equipment has been decontaminated and clean hands/dirty hands protocols are followed, per SOP-0036.
4. Set up equipment needed to collect samples and extend measuring tape to establish a 20-foot transect parallel to stream/creek/drainage. The transect may be adjusted to account for significant obstacles. The midpoint of the transect should be the pre-determined sample location.
5. Measure and record the water depth at the sample location immediately prior to sample collection using the survey rod. Sediment will be collected from inundated areas beneath a water column depth of a few inches or more. Do not wade into the water to a depth above knees.

6. One primary composite analytical sample will be collected from each sediment sampling location. Sediment samples will be collected at the center and each end of the transect (3 increment locations total, making up the composite sample). Samples will be collected from inundated areas using Lexan tubes.
    a. Push the Lexan tube into the sediment by hand with a straight vertical entry until refusal or target depth (six inches).
    b. Place a cap on top on the tube and slowly pull the tube from the sediment, twisting slightly as it is removed (if necessary).
    c. Before the tube is fully removed from the water, place a cap on the bottom end of the tube (while it is still submerged).
    d. Measure the length of sediment recovered and evaluate the integrity of the core. If the core is not suitably intact, repeat coring procedure at the location adjacent to the previous one sampled, approximately 6-12 inches away to minimize disturbance.
        i. If the sediment has a loose texture and falls out of the tube when pulling out of the sediment, repeat the steps above, but push your gloved hand down around the bottom of the core to hold the sediment in place while pulling the tube from the sediment, and then place the bottom cap after the core is removed.
    e. Remove the top cap and decant the overlying water column above the sediment from the top of the Lexan tube using the turkey baster or plastic syringe barrel and tubing. Avoid the removal of fine sediment with the turkey baster; if fine sediment is suspended in the water column, allow fines to settle before removing water.
7. Composite the three Lexan tube samples into one container for analysis.
    a. Empty the contents of the three Lexan tubes into a clean 1-gallon or larger Ziploc bag by removing the bottom cap from each of the Lexan tubes over the bowl. If the sediment does not slide out of the tube, gently tap the core tube on the bowl or tap the side of the core with the spoon.
    b. Photo-document the sample in the bag. Photos will include a view of a dry-erase board marked with the sample identification and a tape measure for scale.
    c. Thoroughly homogenize the sample by repeatedly squeezing the outside of the bag.
    d. Transfer subsamples of the fully homogenized composite sample into the specified laboratory containers as required using a clean plastic spoon. Transfer quickly to avoid air exposure, water evaporation, and potential oxidation. Remove the air from the Ziploc bag, seal, and triple-bag.
        i. Use clean hands/dirty hands protocol when transferring sample out of the bag. Specifically, Clean Hands should handle transfer of sample to separate containers.
        ii. If possible, the sample should be sent to the laboratory in the original Ziploc bag for most analyses to limit sample handling in the field.
    e. Remove the air from the Ziploc bag, seal, and triple bag.
    f. Label each of the sample containers and place the samples on ice in a cooler.
8. Decontaminate reusable sampling equipment.

If Lexan tubes are impractical at the sampling location, proceed with the following alternate procedure utilizing a sample scoop/trowel.

1. Follow Steps 1 through 5 above, targeting a water column depth approximately two inches.
2. Slowly lower the scoop or trowel through the water column, ensuring not to stir up sediments.
3. Scoop the sediment to the sample depth.
4. Slowly raise the scoop through the water. The rate of raising the scoop through the water should prevent sediment from falling out of the scoop and prevent a turbidity plume from the scoop.
    a. Several scoops may be required to target a volume similar to the 2-inch diameter x 6-inch Lexan tube.
    b. If a clean plastic scoop is used, the sample can be directly transferred to the sample container.
    c. If a metal trowel is being used, Clean Hands must scoop a sample off of the trowel using a plastic scoop/spoon, taking care to not sample sediment in direct contact with the metal trowel.
5. Place sediment into the Ziploc bag and proceed with Steps 7 and 8 above.

DATA RECORDING AND MANAGEMENT

Data will be recorded in a project-dedicated field notebook, field data sheets, and chain-of-custody forms. Following completion, copies of all field documents will be maintained in the project files.

QUALITY ASSURANCE

Quality assurance samples (replicates, trip blanks, etc.) will be collected at the frequency specified in the QAPP to achieve the project quality objectives. Dedicated or disposable sampling equipment and tubing will be either cleaned and stored for future sampling or disposed of in accordance with established waste management procedures.

REVISION HISTORY

Revision #	Description of Change	Prepared By	Date
1	Drafted Document	Arcadis	6/11/2021

Appendix B
Donlin Gold Field Forms

Groundwater Monitoring Field Form

General Information

Well ID:		On site Date:		Time:	
Monitoring Performed By (Full Names):					
Well Head Condition - Locked?	☐ Yes ☐ No	Damaged?	☐ Yes ☐ No		
If damaged, describe:					

Well Thawing (if needed)

Frozen? ☐ Yes ☐ No	if so, at what depth?		☐ feet ☐ meter		
Heat Trace energized	Date:	Time:	Heat Trace de-energized	Date:	Time:
Riser thawed successfully ☐ Yes ☐ No					
Notes/comments:					

Water Level Measurement Information

Depth to Water: ☐ feet ☐ meter		Measurement Point:	/
Total Well Depth: ☐ feet ☐ meter		Height of Water Column:	☐ feet ☐ meter
Elevation of Meas. Pt.: feet AMSL		Water Level Elevation:	feet AMSL

Well Purging/Field Measurements Information

Minimum Purge Volume*: gals		*0.5 gal/ft of water column for 2" dia. well *2 gal/ft of water column for 4" dia. well		
Field Parameter	First	Second	Third	**Final**
Date/Time:	Date Time	Date Time	Date Time	Date Time
Volume Purged (gals):				
Color/Clarity:	Color Clarity	Color Clarity	Color Clarity	Color Clarity
pH (su):				
Conductivity (µmhos/cm):				
Temperature (deg C):				
ORP (mv):				
Dissolved Oxygen (mg/L):				
Water Quality Sample Collected	Date:		Time:	
Parameter List Requested:	☐ ***Long List-1***	☐ ***Short List-1***	☐ ***Other***	
Date Shipped to Lab:				

Weather/Notes:

Surface Water Monitoring Field Form (page 1)

1. Station Name and Location:

Station ID:		Sample Date:	Time:
Monitoring Performed By (Full Names):			
Site Conditions:		Ice Present? ☐ YES ☐ NO	Ice thickness (if YES):
Stream Flow Conditions (check): ☐ High Flow ☐ Medium Flow ☐ Low Flow ☐ Frozen to stream bed			
UTM Z4 Easting (NAD83):			
UTM Z4 Northing (NAD83):			

2. Water Quality Sample Type

Check one:		
☐ Routine Monitoring		
☐ Field Blank		
☐ Equipment Rinse blank		
☐ Field Duplicate	DUPLICATE OF:	
☐ Field Generated Reference Material	Ref. Std I.D.:	

3. Field Parameters:

Air Temperature:		°C
pH:		pH units
Conductivity:		µmhos/cm
Water Temperature:		°C
Oxidation/Reduction Potential (ORP):		millivolts (mv)
Dissolved Oxygen (DO):		mg/L
Turbidity:		ntu

4. Water Quality Sample Information:

Parameter List Requested (Check one):	☐ Long List-1	☐ Short List-1	☐ Other:	
Date Shipped to Lab (must be filled):		Time:		

5. Weather and Notes:

Surface Water Monitoring Field Form (page 2)

Stream Velocity Measurements (used for determining stream flow)

1. Station Location and Basic Information

Station ID:		Date:	Time:
Personnel on site (Full Names):			
Measurement site condition (check): ☐ **High Flow** ☐ **Medium Flow** ☐ **Low Flow** ☐ **Frozen to stream bed**			
Staff gauge present? (check):	☐ **YES**	☐ **NO**	
Staff Gauge Reading (record to nearest 0.01 m):		m	

2. Velocity Measurement Data

Distance at LEFT bank (m):	m	Distance at RIGHT bank (m):	m
Stream Width in meters (left bank – right bank):		m	

METER CALIBRATION

Station (m)	Water depth	Measurement depth (6/10 of water depth)	Velocity (m/sec)	Notes

3. Additional Notes:

DONLIN GOLD YSI METER CALIBRATION LOG				**PH**		**CONDUCTIVITY**		**ORP**		**Calibration by:**
	Serial of YSI	***Date***	***Time***	*Calibration Reading (Circle one)*	*Temp.*	*Calibration Reading*	*Temp.*	*Calibration Reading*	*Temp.*	*Initial for first name, written out last name*
				4.00 7.00 10.0						
Initial calibration (Start, Before Sampling)										
Final calibration (End of Day)										
Initial calibration (Start of Day)										
Final calibration (End of Day)										
Initial calibration (Start of Day)										
Final calibration (End of Day)										
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Initial calibration (Start of Day)										
Final calibration (End of Day)										

DONLIN GOLD YSI METER INSTRUMENT MAINTENANCE LOG	Serial No. of YSI	Date	Time	Issued by:	NOTES/ISSUES

Well Inspection Checklist

DONLIN GOLD	Well ID:	Date Of Inspection:
	Inspector Name:	

Well Depth (m): (Ref: ENV-SOP-0037)		Water Level (m):		Diameter of riser pipe (cm):	
Stick up Height of Steel Casing (m): Using Pull Over method		Stick up height (m) of PVC above steel casing? (N/A if not applicable)		Are there other monitoring wells in the vicinity? If so, please list.	

Well ID readily found? ☐ Yes ☐ No	Artesian Conditions? ☐ Yes ☐ No	Body of water in close proximity to well? ☐ Yes ☐ No Is there water inside the outer casing and PVC? ☐ Yes ☐ No
Heat Trace Available? ☐ Yes ☐ No In Working Condition? ☐ Yes ☐ No	Cracked or corroded well casing? ☐ Yes ☐ No	Erosion around well base? ☐ Yes ☐ No
Frost heaving? ☐ Yes ☐ No Is casing frost- jacking into well protector? ☐ Yes ☐ No	Dedicated Pump? ☐ Yes ☐ No Damage to dedicated pump? ☐ Yes ☐ No BarCad System Pump? ☐ Yes ☐ No	Silt accumulation (encountered during well depth)? ☐ Yes ☐ No
Foreign material observed in the well casing (observing for a damaged casing)? ☐ Yes ☐ No Grout? ☐ Yes ☐ No Sand? ☐ Yes ☐ No	Did PVC need to be cut so that the PVC is below the protector level of the outers tell casing? ☐ Yes ☐ No If so, PVC length cut off? Amount: _____	Additional Observations:

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SGS Environmental Services Inc.
Laboratory Division

Locations Nationwide

Alaska Hawaii
Maryland Louisiana
New Jersey West Virginia
www.sgs.com

CLIENT: **Donlin Gold LLC**

CONTACT: **Tisha Woolley** PHONE NO: **(907) 569-0342**

PROJECT: **Donlin Gold GW** SITE/PWSID#:

REPORTS TO: **Nick Enos and Tisha Woolley**

Donlin Gold LLC , 4720 Business Park Blvd.Suite G-25, Anchorage, AK 99503

INVOICE TO: **Nick Enos** QUOTE #:

Donlin Gold LLC , same as above P.O. NUMBER:

LONG LIST - 1
Donlin Gold Ground Water (GW)

page _____ of _____

LAB NO.	SAMPLE IDENTIFICATION	DATE	TIME	MATRIX	No CONTAINERS	PRES USED	NONE	NONE	HNO3	HNO3	HCL	H2SO4	NaOH						REMARKS
						SAMPLE TYPE C = COMP G = GRAB	pH, Cond, TDS, Alk*, Cl, SO4, Fluoride	TSS	Metals, Total	Cations (Ca, Mg, Na, K), Dissolved and Dissolved Metals	Mercury (LL-1631)	Nitrate + Nitrite (as N), Ammonia	Cyanide (Tot & WAD)						
				GW															
				GW															
				GW															
				GW															
				GW															
				GW															
				GW															
				GW															
				GW															
				GW															

Collected/Relinquished By: (1)	Date	Time	Received By:	Shipping Carrier: Shipping Ticket No:	Samples Received Cold? YES NO Temperature °C: _____._____
Relinquished By: (2)	Date	Time	Received By:	Special Deliverable Requirements: **KEEP COOL / DO NOT FREEZE**	Chain of Custody Seal: (Circle) INTACT BROKEN ABSENT
Relinquished By: (3)	Date	Time	Received By:	Requested Turnaround Time and Special Instructions: **Alk* - Alkalinity, CO3, HO3, OH** **Metals, Total: Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Li, Pb, Mn, Mo, Ni, Se, Ag, Tl, V, Zn (200.7/200.8)**	
Relinquished By: (4)	Date	Time	Received For Laboratory By:		

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SGS Environmental Services Inc.
Laboratory Division

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CLIENT: **Donlin Gold LLC**

CONTACT: **Tisha Woolley** PHONE NO: **(907) 569-0342**

PROJECT: **Donlin Gold SW** SITE/PWSID#:

REPORTS TO: **Nick Enos and Tisha Woolley**

Donlin Gold LLC , 4720 Business Park Blvd.Suite G-25, Anchorage, AK 99503

INVOICE TO: **Nick Enos** QUOTE #:

Donlin Gold LLC , same as above P.O. NUMBER:

LONG LIST - 1
Donlin Gold Surface Water (SW)

page _____ of _____

LAB NO.	SAMPLE IDENTIFICATION	DATE	TIME	MATRIX	No CONTAINERS	PRES USED	NONE	NONE	HNO3	HNO3	HCL	H2SO4	NaOH	HCL					REMARKS
						SAMPLE TYPE C = COMP G = GRAB	pH, Cond, TDS, Alk*, Cl, SO4, Fluoride	TSS	Metals, Total	Cations (Ca, Mg, Na, K), Dissolved and Dissolved Metals	Mercury (LL-1631)	Nitrate + Nitrite (as N), Ammonia	Cyanide (Tot & WAD)	Methyl Mercury (Method 1630 - BrooksRand)					
				SW															
				SW															
				SW															
				SW															
				SW															
				SW															
				SW															
				SW															
				SW															

Collected/Relinquished By: (1)	Date	Time	Received By:	Shipping Carrier: Shipping Ticket No:	Samples Received Cold? YES NO Temperature °C: _____._____
Relinquished By: (2)	Date	Time	Received By:	Special Deliverable Requirements: **KEEP COOL/ DO NOT FREEZE**	Chain of Custody Seal: (Circle) INTACT BROKEN ABSENT
Relinquished By: (3)	Date	Time	Received By:	Requested Turnaround Time and Special Instructions: **Alk* - Alkalinity, CO3, HO3, OH** **Metals, Total: Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Li, Pb, Mn, Mo, Ni, Se, Ag, Tl, V, Zn (200.7/200.8)**	
Relinquished By: (4)	Date	Time	Received For Laboratory By:		

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CLIENT: **Donlin Gold LLC**

CONTACT: **Tisha Woolley** PHONE NO: **(907) 569-0342**

PROJECT: **Donlin Gold GW** SITE/PWSID#:

REPORTS TO: **Nick Enos and Tisha Woolley**

Donlin Gold LLC , 4720 Business Park Blvd.Suite G-25, Anchorage, AK 99503

INVOICE TO: **Nick Enos** QUOTE #:

Donlin Gold LLC , same as above P.O. NUMBER:

SHORT LIST - 1
Donlin Gold Groundwater (GW)

page _____ of _____

LAB NO.	SAMPLE IDENTIFICATION	DATE	TIME	MATRIX	No CONTAINERS	PRES USED / SAMPLE TYPE (C = COMP, G = GRAB)	NONE: pH, Cond, TDS, Alk*, Cl, SO4, Fluoride	NONE: TSS	HNO3: Metals, Total	HNO3: Cations (Ca, Mg, Na, K), Dissolved and Dissolved Metals	HCL: Mercury (LL-1631)	H2SO4: Nitrate + Nitrite (as N), Ammonia	NaOH: Cyanide (Tot & WAD)						REMARKS
				GW															
				GW															
				GW															
				GW															
				GW															
				GW															
				GW															
				GW															
				GW															

Collected/Relinquished By: (1)	Date	Time	Received By:	Shipping Carrier: Shipping Ticket No:	Samples Received Cold? YES NO Temperature °C: _____._____
Relinquished By: (2)	Date	Time	Received By:	Special Deliverable Requirements: **KEEP COOL / DO NOT FREEZE**	Chain of Custody Seal: (Circle) INTACT BROKEN ABSENT
Relinquished By: (3)	Date	Time	Received By:	Requested Turnaround Time and Special Instructions: **Alk* - Alkalinity, CO3, HO3, OH** **Metals, Total: Al, As, Ba, Cd, Fe, Li, Mn, Ni, Zn (200.7/200.8)**	
Relinquished By: (4)	Date	Time	Received For Laboratory By:		

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SGS Environmental Services Inc.
Laboratory Division

Locations Nationwide

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CLIENT: **Donlin Gold LLC**

CONTACT: **Tisha Woolley** PHONE NO: **(907) 569-0342**

PROJECT: **Donlin Gold SW** SITE/PWSID#:

REPORTS TO: **Nick Enos and Tisha Woolley**

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SHORT LIST - 1
Donlin Gold Surface Water (SW)

page _____ of _____

LAB NO.	SAMPLE IDENTIFICATION	DATE	TIME	MATRIX	No CONTAINERS	PRES USED	NONE	NONE	HNO3	HNO3	HCL	H2SO4	NaOH	HCL					REMARKS
						SAMPLE TYPE C = COMP G = GRAB	pH, Cond, TDS, Alk*, Cl, SO4, Fluoride	TSS	Metals, Total	Cations (Ca, Mg, Na, K), Dissolved and Dissolved Metals	Mercury (LL-1631)	Nitrate + Nitrite (as N), Ammonia	Cyanide (Tot & WAD)	Methyl Mercury (Method 1630 - BrooksRand)					
				SW															
				SW															
				SW															
				SW															
				SW															
				SW															

Collected/Relinquished By: (1)	Date	Time	Received By:	Shipping Carrier: Shipping Ticket No:	Samples Received Cold? YES NO Temperature °C: _____._____
Relinquished By: (2)	Date	Time	Received By:	Special Deliverable Requirements: **KEEP COOL / DO NOT FREEZE**	Chain of Custody Seal: (Circle) INTACT BROKEN ABSENT
Relinquished By: (3)	Date	Time	Received By:	Requested Turnaround Time and Special Instructions: **Alk* - Alkalinity, CO3, HO3, OH** **Metals, Total: Al, As, Ba, Cd, Fe, Li, Mn, Ni, Zn (200.7/200.8)**	
Relinquished By: (4)	Date	Time	Received For Laboratory By:		

Appendix C
Contract Laboratory SOPs and QAP

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 Reuter	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.
\\usfs700\ank_groupdata\Public\DOCUMENT\SOP\~Approved_SOPs~

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:

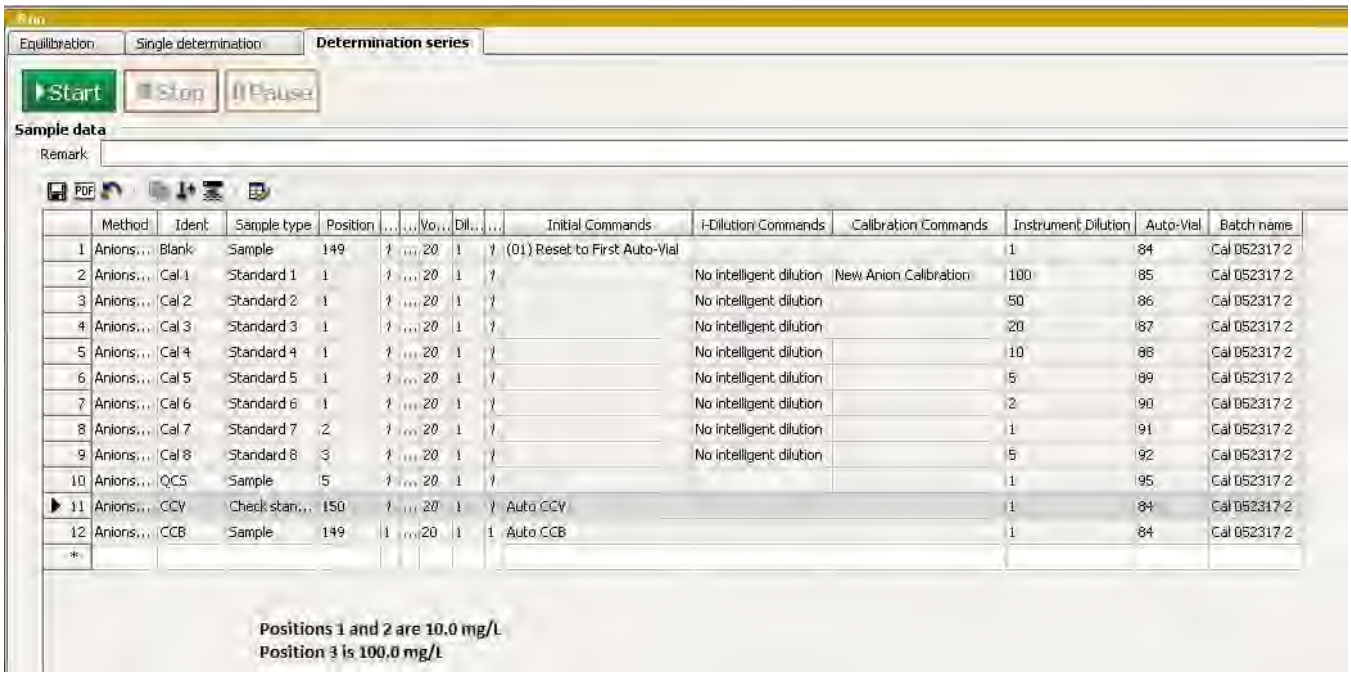
10.1. Recalibration for the instrument does not need to be done daily. It should be done when the QC fails more than once for instrument related reasons. It should also be done following any major maintenance on the instrument, such as changing the column. **Full instructions can be found in the MagIC 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	Initial Commands	i-Dilution Commands	Calibration Commands	Instrument Dilution	Auto-Vial	Batch name
1	Anions...	Blank	Sample	149	(01) Reset to First Auto-Vial			1	84	Cal 052317 2
2	Anions...	Cal 1	Standard 1	1		No intelligent dilution	New Anion Calibration	100	85	Cal 052317 2
3	Anions...	Cal 2	Standard 2	1		No intelligent dilution		50	86	Cal 052317 2
4	Anions...	Cal 3	Standard 3	1		No intelligent dilution		20	87	Cal 052317 2
5	Anions...	Cal 4	Standard 4	1		No intelligent dilution		10	88	Cal 052317 2
6	Anions...	Cal 5	Standard 5	1		No intelligent dilution		5	89	Cal 052317 2
7	Anions...	Cal 6	Standard 6	1		No intelligent dilution		2	90	Cal 052317 2
8	Anions...	Cal 7	Standard 7	2		No intelligent dilution		1	91	Cal 052317 2
9	Anions...	Cal 8	Standard 8	3		No intelligent dilution		5	92	Cal 052317 2
10	Anions...	QCS	Sample	5				1	95	Cal 052317 2
11	Anions...	CCV	Check stan...	150	Auto CCV			1	84	Cal 052317 2
12	Anions...	CCB	Sample	149	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.

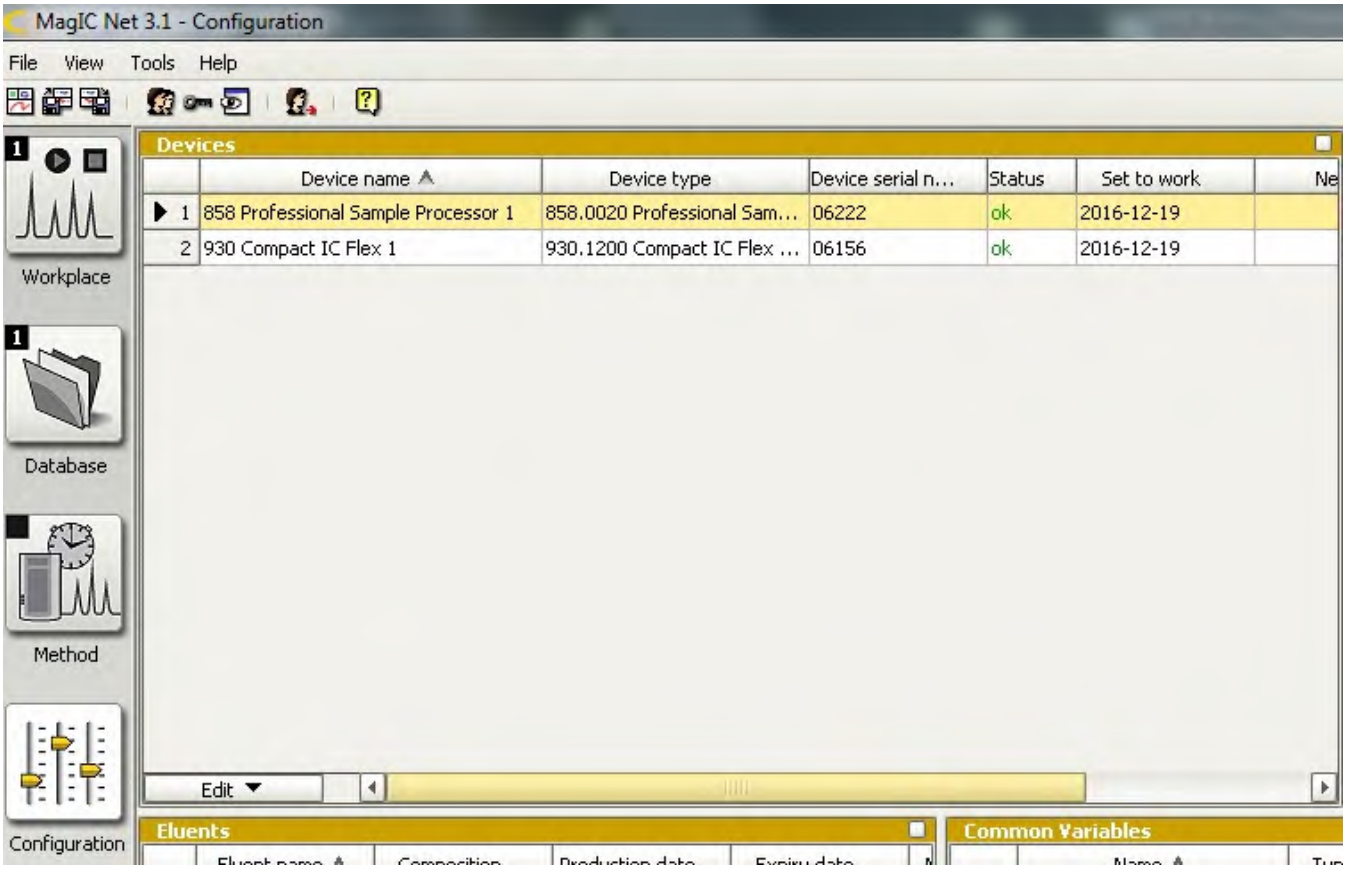


Figure 2 Configuration tab

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.

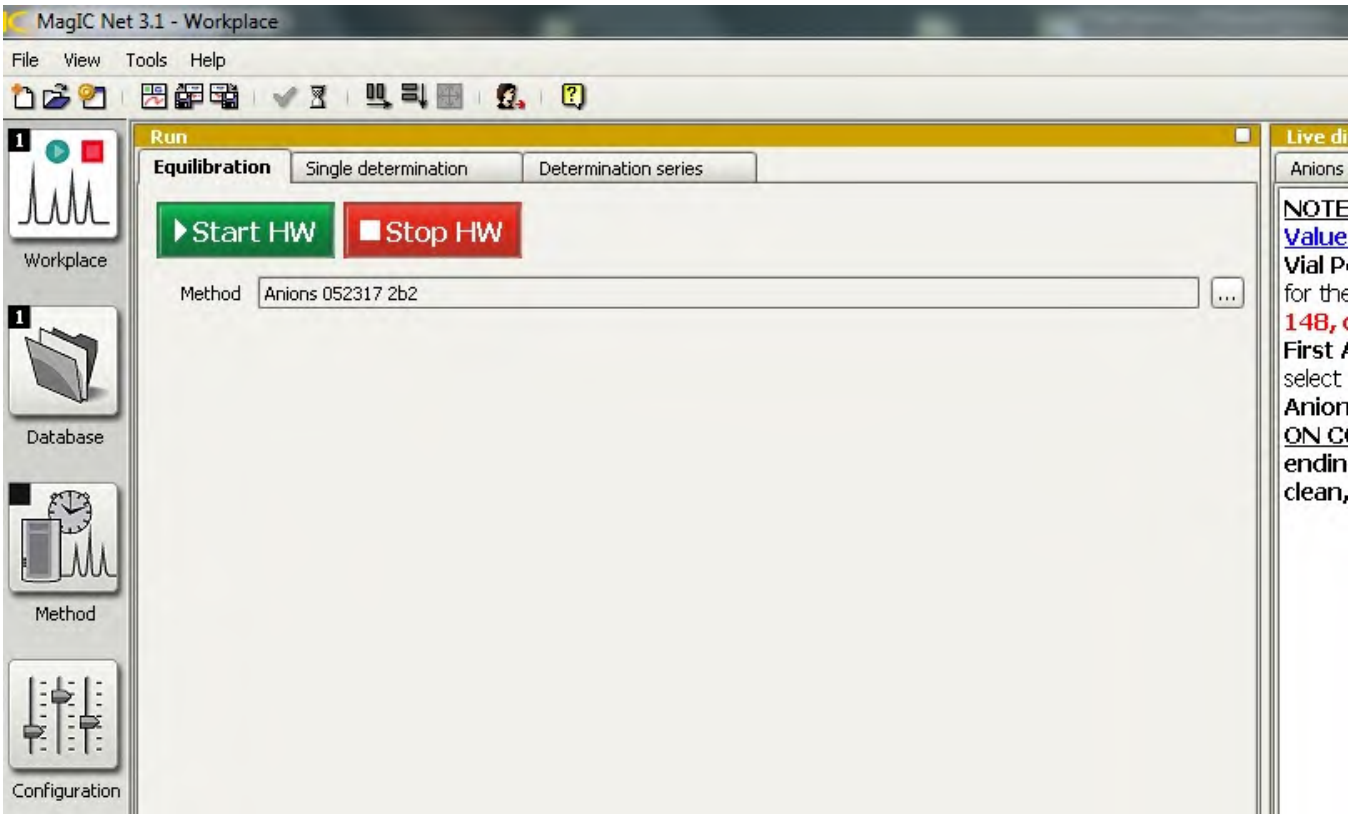


Figure 3 Equilibration tab

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.

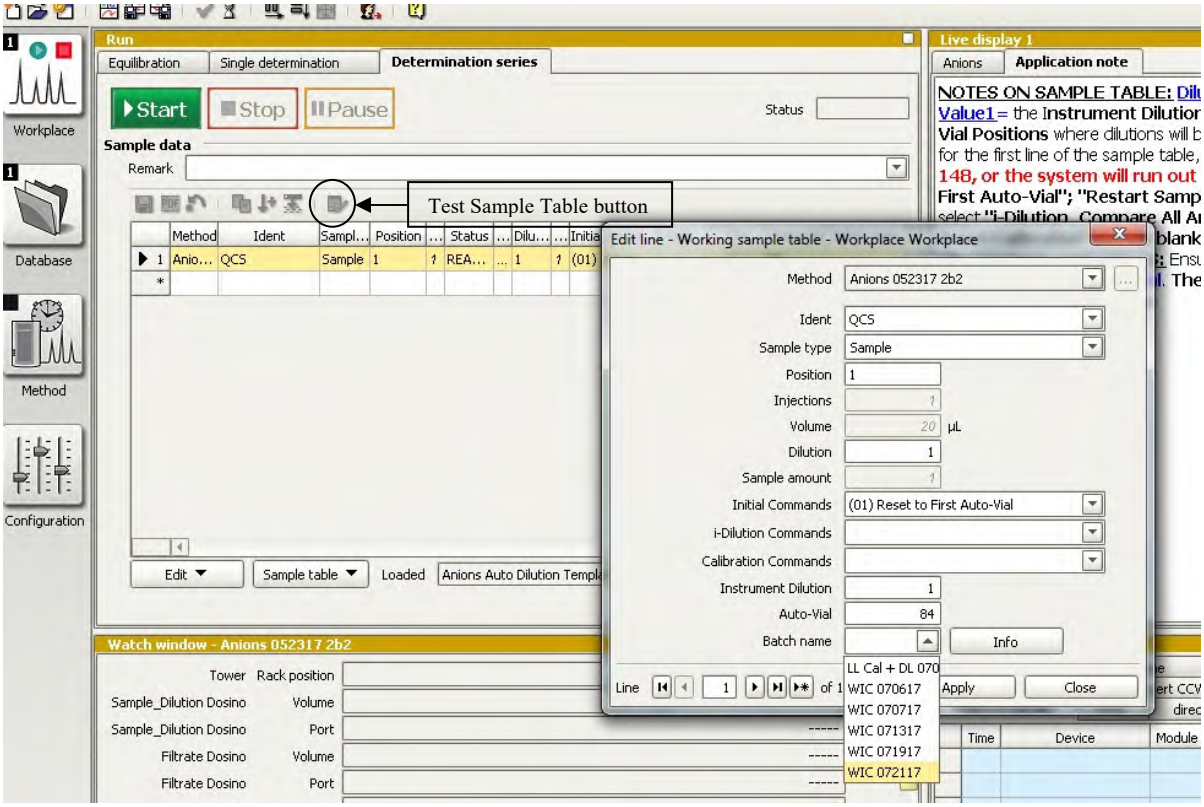


Figure 4 Sample scheduling window

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.	
Title: Total Fixed, & Volatile / Filterable & Non-Filterable Solids in Liquid **(TDS, TSS & DVS, SVS)**	**Revision Date**: October 2018
Method No: SM 2540 C, D, & E	**SOP No**: 329r14
Page: 1 of 16	**Supersedes**: 329r013

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	1/10/20	Samara Petty	01/10/20
Stephen C. Ede	10/23/18		10/23/18

Original cover pages with wet signatures and the digitally signed electronic SOP versions are available in the Quality Assurance Office.
A limited number of controlled hard copies will be issued for the Section Method SOPs & Technical Director's offices.

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: _____

Document Control Number _____ Issued by _____ Date _____

Addendum 1 added 1/27/2020 TPR

Morgan Morris 2018.10.26 10:31:29 -08'00'

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NOTE: This document contains CONFIDENTIAL business information and is not intended for distribution.	
S.O.P. Title: Total Fixed, & Volatile / Filterable & Non-Filterable Solids in Liquid **(TDS, TSS & DVS, SVS)**	**Revision Date**: January 2020
Method No: SM 2540 C, D, & E	**SOP No**: 329r14 Addendum #1
Page: 1 of 1	**Supersedes**: 329r13

Signatures below reflect approval for the following changes to the current SOP. These changes will be incorporated into the SOP during the next review. This addendum will be incorporated into the electronic SOP (i.e., PDF file).

Technical Director	Date	Quality Assurance (QA) Manager, QA Staff or their Designee	Date
Stephen C. Ede	1/27/20	Jamaica Pentry	1/27/2020

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: _____

The above referenced SOP should be modified as follows:

Change:

8.2 **TDS Standard**: 10000µs standard Conductivity/TDS Standard purchased certified, ~ 6,600 mg/L as KCl depending on lot number. Fisher brand 09-328-4 (or equivalent).

To:

8.2 **TDS Standards**:

8.2.1 10,000µs/cm Conductivity / TDS Standard purchased certified, ~ 6,600 mg/L as KCl depending on lot number. Fisher brand 09-328-4 (or equivalent).

8.2.2 1,000µs/cm Conductivity / TDS Standard purchased certified, ~ 660 mg/L as KCl depending on lot number. Fisher brand 09-328-3 (or equivalent).

Change:

12.1.3. Laboratory Control Sample / Laboratory Control Sample (LCS/LCSD): 1 set per batch of 20 or fewer samples. Use a 5.0mL pipette to dilute 5 ml of the Conductivity/TDS Standard to a final volume of 100mL with DI water, yielding a 330 mg/L concentration. The stock solution must be thoroughly mixed immediately before removing the portion to be filtered. Process as a sample. Recovery acceptance criterion is ± 25 %, Duplicate RPD acceptance criterion is ≤ 5 % of their average weight.

To:

12.1.3. Laboratory Control Sample / Laboratory Control Sample (LCS/LCSD): 1 set per batch of 20 or fewer samples. Use a 5.0mL pipette to dilute 5 ml of the 10,000µs/cm Conductivity / TDS Standard to a final volume of 100mL with DI water, yielding a 330 mg/L concentration. The stock solution must be thoroughly mixed immediately before removing the portion to be filtered. Process as a sample. Recovery acceptance criterion is ± 25 %, Duplicate RPD acceptance criterion is ≤ 5 % of their average weight.

Add section and renumber the following sections:

12.1.4. For drinking water samples, a low-level quantitation check (LLQC) needs to be evaluated for each batch of 20 or fewer samples. Use a 5 mL pipette to dilute 1.5 mL of the 1,000µs/cm Conductivity / TDS standard to a final volume of 100 mL with DI water. Process as a sample.

Summary of Changes from Previous Revision:

- Addendum 1 incorporated into SOP
- Addendum 2 incorporated into SOP
- Updated Sections 5.3.2., 11.3.4., and 11.5.4. to have a minimum residue of 1.0 mg to match LOQ value.
- Added 6.3. to mention samples are unpreserved
- Updated 17.2. to remove annual DL requirements for TDS. Removed mention of ADEC.
- Updated attachments C and D Duplicate RPD failure corrective action

Table of Contents

1.0. OBJECTIVE:

This document details a procedure for determining the Total, Fixed, and Volatile, filterable, and non-filterable solids in drinking, surface, and saline waters, domestic and industrial wastes.

2.0. SCOPE AND APPLICATION:

2.1. A well-mixed sample is evaporated in a prepared, dried and weighed "dish". Depending on the analysis required the sample may or may not be filtered.

2.2. The "dish" or filter is then dried at 105° or 180ºC.

2.3. If Volatile solids are needed the dried and weighed sample is ignited at 550º C in a muffle furnace.

3.0. DEVIATIONS FROM REFERENCE METHOD:

3.1. SM 2540 C for Total Dissolved Solids states that sample should be stirred with a magnetic stir bar prior to removing an appropriate volume into filtration system. Deviation: Samples are not stirred with a magnetic stir bar prior to use, rather samples are vigorously shaken prior to removing the sample volume with a class A graduated cylinder as stated in USEPA 160.2. **See control charts in method development folder for 2016**

3.2. SM 2540 D for Total Suspended Solids states that sample residue is dried for one hour, then cooled in a desiccator and weighed. Sample is weighed until a constant weight is achieved. Deviation: All samples are dried overnight and then weighed once.

3.3. SM 2540 E for Fixed and Volatile Solids Ignited at 550ºC states that ignition time for samples should be approximately 15 to 20 minutes. Deviation: All samples are ignited for 30 minutes.

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. This includes destruction of controlled copies of expired and retired SOPs. 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 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. A limited number of controlled hardcopies are to be distributed by the QA Office.

5.0. INTERFERENCES:

5.1. **TDS**

5.1.1 Hygroscopic samples containing highly mineralized waters require prolonged drying, desiccation and rapid weighing.

5.2. **TSS**

5.2.1 Remove non-representative particulates such as leaves, sticks, insects, etc. before analysis.

5.2.2 Suspended solids samples high in dissolved matter, such as saline waters, and some wastes, may retain dissolved matter such as salts and sugars on the filter. Additional washing of the filter may be necessary.

5.3. **TSS / TDS**

5.3.1 Clogging of the filter with too fine or too much material will prolong the filtering time and retain smaller particles that would normally pass through the filter. If complete filtration takes more than 10 minutes, decrease the sample volume.

5.3.2 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Choose sample volume to yield between 1.0 and 200 mg dried residue.

5.4. **Volatile Solids**

5.4.1. Negative values for volatile solids analysis may be produced by loss of volatile matter during ignition.

6.0. SAMPLE HANDLING:

6.1. Analysis must be initiated within seven days of collection.

6.2. Refrigerate the sample at 0-6^{o}C to minimize microbiological decomposition of solids.

6.3. Samples are unpreserved.

7.0. APPARATUS:

7.1. **TDS**: Glass Fiber Filter Discs, 4.7 cm without organic binder, Whatman, type 934-AH, Gelman type A/E, or equivalent.

7.2. **TSS**: XenoSep pre-weighed 47mm TSS filters, bar coded, Hach order # 2546200 or equivalent.

7.3. Porcelain crucibles (for Volatile solids)

7.4. 150mL pyrex beakers

7.5. Vacuum Pump and Manifold.

7.6. Membrane Filter Funnel.

7.7. Drying ovens, 180ºC ± 2°C (TDS) and 103ºC - 105°C (TSS).

7.8. Muffle Furnace

7.9. Desiccator.

7.10. Balance capable of weighing to 0.1 mg.

7.11. Tweezers

7.12. Class A Graduated Cylinder

7.13. Eppendorf pipetters and appropriate tips

7.14. Drierite® 10 – 20 mesh

7.15. 50 mL Class A Volumetric Pipette

7.16. For instrument and equipment maintenance, refer to the appropriate manual. For computer hardware/software, refer to IT.

8.0. REAGENTS:

8.1 Deionized (DI) water.

8.2 **TDS Standard**: 10000µs standard Conductivity/TDS Standard purchased certified, ~ 6,600 mg/L as KCl depending on lot number. Fisherbrand 09-328-4 (or equivalent).

8.3 **TSS standard**: NSI Lab Solutions (or equivalent) High Level Solids Standard (500 mg/L, Environmental Express order # NSIQCI-055H): Used as LCS for TSS.

9.0. EXTRACTION:

N/A

10.0. CALIBRATION:

The balance must be calibrated prior to use.

11.0. ANALYSIS:

11.1. TSS /SVS: Quality Approval Process for XenoSep pre weighed filters:

11.1.1. Each lot of filters will be approved by testing 2 filters.
Wash each filter through the vacuum system with 1000mL of distilled water. Continue to apply vacuum after the water has passed through to remove all traces of water.

11.1.2. Place filter in bar coded pan and dry in oven at 103 to 105°C to a constant dried weight. Place in desiccator until room temperature is reached.

11.1.3. Verify that the dried weight is equal to the documented weight recorded for that filter set ± 0.1mg. This is the verification for the lot # of filters to be used.

11.1.4. QC will assign a "L" number to that lot of filters.

11.2. For SVS: Do not use pre weighed filters use Watman 934-AH filters.

11.2.1. Wash each glass fiber filter through the vacuum system with 3 X 100mL of distilled water.

11.2.2. Place the filter in a porcelain crucible and ignite at 550ºC in the muffle furnace for 30 minutes.

11.2.3. Cool in the desiccator to room temperature and record the weight.

11.2.4. Process the sample by following steps from 11.3.

11.3. **Analysis TSS:**

11.3.1. Build a batch in Horizon.
- 11.3.1.1. Open Horizon
- 11.3.1.2. Select "Batching" followed by "New Batch"
- 11.3.1.3. Enter "STS" for queue and double click on "Total Suspended Solids"
- 11.3.1.4. Select "Clear Selections"
- 11.3.1.5. Check all desired samples. Then click "Build Batch"
- 11.3.1.6. Add necessary QC by selecting "Add QC" and selecting what is necessary
- 11.3.1.7. Open the ELN (Electronic LIMs Network)
- 11.3.1.8. Your user name and password are the same as your Horizon user name and password.
- 11.3.1.9. Enter the batch number in the "Batch:" box at the top left of the screen and click the arrow point to the right of the box to open the file.
- 11.3.1.10. Put the curser on a sample line in the "Pan Label" column, and scan the bar code on the filter pan, save.
- 11.3.1.11. Continue the process for the remaining samples.
- 11.3.1.12. Once samples have been filtered, enter the sample volumes, save.

11.3.2. Sample Preparation

11.3.3. Place XenoSep filter on membrane base and attach funnel.

11.3.3.1. Wet the filter with enough DI water to saturate the filter surface.

11.3.4. Shake sample vigorously and transfer an appropriate volume of sample to obtain minimum of 1.0 mg residue on filter (no more than 200 mg) or 1000mL of sample.

11.3.5. If entire sample volume is used, sample bottle must be rinsed and filtered through the filtration system. Also, the graduated cylinder used to measure the volume of the sample must be rinsed with DI water and added to the filtered sample.

11.3.6. When less than the full volume is used for analysis, insure that the portion analyzed is a homogenized representation of the total sample. Shake sample vigorously and measure an appropriate volume in a class A cylinder. Rinse the graduated cylinder used to measure the homogenized sample with DI water and add to the filtered sample.

11.3.6.1. If this lesser volume does not pass through the filter, the entire procedure must be repeated with a fresh filter.

11.3.7. Rinse the filter and holder three times with approximately 10-mL of DI water.

11.3.8. Continue to apply vacuum until filtration is complete and as much water as possible is removed from the filter. Remove filter from apparatus and place into drying pan.

11.3.9. Place the filter and pan in the 103º-105°C oven overnight. If rush results are required filters are dried at least 1 hour in the oven, weighed, and replaced in the oven for 1 more hour. A second weight must verify that a constant weight has been reached. The acceptance criteria are less than a 4% change from the previous weight or 0.5mg.

11.3.10. Cool in the desiccator ***to room temperature***.

11.3.11. Open the batch in ELN.

11.3.11.1. Tare the balance
11.3.11.2. Place each filter on the balance
11.3.11.3. Select the cell in the “Dry Weight” Column on the row of the current sample
11.3.11.4. Press “Print” on the balance to record the dry weight
11.3.11.5. Continue to complete all samples in the batch, save
11.3.11.6. For samples that require VSS, record the Container ID of the crucible used in the comments column
11.3.11.7. When all required fields have been filled out, select “Post Batch”
11.3.11.8. Open the batch in Horizon, open “auto post pipe” and select “auto post.”

11.4. TSS results are calculated in mg/L. Residue greater than 200mg may require reanalysis.

11.4.1 If SVS analysis is required, place the 105ºC dried & weighed filter in the muffle furnace for 30 minutes at 550°C. Cool in the desiccator and weigh.

11.4.1.1. Calculate VSS by subtracting the muffled weight from the dried TSS weight and divide the result by the sample volume. VSS should be calculated automatically by VSS/VDS spreadsheet

11.4.2. Verify the weight is constant by replacing sample in furnace for 30 minutes.

11.4.3. Repeat cooling and weighing process until the weight change obtained is within 4% or 0.5 mg of the original weight.

11.5. **TDS:**

11.5.1. **Preparation of evaporating dishes:**
Clean and heat numbered evaporating dish (150mL beakers) to 180°C ± 2°C for one hour. Cool in desiccator ***to room temperature***

11.5.2. **Build a batch in Horizon.**

11.5.2.1. Refer to 11.3.1.1 – 11.3.3.6 to create a batch in Horizon, apart from selecting "Total Dissolved Solids"

11.5.2.2. Open the ELN (Electronic LIMs Network) TDS spreadsheet.

11.5.2.3. Your user name and password are the same as your Horizon user name and password.

11.5.2.4. Enter the batch number in the "Batch:" box at the top left of the screen and click the arrow point to the right of the box to open the file.

11.5.2.5. Put the beaker on the balance and the curser on a sample line, enter weight. After all the tare weights are entered, "save".

11.5.2.6. Enter the Beaker ID in the "Pan ID" column

11.5.2.7. Once samples have been filtered, enter the volume used, save.

11.5.3. **Filtering:**

11.5.3.1. Place filter on assembled filtering apparatus and attach to a tared beaker with the sample number.

11.5.3.1.1. Wet the filter with enough DI water to saturate the filter surface.

11.5.3.2. Shake sample vigorously and transfer an appropriate measured volume of sample (typically 100mL) through filter apparatus.

11.5.3.3. Rinse and filter the graduated cylinder three times with approximately 10 mL of DI water.

11.5.4. Shake sample vigorously and transfer an appropriate volume of sample to obtain minimum of 1.0 mg residue on filter (no more than 200 mg) or 100mL of sample.

11.5.5. If entire sample volume is used, sample bottle must be rinsed and filtered through the filtration system. Also, the graduated cylinder used to measure the volume of the sample must be rinsed with DI water and added to the filtered sample.

11.5.6. When less than the full volume is used for analysis, insure that the portion analyzed is a homogenized representation of the total sample. Shake sample vigorously and measure an appropriate volume in a class A cylinder. Rinse the graduated cylinder used to measure the homogenized sample with DI water and add to the filtered sample.

11.5.6.1. If this lesser volume does not pass through the filter, the entire procedure must be repeated with a fresh filter.

11.5.7. Continue to apply vacuum until filtration is complete and as much water as possible is removed from the filter. Turn off vacuum when complete.

11.5.8. Remove the filter apparatus from the TDS beaker.

11.5.9. Place the beaker containing the sample in a 180°C ± 2°C oven overnight, or until dried to a constant weight.

11.5.10. Remove beakers from oven and cool ***to room temperature*** in the desiccator.

11.5.11. Open the batch in ELN.

11.5.11.1. Place the beaker on the balance, in the ELN click on the cell in the "dry weight" column. Press "Print" on the balance to record the dry weight

11.5.11.2. Continue with the remaining samples. Save the batch and click the "post" button.

11.5.11.3. Open the batch in Horizon, open "auto post pipe" and "auto post"

11.5.11.4. TDS is calculated in mg/L.

11.5.12. **For VDS: Samples that require VDS should not be placed in a batch with samples requiring only TDS. For samples that require VDS, use the VSS/VDS spreadsheet for both TDS and VDS batches in place of the ELN.**

11.5.12.1. Open the VDS/VSS excel spreadsheet and save a new copy in the "VDS" folder

11.5.12.2. Record HSN, volume, tare weight, and container ID (for crucibles / beaker)

11.5.12.3. Clean and heat numbered evaporating crucibles to 550°C for one hour. Cool in desiccator ***to room temperature***. Weigh & record the tare weight.

11.5.12.4. Follow TDS procedure using 30 ml and crucibles for the MB and samples. The LCS/LCSD are still in beakers, and 100 ml is used. Transfer the whole sample without exceeding the capacity of the crucible.

11.5.12.5. Once dried at 180ºC, cool in the desiccator to room temperature and record the dry weight.

11.5.12.6. The TDS results should be calculated automatically.

11.5.12.7. For VDS, place the 180ºC dried & weighed sample in the muffle furnace for 30 minutes at 550°C. **Do not place beakers in the muffle furnace. LCS/LCSD is not required for the VDS batch**

11.5.12.8. Cool in the desiccator and record the muffled weight (ign. Weight at 550°C).

11.5.12.9. Calculate VDS by subtracting the muffled weight from the dried TDS weight and divide the result by the sample volume. The spreadsheet should calculate VDS automatically

11.5.12.10. Verify the weight is constant by replacing sample in the furnace for 30 minutes.

11.5.12.11. Repeat cooling and weighing process until the weight change obtained is within 4% or 0.5 mg of the original weight.

12.0. QUALITY CONTROL:

12.1. **TDS:**

12.1.2. **Blank (MB)**: 1 per batch of 20 samples by filtering 100mL of DI water. Acceptance criterion is ≤ LOQ

12.1.3. **Laboratory Control Sample / Laboratory Control Sample (LCS/LCSD)**: 1 set per batch of 20 or fewer samples. Use a 5.0mL pipette to dilute 5 ml of the Conductivity/TDS Standard to a final volume of 100mL with DI water, yielding a 330 mg/L concentration. The stock solution must be

thoroughly mixed immediately before removing the portion to be filtered. Process as a sample. Recovery acceptance criterion is ± 25 %, Duplicate RPD acceptance criterion is ≤ 5 % of their average weight.

12.1.4. **Duplicate sample (DUP)**: 1 duplicate with each 10 samples (10%). The acceptance criterion for the sample / sample duplicate RPD is ≤ 5 % of their average weight.

12.1.5. **Weight verification**: Once every six months ten samples will be dried and weighed a second time to verify that overnight drying produces a constant weight. The acceptance criteria are less than a 4% change from the previous weight or 0.5mg. This verification is tracked in the run log.

12.2. **TSS:**

12.2.1. **Blank (MB)**: 1 per batch of 20 samples by filtering 1.0 L of DI water. Acceptance criterion is ≤ LOQ.

12.2.2. **LCS & LCSD:** 1 set per batch of 20 or fewer samples. Recovery acceptance criterion is ± 25 %, Duplicate RPD acceptance criterion is ≤ 5 % of their average weight.

12.2.2.1. Add a stir bar to the High Level Solids Standard (8.3.) and place on a magnetic stir plate. Measure 50 mL of High Level Solids Standard using a 50 mL volumetric pipette. Pipette to a 1000 mL graduated cylinder partially filled with DI water. Rinse the pipette with DI and bring to a final volume of 1000 mL. Process as a sample. LCS = 25 mg/L.

12.2.3. **Duplicate sample (DUP)**: 1 duplicate with each 10 samples (10%). The acceptance criteria for the sample / sample duplicate RPD is ≤ 5 % of their average weight.

12.2.4. **Weight verification**: Once every six months, ten samples will be dried and weighed a second time to verify that overnight drying produces a constant weight. The acceptance criteria are less than a 4% change from the previous weight or 0.5mg. This verification is tracked in the run log.

12.3.1. SVS/DVS:

12.3.1.1. Process the MB and duplicate samples in the batch through the 550ºC ignition. The LCS & LCSD are not required for volatile analysis.

12.4. Refer to Attachment C and D for appropriate corrective actions. Any corrective action required to address a QC outlier which is not listed in this SOP requires the approval of the QA Manager or Technical Director.

13.0. CALCULATIONS:

For TDS & TSS (13.1 & 13.3) the tare weight and dry weight are entered electronically from the balance to the ELN. The volume and container ID are entered in the ELN by the analyst. The following calculations are a product of the ELN. An Excel Spreadsheet is used in place of the ELN for VSS and VDS.

For Volatile Solids (13.2, 13.4, & 13.5) determination, the controlled Excel spread sheet is found at:

\\usfs700ankgroupdata\Public\DOCUMENT\Calculations\Waters

13.1. **TSS**: **mg/L Total Suspended Solids =** $\frac{\text{(dry wt. @105º - tare wt.) X 1000}}{\text{(volume in mL)}}$

13.2. **SVS: mg/L Volatile SS** = [(dry wt. @105º) - (ignited wt. @550º)] X 1000
(volume in mL)

13.3. **TDS**: **mg/L Dissolved Solids =** (dry wt. @180º - tare wt.) X 1000
(volume in mL)

13.4. **DVS: mg/L Volatile DS** = [(dry wt. @180º) - (ignited wt. @550º)] X 1000
(volume in mL)

13.5. **Fixed Solids: mg/L** = (ignited wt. @550º - tare wt.) X 1000
(volume in mL)

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.

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. 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. Further guidance on performing a DL study can be found in SOP 116.

17.2. **TDS:** DL studies are performed initially, when a new operator is trained, when a new instrument is purchased for analysis, or when a major modification to the methodology is made.
17.2.1. The suggested DL spiking level for TDS is 10 mg/L. The current DL for TDS is 3.1 mg/L.

17.3. **TSS:** A DL study is performed initially, when a new instrument is purchased for analysis or when a major modification to the methodology is made.
17.3.1. The suggested DL spiking level for TSS is 0.5 mg/L. The current DL for TSS is 0.15 mg/L.

18.0. LIMIT OF DETECTION (LOD):

The LOD is defined per SOP 116; LOD studies are not required for TDS or TSS.

19.0. LIMIT OF QUANTITATION (LOQ):

The LOQ is defined per SOP 116; LOQ studies are not required for TDS or TSS.

20.0. REFERENCES:

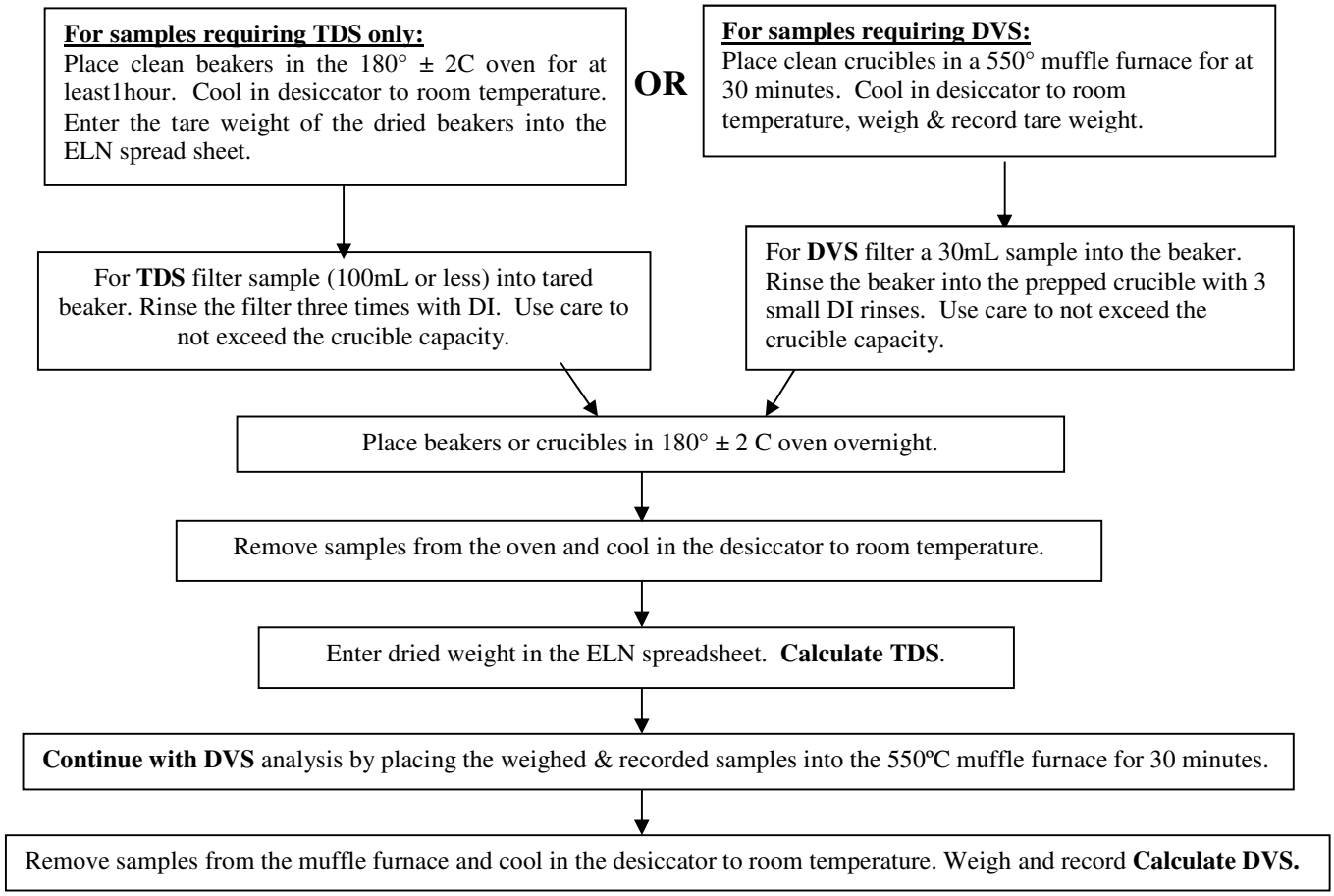
SM 22nd Edition, 2540 C. Total Dissolved Solids Dried at 180ºC
SM 22nd Edition, 2540 D. Total Suspended Solids Dried at 103 - 105ºC
SM 22nd Edition, 2540 E. Fixed and volatile Solids Ignited at 550ºC

21.0. ATTACHMENTS:

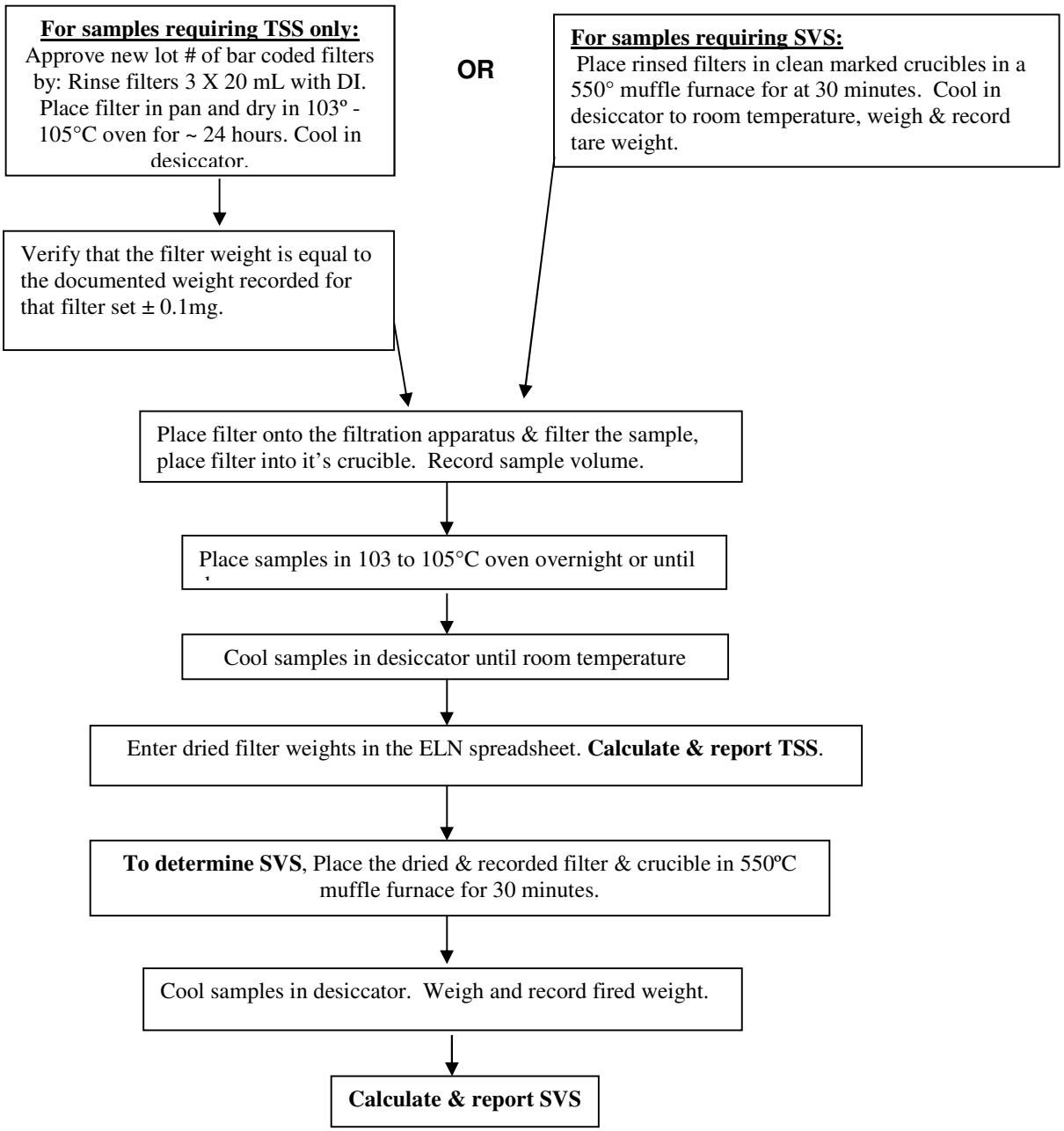
Attachment A: Flow Chart (TDS/DVS)
Attachment B: Flow Chart (TSS/ SVS)
Attachment C: Corrective Action Table (TSS/TDS)
Attachment D: Corrective Action Table (SVS/DVS)

ATTACHMENT A: FLOW CHART

TDS / DVS



ATTACHMENT B: FLOW CHART
TSS / SVS



ATTACHMENT C: CORRECTIVE ACTION TABLE (TSS / TDS)

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM 2540C SM 2540D (TSS/TDS)	Method Blank	1 per batch of ≤ 20 samples.	Result must be < the LOQ.	1. Reanalyze any sample ≥LOQ and ≤10X level of blank contamination.
	LCS LCSD	1 set per batch of ≤ 20 samples.	Recovery ± 25% RPD ≤ 5%	1. If the QC recovery >125% reanalyze the batch. 2. If the recovery <75% reanalyze all samples > LOQ. 3. LCSD used for RPD only when needed.
	Sample Duplicate	1 duplicate sample at 10% interval	≤ 5% of the average weights	1. Qualify Duplicate if weight difference < LOQ 2. If result is still out, qualify with the LCS/LCSD RPD and flag the sample as heterogeneous.

ATTACHMENT D: CORRECTIVE ACTION TABLE (SVS / DVS)

Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM 2540D SM 2540E (DVS/SVS)	Method Blank	1 per batch of ≤ 20 samples.	Result must be < LOQ.	1. Reanalyze any sample ≥LOQ and ≤10X level of blank contamination.
	Sample Duplicate	1 duplicate sample at 10% interval	≤ 5% of the average weights	1. Qualify Duplicate if weight difference < LOQ. 2. Reanalyze batch if sample volume allows

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 in Drinking Water and Wastewater by ICP/MS	**Revision Date**: April 2020
Method No: EPA 200.8	**SOP No**: 340r14
Page: 1 of 22	**Supersedes:** 340r13

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	4/13/20	Jamara Penton	4/13/2020

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

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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: _____

Addendum added 7/20/2020 by TPR

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 in Drinking Water and Wastewater by ICP/MS	**Revision Date**: July 2020
Method No: EPA 200.8	**SOP No**: 340r14 Addendum 1
Page: 1 of 1	**Supersedes**: 340r13

Signatures below reflect approval for the following changes to the current SOP. These changes will be incorporated into the SOP during the next review. This addendum will be incorporated into the electronic SOP (i.e., PDF file).

Technical Director	Date	Quality Assurance (QA) Manager, QA Staff or their Designee	Date
Stephen C. Ede	7/17/20	Jamaica Rentty	7/17/2020

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: _____

The above referenced SOP should be modified as follows:

Change:

2.3. Samples will be routinely digested by the 200.2 method before analysis. Samples that require Mercury will be screened for turbidity. If the turbidity is <1 NTU then the sample will be analyzed without being digested. If the turbidity is ≥ 1 NTU, the sample will not be run by EPA 200.8. The sample may be analyzed by EPA 245.1, either in-house or it may be subcontracted.

To:

2.3. Samples will be routinely digested by the 200.2 method before analysis. Samples that are a matrix 0 (PWSID Drinking Water) and require Mercury will be screened for turbidity. If the turbidity is <1 NTU then the sample will be analyzed without being digested. If the turbidity is ≥ 1 NTU, the sample will not be run by EPA 200.8. The sample may be analyzed by EPA 245.1, either in-house or it may be subcontracted. Samples that are a matrix 1, 6 or 9 (non PWSID) that require Mercury will not be screened for turbidity and will be analyzed without being digested with an additional dilution.

Change:

11.3.3 Pour all digested samples into 14 mL test tubes and place in the appropriate autosampler position. Undigested mercury samples must be diluted by a factor of 2.5X with the appropriate diluent (Section 8.15). Further dilutions can be made if the sample exhibits a difficult matrix or has proven to exceed the linear range for an element of interest.

To:

11.3.3 Pour all digested samples into 14 mL test tubes and place in the appropriate autosampler position. Undigested matrix 0 mercury samples must be diluted by a factor of 2.5X with the appropriate diluent (Section 8.15). Undigested matrix 1, 6 or 9 mercury samples must be diluted by a factor of 5X with the appropriate diluent (Section 8.15). Further dilutions can be made if the sample exhibits a difficult matrix or has proven to exceed the linear range for an element of interest.

Summary of Changes from Previous Revision:

- Updated section 12.1.1
- Updated section 12.2.2
- Added EPA 200.8 method in the reference section

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 EPA 200.8[1] using the NexION 300 Inductively Coupled Plasma-Mass Spectrometer or ICP-MS.

2.0. SCOPE AND APPLICATION:

2.1. This Standard Operating Procedure describes the daily operation, tuning, optimization, and analysis procedures for the analysis of samples according to U.S. EPA Method 200.8 Rev 5.4, 1994.

2.2. This method is applicable to ground waters, surface waters, drinking waters, and wastewaters.

2.3. Samples will be routinely digested by the 200.2 method before analysis. Samples that require Mercury will be screened for turbidity. If the turbidity is <1 NTU then the sample will be analyzed without being digested. If the turbidity is $\geq$ 1 NTU, the sample will not be run by EPA 200.8. The sample may be analyzed by EPA 245.1, either in-house or it may be subcontracted.

2.4. Routine operation and maintenance procedures for the NexION 300 ICP-MS may be found in the NexION Training Manual provided by the instrument manufacturer.

2.5. Detailed instructions on operating the NexION 300 ICP-MS operating software may be found in the NexION Training Manual.

2.6. Detailed information regarding EPA Method 200.8 requirements may be found in version 5.4 of Method 200.8.

2.7. This SOP is designed for use with the Method 200.8 for NexION 300 method.

2.8. Initial Performance Data: It is the responsibility of the user of this SOP to generate the required performance data on the user's specific instrument before the analysis of any samples.

2.9. Aqueous samples, 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 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. Standards are matrix matched at 2% nitric acid and 0.2% hydrochloric acid as opposed to 1% nitric acid as stated in Method 200.8.

3.2. Correction equations for polyatomic interferences are those recommended in Table 5 of Method 200.8 and are not established daily. For elements requiring correction equations that are not listed in Method 200.8, equations from the instrument manufacturer are used.

3.3. Internal standards typically used are Sc, Ge, In, and Th as opposed to the mix of Sc, Y, In, Tb, and Bi as stated in Method 200.8.

3.4. Method 200.8 states in Section 3.5 that the IDL is three times the standard deviation of a series of ten replicate measurements of a calibration blank. This laboratory is currently using the SW846 protocol to determine the IDL so that the IDL can be utilized for both methods. SW 846 criteria are more detailed and must meet more stringent criteria (see Section 12.1.1. of this SOP).

3.5. The instrument is tuned to Be, Mg, In, U, and Ce rather than Be, Mg, Co, In, and Pb as stated in Method 200.8

3.6. The LFB/LCS analyte concentrations are not within the recommended range of Method 200.8 Section 7.9.

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 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 ICP/MS 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. This method is suitable for samples containing < 0.1 mg/L silver. For samples containing silver at concentrations ≥ 0.1 mg/L, notify the supervisor or project manager. A sample may need to be prepared a second time, or diluted in an approved manner.

6.0. SAMPLE HANDLING:

Refer to SOP 367 (Total Recoverable and Dissolved Metals Preparation) for sample preservation. Digests are stored for one month prior to disposal.

7.0. APPARATUS:

7.1. Perkin-Elmer NexION 300 ICP-MS system, or equivalent, includes the NexION 300 instrument, computer system, ELAN NT software, printer, and auto sampler. Instrument capable of scanning the mass range 5-250 amu with a minimum resolution of 1 amu peak width at 5% peak weight.

7.2. Instrument maintenance logs must be maintained per SGS SOP 111 and 500.

7.3. Recommended peristaltic pump tubing (other sizes may be used to enhance performance or reduce pulsations produced by the pump):

Tab colors	I.D. mm	Purpose
Black – Black	0.75	Sample introduction
Green – Orange	0.51	Internal standard introduction
Grey – Grey	1.3	Spray chamber drain

7.4. SC-2 Autosampler (ESI no. SC-8102-1341-54) or equivalent

7.5. Calibrated mechanical pipettes: 20–200 µL, 200–1000 µL, 1000–5000 µL

7.6. Class A volumetric labware for the preparation of calibration standards.

7.7. Metal-free plastic pipette tips (for the pipettes specified in Section 7.5).

7.8. 14 mL disposable auto sampler tubes. (VWR # 60818-614 or equivalent)

7.9. 50 mL freestanding graduated digestion vessels for standards (VWR # 21008-480 or equivalent)

7.10. Argon gas: High purity grade (99.99%)

8.0. REAGENTS:

8.1. All stock solutions/chemicals/reagents must be traceable back to documented records. Refer to SGS SOPs 500 and 112 and PX-001 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.

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) sub-boiled distilled according to the most recent approved revision of SOP 348.

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, Au, Th,
Cd, Hg, In, Sn, Sb, Sr, Ba, Tl, Pb, Bi, U, Na, Mg, Si, P, K, Ca, Ti, Fe, Ce, Ir.

8.6. Daily Tuning Stock Solution:

For example, prepare by filling a 50 mL volumetric vessel with about 20 mL of reagent water and 2.5 mL concentrated nitric acid. Pipette the appropriate amount of each element stock solution into the vessel. Dilute to the 50 mL mark with reagent water and mix well. Refer to **CX-0003** for the current preparation.

8.7. Daily Tune Solution:

Prepare by pipetting 50 µL of Daily Tuning Stock Solution (Section 8.6) into a 50 mL volumetric vessel filled with 20 mL of reagent water and 1.0 mL of concentrated nitric acid. Dilute to the 50 mL mark with reagent water and mix well.

8.8. Internal Standard Solution of Sc, In, Ge, and Ir. Enriched Li^6 may also be used as an option to Sc, if the need arises, for isotopes with atomic mass units less than 20. Prepare by pipetting the elements at listed volumes into a 4 liter container with approximately 1,000 mL of reagent water, 80 mL of nitric acid and 4 mL of a 10,000 µg/mL gold standard for a final concentration of 10 µg/mL gold. 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.

8.9. Stock Calibration Standard Solutions: Standards may be prepared from single element solutions or a custom blended solution. All solutions for each stock standard are pipetted into a 100 mL Class A Teflon volumetric flask with about 30 mL of reagent water and 5 mL nitric acid. For the Hg standard 0.2 mL of 1,000 µg/mL gold is added for a concentration of 2 µg/mL. After all elements for each solution have been added, fill the flask to the mark with reagent water. Refer to **CX-0005** for the current preparations for 200.8 Cal 1-4. Refer to **CX-0022** for the current preparation of Hg Cal.

8.10. Stock QCS (Quality Control Sample) solutions: The QCS stock solutions 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 pipetted into a 100 mL Class A Teflon volumetric flask with about 30 mL of

reagent water and 5 mL nitric acid. For the Hg standard 0.2 mL of 1,000 µg/mL gold is added for a concentration of 2 µg/mL. After all elements for each solution have been added, fill the flask to the mark with reagent water. Refer to **CX-0005** for the current preparations for 200.8 QCS 1-4. Refer to **CX-0022** for the current preparation of Hg QCS.

8.11. Post Digestion Spike (BND): Post Digestion Spike (BND): Pipette 50 µL of Hg QCS and QCS 1-4 (Section 8.10) into a 14-mL test tube, match the analytical dilution and pipette enough diluent for a final volume of 5 mL. If there is no analytical dilution, pipette enough sample (4.75 mL) for a final volume of 5 mL. Mix.

8.12. Working calibration scheme: Prepare fresh calibration standards daily in Class A volumetric labware. Prepare the calibration standards according to the chart 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.

A/S Position	Solution	Ingredients	Acids/Au	Final vol. (mL)
1	Blank	Reagent water	1.0 mL HNO_3 100 µL HCl	50
6	Standard 5	500 µL each of stock Cal Hg, 1,2,3,4	1.0 mL HNO_3 100 µL HCl	50
5	Standard 4	10 mL of Standard 5	0.8 mL HNO_3 80 µL HCl	50
4	Standard 3	10 mL of Standard 4	0.8 mL HNO_3 80 µL HCl	50
3	Standard 2	10 mL of Standard 3	0.8 mL HNO_3 80 µL HCl	50
2	Standard 1	10 mL of Standard 2	0.8 mL HNO_3 80 µL HCl	50
7	ICV / CCV	100 µL each of stock Cal Hg, 1, 2, 3, 4	1.0 mL HNO_3 100 µL HCl	50
8	QCS	500 µL each of stock QCS Hg, 1, 2, 3, 4	1.0 mL HNO_3 100 µL HCl	50

8.13. 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.

8.14. Sample Diluent/Carrier Solution: 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.

8.15. Diluent for undigested mercury samples: diluent contains 2.0% (v/v) nitric acid and 0.0167% HCl. Volumes may be made as necessary at a ratio of 20.0 mL nitric and 1.67 mL HCl per 1000 mL of reagent water.

8.16. Rinse: containing 4.0% (v/v) hydrochloric acid, 2.0% (v/v) nitric acid, and 1 µg/mL Au. Volumes may be made as necessary at a ratio of 80.0 mL of HNO_3, 160.0 mL of HCL, and 0.4 mL of 10,000 µg/mL Au per 4,000 mL of reagent water.

9.0 EXTRACTION:

Refer to SOPs 367 (Total Recoverable and Dissolved Metals Preparation) for sample preparation.

10.0 CALIBRATION:

10.1 Multipoint calibration (default calibration method). 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. Weighted calibration is allowed with approval from QA for select elements.

10.1.1 Prepare the calibration standards as described in Section 8.12 to produce standards at concentrations in µg/L listed in the chart below and entered into the calibration page of the analytical method in the ICP/MS software.

10.1.2 The lowest concentration listed for each analyte should be equal to or less than the LOQ

Element	Std 1	Std 2	Std 3	Std 4	Std 5	Element	Std 1	Std 2	Std 3	Std 4	Std 5
Li			4	20	100	Sb	0.4	2	10	50	250
Be	0.16	0.8	4	20	100	Ba		1	5	25	125
B		4	20	100	500	Tl		0.2	1	5	25
Al			8	40	200	Pb	.08	0.4	2	10	50
V			8	40	200	Bi	0.4	2	10	50	250
Cr	0.4	2	10	50	250	Th	.08	0.4	2	10	50
Mn	0.4	2	10	50	250	U	.08	0.4	2	10	50
Co		1.6	8	40	200	Na		100	500	2500	12,500
Ni		0.8	4	20	100	Mg	20	100	500	2500	12,500
Cu	0.4	2	10	50	250	Si		80	400	2000	10,000
Zn		2	10	50	250	P			80	400	2000
As		2	10	50	250	K		100	500	2500	12,500
Se		2	10	50	250	Ca		100	500	2500	12,500
Mo		0.8	4	20	100	Ti		2	10	50	250
Ag		0.2	1	5	25	Fe		100	500	2500	12,500
Cd	0.2	1	5	25	125	Sr	2	10	50	250	1250
Sn	0.4	2	10	50	250	Hg	0.032	0.16	0.8	4	20

10.2 The ICP/MS software labels calibration solutions as follows: Blank, Standard 1, Standard 2, Standard 3, Standard 4, and Standard 5.

10.3 The R-value (linear regression correlation coefficient) for each analyte must be greater than or equal to 0.995.

10.4 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 minutes.

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 Open the "SGS SmartTune Daily.wrk" workspace.

11.2.2 While using the Dual Detector Solution (Section 8.13), 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 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.

11.2.3 Switch to the Daily Tune Solution (Section 8.7) after rinsing the lines. Select the "Mass Calibration and Resolution" tab, 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.

11.2.3.1 The measured mass for each analyte must be +/- .05 AMU of the exact mass.

11.2.3.2 The measured peak width must be 0.7 amu, +/- 0.1 amu at 10% peak height (per Perkin Elmer recommendations). EPA 200.8 states 0.75 amu at 5% peak height. The peak width of 10% at 0.7 amu will be less than 5% at 0.75 amu. The decrease in peak width is accounted for by the increase in resolution from 0.75 to 0.7 amu.

11.2.4 Select the "Autolens" 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.

11.2.5 Select the "Daily Performance Check" tab, right click and select "Quick Optimize". The software will automatically check the limits except for the RSD. Make adjustments and rerun if there is a failure. After each run the results will print out.

11.2.5.1 The RSDs for the five replicates of Be, Mg, In and U need to be less than or equal to 5%.

11.2.5.2 Monitor daily performance measures for Be sensitivity, Mg sensitivity, In sensitivity, U sensitivity, background, % double charged and % oxide levels.

Background at mass 220	< 5 cps
Ce++ double charged	≤3%
CeO/Ce Oxide	≤3%
Be intensity	> 2,000 CPS
Mg intensity	> 15,000 CPS
In intensity	> 40,000 CPS
U intensity	>30,000 CPS

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. **This performance report must be printed and submitted with each analytical batch.

11.3 Open the "SGS 200.8.wrk" workspace that contains the method and sample worksheet for analysis.

11.3.1 Calibration standards and QC solution prepared in Section 8.12 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. Ensure that the proper dilution factor is entered for each sample. Save the sample window with the date of analysis.

11.3.3 Pour all digested samples into 14 mL test tubes and place in the appropriate autosampler position. Undigested mercury samples must be diluted by a factor of 2.5X with the appropriate diluent (Section 8.15). Further dilutions can be made if the sample exhibits a difficult matrix or has proven to exceed the linear range for an element of interest.

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 Select the samples to be analyzed 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 Press the Analyze Batch button.

11.3.7 All samples containing target analytes above linear range shall be diluted and re-analyzed.

11.3.8 Any samples that have Hg above 5 mg/L will be re-analyzed at a dilution in order to have the result from the instrument be less than 5 µg/L.

11.4 At the end of the analytical run, print out the following and include them with the raw data:

11.4.1 Open the "report option window."

11.4.2 Open "CAL REPORT.rop" file and print the report view.

11.4.3 Open "RUN-COVER.rop" file and print the report view.

11.4.4 Click back on the "report option window."

11.4.5 Open "SGS.rop" file to reset.

11.5 A low level quantitation (LLQ) is extracted and analyzed with each drinking water batch.

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) - 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 Limits (DLs) - In order to determine the DL in a matrix, the analytes should be spiked into the matrix of interest (e.g. 200.2 sample preparation blank, ground water matrix, or other sample preparation procedure matrix) at a level that is two 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 As defined by EPA Method 200.8, the linear range "…should be an observed signal no more than 10% below the level extrapolated from lower standards." Analyte concentrations that are greater than 90% of the determined Linear Range must be diluted and re-analyzed.

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:

- 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)

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 *Initial Calibration Verification (ICV)*: the ICV is analyzed immediately after completion of calibration procedures to verify that the generated calibration curve is valid. All analytes of interest must fall within 10% of the expected value. If that 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 re-calibration must be performed.

12.3.2 *Quality Control Sample (QCS*): the QCS is analyzed immediately following the ICV to verify the accuracy of the calibration curve. All analytes of interest must be within 10% of the expected 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 re-calibration must be performed.

12.3.3 *Continuing Calibration Blank (CB)*: the CB is analyzed following QCS and CCV samples. In the CB all analytes of interest should be below the established LOQ. The CB may be analyzed a second time if the analytes of interest are not below the LOQ. If the CB cannot be brought below the LOQ for the analytes of interest, there are several options. If an analyte is detected in the CB but is not detected in the sample, or if the analyte is greater than ten times the level detected in the CB, the data can be reported with appropriate comments. All samples that do not meet those criteria must be re-analyzed after the instrument has been recalibrated. If a CB failure occurs consistently with one or more elements, then a re-evaluation of the IDL and DL for those analytes may be required.

12.3.4 *Continuing Calibration Verification (CCV)*: the CCV is analyzed at a rate of not greater than every 10 samples and at the end of an analytical batch. All analytes of interest must be within 15% of the expected results. If the 15% criteria is not met, 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 re-calibration must be performed.

12.3.5 *Internal Standards*: the internal standards must be monitored in all solutions to correct for instrumental drift. The ICP/MS software will report the % recovery for each internal standard being used. The intensities of internal standards in all solutions analyzed must be within 60-125% of the levels in the blank used for calibration.

12.3.5.1 Samples of significantly different matrix may cause the internal standards to fall outside tolerance levels. These samples may be serially diluted by additional factors of 5 until the internal standards fall within limits.

12.3.5.2 Persistent failure of internal standards indicates that the instrument has drifted outside of acceptable limits relative to the initial calibration and requires the instrument to be re-calibrated and to re-analyze all affected samples.

12.3.6 *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 LOQ values. If results for analytes of interest exceed the LOQ, then all associated samples must be re-processed through the digestion procedure unless the associated samples are non-detect or contain concentrations of analyte greater than 10x the MB contamination. All samples reported with MB contamination above the LOQ must have a comment with appropriate qualifiers.

12.3.6.1 The MB will be evaluated at the DL for drinking water.

12.3.7 *Laboratory Control Sample (LCS)*: the LCS is reagent water that has been spiked with known concentrations of analytes that are 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. Results for the LCS must fall within 15% of expected concentrations for all analytes of interest. If an analyte of interest in the LCS is greater than 115% of the expected value and the associated sample results for that analyte are below the LOQ, then those samples may be reported with a comment. If an analyte of interest in the LCS is less than 85% of the expected value, then those samples affected must be re-processed through the digestion procedure.

12.3.7.1 *Low Level Quantitation (LLQ):* the LLQ is reagent water that has been spiked wat the concentration of the LOQ. One LLQ will be prepared and analyzed for each batch of 20 samples or less for drinking water samples.

12.3.8 *Matrix Spike (MS)*: the MS is prepared and analyzed to determine the accuracy of the analytical system. At least 10% of the samples within an analytical batch must be spiked with known concentrations of all analytes of interest and evaluated for spike recovery. Samples are spiked at a level equal to that of the LCS. Spike recoveries must be between 70% and 130% for all analytes of interest in which the sample concentration is not greater than 4x the spike concentration. If any analyte does not meet these recovery criteria in the matrix spike perform a bench spike (BND).

12.3.9 *Matrix Spike Duplicate (MSD)*: the MSD is performed only on a client request basis and is used to gauge the precision of the analytical system. Spike recoveries must be between 70% and 130% for all analytes of interest in which the sample concentration is not greater than 4x the spike concentration. The relative percent difference (RPD) between the MS and MSD must be 20% or less. A sample with a MS/MSD RPD outside 20% should be commented on appropriately.

12.3.10 *Post-Digestion Spike (BND)*: the BND is performed only on samples which do not meet MS evaluation criteria. An aliquot of digested sample at standard or inflated dilution is spiked with a known concentration of analyte. The concentration of spike should be relative to the naturally occurring concentration in the sample. Recoveries calculated on the BND should be between 70% and 130% of the expected values. If the spike is not recovered within the acceptance limits, dilute the sample and re-spike at that dilution.

12.3.11 See Attachment A for specific corrective actions. Any corrective action needed to address a QC outlier that is not listed in this SOP requires approval of the QA Manager or Technical Director.

13.0 CALCULATIONS, REVIEW AND REPORTING:

13.1 The ICP/MS software performs all calculations necessary to convert raw data (ion counts/second). The calculated quantities are selected by choosing the desired options in the Report Options screen. The default report option for the 200.8 Method is CTE1.rop. If the user desires, this format can be edited and saved under a new name.

13.2 All calculations performed in the ICP/MS software are based on the ratio of analyte intensity (cps) to internal standard intensity (cps). In all calculations where internal standards are used, the ratio of analyte intensity to internal standard intensity is determined before any other calculation is performed.

13.3 Quality Control Sample results may be evaluated using the QC Checking features in the ICP/MS software. All values entered in the default 200.8 method should be checked and edited to match the true values used by the laboratory. The modified method can then be saved under a different name.

13.4 The percent recovery for standard solutions (both digested standards and the periodic quality control standards) is calculated by the following equation:

$$\frac{V_o}{V_e} \times 100 = \% \text{ recovery} \qquad \textit{Equation 1}$$

V_o = observed value of QC
V_e = expected value of QC

13.5 The percent recovery for matrix spiked solutions is calculated by the following equation:

$$\frac{V_o - S_c}{V_e} \times 100 = \% \text{ recovery} \qquad \textit{Equation 2}$$

V_o = observed value of spiked sample
S_c = observed value of the sample
V_e = expected value of spike

13.6 The relative percent difference between duplicate samples is calculated by the following equation:

$$\frac{|S_c - D_c|}{((S_c + D_c)/2)} \times 100 = \text{relative \% difference (RPD)} \qquad \textit{Equation 3}$$

S_c = observed value of sample
D_c = observed value of duplicate sample

13.7 The post-digestion spike (BND) recovery is calculated by the following equation:

$$\frac{BS_c - S_c}{BS_e} \times 100 = \% \text{ recovery} \qquad \textit{Equation 4}$$

BS_c = observed value of post-digestion spike
S_c = observed value of sample
BS_e = expected value of post-digestion spike

13.8 Samples that have been concentrated during the digestion procedure must have the concentration values 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 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.

14.8 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:

Detection Limit (DL) studies are performed annually for each EPA 200.8 analyst, 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 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.

19.0 LIMIT OF QUANTITATION (LOQ):

The LOQ is defined per SOP 116. 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 (µg/L)
Ag	1
Al	20
As	5
B	50
Ba	3
Be	0.4
Bi	1
Ca	500
Cd	0.5
Co	4
Cr	2
Cu	1
Fe	250
Hg	0.2
K	500
Li	10
Mg	50
Mn	1
Mo	2
Na	500
Ni	2
P	200
Pb	0.2
Sb	1
Se	5
Si	200
Sn	1
Sr	25
Ti	25
Tl	1
U	1
V	20
Zn	5

20.0 REFERENCES

20.1 "Methods for the Determination of Metals in Environmental Samples - Supplement 1", EPA-600/R-94-111, May 1994, Available at NTIS, PB 94-184942

20.2 ICP-MS 300 Training Manual, 2009, Perkin-Elmer Corporation

20.3 EPA 200.8 Rev.5.4: "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry, 1994

21.0 ATTACHMENTS:

Attachment A: Corrective Action Table
Attachment B: Method Nomenclature
Attachment C: ICP/MS Isotopes

Attachment A: CORRECTIVE ACTION TABLE

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
EPA200.8	Calibration	Daily before each method.	Correlation coefficient acceptance criterion ≥ 0.995.	1. Find source of problem and correct. 2. Repeat calibration.
EPA200.8	Instrument Performance	Daily before each method.	1. Background at mass 220 <5 cps 2. Ba^{++}/Ba^{+} double charged < 3%. 3. CeO/Ce Oxide <3% 4. Be intensity > 2,000 cps. 5. Mg intensity > 15,000 cps. 6. In intensity > 40,000 cps. 7. U intensity > 30,000	1. Fix problem and rerun.
EPA200.8	Calibration Blank (CB)	After calibration, 1 per 10 sample Readings, and at the end of the analytical run.	Concentration < LOQ	1. Rinse with acid and repeat. 2. Evaluate samples; if N.D. or concentration > 10 times blank contamination level, ok to report. Comment if results reported without compliant blank. 3. Recalibrate 4. Reanalyze all affected samples.
EPA200.8	Calibration Verification Std. (CCV)	1 per 10 sample readings and at the end of the analytical run.	± 15%	1. Repeat analysis once. 2. Fix problem. 3. Recalibrate. 4. Reanalyze all affected samples.
EPA200.8	Initial Calibration Verification Std. (ICV)	After Calibration	± 10%	1. Repeat analysis once. 2. Fix problem. 3. Recalibrate.
EPA200.8	Quality Control Standard (QCS) Second Source	After ICV	± 10%	1. Repeat analysis once. 2. Fix problem. 3. Recalibrate.
EPA200.8	Method Blank (MB) **MB**	1 per batch of 20 or less.	Concentration < LOQ **Evaluated at the DL for drinking water**	1. Repeat analysis once. 2. Evaluate samples; if ND or sample concentration > 10 times blank contamination level, ok to report. Comment on MB if results reported without compliant blank. 3. Re-digest and reanalyze samples with concentration of contaminant > LOQ and < 10x LOQ.

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
EPA200.8	Laboratory Control Sample (LCS)	1 per batch of 20 or less	Recovery ± 15%	1. Repeat analysis once. 2. Evaluate samples; if LCS is high but samples are ND for that analyte, ok to report; comment on sample. Re-digest and reanalyze samples with concentration of contaminant > LOQ. 3. If LCS is low, re-digest and reanalyze samples for all failed analytes.
EPA200.8	Matrix Spike (MS)	1 per 10 samples Digested	70-130% if analyte concentrations are < 4 times the spike	1. If MS recovery is not within limits perform a BND.
EPA200.8	Matrix Spike Dup. (MSD)	Per client request	70-130% if analyte concentrations are < 4 times the spike RPD ≤ 20	1. If MSD recovery is not within limits perform a BND. 2. If RPD is not within limits, comment that the parent sample data is estimated.
EPA200.8	Post Digest Spike (BND)	As needed	70 – 130%	1. If BND recovery is not within criteria, dilute and re-spike at dilution.
EPA200.8	Internal Standards	In all solutions	In CCV/CB: 60-125% original cal blank intensity.	1. Terminate analysis. 2. Correct problem.
			In Samples ICS stds.: 60 –125% original cal blank intensity.	1. Dilute the sample 5x and reanalyze. 2. Repeat until criteria are met.

Attachment B: Method Nomenclature

Method Symbol	SGS Symbol	Method Name	SGS Name
CAL	ICV,CCV	Calibration Standard	Continuing Calibration Verification
LD1, LD2	DUP	Laboratory Duplicates	Duplicates
LFB	LCS	Laboratory Fortified Blank	Laboratory Control Sample
LFM	MS/MSD	Laboratory Fortified Matrix	Matrix Spike/ Matrix Spike Duplicate
LRB	MB	Laboratory Reagent Blank	Method Blank
QCS	QCS	Quality Control Sample	Quality Control Sample

Attachment C: 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.

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**	

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	Use 78 only for method 3051
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	

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

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: Nitrate + Nitrite Nitrogen	**Revision Date:** May 2019
Method No: SM4500NO3-F	**SOP No:** 351r13
Page: 1 of 15	**Supersedes:** 351r12

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	5/16/19	Jamaica Renty	5/16/19
Stephen C. Ede	4/27/20	Jamaica Renty	4/27/2020

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 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: _____

Document Control Number _____ Issued by _____ Date _____

Addendum 1 added 7/11/19

Mary C McDonald
Mary Mcdonald
2019.07.11
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SGS	SGS North America, Inc. - Alaska Division Standard Operating Procedure
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S.O.P. Title: Nitrate + Nitrite Nitrogen	**Revision Date**: June 27 2019
Method No: SM4500NO_3-F	**SOP No**: 351r13 addendum #1
Page: 1 of 2	**Supersedes**: 351r13

Signatures below reflect approval for the following changes to the current SOP. These changes will be incorporated into the SOP during the next review. This addendum will be incorporated into the electronic SOP (i.e., PDF file).

Technical Director	Date	Quality Assurance (QA) Manager, QA Staff or their Designee	Date
Stephen C. Ede	7/11/19	Mary C. McDonald	7/11/19

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: _____

The above referenced SOP should be modified as follows:

ADD TO Section 13.0. Calculations, Review and Reporting:

13.0. Calculations, Review and Reporting:

13.1. **Notify the client immediately** (within 24 hours) of unsatisfactory results by emailing a completed ALERT: Nitrate-N over 10 mg/L report or Nitrite-N over 1.0mg/L.

13.2. Record the date, time, and name of the person contacted in the appropriate area of the form.

13.3. **ADEC must also be notified immediately if a PWSID number is on the Chain of Custody.**

1.3.4 Email the form 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: ..\..\..\FORMS\Approved\FW\FW-0098_Current contacts_ADEC_Divisions_20170830.docx

13.5. 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.

Notify the Project Manager immediately so the results may be submitted to ADEC via

CMDP.

ALSO ADD TO: NO2/NO3 Analysis by Flow Quick Reference Guide

Use form below; usfs700\ANK -Groupdata\Public\Alert-Nitrate over 10mg/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

Summary of Changes from Previous Revision:

- Addendum #1 was incorporated into sections 8.9., 8.10., 10.1.1., and Attachment C
- Addendum #2 was incorporated into sections 10.4. and 10.4.1.
- Section 8.8.1. was formatted to emphasize final buffer pH over amount of ammonium hydroxide used
- Section 8.12.1 was edited to remove mention of filtering Color reagent
- Section 8.16. formatting was changed.
- Section 8.18.1.2. formatting was changed.
- Section 12.2.2 was changed from evaluating drinking water MB at DL to ½ LOQ
- Section 12.5. was edited to current QCS concentrations
- Section 12.6. was edited
- Section 13.6. was edited to mention modifying the data file before using LIMSBridge
- Section 13.9. was edited to include correct dilution factors of all QC
- Section 13.12. was edited to correct LIMS posting procedure.
- Section 13.13. was edited to include LCS and correct dilution factor
- Section 17.0. was edited to match current DL practices. The DL was updated
- Section 19.0. was updated to current LOQ
- Attachment B was edited to mention evaluating drinking water MB at ½ LOQ
- Attachment C was edited to current LOQ and LOQ concentrations at 2X

Table of Contents

1.0. OBJECTIVE:

Nitrate is reduced quantitatively to nitrite by cadmium metal in the form of an open tubular cadmium reactor. The nitrite thus formed, plus any originally present in the sample, is determined as an azo dye at 510 nm following its diazotization with sulfanilamide and subsequent coupling with N-1-naphthylethylenediamine in an acidic solution. Nitrite is analyzed in tandem on a separate channel. Nitrate is determined mathematically by subtracting the nitrite value from the total determination.

2.0. SCOPE AND APPLICATION:

This method is used for the determination of nitrite or nitrate plus nitrite in drinking, surface water, domestic and industrial wastes.

3.0. DEVIATIONS FROM REFERENCE METHOD:

3.1. The cadmium column is not constructed with granular cadmium.

3.2. The sample pH is not adjusted before analysis. The small volume and buffer addition make this an unnecessary step in the analysis.

3.3. The sample flow setup is designed for the Astoria segmented flow analyzer.

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. This includes destruction of controlled copies of expired and retired SOPs. 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 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. A limited number of controlled hardcopies are to be distributed by the QA Office.

5.0. INTERFERENCES:

5.1 Filter turbid samples prior to analysis.

5.2 Interferences from iron, copper, or other metals can be eliminated with the addition of EDTA.

5.3 Samples containing large concentrations of oil and grease must be pre extracted with an organic solvent.

5.4 Residual chlorine can interfere by oxidizing the cadmium coil, reducing its efficiency. This interference is eliminated by dechlorinating with thiosulfate.

6.0. SAMPLE HANDLING:

6.1 Surface and sewer waters and industrial wastes may be analyzed by this method.

6.2 The samples must be unaltered and unopened prior to analysis.

6.3 Collect at least 60mL of sample into a clean container.

6.4 Samples may be unpreserved or preserved with sulfuric acid to pH < 2.0. The samples are stored at 0-6 ºC.

6.5 Holding Times –

6.5.1 Preserved samples have a hold time of 28 days.

6.5.2 Unpreserved samples should be analyzed as soon as possible and have a hold time of 48 hours.

7.0. APPARATUS:

7.1. Astoria 2 Auto-Analyzer

7.2. Auto-Sampler model 311 M / with sample wash pump

7.3. Data Acquisition system, FASPac II

7.4. Multitest Cartridge with a 510 nm filter.

7.5. Nitrite Cartridge with a 540 nm wavelength filter and a 90 neutral density filter.

7.6. Gas pillow - Nitrogen

8.0. REAGENTS:

8.1. Nitrate as Nitrogen Primary standard 1000mg/L, AccuStandard or equivalent.
8.1.1. Shelf life 6 months.

8.2. Nitrite /Nitrogen Primary standard 1000mg/L, AccuStandard or equivalent.
8.2.1. Shelf life 1 month.

8.3. Nitrate as Nitrogen 2nd Source standard, 1000mg/L, Spex CertiPrep or equivalent.
8.3.1. Shelf life 6 months.

8.4. Nitrite /Nitrogen 2nd Source standard,1000mg/L, Spex CertiPrep or equivalent.
8.4.1. Shelf life 1 month.

8.5. Ammonium Chloride, Fisher order # A661 or equivalent.

8.6. Ethylenediamine Tetraacetic Acid: EDTA, Fisher order # S311 or equivalent.

8.7. Brij-35, 30%, Astoria-Pacific reagent.

8.8. Stock Ammonium Chloride – EDTA Buffer, pH 8.5
8.8.1. Dissolve 425g of ammonium chloride and 0.5g of disodium EDTA in 1500mL of DI water. Using approximately 15ml of concentrated ammonium hydroxide, adjust the pH to 8.5. Transfer the solution to a 2L volumetric flask and dilute to the mark with DI water. Store at 0 – 6ºC.

8.8.2. Working Ammonium Chloride: Add 5-7 drops of Brij–35 to 500mL of buffer. Mix well.

8.9. Phosphoric Acid, concentrated, Fisher order # A242-500 or equivalent.

8.10. Sulfanilamide, Acros Organics # 13285-100 or equivalent.

8.11. N-1-napthylethylenediamine dihydrochloride, Sigma Aldrich # 222488 or equivalent.

8.12. Color Reagent, 500mL. Store in a brown bottle and keep in the dark when not in use.

8.12.1. Cautiously, add 50mL of concentrated phosphoric acid to 400mL of DI water. Dissolve 20g of sulfanilamide and 1g N-1-napthylethylenediamine in the acid solution. Bring to 500mL with DI water. Pour into a brown bottle and store in the dark (in the refrigerator at 0-6ºC) when not in use. Reagent is stable for several months. Discard if it turns dark pink.

8.13. Startup / Shutdown solution: ~5-7 drops of Brij to 500mL DI water.

8.14. Sampler wash solution: DI water.

8.15. Copper(II) Sulfate, anhydrous 98%,
8.15.1. Cupric Sulfate Solution: Dissolve 20g $CuSO_4$ in 1.0L DI water.

8.16. Hydrochloric Acid, concentrated.
8.16.1. 1N HCl: 100mL: add 8.3mL HCl to 100mL DI water.

8.17. Cd column (OTCR) Activation: The OTCR is a coiled cadmium column sleeved in heat wrap.

8.18. Procedure for new cadmium columns generation or used OTCR regeneration:

8.18.1. Using a 10mL plastic syringe with a short tubing extension, wash the column with the following sequence of solutions: Push solutions through gently, without introducing air into the column.
8.18.1.1. DI water

8.18.1.2. 1N HCl

8.18.1.3. Follow quickly with a DI wash

8.18.1.4. 2% $CuSO_4$, flush slowly, twice, let sit 5 or 10 minutes

8.18.1.5. DI water: flush through forcefully until no more black precipitated copper is flushed from the reactor.

8.18.1.6. Stock ammonium chloride buffer – Store the reactor filled with this solution

8.18.1.7. Once a column is generated, a solution of 1 mg/L for nitrate is to flow continuously through the column for approximately 10 minutes before use. This is only to be done when a new column is generated. If regenerating a column already in use, then this step can be skipped.

9.0. EXTRACTION:

N/A

10.0. CALIBRATION:

10.1. Calibration Criteria - Create a six point curve as follows:

10.1.1. Make an intermediate Working NO_2/NO_3 standard solution daily because nitrite is unstable in the solution mix. Use 250 µl of each primary nitrate standard (8.1) and primary nitrite standard (8.2), in a 25 mL volumetric flask. Bring to volume with DI water. This solution concentration is 10.0 mg/L nitrite and 20.0 mg/L total nitrite/nitrate – N after Cd reduction. Make 10.0 mL calibration standards from the intermediate working standard following the chart below.

Concentration, mg/L	Volumetric Flask	Volume of Working Standard	NO_2 Concentration	Total NO_2/NO_3 calibration Concentration
5.0	10mL	2.5mL	2.5mg/L	5.0mg/L
2.5	10mL	1.25mL	1.25mg/L	2.5mg/L
1.0	10mL	0.5mL	0.5mg/L	1.0mg/L
0.5	10mL	0.25mL	0.25mg/L	0.5mg/L
0.05	10mL	0.025mL	0.025mg/L	0.05mg/L
Blank	DI Water		0.0mg/L	0.0mg/L
ICV/CCV/LCS	10mL	1.25mL	1.25mg/L	2.5mg/L

10.2. Make an intermediate 2nd source standard (QCS) from separate source nitrite and nitrate solutions. Dilute 250µl of each solution to 25mL.

10.2.1. Dilute 0250 µl of the 2nd source intermediate to 10mL with DI water. 2nd source concentration is 0.5mg/L nitrite, and 1.0mg/L total nitrate/nitrite - N.

10.3. The SYNC sample is the highest calibration point. (~~10mg/L~~ 5 mg/L point)

10.4. The column efficiency sample is nitrate only at 4.0mg/L. This can be made up weekly and is used each day.

10.4.1. The column efficiency solution is made by diluting 100 µl of the primary nitrate standard to 25mL.

10.5. The LCS / CCV concentration is 1.25mg/L nitrite and 2.5mg/L total nitrate/nitrite - N.

10.5.1. The initial CCV (ICV) is also posted as the LCS. A LCS is posted each batch of 20 samples

10.6. Matrix spikes and MSD's (Matrix Spike Duplicate) are 0.5ml of the intermediate standard in the two cut dilution (4.0mL) of the sample, remembering to remove 0.5mL of the 2 cut dilution before adding the intermediate standard. Nitrite concentration is 1.25mg/L and Total nitrate/nitrite is 2.5mg/L. As noted in section 5.1, turbid samples should be filtered to prevent interference. If samples have been filtered, then associated QC samples must also be filtered.

11.0. ANALYSIS:

11.1 All samples will be diluted 2 to 2 (2X). Place 2.0mL of DI water in a sample cup, add 2.0mL sample to and mix well.

11.1.1. Samples with values over the high point of the curve must be diluted to read within the curve limits.

11.2 Verify that the correct cartridge, filters, and flow cell are installed.

11.3 Make sure there are no loose fittings or connections

11.4 Attach the gas pillow to the air line on the multi-cartridge.

11.5 Turn the sampler and the auto-analyzer on and latch the pump platens.

11.6 Open the software

11.7 Select the appropriate configuration from the list box in the tool bar.

11.8 Enter a name for the run (MM-DD-YYRUN#) and click OK.

11.9 Select System – Connect from the main menu.

11.10 Sampler line wash solution is MilliQ DI water.

11.11 Place all reagent lines in fresh DI water to stabilize the baseline.

11.12 Run a minimum of 30 minutes to stabilize the baseline.

11.13 Select Options – Show % light, - Display Signal All, - Zero Signal All.

11.14 Click the Sample Table button to the batch.

11.15 The first sample in every batch must be a SYNC sample, (the highest point on the curve). Follow this by the curve, initial QC, method blank & samples.

11.16 Using the sample table, fill the standard and sample racks.

11.17 Place the nitrite cartridge color line in the color solution.

11.18 Place the multi-cartridge lines 1 buffer/Brij solution, line 4 and diluent line in Startup/Shutdown solution, and line 5 and color line in color reagent approximately for 5 to 10 minutes before inserting the cadmium tubing.

11.19 Insert the activated OTCR, attaching the flow **IN** first (to assure that no air is introduced inside the OTCR). Be sure that buffer is in the reagent flow before the OTCR is put in place. Allow the baseline to stabilize.

11.20 Select Run – Begin

11.21 At the end of the run, remove the OTCR and flush with buffer to store.

11.22 Run DI through system for at least 30 minutes.

12.0. QUALITY CONTROL:

12.1 Accuracy Measurements :

12.1.1 The LCS concentration is 1.25mg/L nitrite and 2.5mg/L total nitrate/nitrite - N. The LCS can either be made daily and ran as separate injections within the analysis, or the CCV can also be posted as a LCS for every 20 samples.

12.2 Blank Criteria - MB must be < LOQ
12.2.1 DOD clients require <½ the LOQ
12.2.2 For drinking water samples, the MB will be evaluated at ½ the LOQ.

12.3 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 QA Office or Technical Department.

12.4 A six point calibration curve must have a correlation coefficient of 0.995 or better. The preferred curve type is 2nd Order Polynomial.

12.4.1. Each calibration must be evaluated by read back of each point; validation for the low point is ± 50% of the true value. The criterion for all other points is ± 10% of the true value.

12.5 The initial (ICV) and continuing calibration verification (CCV) concentrations are 2.5mg/L total nitrate/nitrite - N / 1.25mg/L NO_2. The 2nd source (QCS) is 0.5 mg/L total nitrate/nitrite - N / 0.25 mg/L NO_2. They must be ± 10% of the true value. If it fails to meet the criteria it may be run one more time. If the second run fails, all samples run after the last passing CB & CCV must be re run.

12.5.1 The nitrate concentration is determined by subtracting NO_2 from total N/N. The recovery criterion is ± 30%.

12.6 The CCV and CB must be run after every 10 injections and at the end of the run.
12.6.1 For drinking water samples, a low level quantitation (LLQC) needs to be evaluated each analysis day. The lowest calibration point will be posted as the LLQC.

12.7 An MB and an LCS are run with each batch of 20, or less, samples.

12.8 A Matrix Spike/ Matrix Spike Duplicate (MS/MSD) must be analyzed at a 5% frequency. The allowable recovery is 90 – 110% for total nitrate/ nitrite, & ± 30% for nitrite. The RPD criterion is ± 25%.

12.9 The column efficiency sample (4mg/L nitrate) must be within 20% of the true value. Failed criteria require that the column be reconditioned per section 8.18.

12.10 When warranted, manual integration can be done on this instrument. For guidance regarding manual integration, refer to SOP 144.

12.10.1 For all injections affected by integration (all instrument QC, batch QC, and each paying sample) print outs of both before and after integration must be initialed and dated by the analyst, with a brief comment justifying the integration. Each before and after must be included in Peer Review Report for review.

12.10.2 When a manual integration is warranted, tips for correctly completing the manual integration process are as follows:

12.10.2.1 When the analyst attempts to correct a peak, the software will ask if the user would like to search for peaks to the right. In this case, the software is asking whether it is acceptable to adjust the quantitation line to the tallest point of the closest peak to the right.

12.10.2.2 When one peak is corrected, every peak following will also be corrected with the same change as was applied to the initial target peak. Unless each sample needs peak adjustment, it is important to return the peaks that did not need the correction to their original position.

13.0. CALCULATIONS, REVIEW AND REPORTING:

13.1 Units/Significant Figures – Waters are reported in mg/L.

13.2 Equations – 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:

13.3 3rd Order Quadratic Regression:

$$Y = K_3 X_i^3 + K_2 X_i^2 + K_1 X_i \quad \text{EQUATION 1}$$

Where: Y = predicted instrument response
K_3, K_2, K_1 = coefficients
X_i = concentration of standard i

13.3.1 FASPac software does these calculations automatically.

13.4 Spike Recovery:

$$\%\,\text{Recovery} = \frac{(V_0 - S_0)}{V_E} \times 100$$

Where V_0 = observed value of the spike
S_0 = observed value of the sample
V_E = expected value of the spike

13.5 At the end of the run, print the plot showing both channels (analysis), the run table, and each curve correlation for both channels. Write the run data into the log book.

13.6 Export the days run under File: - Export: - Results: - choose the run name (run date) and OK. Locate the exported file and highlight. Right click and select, "Edit with Notepad++." In the first row of text replace *"Cor Ht","NO3NO2","Cor Ht","NO2"* with *"Raw Ht","mg/L\NN","Raw Ht"," mg/L\N"*. Select "Save As" and rename the file to indicate the file has been modified.

13.7 Build the day's batch in LIMS under the queue, WFI, adding MS samples and recording the MS HSN designation in the log book.

13.8 Open LIMS bridge. Be sure that FASPac is designated. Get Data – choose the modified file name, (run date), Open – OK. Maximize the window.

13.9 "NO" all data not to be posted. Ensure CCV, CB, QCS and LLQC have a dilution factor of 1 listed. The dilution for MB and LCS should be 2.

13.10 Change the sample number for the MS & MSD samples to the HSN designation. Correct any dilution that is not 2.

13.11 Enter the queue, WFI, down arrow, YES. (This is the auto fill sequence). Repeat for Batch #, Analyst, and instrument, (FI). Check to verify and POST SAMPLES – YES – **NO**. Minimize the screen.

13.12 Open LIMS, choose Operations – Autopost – Autopost Pipe. Enter queue "WFI." Your data will be posted in LIMS. Use the Refresh button to track the progress. When done, minimize the window.

13.13 Go back to LIMS Bridge. Change required CCVs to LCS. Change required CBs to MB. "NO" everything else in the window. Make sure that the dilution for MB and LCS is 2. Re-enter the batch #, up arrow, to reset the data. "Post Samples".

13.14 When the posting is complete, open the WFI batch to Edit. With the cursor in an empty space, hit control – P. this puts the batch in order. SAVE.

13.15 Review/Peer Review Steps – A peer reviewer must date and initial all chromatograms that have been manually integrated.

13.16 Archive Policy (hardcopy and electronic) – Electronic archive is done on a once monthly basis.

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.

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:

N/A

17.0. *DETECTION* Limit *(DL)* Study:

Per ADEC drinking water requirements the DL is verified annually. DL studies are performed when a new operator is trained, when a new instrument is purchased, or when a major modification to the methodology is made. 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 current DL is 0.05mg/L for waters.

18.0. LIMIT OF DETECTION (LOD):

The LOD is set as ½ the established LOQ.

19.0. LIMIT OF QUANTITATION (LOQ):

LOQs may change by the lab's discretion and do not require an update to this document. The current LOQ for both Nitrate/ Nitrite is 0.2 mg/L.

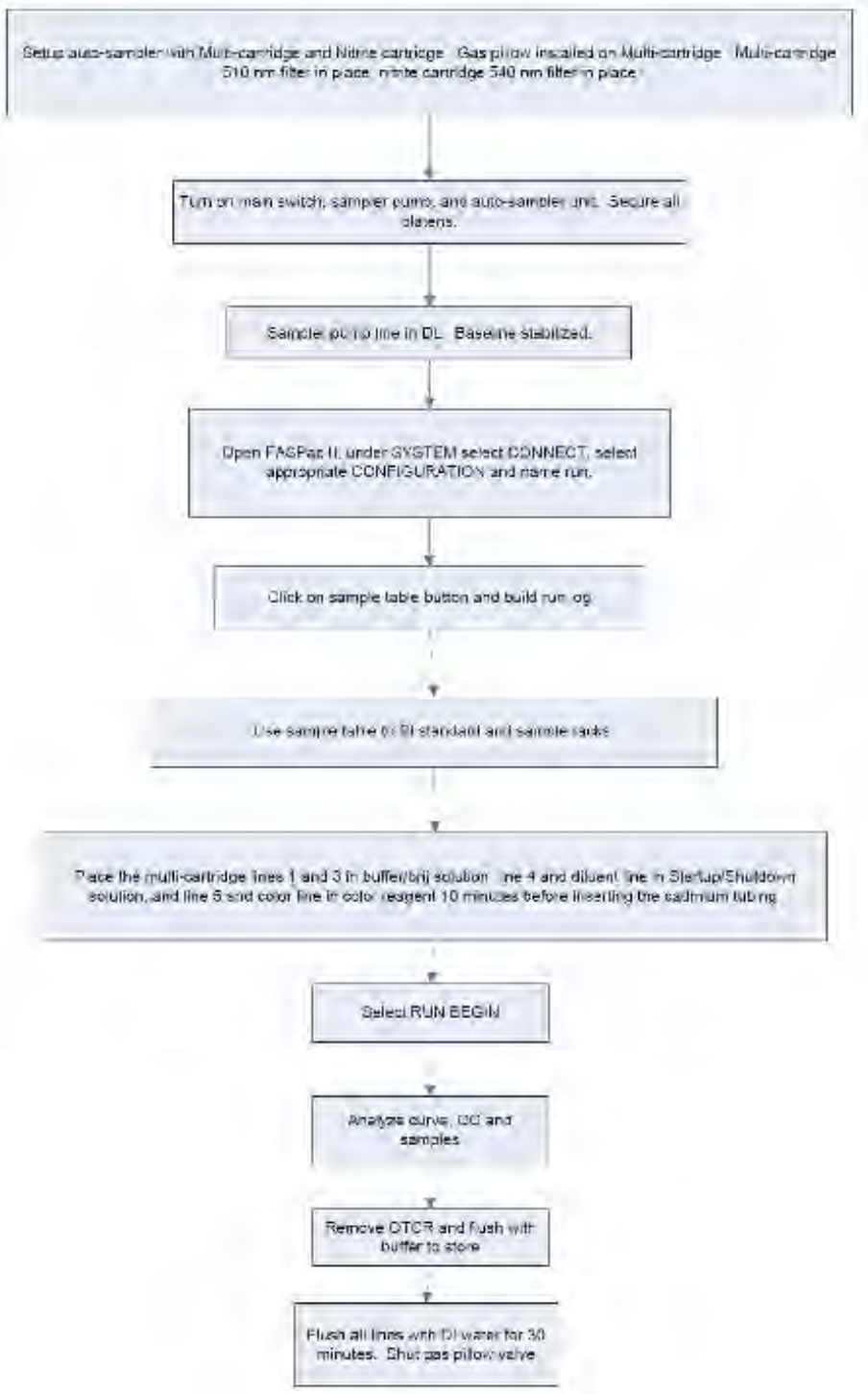
20.0. REFERENCES:

Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 1981, American Public Health Association, Washington, D.C.

21.0. ATTACHMENTS:

Attachment A: Flow Chart
Attachment B: Corrective Action Table
Attachment C: Quick Reference Guide

ATTACHMENT A: FLOW CHART



ATTACHMENT B: CORRECTIVE ACTION TABLE

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM4500 NO3-F	Multipoint Calibration	Before each run	Correlation coefficient $r^2 \geq 0.995$	1. Find source of problem and correct. 2. Repeat calibration.
	Initial Calibration Verification (ICV) with Calibration point Read Back	After the curve.	ICV ± 10% Read Back: low point ±50% of the true value, all other points ± 10%	1. Repeat ICV analysis once. If it again fails Recalibrate. 1. If read back values fail to meet criteria Recalibrate
	Initial Calibration Blank & Method Blank (ICB) & (MB)	Immediately after ICV (ICB) 1 MB per batch of ≤ 20 samples	Concentration <LOQ (DOD clients and Drinking Water Require< 1/2 LOQ)	1. Evaluate samples before further analysis. If <LOQ – no reanalysis is required. If >10X the 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.	Recovery Total ± 10% NO_3 ± 30%	1. Repeat analysis once. 2. If results remain outside limits, correct the problem and recalibrate
	Continuing Calibration Verification (CCV)	Every 10 injections, and at end of the run.	Recovery Total ± 10% NO_3 ± 30%	1. Repeat analysis once. 2. If results remain outside limits, rerun all samples after last passing CB CCV pair.
	Calibration Blank (CB)	Every 10 injections, and at end of the run.	< LOQ (DOD clients require <1/2 the LOQ.)	1. Evaluate samples before further analysis. If <LOQ – no reanalysis is required. If >10X the concentration in blank – no reanalysis is required. All other samples using the contaminated blank for QC will be reanalyzed.
	Laboratory Control Sample (LCS)	1 per 20 samples or 1 per batch	Recovery Total ± 10% NO_3 ± 30%	1. Repeat analysis once. 2. If results remain outside limits, correct the problem and re analyze samples.
	Matrix Spike Matrix spike Duplicate. (MS/MSD)	1 per 20 samples, (5%) or 1 per batch	Recovery Total ± 10% NO_3 ± 30% RPD = 25%	1. Report LCS; flag sample results. 1. Repeat analysis once. Failure, flag results.

Attachment C:

NO_2/NO_3 Analysis by Flow Quick Reference Guide

Reagents

Start-Up: 500mL of fresh DI with 5-7 drops of Brij-35
Buffer: 500mL of buffer solution with 5-7 drops of Brij-35
Color: Filter color reagent through a 0.45µm filter if needed, protect from light

Standards

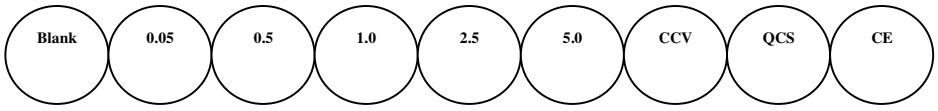
Intermediate Working Standard (20.0mg/L): 0.250mL of both primary NO_2 and NO_3 standards into 25mL vol. flask
Column Efficiency (CE) sample (4.0mg/L): 0.100mL of NO_3 primary standard into 25mL vol. flask
QCS intermediate (20.0mg/L): 0.250mL of both 2nd source (8.3 and 8.4) NO_2 and NO_3 standards into 25mL vol. flask

Curve

Concentration, mg/L	Volumetric Flask	Volume of working Standard	NO_2 calibration Concentration	Total NO_2/NO_3 calibration Concentration
5.0	10mL	2.5mL	2.5mg/L	5.0mg/L
2.5	10mL	1.25mL	1.25mg/L	2.5mg/L
1.0	10mL	0.5mL	0.5mg/L	1.0mg/L
0.5	10mL	0.25mL	0.25mg/L	0.5mg/L
0.05	10mL	0.025mL	0.025mg/L	0.05mg/L
Blank	DI Water		0.0mg/L	0.0mg/L
ICV/CCV/LCS	10mL	1.25mL	1.25mg/L	2.5mg/L
QCS	10mL	0.25mL of	2nd source	Working Std.

Calibration acceptance criterion for 0.05mg/L readback is +/- 50%
Calibration acceptance criterion for all other calibration readbacks is +/- 10%

Place standards in 16x100mm culture tubes and fill the "Rear" side of the auto sampler rack, using the following order from the left side of the rack:



Sample Prep: Add 2mL of sample to 2mL of DI, mix. Pour into sample cuvette and place on autosampler tray.
MS/MSD: Add 2mL of sample to 2mL of DI, mix. Remove 0.5 mL, add 0.5mL of the Working Standard. Pour into sample cuvette and place on auto sampler tray.

True Values for 2X

ICV/LCS/CCV = 2.5mg/L total NO_2/NO_3, 1.25mg/L NO_2
QCS = 0.5mg/L total NO_2/NO_3, 0.25mg/L NO_2
CE = 4.0mg/L total NO_2/NO3, 0.0mg/L NO_2
MS/MSD = 2.5mg/L total NO_2/NO_3, 1.25mg/L NO_2
LOQ = 0.1mg/L total NO_2/NO_3
LOD = 0.05mg/L total NO_2/NO_3

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 Beatty	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~

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 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: Acid Digestion of Soils, Sludges and Sediments for ICP-MS	**Revision Date**: January 2020
Method No: SW846 3050B	**SOP No**: 361r17
Page: 1 of 11	**Supersedes:** 361r16

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	1/23/20	Jamaica Beatty	1/23/2020

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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 coverpage 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:

- **7.0** removed reference to centrifuge and centrifuge tubes.
- **8.7** correct instructions for establishing expiration dates for reagents.
- **9.0** added instructions for weighing and digesting MI soil samples**.**
- **9.0** added procedure for glycols.
- **17.0** updated to reflect changes made to DL Study trials.
- Various grammatical/formatting corrections.

Table of Contents

1.0. OBJECTIVE:

This document outlines a procedure for acid digestion of sediments, sludges, soils, and oils samples for metals.

2.0. SCOPE AND APPLICATION:

This SOP outlines the preparation of sediments, sludges, soil, and oil samples for analysis by inductively coupled plasma mass spectrometry (ICP-MS).

3.0. DEVIATIONS FROM REFERENCE METHOD:

3.1 The reference method (SW846 3050B) is designed to accommodate large reagent volumes, glassware, and hardware. The digestion times and reagent amounts have been reduced for this method because the hotblocks and digestion vessels used are smaller than those of the reference method.

3.2 Chapter Three of SW 846 discourages the use of HCl for the digestion procedure for ICP-MS analysis unless needed to enhance performance. SGS experience has shown that no significant interference occurs from the addition of HCl. The use of HCl has shown marked improvement in the recovery of Silver (Ag) and Barium (Ba). HCl is used in all digestions for ICP-MS digestions as documented in this procedure.

4.0. RESPONSIBILITIES:

4.1 The QA Office maintains a master file of this SOP to insure review on a timely basis. The filing system serves as an accounting of SOP distribution and insures that distributed SOPs are current and complete. The accounting includes destruction of controlled copies of expired and retired SOPs. The QA Office also maintains a historical file of original and electronic versions of this SOP; including the current revision and any versions archived within the past 5 years.

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All staff have “read” access to these SOPs. Only QA/QC has access to “write” on SOPs. Staff is directed to use the controlled electronic versions of SOPs.

5.0. INTERFERENCES:

Sediment, sludges, and soil samples can contain diverse matrix types, each of which can pose its own analytical challenges. Laboratory Control Sample (LCS) and Matrix Spike/ Matrix Spike Duplicate (MS/MSD) samples are prepared with each digest batch to determine the validity of the method, 3050B, for a particular sample.

6.0. SAMPLE HANDLING:

Soils, sediments, and sludges are refrigerated upon receipt at 0-6°C and analyzed as soon as possible. The holding time is six months from collection to analysis. Digests are discarded one month after the analysis date. The holding time for samples is 180 days. If mercury analysis is required, the holding time is 28 days.

7.0. APPARATUS:

7.1. Environmental Express 36 or 54 well digestion block with temperature control (or equivalent).

7.2. Environmental Express HotBlock digestion vessels (or equivalent). Vessels are graduated every 5 mL from 5 mL to 50 mL with a maximum capacity of 62 mL. The graduations have a certified tolerance of $\pm$0.2 mL.

7.3. Eppendorf Reference Pipettes (or equivalent): 0.02 – 0.2 mL, 0.2 – 1.0 mL, and 1.0 – 5.0 mL with an accuracy of $\pm$1% (*note*, micro-pipettes accuracy tolerance may be extended to 2% per SGS SOP #104).

7.4. Analytical balance capable of measuring to 0.1 mg.

8.0. REAGENTS:

8.1. Milli-Q filtered ultra-pure water.

8.2. Concentrated nitric acid (HNO_3), reagent grade.

8.3. Concentrated hydrochloric acid (HCl), reagent grade.

8.4. Hydrogen peroxide, 30% (H_2O_2).

8.5. ICP-MS Matrix Spike: following table lists the concentration of each analyte in the spike solution.

Aluminum	50 µg/mL	Cobalt	25 µg/mL	Selenium	50 µg/mL
Antimony	50 µg/mL	Copper	50 µg/mL	Silver	5 µg/mL
Arsenic	50 µg/mL	Iron	250 µg/mL	Sodium	500 µg/mL
Barium	50 µg/mL	Lead	50 µg/mL	Strontium	50 µg/mL
Beryllium	5 µg/mL	Magnesium	500 µg/mL	Thallium	0.5 µg/mL
Bismuth	5 µg/mL	Manganese	25 µg/mL	Tin	5 µg/mL
Boron	50 µg/mL	Molybdenum	20 µg/mL	Titanium	5 µg/mL
Cadmium	5 µg/mL	Nickel	50 µg/mL	Vanadium	10 µg/mL

Calcium	500 µg/mL	Phosphorus	25 µg/mL	Zinc	50 µg/mL
Chromium	20 µg/mL	Potassium	500 µg/mL	Gold	5 ug/mL
Lithium	10 µg/mL	Uranium	5 µg/mL	Mercury	0.5 ug/mL

8.6. Preparation of the ICP-MS Matrix Spike.

8.6.1. In a 100 mL class A volumetric Teflon flask, add 20 to 30 mL DI water then add 15 mL of concentrated HCl and 7 mL of concentrated HNO_3.

8.6.2. Refer to CX-0011 for the list of element stock solutions and correlating spike volumes. Note that "ICAL" refers to a mixture of Ca, Mg, K, and Na.

8.6.3. Bring up to volume (100 mL) using deionized water and transfer to a 100-mL plastic Nalgene bottle wrapped in electrical tape. Cap bottle tightly, invert, and give to analyst to verify the concentrations.

8.6.4. Silicon Standard: 1,000 µg/mL single element standard of which 0.5 mL is used in digestion. Solution is used as is without being mixed into any other solutions.

8.7. All reagents must be labeled following the criteria in SOP #112. Expiration dates for HCL, HNO3, and H_2O_2 are five years from the date opened. The expiration dates for spike solutions are one year from the date made or the earliest expiration date from the stock standards used to make the spike solution, whichever is earlier.

9.0. EXTRACTION:

9.1 Label digestion vessels (section 7.1) with work order and sample number. Label QC vessels (MB, LCS, MS,MSD,DUP), see 9.3 below.

9.2 See SOP#143 for the proper procedure for weighing 1.0-1.1 grams of sample. For glycol batches, measure 1.0 mL of sample into digestion vessels. Record the actual weight in the logbook (except glycols, record 1 mL). See SOP#149 for Multi-Incremental Soil sample weighing procedure. Record total weight of MI sample in logbook (will be between 10-11 grams). Digest each MI sample in 10 separate vessels following the procedure outlined in section 9.3. Please note one MI sample (10 vessels) equates one paying sample.

9.3 Preparation of batch QC is as follows:

9.3.1. Method Blank (MB): A MB is prepared for each digestion batch of $\leq$ 20 paying samples. Teflon stones are used for the MB to represent a solid matrix. For oils batches the base oil standard is used in place of Teflon. Weigh out 1.0-1.1 g of Teflon chips into a tared digestion vessel, then proceed to step 9.3.5. For oils batches, weigh out 1.0-1.1 g of the base oil standard. For glycol batches, measure 1.0 mL DI water.

9.3.1.1. For glycols batches, a Method Blank Filter (MBF) is prepared at the same time as any glycol samples requiring lab filtering. The MBF is batched in LIMS and given a sample ID number. The blank is carried through the digestion process along with the associated samples.

9.3.2. Laboratory Control Sample (LCS): An LCS is prepared for each digestion batch of ≤ 20 paying samples. Weigh out 1.0-1.1 grams of Teflon stones into a tared digestion vessel. For oils batches, weigh out 1.0-1.1 g of the base oil standard. For glycol batches, measure 1.0 mL DI water. The LCS is prepared by adding 1.0 mL of ICP spike solution (section 8.5) and 0.5 mL of Silicon Standard solution (section 8.6.4).

9.3.3. Matrix Spike (MS) and Matrix Spike Duplicate (MSD): Choose a random sample within the batch to spike (MS/MSD) unless client specifies BMS/BMSD on a sample. Weigh out 1.0-1.1 g (1.0 mL for glycols) of sample into the tared and labeled digestion vessels. The MS\MSD is prepared by adding 1.0 mL of ICP spike solution (section 8.5) and 0.5 mL of Silicon spike solution (section 8.6.4).

9.3.4. Duplicate (DUP): The sample chosen for the MS/MSD needs to be prepared in duplicate. Weigh out 1.0-1.1 g (1.0 mL for glycols) of sample into the tared and labeled digestion vessel.

9.3.5 **Note:** This digestion procedure is applicable to the digestion of air sampling filters and sample wipes. The entire filter or wipe is used for the digestion – do not cut or otherwise subdivide a filter or wipe. Filters and wipes do not require weighing before digestion, record the initial weight as 1.0 g. Digest according to section 9.0, and fill to the final volume of 50 mL, as usual. Wipes are typically digested on batches containing other solid/soil samples. The parent sample of the MS/MSD/DUP is selected from the solid/soil samples. If there are only wipes making up the digestion batch, an LCS and LCSD set must be prepped (in place of MS/MSD/DUP).

9.4. Add 2.5 mL of Milli-Q water (section 8.1) and 2.5 mL of concentrated HNO_3 (section 8.2) to each digestion vessel.

9.5. Cover digestion vessels loosely with the lids (DO NOT TIGHTEN) and heat in the hot block for 15 minutes at 95 ± 5ºC. This step is to ensure that the samples are up to temperature. Monitor samples closely for reactivity as they heat.

The temperature of the hot block is monitored using a thermometer. The thermometer is placed in a digestion vessel with a hole in the cap. The thermometer must be suspended above the bottom of the vessel and cannot touch the side of the walls. Any space in the hole of the cap should be sealed to ensure that the water does not evaporate. The position of the thermometer must be placed in a different cell of the hot block each day of use to track the temperature of the entire hot block. A grid is used to identify the location of each cell in the hot block, where letters (i.e. A-I) read from left to right and numbers (i.e. 1-6) read from top to bottom, this is illustrated in Figure 1 below. The temperature and position will be monitored and recorded in the prep logbook for a different cell during each day of use. The thermometer will move to a new location each day of use, using all locations in no more than a 60 day of use period.

	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
1	1A	1B	1C	1D	1E	1F	1G	1H	1I
2	2A	2B	2C	2D	2E	2F	2G	2H	2I
3	3A	3B	3C	3D	3E	3F	3G	3H	3I
4	4A	4B	4C	4D	4E	4F	4G	4H	4I
5	5A	5B	5C	5D	5E	5F	5G	5H	5I

6	6A	6B	6C	6D	6E	6F	6G	6H	6I

Figure 1. HotBlock Grid

9.6. Remove samples and allow to cool for 5 minutes; then add 2.5 mL of concentrated HNO_3.

9.7. Place samples into hot block and heat for 45 minutes at 95 ± 5ºC. If sample is emitting reddish-brown fumes after cooling (approximately 5 minutes after removing from hot block), repeat steps 9.5 and 9.6 until sample no longer emits fumes. Monitor samples closely for reactivity.

9.8. Allow samples to cool for approximately 5 minutes. For soils/wipes add 1.5 mL Milli-Q water and 1.5 mL 30% H_2O_2 (**for oil and glycol batches add 1.5-2.5 mL 30% H_2O_2**) to each vessel. Allow initial effervescence to subside. Return samples to the hot block to continue the peroxide reaction. Heat samples for 30 minutes (90 min-150 min for oils and glycols). If no effervescence is observed proceed to step 9.8. For oil and glycol batches, follow procedure below for additional required 30% H_2O_2 steps. If effervescence is still observed then cool, add 0.5 mL of 30% H_2O_2. Heat for an additional 30 minutes. Repeat until effervescence mostly subsides. Do not exceed 5 mL of 30% H_2O_2 for soils/wipes.

9.8.1. For **oil** batches continue to add 0.5 mL-1.0 mL of 30% H_2O_2 every 30-60 minutes until a final volume of 8-10 mL 30% H_2O_2 has been added (digestate will be mostly clear and no longer effervescing). Heat for 30 minutes then proceed to step 9.9.

9.8.2. For **glycol** batches continue to add 0.5-1.0 mL of 30% H_2O_2 every 30-60 minutes until a final volume of 5.0-6.0 mL 30% H_2O_2 has been added (or when digestate is clear and no longer effervesces). Heat for 30 minutes then proceed to 9.9.

9.9. Remove samples and allow them to cool for approximately 5 minutes. Add 1.0 mL of concentrated HCl. Place samples on the hot block for an additional 15 minutes.

9.10. Remove from hot block and allow to cool.

9.11. Dilute to 50 mL with Milli-Q water, cap digestion vessels, invert and shake well. Prior to analysis, particulates in the digestate must settle.

9.11.1. For **MI** samples, dilute each vessel (10 per paying sample), to 50 mL with Milli-Q water. Shake, and combine all 10 subaliquots into a 1 L HDPE bottle. Record the final volume of 500 mL in the logbook.

9.12. Post the samples in LIMS, label them, and deliver the batch to the analyst.

10.0. CALIBRATION:

N/A

11.0. ANALYSIS:

N/A

12.0. QUALITY CONTROL:

12.1. Method blank: A MB is prepared for each digestion batch of ≤ 20 samples as a check for contamination.

12.2. Laboratory Control Sample: A LCS is prepared for each digestion batch of ≤ 20 samples.

12.3. Matrix Spike / Matrix Spike Duplicate: A MS/MSD set is prepared for each digestion batch of ≤ 20 samples. In the case of a "wipe-only" batch, this requirement will be met by preparing an LCS/LCSD set.

12.4. Duplicate: A DUP is prepared for each digestion batch of ≤ 20. The sample chosen for the MS/MSD will also be prepared as the DUP.

12.5. The digestion batch cannot exceed a total of 20 paying samples.

13.0. CALCULATIONS, REVIEW AND REPORTING:

N/A

14.0. HEALTH AND SAFETY:

14.1. Appropriate eye protection, goggles, and gloves will always be worn.

14.2. All digestion steps will be performed inside the designated hood.

14.3. A face shield, apron and sleeves will be worn when handling concentrated acid solutions.

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

14.5. Once it has been established that no further analysis of a sample will be required, acid and alkaline preserved samples will 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.

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

14.7. Proper Personal Protective Equipment (PPE) must always be worn. 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, apron and sleeves must be worn.

15.0. POLLUTION PREVENTION:

SGS is committed to evaluate all areas of the lab regarding 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:

Method performance does not apply to this SOP.

17.0. DETECTION LIMIT (DL) STUDY:

DL Studies are completed in 3 sets with 3 spiked vessels, one MB and one LCS and digested on 3 separate days. The process for DL studies follow the same procedure listed in Section 9.0. For the DL spike solution refer to **CX-0015**. Spike levels may be adjusted based off the first DL Study trial. Refer to SOP#116 for further guidance.

18.0. LIMIT OF DETECTION (LOD):

N/A

19.0. LIMIT OF QUANTITATION (LOQ):

The LOD/LOQ spike is prepared using **CX-0015.** Prepare the digests following the same procedure listed in Section 9.0, using appropriate spike volumes for the LOD/LOQ sample preparation. Refer to SOP#116 for further guidance.

20.0. REFERENCES:

SW846 3050B

21.0. ATTACHMENTS:

Attachment A: Flow Chart

Attachment A: FLOW CHART

Label digestion vessels and weigh 1 gram of homogenized sample into appropriately labeled vessel. Weigh 1.0-1.1 g Teflon stones for MB, LCS (and LCSD if applicable). OIL: 1.1-1.0 g oil base standard. GLYCOL: 1.0 mL DI water. Also requires filter blank. Ensure sample chosen for QC has MS, MSD, DUP (1.0-1.1 g each or 1.0 mL for glycols).

↓

Spike the LCS (and LCSD if applicable), MS, and MSD with 1.0 mL ICP/ICP-MS Matrix Spike Solution and 0.5 mL Silicon Spike.

↓

Add 2.5 mL of Milli-Q water, then 2.5 mL of concentrated HNO_3. Cover loosely with lids. Place into preheated 95±5ºC hot block and heat for 15 minutes.

↓

Remove from hot block. Cool 5 min. Add 2.5 mL of concentrated HNO_3. Place samples back onto 95±5ºC Hot Block. Heat for 45 minutes.

- Red fumes observed after 5 minutes (see step 9.6) → return to "Remove from hot block. Cool 5 min. Add 2.5 mL of concentrated HNO_3. Place samples back onto 95±5ºC Hot Block. Heat for 45 minutes."
- Red fumes not observed after 5 minutes (see step 9.6) ↓

Remove from hot block and cool to room temperature. Add 1.5 mL of Milli-Q water and 1.5 mL of 30 % H_2O_2 (or 0.5 mL 30% H_2O_2 if this step is being repeated). Place samples onto 95±5ºC Hot Block for 30 minutes. Do not exceed 5 mL H_2O_2 if this step must be repeated several times. See section 9.8 for oils and glycols.

- Effervescence observed after 30 minutes → return to "Remove from hot block and cool to room temperature. Add 1.5 mL of Milli-Q water and 1.5 mL of 30 % H_2O_2 (or 0.5 mL 30% H_2O_2 if this step is being repeated). Place samples onto 95±5ºC Hot Block for 30 minutes. Do not exceed 5 mL H_2O_2 if this step must be repeated several times. See section 9.8 for oils and glycols."
- Effervescence not observed after 30 minutes ↓

Add 1.0 mL of concentrated HCl and reflux on hot block for 15 minutes

↓

Cool, dilute to 50 mL, cap tightly, invert and shake samples. Particulates must be allowed to settle prior to analysis.

↓

Post, label and give to analyst.

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NOTE: This document contains CONFIDENTIAL business information and is not intended for distribution.	
S.O.P. Title: Ammonia Nitrogen by Discrete Analyzer	**Revision Date**: January 2021
Method No: 4500-NH_3 (B,F,G)	**SOP No**: 378r14
Page: 1 of 16	**Supersedes**: 378r13

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Technical Director	Date	Quality Assurance (QA) Manager, QA Staff or their Designee	Date
Stephen C. Ede	1/25/21	Jermana Penty	1/25/21

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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:

- Addenda 1 and 2 are incorporated into this version.
- Minor spelling and grammatical changes were made throughout.

Table of Contents

1.0. OBJECTIVE:

This document outlines a procedure for the determination of nitrogen as ammonia in aqueous and solid samples using discrete analyzer instrumentation.

2.0. SCOPE AND APPLICATION:

This method may be used for the determination of ammonia-nitrogen in soils, surface and domestic waters, saline, and industrial wastewaters using the Seal AQ2 discrete analyzer. The applicable range of the method is 0.1 to 5.0 mg/L ammonia-nitrogen. The ammonia-nitrogen concentration is determined by a colorimetrical means using the automated phenate method referenced in the 23rd edition of Standard Methods.

3.0. DEVIATIONS FROM REFERENCE METHOD:

3.1. The cuvette used for the Seal AQ2 is 10mm.

3.2. The calibration range used to determine ammonia-nitrogen is 0.1 to 5 mg/L. Higher concentrations may be determined through dilution of the sample.

3.3. *Sulfuric acid*, H_2SO_4, 5N, air scrubber solution is not used because the samples are determined via discrete analyzer instead of flow injection analysis.

3.4. Colorimetric reagents are added in the instrument specified order.

3.5. The AQ2 incubates samples for color development at a temperature of 40°C.

3.6. The distillation reagent (8.10) used in the distillation procedure assumes that residual chlorine is present in the sample at a concentration less than 25mg/L.

3.7. Ammonia on the AQ2 is analyzed at wavelength 660 nm.

4.0. RESPONSIBILITIES:

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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. Glycine, urea, glutamic acid, cyanates, and acetamide hydrolyze slowly on standing. Only urea and cyanates will hydrolyze on distillation at pH 9.5.

5.2. Volatile alkaline compounds (i.e.: ketones, aldehydes, and alcohols) may cause an off-color upon using the automated phenate method. Boiling off at a low pH (2 to 3) may eliminate some of these, such as formaldehyde.

5.3. Seawater and saline samples contain calcium and magnesium ions in sufficient concentrations to cause precipitation during analysis and must be distilled prior to analysis.

5.4. Eliminate any marked variation in acidity or alkalinity among samples because the color development for analysis is pH-dependent. Ensure that the pH of water and standard ammonia solutions approximates that of sample. This is especially important for samples that do not undergo distillation. For example, if the sample has been preserved with 0.8 mL conc H2SO4/L, include H2SO4 in diluent and standards at the same ratio. High buffering capacity in samples can also interfere with distillation and may result in low sample recovery.

5.5. Residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate before distillation.

5.6. Ammonia-nitrogen must not be determined on the Seal AQ2 concurrently as analyses that require alkaline matrices or solutions as it may cause matrix interference problems.

5.7. Turbidity and color may create interferences in those samples that are not distilled prior to determination. Drinking waters, clean surface or ground water, and good-quality nitrified wastewater effluent may be filtered to remove these interferences. Other types of water, and water that remains turbid or colored after filtration, must be distilled prior to determination of ammonia-nitrogen.

6.0. SAMPLE HANDLING:

6.1. Water samples are collected in a 125-mL clean container supplied to the client containing 0.5mL of concentrated H_2SO_4; this will adjust the contents of a full bottle to pH<2. If the sample is aqueous and not previously preserved immediately preserve by adding 0.5mL of concentrated H_2SO_4. Store at 0 - 6° C. Analyze as soon as possible within 28 days.

6.1.1. If a supplied preserved container is not filled with sample, (half full), the sample cannot be analyzed.

6.2. Soil samples are stored at 0 - 6° C.

6.3. For preserved aqueous samples the holding time is 28 days. The holding time SGS applies to solid samples is also 28 days.

6.4. Water samples received without preservation are preserved with H_2SO_4 to a pH of less than 2 upon receipt.

7.0. APPARATUS:

7.1. Seal AQ2 discrete analyzer with:

- Instrument appropriate cuvettes and reagent bottles.
- 2ml disposable polystyrene auto-analyzer sample cups.
- 40mL clear glass vials with closed top screw cap lids.
- Disposable labeled culture tubes.

7.1.1. For instrument maintenance and troubleshooting, refer to SOP 397. For computer, hardware, or software refer to IT.

7.2. 0.45µm filter.

7.3. 10mL disposable syringe.

7.4. Lachat MicroDist Distillation Block

7.5. Lachat MircoDist Tubes – User Fill Option-Ammonia Part #:A17117A

NOTE: The Lachat MicroDist Tubes, Part #:A17117, used for cyanide distillation should not be used for ammonia analysis due to ammonia contamination).

8.0. REAGENTS:

8.1. Reagent water, ammonia free: Deionized (DI) water.

8.2. Sulfuric Acid Concentrated high purity (low NH_3) H_2SO_4:

8.2.1. **Non-distilled Sample Diluent**: **0.06N H_2SO_4:** Dilute 0.75mL to 500mL with DI (8.1). Use for samples and instrument QC.

8.2.2. **Distilled Sample Diluent 0.032N H_2SO_4:** Dilute 0.4mL H_2SO_4 to 500mL of DI (8.1). used for distilled samples and instrument QC.

8.3. Sodium Hydroxide (NaOH) Pellets, Reagent grade:

8.3.1. 0.1M NaOH solution: Dissolve 4g of NaOH pellets in 1Lof DI. Bring to 1.0L after the solution has cooled.

8.4. Liquefied Phenol ~89 %:

8.4.1. Alkaline Phenate Solution: Dissolve 10g of NaOH pellets (8.3) in ~ 200mL DI. Add 28.1mL of liquefied phenol (8.4) to the cooled NaOH solution. Bring to 250mL with DI. Refrigerate overnight before using. Store in an amber bottle at 0-6ºC up to 1 month or until it becomes discolored.

8.5. EDTA (Ethylenediamine Tetraacetic Acid Disodium Salt Dihydrate) ACS grade:

8.5.1. Modified **EDTA Buffer** (75g/L):

8.5.1.1. For **Non-Distilled** Samples: Dissolve 37.5g EDTA (8.5) and 3.3g NaOH pellets (8.3) in ~400mL DI. Dilute to 500mL when cooled.

8.5.1.2. For **Distilled Samples**: Dissolve 37.5g EDTA (8.5) and 1.6g NaOH pellets (8.3) in ~400mL DI. Dilute to 500mL when cooled.

8.6. Nitroferricyanide (Sodium Nitroferricyanide) ACS grade: Dissolve 1.0g Nitroferricyanide in 500mL DI. This solution is good for 1 month. Store at 0-6ºC in amber jar.

8.7. Sodium hypochlorite (Clorox) 6% or 8.25% without any additives. Replace 1 months from opening.

8.8. Distillation reagents:

8.8.1. Sodium Thiosulfate Pentahydrate ACS grade:
NH_3 Distillation/Dechlorinating Reagent: Dissolve 6.5g of NaOH (8.3) and 0.35g of sodium thiosulfate into DI water Bring to 100mL volume.

8.8.2. Sodium Tetraborate Anhydrous ($Na_2B_4O_7$) /Sodium Tetraborate10Hydrate Crystals ($Na_2B_4O_7$-$10H_2O$):

8.8.2.1. **Sodium Tetraborate solution 0.025M**: Dissolve 5.0g ($Na_2B_4O_7$) anhydrous or 9.5g ($Na_2B_4O_7$-$10H_2O$) into 500mL of DI water. Dilute to 1000ml.

8.8.3. **Borate Buffer**: Combine 50mL of Sodium Tetraborate solution (8.8.2.1.) and 8.8mL of 0.1M NaOH solution (8.3.1). Total volume = 58.8mL.

8.9. **Stock Ammonia-Nitrogen Standard Solution (100 mg/L as NH_3-N)** purchased commercially (Hach item # 24065-49) or equivalent. If needed can be prepared by dissolving 0.3819g of anhydrous NH_4Cl in 1000 mL DI water.

Note: *This 100mg/L stock solution is used to prepare non-distilled standards.*

8.9.1. **Non Distilled** Calibration Curve Top Standard (5mg/L): Dilute 500µL of stock standard (8.9.) to 10mL with the appropriate sample diluent (8.2.1).

8.9.2. **Non Distilled** CCV Standard (2.5mg/L): Dilute 250µL of stock standard (8.9.) to 10mL with the appropriate sample diluent (8.2.1).

8.9.3. **Distilled Ammonia-Nitrogen Working Standard Solution (10 mg/L as NH_3-N):** Dilute 1.0mL NH_3-N stock (8.9.) to 10.0ml with distilled diluent 0.032^N H_2SO_4 (8.2.2.)

8.10. **2nd Source Stock QC Ammonia-Nitrogen Standard (100 mg/L as NH_3-N)** purchased commercially (RICCA item # 5453-4) or equivalent. This must be a different source then the stock standard.

8.10.1. **2nd Source Distilled Ammonia-Nitrogen Working Standard Solution (4 mg/L as NH_3-N)**
Non Distilled QCS: Dilute 0.4mL NH_3-N stock (8.10.) to 10 mL with 0.06^N H_2SO_4 (8.2.1.)

8.10.2. **Distilled QCS:** Dilute 0.24mL NH_3-N stock (8.10.) to 10.0ml with distilled diluent 0.032^N H_2SO_4 (8.2.2.)

9.0. DISTILLATION:

9.1. Samples that will not be distilled must be filtered using a 0.45µm filter (7.3.). Filtration must be documented in the logbook by reference to the lot number for filters used. The sample is now ready for determination on the discrete analyzer. A MB, LCS, LCSD is required for a batch of 20 samples or less. A matrix spike (MS) and matrix spike duplicate (MSD) is required for every batch of 20 samples or less. Prepare and apply appropriate QC controls to the system. See section 12.0 'Quality Control' for a description of QC standards and suggested preparatory schemes.

9.2. For samples that require distillation, perform the distillation procedure listed below.

9.2.1. The MicroDist heating block should be set at 120°C.

9.2.2. With the **M** end up; add 1 mL of 0.032N H_2SO_4 (8.2.2) into the tube. Place a filter membrane over the open end of the tube and push a tube cap over the membrane.

9.2.3. Label all the sample/distillation tubes.

9.2.4. Preparation of samples and standards into the sample tube are as follows:

9.2.4.1. **Curve Top Standard (5ppm NH_3):** Add 0.3mL of Ammonia Standard (8.9) into 6mL of 0.032^N H_2SO_4 (8.2.2).

9.2.4.2. **CCV (2.5mg/L NH_3):** Add 0.15mL of Ammonia Standard (8.9) into 6mL of 0.032N H_2SO_4 (8.2.2).

9.2.4.3. **QCS (4mg/L NH_3):** Add 0.24mL of Ammonia Standard, secondary source (8.10) into 6mL of 0.032N H_2SO_4 (8.2.2).

9.2.4.4. **MB/CB:** Add 6 mL of 0.032N H_2SO_4 (8.2.2).

9.2.4.5. **LCS/LCSD (1mg/L):** Add 60µl of Ammonia Standard (8.9) into 6mL of 0.032N H_2SO_4 (8.2.2).

9.2.4.6. **PS**: Add 6mL of sample.

9.2.4.7. **MS/MSD (1mg/L):** 5% or one per each batch of 20 or less samples: Add 6mL of sample and 60µl of Ammonia Standard (8.9).

9.2.4.8. **For Soil** samples, weigh approximately 0.5-1g of sample into sample tube and add 4mL of 0.032N H_2SO_4 (8.2.2).

9.2.5. Add 0.4mL of Distillation/dechlorinating reagent (8.8.1) to the samples.

9.2.6. Add 1mL of Borate Buffer (8.8.3) to the samples and clamp the sample tube to the distillation tube.

9.2.7. Place the tubes on the distillation block for 30 minutes.

9.2.8. When the 30 minutes is up, put on heat resistant gloves. Remove the first tube from the distillation block and **immediately** pull off the sample tube using a downward, twisting motion. ***Note: The liquid is boiling hot. This must be done immediately, or the distillate will be lost.*** The liquid

from the sample tube is discarded into the acid waste. Invert the distillation tube and place into rack with the **D** end up.

9.2.9. Hold the tube horizontally and rinse tube walls with the distillate in order to homogenize it. Slowly roll the distillate around the tube walls, gathering all the droplets clinging to the tube walls into the bulk of the distillate. Slowly return the collector tube to an upright position, **D** end up. Break the tube in the middle. Rinse the **D** end of the tube with 3 small 0.032N H_2SO_4 rinses, pouring each rinse into the **M** end. Be sure not to exceed the 6.0mL volume marked on the **M** end. Discard the **D** end. Fill to the 6 mL mark of the **M** end with 0.032N H_2SO_4 and pour into a labeled sample vial and cap securely.

9.2.10. The samples are now ready to be analyzed using the Ammonia Distillation method. Calibrate with the digested standard in 9.2.4.

10.0. CALIBRATION:

10.1. Place the Ammonia top standard (8.9.1) for undistilled samples or the digested standard (9.2.4.1) for digested samples in the sample wheel. The instrument will auto-dilute the top standard into the following points for the calibration curve:

Std	Conc (mg/L)	% of 5mg/L
1	0	0
2	0.1	2
3	0.25	5
4	0.5	10
5	1.25	25
6	2.5	50
7	5	100

10.2. **For Undistilled:** Place the Amm CCV (8.9.2) and Amm CB (8.2). Place the Amm QCS (8.10.1) in the sample wheel.

10.3. Place the reagents, **fresh daily**, in the reagent wheel containers. Verify that the reagent mixture is between 12.15 and 12.4 optimum pH. This is achieved be checking the pH of the reagent mixture at these volumes:

Reagent	pH Test Vol, mL
(8.2.1.) Sample matrix (Diluent)	3.75
DI Water	15.0
(8.5.1.1.) EDTA Buffer **(Undistilled)**	1.75
(8.5.1.2.) EDTA Buffer **(Distilled)**	1.75
(8.4.1.) Phenate	3.1
(8.7.) Bleach	1.3
(8.6.) Nitroferricyanide	1.0

Note: If the pH is not within the ideal range, the bleach is most likely the first reagent to need replacing.

10.4. Follow the start-up procedures outlined in SOP 397 “Seal AQ2 Operation Procedures”

11.0. ANALYSIS:

11.1. Follow the Seal Operation Procedures SOP 397 and the table below for ammonia analysis on the SealAQ2.

TEST PARAMETERS

PARAMETER	AQ2 SETTING
Test name	Ammonia 10
Units	Mg N/L
Decimals	3
Test Type	End point
Sample Volume (µl)	75
Water Volume (µl)	300
Number of mixes	1
Cuvette primes	2
Cuvette washes	2
Reaction time (seconds)	600
Wavelength (nm)	660
Polynomial order	1
Number of reagents	4
1. EDTA buffer (µl)	35
2. Phenate (µl)	62
3. Hypochlorite (µl)	26 (8.25% NaOCl)
4. Nitroferricyanide (µl)	20
Advanced test Parameters	Eliminate air from test transfer Extra Debubbling Action

11.2. Name the samples in the scheduling window.

11.3. Pour approximately 2mL of filtered sample into sample cups and place in the sample wheel.

11.4. Select ammonia analysis.

11.5. For sample results outside the calibration curve, the discrete analyzer will perform an auto-dilution up to 100x. If the sample is still outside the curve a hand dilution is required.

12.0. QUALITY CONTROL:

12.1. The discrete analyzer will analyze the calibration curve using linear regression. The correlation coefficient for the curve must be greater than or equal to 0.995. If the correlation coefficient is outside of acceptable control limits it must be re-analyzed.

12.1.1. Each calibration point must be evaluated with a 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.

12.2. The concentrations given for the CCV, LCS, MS/MSD, and QCS solutions are suggested values only. The QCS concentration is to be confined to the mid-portion of the curve. The flexibility of variable concentrations allows, over the course of time, the verification of the entire range of the calibration curve and permits a more thorough assessment of sample matrices. ***NOTE: values for the QC standards must be logged appropriately in logbooks and in LIMS. Discretion must be used when altering values in LIMS in order to maintain accurate and complete traceability.***

12.3. The instrument is set up to run a CCV and CB at the beginning of each run, after every 10 injections, and at the end of the run. The control limit for the CCV is ±10% of the true value. The CB must be less than the LOQ. If the CCV sample or the CB falls outside acceptable control limits, the CB and or CCV may be run one more time, if they do not pass the problem must be identified and corrected. The instrument is recalibrated, if necessary. All samples run after the last acceptable CCV/CB must be re-analyzed.

12.4. A QCS (2nd Source) standard must be analyzed after the calibration curve prior to any sample analysis to assess the validity of the calibration curve. The control limit for the QCS is ±10% of the true value.

12.5. A Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) are prepared with every prep batch of 20 samples or less. For filtered samples, create the LCS using filtered sample diluent. The acceptance criteria are ±25% of the true value. LCS failure action: Rerun once. If still outside of the acceptance limits, re-extract the batch. ***NOTE:*** The LCSD is intended to evaluate RPD precision only (not recovery). However, any QC value falling outside of limits should be narrated. A LCS is prepared by adding 100µl of stock standard (8.9) to 10ml of appropriate diluent (8.2) for a concentration of 1.0mg/L

12.6. A MS/MSD is required at a frequency of 5%, a set every batch of 20 or less samples. The recovery limit for the MS is ±25% of the known value. Matrix spike failure action: Verify batch integrity with LCS data, commenting on sample matrix interference. The RPD between the MS and MSD must be ±25. If the MSD fails to meet QC criteria, the passing RPD of LCS/LCSD can be used FOR lab precision QC. In these cases, the result will be reported and flagged. The MS/MSD are prepared by adding 100µl of stock standard (8.9) to 10ml of sample for a concentration of 1.0mg/L

12.7. A Method Blank (MB) will be prepared with every prep batch for a minimum of one MB per 20 samples. The acceptance criterion is less than the LOQ. MB contamination may require re-distillation (i.e., those with detectable results between the PQL and 10x LOQ). Samples having a concentration >10 times the blank value or < the LOQ may be reported. All other samples will require re-distillation.

12.8. 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 QA Office or Technical Department.

13.0. CALCULATIONS, REVIEW AND REPORTING:

13.1. The instrument will calculate the concentration of ammonia of unknown samples by entering the sample absorbance into the curve generated in section 10.0. ***NOTE:*** Assure that all hand dilutions are properly accounted for in the instrument's software.

13.2. CCV/QCS Recovery.

$$\frac{Vo}{Ve} \times 100 = \%\ \text{recovery} \qquad \text{EQUATION 1}$$

Vo = the observed value
Ve = the expected value

13.3. MS recovery

$$\frac{Vo-Sc}{Ve} \times 100 = \%\ \text{recovery} \qquad \text{EQUATION 2}$$

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

13.4. MS/MSD or LCS/LCSD Relative Percent Difference. (RPD):

EQUATION 3

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

Sc = observed sample concentration
Dc = observed duplicate sample concentration

13.5. Soil sample results are reported in terms of mg/Kg, corrected for percent solids. The dry correction is performed by the LIMS.

13.6. Review, Peer Review, and Reporting criteria are found in SOP 101 current revision.

13.7. Analytical results are calculated with 4 significant figures and reported in 3 significant figures.

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.

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. A DL study is performed when a new instrument is purchased, when a new method is developed or when repair or modification are made to parts that could affect reproducibility.

17.1.1 The suggested replicate spiking level for DL determination is 0.05 mg/L.

18.0. LIMIT OF DETECTION (LOD):

The LOD is ½ of the established LOQ.

19.0. LIMIT OF QUANTITATION (LOQ):

The LOQ is defined per SOP 116. LOQ verification shall be performed quarterly according to the schedule set by the QC office. The LOQ for this method is currently 0.10mg/L.

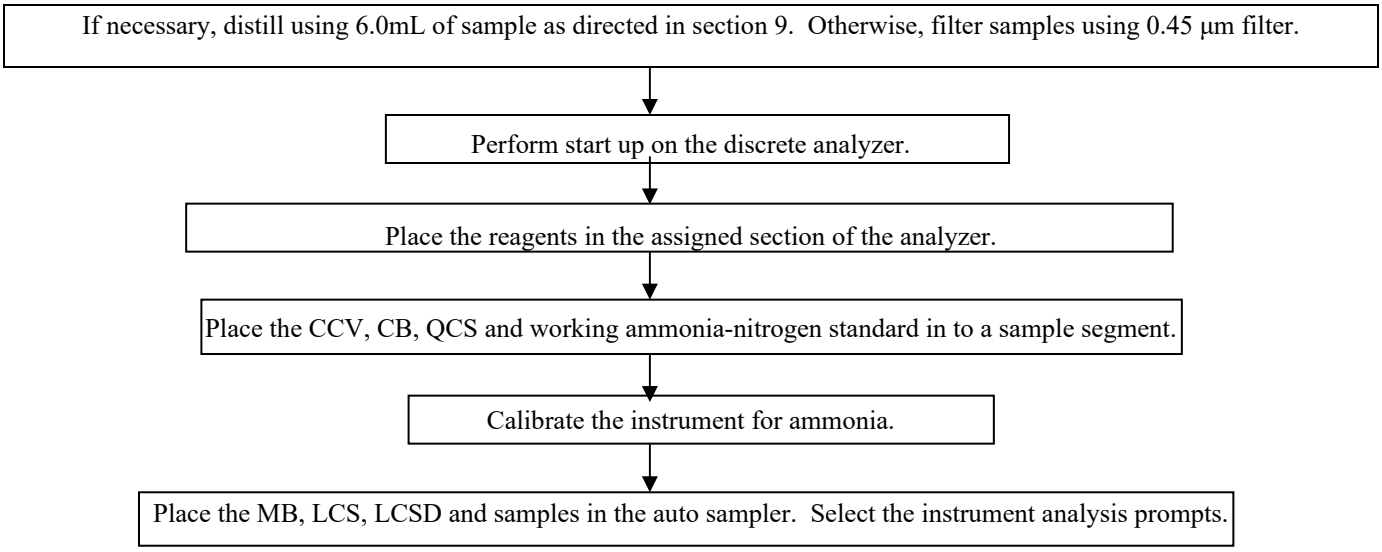
20.0. REFERENCES:

Standard Methods for the Examination of Water and Wastewater 4500-NH_3-23rd edition.

21.0. ATTACHMENTS:

ATTACHMENT A: Flow Chart
ATTACHMENT B: Corrective Action Table
ATTACHMENT C: Distilled Ammonia Prep Quick Reference Guide
ATTACHMENT D: Ammonia Analysis Quick Reference Guide

ATTACHMENT A: FLOW CHART



ATTACHMENT B: CORRECTIVE ACTION TABLE

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM4500-NH3 (B,F)	Calibration, 6 Point w/read back verification	Before each analytical batch	Correlation coefficient ≥ 0.995 Read back: Low pt: +/- 50% TV All other pts: +/- 10% TV	1. Find source of problem and Correct 2. Repeat calibration.
	Calibration Blank	After calibration, every 10 samples, and at end of run.	Concentration < the LOQ	1. Reanalyze once. 2. If it still fails, find source of problem and correct. 3. Evaluated samples having a concentration of >10X the CB or < the LOQ may be reported. All other samples must be reanalyzed
	Method blank (MB)	1 per batch of ≤ 20 samples.	< LOQ	Evaluated samples having a concentration >10 times the blank value or < the LOQ may be reported. All other samples must be refiltered / redistilled and reanalyzed.
	Laboratory control sample (LCS) Laboratory Control Sample Duplicate (LCSD)	1 per batch of ≤ 20 samples.	LCS Recovery ± 25% LCSD RPD ≤ 25%	1. Repeat analysis once. 2. Re-extract batch. 1. Use for batch QC if MS/MSD RPD is not within limits.
	Continuing calibration verification std. (CCV)	After calibration every 10 samples, and at end of run	Recovery ± 10%	4. Reanalyze once. 5. If it still fails, find source of problem and correct 6. Rerun all samples after last passing CCV.
	QC sample (QCS) (2^{nd} source)	After calibration	Recovery ± 10%	1. Reanalyze one time. 2. If it still fails, recalibrate
	Matrix Spike	1 per every batch of 20 or less samples.	Recovery ± 25%	Verify batch with LCS data. Comment sample matrix interference.
	Matrix Spike Duplicate	1 per every batch of 20 or less samples.	RPD ≤ 25%	Use LCS, LCSD RPD. Samples will be reported and flagged.

ATTACHMENT C: DISTILLED AMMONIA PREP

Ensure you are using the tubes specifically for ammonia distillation (different from the CN distillation)
Label, add 1mL of 0.032N H_2SO_4, and cap each tube with a membrane and cap

Curve = 6mL of 0.032N H_2SO_4 + 0.3mL stock Ammonia Spike
QCS = 6mL of 0.032N H_2SO_4 + 0.24mL 2nd source stock Ammonia Spike
CCV = 6mL of 0.032N H_2SO_4 + 0.15mL stock Ammonia Spike
CB/MB = 6mL of 0.032N H_2SO_4
LCS/LCSD = 6mL of 0.032N H_2SO_4+ 60µL of stock Ammonia Spike
Samples = 6mL of sample
MS/MSD = 6mL of sample + 60µL of stock Ammonia Spike

Add 1mL of Borate Buffer (8.8.3) to each sample
Add 0.4mL of Distillation/Decoloring Solution (8.8.1) to each sample
Press the top portion of the tube onto the sample cup
Place on hot block at 120°C for 30 minutes
Remove from hot block, quickly remove sample cup, and invert tube

Once cool, gently rock tube to collect condensed droplets into the M end, crack tube at middle perforation, rinse D end with 3 small 0.032N H_2SO_4 portions into the M end, and bring to 6mL mark on D end
Pour into sample storage tube and cap

ATTACHMENT D: AMMONIA ANALYSIS QUICK REFERENCE GUIDE

Reagents:

0.06N Diluent (**undistilled**) = 0.75mL concentrated H_2SO_4 diluted to 500mL
EDTA (**undistilled**)
Alkaline Phenate
Bleach – fill fresh daily
Nitroferricyanide
EDTA **(distilled**)
0.032N H_2SO_4 (**distilled**)

For Undistilled Samples

Curve = 0.500mL of stock Ammonia Spike + 9.5mL of diluent
CCV (x2) = 0.250mL of stock Ammonia Spike + 9.75mL of diluent
QCS = 0.400mL of 2nd Source Ammonia stock Spike + 9.6mL of diluent
LCS/LCSD = 0.100mL of stock Ammonia Spike + 9.9mL of diluent
MS/MSD = 0.100mL of stock Ammonia Spike + 9.9mL of sample

Filter all samples with a 0.45µM filter prior to analysis

True Values distilled & non distilled

Top Point = 5.0mg/L
CCV = 2.5mg/L
QCS = 4.0mg/L
LCS/LCSD = 1.0mg/L

MS/MSD =1.0mg/L

LOQ = 0.1mg/L
LOD = 0.05mg/L

For Distilled Samples
Pour all samples/QC into sample cups

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: Total & WAD Cyanide by Discrete Analyzer		**Revision Date**: February 2021
Method No: SM4500CN-B,C,E,I and 10-204-00-1-X-Hach		**SOP No**: 379r13
Page: 1 of 17		**Supersedes:** 379r12

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	2/4/21	Jamaica Rentz	2/4/21

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 coverpage 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:

- Addenda 1 and 2 have been incorporated into this version.
- Section 8.20 modified to reflect current reagent used for chlorine treatment.
- Minor spelling and grammatical changes were made throughout.

Table of Contents

1.0. OBJECTIVE:

This document outlines a procedure for testing cyanide in aqueous and solid samples using the Seal AQ2 discrete analyzer. This SOP also outlines the procedure for determining weak acid dissociable (WAD) cyanide in aqueous and solid samples using the Seal AQ2 discrete analyzer. Cyanide and WAD cyanide are converted to cyanogen chloride by reaction with chloramine-T that subsequently reacts with pyridine and barbituric acid to give a red colored complex that is measured colorimetrically. Cyanide often exists in metallic complexes such as ferricyanide, zinc cyanide, cupric cyanide, etc.

2.0. SCOPE AND APPLICATION:

2.1. This method is applicable to drinking, surface and saline water, domestic and industrial wastes. The applicable range of the method is 0.003 to 0.25 mg cyanide/L. This range may be extended with sample distillate dilution.

2.2. These test methods do not distinguish between cyanide ions and metallocyanide compounds and complexes. Furthermore, they do not detect cyanates.

2.3. Cyanide is highly toxic to humans, but more so to fish and other aquatic life. The presence of cyanide in industrial, domestic, and surface water is cause for concern.

2.4. "Cyanide" refers to all of the CN groups in cyanide compounds that can be determined as the cyanide ion, CN^-. The cyanide compounds in which cyanide can be obtained as CN^- are classified as simple and complex cyanides. When total cyanide is determined, the non-dissociable cyanides, as well as cyanide bound in complexes that are readily dissociable and complexes of intermediate stability are measured. The free and potentially dissociable cyanides also may be estimated when using the *Weak Acid Dissociable Cyanide* (SM4500 CN-I) procedure.

2.5. The maximum allowable limit for total cyanide concentration in water samples in Alaska is 0.20 mg/L. The maximum allowable contamination limit for the Municipality of Anchorage wastewater pretreatment is 0.30 mg/L. The TCLP/EPTOX inorganic waste management profile is 250 mg/kg.

3.0. DEVIATIONS FROM REFERENCE METHOD:

3.1. The discrete analyzer uses a wavelength of 578 nm to analyze total cyanide and WAD cyanide.

3.2. The distillation system used is the Lachat Micro Dist heating block and plastic closed system distillation tubes.

3.3. The AQ2 cuvette has a light path of 10 mm.

3.4. The concentration of standard cyanide is not titrated weekly. Certified commercially prepared, primary and secondary cyanide standards are purchased, alternating months, so that each standard is checked against another standard which is no more than one month old from date of purchase.

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 revisions to make, the SOP cover page is signed and dated by the Technical Director and QA to document the review, and then the updated cover page and SOP are 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. Common interferences in the analysis for cyanide include oxidizing agents, sulfides, aldehydes, glucose and other sugars, high concentration of carbonate, fatty acids, thiocyanate, and other sulfur containing compounds. Chlorinated samples need to be treated before preservation at the time of collection; clients can make arrangements with SGS for sample kits to pretreat samples with sodium arsenite to remove chlorine before preservation with sodium hydroxide. See procedure form PS0039.

5.2. Sulfides adversely affect the procedure by converting CN^- to SCN rapidly, especially at a high pH. Test for S^{2-} by placing a drop of sample on lead acetate test paper. Darkening of the paper indicates the presence of S^{2-}. Add lead acetate, or if the S^{2-} concentration is too high, add powdered lead carbonate [$Pb(CO_3)_2$] to avoid significantly reducing pH. Repeat this operation until a drop of treated sample solution does not darken the lead acetate paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be analyzed.

5.3. High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. Oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

6.0. SAMPLE HANDLING:

6.1. Samples must be preserved to pH 11 with NaOH at the time of sampling and are collected in amber HDPE plastic bottles. Chlorinated samples must be treated with sodium arsenite prior to preservation with NaOH.

6.2. Refrigerate samples at 0 to 6ºC. Amber HDPE prevents ultraviolet radiation penetration, so storage in the dark is not necessary.

6.3. Analysis must be complete within 14 days of sampling and preservation. Sample pH must be checked prior to analysis and recorded in the preparation notes. If the sample has been incorrectly preserved, contact the project manager for further instructions.

6.4. Samples containing sulfide are treated with lead carbonate.

6.5. Samples received in lab that test positive for chlorine cannot be analyzed for cyanide. The Project Manager must be notified immediately.

7.0. APPARATUS:

7.1. **Distillation:**

7.1.1. Lachat Micro Dist.

7.1.2. Assembled Micro Dist polypropylene sample and collector tubes, unfilled.

7.1.3. Appropriate glassware:

7.1.3.1. Volumetric flasks class A, 10mL, 50mL

7.1.3.2. Pipetters, Eppendorf, or equivalent.

7.1.3.3. Disposable culture tubes, 20 x 150 mm

7.1.4. Timer

7.2. **Analysis:**

7.2.1. AQ2 Seal Discrete Analyzer or equivalent.

7.2.1.1. Sample cups

7.2.1.2. Reagent bottles

7.2.1.3. AQ2 reaction Wells

8.0. REAGENTS:

8.1. Deionized water (DI).

8.2. Sodium Hydroxide (NaOH) Pellets ACS Certified, Fisher S318-500 or equivalent.

8.2.1. **CN Diluent** : 0.25^{N} NaOH: Place a two liter volumetric flask containing a stir bar on a stir plate. Fill with about 2/3 with DI water. Add 20 grams of high purity NaOH pellets. Stir until dissolved. Heat will be generated, when cool bring to volume with DI water.

8.3. Concentrated Sulfuric Acid (H_2SO_4) ACS grade

8.4. Sodium Dihydrogenphosphate ($NaH_2PO_4H_2O$) ACS grade:

8.4.1. **Phosphate Buffer 1M:** Dissolve 69 grams of $NaH_2PO_4H_2O$ (8.3) in 500mL of DI water. Keep this solution refrigerated.

8.5. Chloramine-T trihydrate $C_7H_7ClNO_2SNa_3H_2O$:

8.5.1. Chloramine-T 1.0% solution: Dissolve 0.1 grams of chloramine-T into 10 mL DI water. Prepare fresh daily.

8.6. Hydrochloric Acid, ACS grade

8.7. Pyridine ACS reagent grade

8.8. Barbituric Acid 99%:

8.8.1. **Pyridine Barbituric Acid Color Reagent**: Place 3g of barbituric acid in a 200 mL flask and add enough DI water to wash the sides of the flask. Add 15 mL of pyridine and mix. Add 3 mL of concentrated HCl and mix. Add additional DI water and stir to dissolve and break up the lumps of barbituric acid. Fill to the final volume of 200 mL with DI water and stir until mixed. *NOTE: Mixture will not go into solution until brought to volume.* After the mix is in solution add DI to 200mL (some evaporation will have occurred) Store reagent at 0- 6ºC in an amber bottle for up to six months. Replace if particulates form in the bottom of the bottle.

8.9. Magnesium Chloride hexahydrate ($MgCL\text{-}6H_2O$):

8.9.1. **Cyanide Distillation Solution, 11^M H_2SO_4 / 0.79^M MgCl**: Dissolve 32.2 grams of magnesium chloride ($MgCl_2\text{-}6H_2O$) in 100 mL DI water. Slowly add 76 mL concentrated H_2SO_4. Bring to 200mL with DI water and mix. Store in amber bottle.

8.10. Zinc Acetate monohydrate, crystalline Certified ($ZnC_2H_3O_2\text{-}H_2O$)

8.11. Sodium acetate trihydrate anhydrous, ACS reagent ($NaC_2H_3O_2\text{-}3H_2O$).

8.12. Glacial Acetic Acid, ACS certified.

8.13. **WAD Cyanide Distillation Solution (0.50^M zinc acetate / 0.52^M sodium acetate / 0.87^M acetic acid):** Dissolve 35.5g sodium acetate and 50 grams zinc acetate in 400mL DI water. Add 27mL glacial acetic acid, slowly. When cool bring to volume of 500mL with DI water. Store in amber bottle.

8.14. Sulfamic acid 99% pure

8.15. Lead carbonate powder ($Pb(CO_3)_2$)

8.16. Methyl Red Indicator: Dissolve 0.025g powdered methyl red in 50mL DI water. Mix well & store in amber bottle.

8.17. pH test strips readable to 0.5 pH units.

8.18. Lead acetate paper.

8.19. Potassium iodide starch test strips.

8.20. Sodium arsenite (0.1N) - $NaAsO_2$ from Fisher. Kit prep will use 1.92 mL of this solution per cyanide sample bottle. Used for on-site chlorine removal before NaOH preservation.

8.21. **Cyanide Stock Standard (1000 mg/L):** (Spex Certa Prep simple cyanide order # RSCN9-2Y) or equivalent. Purchased commercially every other month**.**

8.21.1. **Intermediate Cyanide Standard (100mg/L):** Dilute 10.0 mL of Cyanide Stock Standard (8.21) to100 mL with 0.25^N NaOH (8.2.1). Final concentration is 100 mg/L. Make fresh every other month. Label appropriately and store in amber at 0-6°C.

8.21.2. **Working Cyanide Standard (5.0 mg/L):** Dilute 0.5mL of Intermediate Cyanide Standard (section 8.21.1) to 10 mL with 0.25^N NaOH (section 8.2.1). Make fresh daily.

8.21.3. **Top Calibration Curve Standard (0.25mg/L):** Dilute 0.5mL of Working Standard (8.21.2) into 10 mL of 0.25^N NaOH (8.2.1).

8.21.4. **CCV Standard (0.1mg/L):** Dilute 200µL of Working Standard (8.21.2) into 10 mL of 0.25^N NaOH (8.2.1).

8.22. **Second Source, Cyanide Stock Standard (1000 mg/L):** This must be a different source than the stock standard. (AccuStandard total cyanide order # WC-CN-10X-1) equivalent. Purchased commercially every other month (opposite month of primary purchase)**.**

8.22.1. **Intermediate 2nd Source Standard (100 mg/L):** Dilute 10.0 mL of 1000 mg/L Stock 2nd Source Standard (section 8.22.) to 100 mL with 0.25^N NaOH (section 8.2.1.). Make fresh every other month. Label appropriately and store in amber at 0 - 6°C.

8.22.2. **Working QCS Standard (2.0mg/L):** Dilute 200µL of Intermediate 2nd Source Standard (8.22.1) to10 mL with 0.25^N NaOH (section 8.2.1). Make fresh daily.

8.22.3. **QCS Standard (0.2mg/L):** Dilute 1.0mL of 2.0mg/L Working QCS Standard (8.22.2) to 10.0 mL with 0.25^N NaOH (section 8.2.1). Make fresh daily.

9.0. DISTILLATION:

9.1. The heating block temperature should be set at 120ºC.

9.2. With the **M** end up; put as many collector tubes as you have samples into a sample rack. Add 2mL of 0.25^N NaOH, place a filter over the open tube end, and push a cap over the filter onto the tube until it clicks into place. Take care not to rip or wrinkle the filter.

9.3. Label all of the sample tubes and distillation / collection tubes.

9.4. Prepare a Method Blank (MB):

9.4.1. Liquid samples: Add 1.0mL 0.25^N NaOH (8.2.1) and 5.0mL DI water to sample tube.

9.4.2. Solid samples: 1.0 gram baked sand, 4mL DI, 1.0mL 0.25^N NaOH.

9.5. Prepare a Laboratory Control Sample/ Laboratory Control Sample Duplicate (LCS/LCSD):

9.5.1. Liquid samples: Add 60µl of 5.0mg/L working primary standard (8.21.2) to 4.mL DI and 2mL 0.25^N NaOH (8.2.1) in the sample tube. Final concentration is 0.05 mg/L.

9.5.2. Soil Samples: Add 60µl of 5.0mg/L working primary standard (8.21.2) to 4.mL DI and 1mL 0.25^N NaOH (8.2.1) in the sample tube. Final concentration is 0.05 mg/L.

9.6. Prepare a Matrix Spike / Matrix Spike Duplicate (MS/MSD):

9.6.1. Liquid samples: Add 60µl of 5.0mg/L working primary standard (8.21.2) to 6 mL of sample in the sample tube. Final concentration is 0.05mg/L.

9.6.2. Solid samples: Add 60µl of 5.0mg/L working primary standard (8.21.2) to 1.0 gram sample, 4mL DI, & 1.0mL 0.25^{N} NaOH.

9.7. Soil Samples: Weigh 1.0 gram of soil sample into the sample tube. Add 1.0mL of 0.25^{N} NaOH and 4mL of DI.

9.8. Liquid Samples: Test pH with test strips (8.17.) and test for chlorine with potassium iodide paper strips (8.19.). Place 6.0mL of the sample into a labeled sample tube.

9.9. For soil samples to be analyzed for cyanide add approximately 0.024 grams of sulfamic acid granules by scoop (8.14) and 0.75mL of the cyanide distillation solution (8.9.1) to the sample tube.

9.10. IMMEDIATELY push the **D** end of the properly labeled collector tube over the open end of the sample tube and place the assembly in the press by putting the sample tube through the hole in the white base.

9.11. **Before pressing, the user should grip the collector tube firmly at the breakaway point to keep the tube from cracking at this point.** The pressing motion should be a smooth, constant pressure which is just enough to slide the sample tube inside the collector tube. Press down on the handle until the stop ring on the sample tube hits the **D** end of the collector tube.

9.12. For samples to be analyzed for WAD cyanide add one drop methyl red indicator (8.16) *caution, too much methyl red will affect the UV absorbance*, and 0.75mL of WAD distillation solution (8.13) indicator will turn from yellow to pink with the addition of the WAD distillation reagent if samples are at the correct pH.

9.13. IMMEDIATELY push the **D** end of the properly labeled collector tube over the open end of the sample tube and place the assembly in the press by putting the sample tube through the hole in the white base.

9.14. Put on heat resistant gloves. Push the collector tube end of each sample tube all the way into the preheated block so that the tube stop ring touches the block.

9.15. Set the timer for **30 minutes**.

9.16. When 30 minutes is up, put on heat resistant gloves, face mask and goggles. Remove the first tube from the block and **immediately** pull off the sample tube using a downward, twisting motion. **CAUTION:** The solution in the tube is ***boiling NaOH*** and may have built up back pressure that will be released when you remove the sample tube. You **must** remove the sample tube within 4 seconds of removing it from the block or "suck-back" of the sample will occur, which invalidates the sample.

9.17. Invert each collector tube and place it into a rack with the **D** end up. Allow to cool at least 10 minutes.

9.18. Hold the tube horizontally and rinse tube walls with the distillate in order to homogenize it. Slowly roll the distillate around the tube walls, gathering all the droplets clinging to the tube walls into the bulk of the distillate. Then, slowly return the collector tube to an upright position so that the **D** end is up. Break the collector tube in half and twist and tear off the **D** end. Rinse the **D** end with 3 small 0.25^{N} NaOH rinses, pouring each rinse into the **M** end. Be sure that you do not exceed 6.0mL volume marked on the **M** end. Discard the **D** end.

9.19. In the remaining **M** end of the collector tube, dilute to the 6.0mL mark with 0.25^{N} NaOH. Decant the 6mL sample into a labeled sample vial and cap securely.

9.20. Test the distillate with dry lead acetate paper strips (8.18) for sulfide. Treat if necessary.

9.21. Store samples in a dark cabinet until analysis.

10.0. CALIBRATION:

10.1. Place the CN top standard (8.21.3) in the sample wheel. The instrument will auto-dilute the top standard into the following points for the calibration curve:

Std	Conc. (mg/L)	% of 0.25mg/L
1	0	0
2	0.003	1.2
3	0.005	2
4	0.013	5
5	0.025	10
6	0.063	25
7	0.250	100

10.2. Place the CN CCV (8.21.4) and CN CB (8.2.1) into the reagent wheel.

10.3. Place the CN QCS (8.22.3) in the sample wheel.

10.4. Follow the start-up procedures outlined in SOP 397 “Seal AQ2 operation procedures”

10.5. Place fresh CN/WAD reagents: phosphate buffer (8.4.1), chloramine T (8.5.1) and barbituric acid (8.8.1) in the reagent wheel.

11.0. ANALYSIS:

11.1. Select the following Test Parameters:

PARAMETER	AQ2 SETTING
Test Name	CYANIDE 335.4
Units	µg/L
Decimals	3
Test type	End point
Sample volume (µl)	250
Water volume (µl)	0
Number of mixes	1
Cuvette primes	1
Cuvette wash	2
Baseline wash	Ticked
Reaction time (seconds)	480
Wavelength (nm)	578
Polynomial order	1
Number of reagents	3
1. CN Neutralizing reagent (µl)	100
2. CN Chloramine-T (µl)	25

3. CN Pyridine barbituric acid (µl)	240
Reagent 3 Delay (sec)	85

11.2. Name the samples in the scheduling window.

11.3. Pour approximately 2mL aliquots of sample into sample cups and place in the sample wheel.

11.4. Select CN or WAD analysis for each sample.

11.5. In those instances where WAD results are greater than the result for Total Cyanide (greater than or equal to the LOQ), the sample will be confirmed by reanalysis.

12.0. QUALITY CONTROL:

12.1. The discrete analyzer will analyze the calibration curve using linear or quadratic regression. The correlation coefficient for the curve must be greater than or equal to 0.995.

12.1.1. Each calibration point must be evaluated with a read back. Validation for the point equal to the LOQ is ± 50% of the true value. The criterion for all other points is ±10% of the true value.

12.1.2. For drinking water samples, a low-level quantitation (LLQ) sample needs to be evaluated each analysis day. The LLQ will be prepared with the samples.

12.2. The instrument is set up to run a Continuous Calibration Verification sample (CCV) and a calibration Blank (CB) at the beginning of each run, after every 10 injections, and at the end of the run. The control limit for the CCV is ±10% of the true value. The CB must be less than the LOQ. If the CCV or the CB falls outside acceptable control limits, you can run it once more. A second failure requires that all samples run after the last acceptable CCV/CB be re-analyzed.

12.3. A Quality Control Sample (QCS), 2nd Source, must be analyzed after the curve. The control limit for the QCS is ±10% of the true value.

12.4. A (LCS/LCSD) are prepared with every prep batch of 20 or less samples. The acceptance criteria is ±25% recovery of the true value. LCS failure action: Rerun once. If sill outside of the acceptance limits, re-extract the batch. *NOTE:* The analysis of the LCSD is to evaluate for precision using the relative percent difference (RPD) calculation if the RPD for the MSD does not meet criteria. However, all QC limit failures should be noted with a sample comment.

12.5. A MS/MSD is required for each batch of 20 samples or less. The recovery limit for the MS/MSD is ±25% of the known value. Matrix spike failure action: Verify batch integrity with LCS data, commenting on sample matrix interference. The RPD criterion for MS/MSD is ≤25. If the MSD fails to meet RPD QC criterion, the LCS/LCSD RPD can be used to demonstrate batch precision. In these cases, the sample shall be reported and flagged with a comment

12.6. A Method Blank (MB) will be prepared with every prep batch one MB per 20 samples or less. The acceptance criterion is less than LOQ. If the MB is outside of QC limits, samples with concentrations greater than 10 times the blank contamination and samples with a concentration less than the LOQ may be reported. All other samples must be re distilled for analysis.

12.6.1. The MB will be evaluated at the DL for drinking water samples.

12.7. Bubbles in the cuvette can cause outliers in the analysis. Routine maintenance and degassed water can lower the chances of bubbles developing in the cuvette. Refer to SOP#377 for further explanation.

12.8. 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 QA Office or Technical Department. Seal software can be programmed to flag samples that have developed bubbles in the cuvette by taking the absorbance of the sample before the final reagent is added. Samples that have been flagged for a high blank should be rerun.

13.0. CALCULATIONS, REVIEW AND REPORTING:

13.1. The instrument will calculate the concentration of cyanide of unknown samples by entering the sample absorbance into the curve generated in section 10.0. *NOTE:* Assure that all hand dilutions are properly entered into the instrument software. The sample Blank Response/Cal. Voltage should be monitored to assure the validity of data. If the Blank Response absolute value is greater than 0.001 run the sample in duplicate to confirm the Blank Response. If the duplicate analysis Blank Response is less than 0.001 use data from this analysis. If not use the data with the lowest Blank Response obtained.

13.2. CCV/QCS Recovery. The Seal is programmed to flag failing CCVs.

EQUATION 1

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

Vo = the observed value
Ve = the expected value

EQUATION 2

13.3. LCS / MS recovery

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

V = the observed value of the spiked sample
Sc = the observed value of the sample
Ve = the expected value of the spike

13.4. MS/MSD or LCS/LCSD Relative Percent Difference. (RPD):

EQUATION 3

$$\frac{Sc - Dc}{\{(Sc + Dc) / 2\}} \times 100 = \text{Duplicate Relative Percent Difference (Dup RPD)}$$

Sc = observed sample concentration
Dc = observed duplicate sample concentration

13.5. Soil sample results are reported in mg/Kg, corrected for percent solids. The percent solids correction is performed by the LIMS system.

13.6. Review, Peer Review, and Reporting criteria are found in SOP 101.

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 any 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. Total Cyanide: Following ADEC drinking water requirements, DL studies are performed annually at a minimum, when a new operator is trained, when a significant change in instrument response is observed, or when a new instrument is purchased for analysis.

17.2. WAD Cyanide: Following SGS SOP 116, DL studies are performed initially, when a significant change in instrument response is observed, upon the failure of a quarterly LOD verification, or when a new instrument is purchased for analysis.

17.3. An update to the DL does not necessitate an update to this document. The suggested DL spiking value for cyanide is 0.005 mg/L.

18.0. LIMIT OF DETECTION (LOD):

18.1 Total Cyanide: LOD reporting is not a requirement for ADEC drinking water methods.

18.2 WAD Cyanide: An LOD verification must be completed on a quarterly, refer to SOP 116.

19.0. LIMIT OF QUANTITATION (LOQ):

19.1. The current LOQ for cyanide in water is 0.005 mg/L.

19.2. The current LOQ for cyanide in soil is 0.06 mg/Kg.

19.3. An update to the LOQ does not necessitate an update to this document.

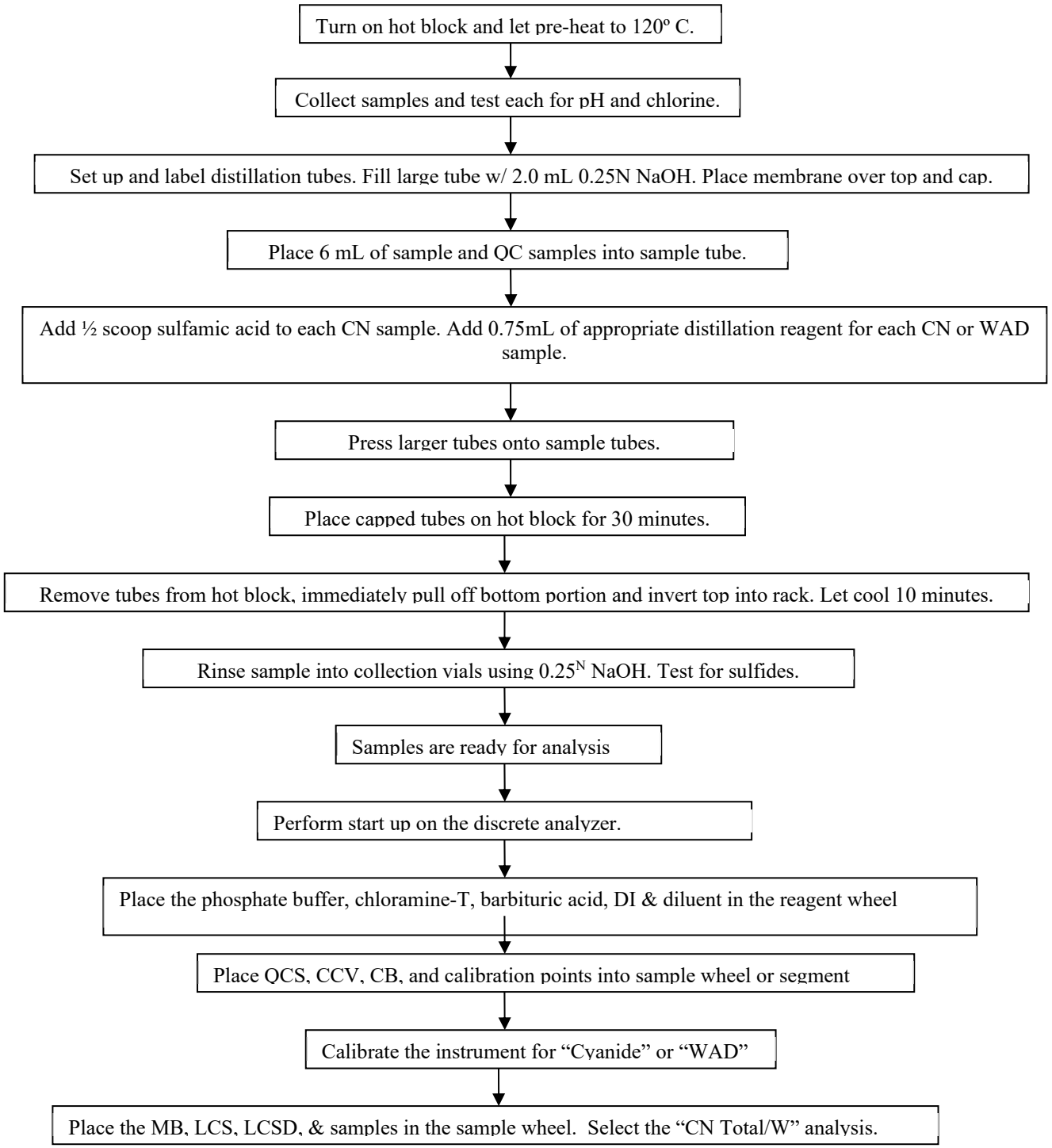
20.0. REFERENCES:

Standard Method 4500-CN, 23rd Edition
HACH Method 10-204-00-1-X

21.0. ATTACHMENTS:

ATTACHMENT A: Flow Chart
ATTACHMENT B: Corrective Action Table
ATTACHMENT C: Cyanide Quick Reference Guide

ATTACHMENT A: FLOW CHART



ATTACHMENT B: CORRECTIVE ACTION TABLE

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM4500-CN-B,C,E,I	Calibration, 6 Point w/read back verification	Before each analytical batch	Correlation coefficient ≥ 0.995 Read back: Pt. at LOQ: +/- 50% TV Pts. >LOQ: +/- 10% TV`	1. Find source of problem and Correct 2. Repeat calibration.
	Calibration Blank	After calibration, every 10 samples, and at end of run.	Concentration < the LOQ	1. Reanalyze once. 2. If it still fails, find source of problem and correct. 3. Evaluated samples having a concentration of >10X the CB or < the LOQ may be reported. All other samples must be reanalyzed
	Method blank (MB)	1 per batch of ≤ 20 samples.	< LOQ CN DW <DL	Evaluated samples having a concentration >10 times the blank value or < the LOQ may be reported. All other samples must be refiltered / redistilled and reanalyzed.
	Laboratory control sample (LCS) Laboratory Control Sample Duplicate (LCSD)	1 per batch of ≤ 20 samples.	LCS Recovery ± 25% LCSD RPD ≤ 25%	1. Repeat analysis once. 2. Re-extract batch. 1. Use for batch QC if MS/MSD RPD is not within limits.
	Continuing calibration verification std. (CCV)	After calibration every 10 samples, and at end of run	Recovery ± 10%	4. Reanalyze once. 5. If it still fails, find source of problem and correct 6. Rerun all samples after last passing CCV.
	QC sample (QCS) (2nd source)	After calibration	Recovery ± 10%	1. Reanalyze one time. 2. If it still fails, recalibrate
	Matrix Spike	1 per every batch of 20 or less samples.	Recovery ± 25%	Verify batch with LCS data. Comment sample matrix interference.
	Matrix Spike Duplicate	1 per every batch of 20 or less samples.	RPD ≤ 25%	Use LCS, LCSD RPD. Samples will be reported and flagged.

ATTACHMENT C: CYANIDE QUICK REFERENCE GUIDE

Cyanide Prep

Prepare working Cn standard 5mg/L: 0.5ml CN intermediate standard (100mg/L) + 9.5mL of 0.25N NaOH.
Prepare working Cn 2nd source standard 2mg/L: 0.2ml CN QCS intermediate standard (100mg/L) + 9.8mL of 0.25N NaOH

Prep distillation tubes: Label, add 2mL of 0.25N NaOH, and cap each tube with a membrane and cap

MB = 5mL of DI + 1mL of 0.25N NaOH
LCS/LCSD = 60µl of working Cn std. (5mg/l) 4mL of DI + 2mL of 0.25N NaOH.Samples = 6mL of sample
MS/MSD = + 60µL of working Cn std. (5mg/l) +6mL of sample.

For TOTAL CN, add 1 scoop of sulfamic acid and 750µL of CN distillation reagent to 6mL sample, then press top portion of tube onto bottom
For WAD CN, add 1 drop of methyl red and 750µL of WAD distillation reagent to 6mL sample, then press top portion of tube onto bottom
Place on hot block at 120°C for 30 minutes
Remove from hot block and quickly remove sample cup and invert tube

Once cool, gently rock tube to collect condensed droplets into the M end, crack tube at middle perforation, rinse D end with 3 small 0.25N NaOH portions into the M end, bring to 6mL mark on D end
Pour into sample storage tube and cap

Chlor-T = 0.5g dissolved in 50mL DI – Make daily

Intermediates:
CCV 0.1mg/L: = 0.2mL of working CN solution (5mg/L) to 9.8mL of 0.25N NaOH
QCS 0.2mg/L: = 1mL of 2nd source working CN solution (2mg/L) to 9.0mL of 0.25N NaOH

Top calibration standard 0.25mg/L: = 0. 5mL of working std (5mg/L) + 9.5mL of 0.25N NaOH

True Values

QCS = 0.2mg/L
CCV = 0.1mg/L
LCS/LCSD = 0.05mg/L
MS/MSD =0.05mg/L
LOQ = 0.005mg/L
LOD = 0.0025mg/L

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: Alkalinity, Acidity, pH, Free CO_2 & Conductivity by Auto-titrator	**Revision Date**: January 2021
Method No: SM2320B, SM2310B, SM4500H-B, 4500-CO_2, SM2510A and B	**SOP No**: 394r09
Page: 1 of 22	**Supersedes:** 394r08

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	1/27/21	Jamaica Beatty	1/27/21

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 coverpage 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:

- Addendum #1 was incorporated into this version
- Attachments F and G were listed at the beginning of section 21
- Reference document updated to current edition

Table of Contents

1.0. OBJECTIVE:

This method outlines a procedure for determining the pH, conductivity, alkalinity and/or acidity of aqueous or solid material by auto-titrator.

2.0. SCOPE AND APPLICATION:

2.1 **Conductivity:** Conductivity is a numerical expression of the ability of an aqueous solution to conduct electric current. This ability depends on the presence of ions; their concentrations, mobility and valence; and on the temperature of the measurement. This method is used to determine the conductivity and resistivity of drinking, surface, saline waters, domestic and industrial wastes, and soils. Laboratory conductivity measurements are used for various purposes such as estimating total dissolved solids in a sample, assessing degree of mineralization or estimating sample size to be used for common chemical determinations.

2.2 **pH:** A pH electrode and a thermistor temperature sensor or a combination electrode is used to determine the pH of drinking water, surface water, and aqueous industrial waste samples.

2.3 **Alkalinity:** This operating procedure is used to determine the alkalinity of surface and groundwater, effluents, and industrial waters by means of an auto-titrator. An unaltered sample is titrated to a predetermined pH of 4.5 using 0.02N H_2SO_4. The end point is determined with a pH meter and results are reported as milligrams per liter. If a lower detection limit is needed the titrator will then titrate the sample to a pH of 4.2. To distinguish different forms of alkalinity the titrator will titrate to a pH of 8.3 when applicable.

2.4 **Acidity:** This operating procedure is used to determine the acidity of drinking water, surface and sewer waters, industrial waters, particularly mine drainage and receiving streams, and other water free of ferrous iron or other polyvalent cations in a reduced state by means of an auto-titrator. An unaltered sample is titrated to a predetermined pH of 8.3 using 0.02N carbonate-free NaOH solution. The end point is determined with a pH meter and results are reported as milligrams per liter.

2.4.1 This operating procedure is also used to determine the acidity of samples containing hydrolysable metal ions and reduced forms of polyvalent cations via hot peroxide treatment.

3.0. DEVIATIONS FROM REFERENCE METHOD:

3.1 The conductivity meter used at SGS incorporates a temperature probe. The cell constant is not adjusted. Calibration is confirmed at the beginning of each batch by reading high and low, NIST traceable, standards.

3.2 Conductivity samples are run at room temperature and are not warmed to 25ºC. PT studies demonstrate that this is an acceptable deviation from the reference method.

3.3 Acidity samples have a 14 day regulatory holding time.

3.4 Acidity and Alkalinity samples are analyzed at 50 mL. PT studies demonstrate that this is an acceptable deviation from the reference method.

3.5 The pH probe is a temperature compensating probe and, therefore, the temperature is not recorded in the run log. The temperature is, however, available in the raw data printed by the auto-titrator.

3.6 pH buffers will be used within the listed expiration date unless they fail to produce a valid calibration. If a buffer begins to respond erratically it will be replaced with an unopened container.

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 An electronic copy of this SOP and any prior versions of this SOP are maintained on the computer network in 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 revisions to make, the SOP cover page is signed and dated by the Technical Director and QA to document the review, and then the updated cover page and SOP are 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.

4.6 It is the responsibility of the analyst to monitor the waste and reagent levels in order to avoid spills and false results.

5.0. INTERFERENCES:

5.1 **Conductivity:**

5.1.1 Temperature variations and corrections represent the largest source of potential error. The probe includes an automatic temperature compensation (ATC) probe.

5.1.2 Conductivity cell must be kept clean. See instrument manuals for recommended cleaning procedures.

5.1.3 Samples containing mineral acids may also contribute to potential errors.

5.2 **pH:**

5.2.1 Samples containing large amounts of particulate or oily films may cause problems with electrode response. Removal of the interfering matter may be accomplished by wiping the electrode, gentle washing with a detergent followed by a thorough rinse with DI water, treatment with dilute hydrochloric acid, or a combination of the above.

5.2.2 The temperature of the sample may interfere with the pH analysis. The temperature could affect the electrode itself, or the sample pH could be temperature dependent. pH analysis should be performed on samples and buffers at room temperature.

5.3 **Alkalinity:**

5.3.1 Response time can become sluggish if the sample is oily or coats pH probe.

5.3.2 If the sample contains inorganic acids or salts of a weak acid they can cause interferences with the electrometric pH meter.

5.3.3 Bubbles in the titrant dispensing line may cause incorrect dispensing volumes. To remove bubbles, follow the steps outlined in section 11.2.10.

5.3.4 If the sample contains mineral acids, it may be necessary to change the end point to a pH of 3.9.

5.4 **Acidity:**

5.4.1 Samples may be subject to microbial action and to loss or gain of CO_2 or other gases when exposed to air. Sample agitation and prolonged exposure to air should be avoided.

5.4.2 Suspended matter present in the sample, or precipitates formed during the titration may cause sluggish electrode response. This may be offset by a slow drop wise addition of titrant as the endpoint pH is approached.

5.4.3 Bubbles in the titrant dispensing line may cause incorrect dispensing volumes. To remove bubbles, follow the steps outlined in section 11.2.10.

5.4.4 Hydrolysable metal ions and reduced forms of polyvalent cations such as acid mine drainage may cause interference. These samples must be prepared using the hot peroxide treatment method.

6.0. SAMPLE HANDLING:

6.1 Sample Matrix – Groundwater Surface and sewer waters and industrial wastes.

6.2 Sample Collection –The samples should be collected in 500mL plastic containers and stored at 0-6ºC.

6.3 Sample Size – The 110mL tubes should be approximately ¾ of the way filled with sample (approximately 80mL). The titrator will take up 50 mL to analyze. Conductivity, pH and alkalinity can be performed with one 110mL tube, but Acidity will need its own 110mL tube for analysis.

6.4 Sample Preservation – Unpreserved.

6.5 Holding Times:

6.5.1 Conductivity samples are to be analyzed within 28 days of collection. If analysis is not completed within 28 days, filter through a 0.45 µm filter. Filter and apparatus should be washed with DI water and pre-rinsed with sample before use.

6.5.2 The pH of samples should be taken as soon after collection as possible. Analysis in the field would be optimal.

6.5.3 Alkalinity and Acidity analysis should take place as soon as possible after collection. The maximum hold time is 14 calendar days from collection.

6.6 Criteria for Acceptance/Rejection of Samples – If samples are not stored at 0-6ºC or if samples have broken hold time, approval from Project Manager (PM) should first be obtained before proceeding with analysis.

7.0. APPARATUS:

7.1 Metrohm 855 Robotic Titrosampler or equivalent. Both the conductivity probe and pH probe are temperature-compensating probes.

7.2 Tiamo titration software or equivalent.

7.3 110 mL plastic tubes or equivalent.

7.4 Autotitrator maintenance

7.4.1 Ensure the stopper on the pH probe is removed when running and is put back in place as soon as the run has ended.
7.4.2 Rinse probe with tap water after each run and put back in storage solution.
7.4.3 Ensure storage solution is kept full and the probe is placed back into this solution after every run.
7.4.4 Empty, clean out and refill the storage solution periodically.

7.5 For further instrument maintenance refer to the manual. For computer hardware/software, refer to IT.

8.0. REAGENTS:

8.1 DI H_2O.

8.2 Conductivity standards:

8.2.1 Inorganic Ventures (or equivalent) 5 µmhos/cm standard (CAT#CON5-25)

8.2.2 Fisher (or equivalent) 10 microsiemens standard (CAT#09-328-1)

8.2.3 Fisher (or equivalent) 100 microsiemens m standard (CAT#09-328-2)

8.2.4 Fisher (or equivalent) 1000 microsiemens standard (CAT#09-328-3)

8.2.4.1 These are NIST Traceable Calibration Standards. Standards are stable for 1 year from date of preparation, or until the expiration date listed on the standard, whichever is first.

8.3 pH 4 & 7 Guide 34 buffers are purchased from Inorganic Ventures. Certified pH 10 buffer is purchased from Fisher Scientific. or other equivalent vendors.

8.4 Electrode Filling Solution and electrode storage solution, 3M KCL.

8.5 Standard H_2SO_4 titrant (0.02N): This reagent is purchased commercially from Fisher, or equivalent.

8.6 Alkalinity Quality Control (QC) Standard, Hach: 25,000 mg/L. Dilute 10 mL (one ampule) to 1,000 mL in a volumetric flask to yield a final concentration of 250 mg/L. The concentration may vary from lot to lot so check the certificate of analysis for the current concentration.

8.7 Acidity QC Standard, Potassium Hydrogen Phthalate. Dissolve 0.15 g in 1,000 mL of DI water to yield a final concentration of 37 mg/L as $CaCO_3$.

8.8 Standard NaOH titrant (0.02N): This reagent is purchased commercially from Fisher, or equivalent.

8.9 Hot peroxide reagents:

8.9.1 Sulfuric acid (0.02N): This reagent is purchased commercially from Fisher, or equivalent.

8.9.2 Hydrogen Peroxide (30%).

9.0. EXTRACTION:

9.1 **Conductivity:**

9.1.1 For soils, a 1:1 extraction with DI water is performed before analysis, if enough soil is available. Weigh 60 grams of soil into a titrator tube or vessel large enough to handle extraction. Add 60 mL of DI water. Swirl the tube for 3-5 minutes and then centrifuge or let soil settle for at least 1 hour or centrifuge. The amount of soil and water can be adjusted according to the needs of the instrument being used, as long as a 1:1 ratio is maintained. Calibration and standard checks should be done as in section 10.0. A duplicate should be prepared for every 10 samples. Analyze the aqueous layer in the same manner as described in section 11.0.

9.2 **Alkalinity:**

9.2.1 For soils, a 1:1 extraction with DI water is performed before analysis. Weigh 50 grams of soil into a titrator tube or a vessel large enough to handle extraction. Add 50 mL of DI water. Swirl the tube for 3-5 minutes and then centrifuge or let soil settle for at least 1 hour. The amount of soil and water can be adjusted according to the needs of the instrument being used, as long as a 1:1 ratio is maintained. Use Teflon chips as the soil matrix for the method blank and LCS. Use DI water for the method blank and the alkalinity standard as the liquid matrix in the LCS. Be sure to use a 1:1 ratio for both. Analyze the aqueous layer in the same manner as described in section 11.0.

9.3 **Acidity:**

9.3.1 Most samples received by SGS are free from hydrolysable metal ions and reduced forms of polyvalent cations. These samples do not require any treatment.

9.3.2 Samples containing, or suspected of containing, hydrolysable metal ions or reduced forms of polyvalent cations must be flagged as such by the PM. These samples must be treated with hot peroxide.

9.3.2.1 *Hot peroxide treatment:* Aliquot a sample into a beaker and measure the pH. If the pH is greater than 4.0 add 5mL increments of 0.02N sulfuric acid until the pH is below 4.0. Carefully note the amount of acid used. Add 5 drops of 30% H_2O_2 and boil for 2 to 5 minutes.

10.0. CALIBRATION:

Conductivity:

10.1 A one-point calibration is performed for conductivity using the 100 µmhos/cm standard. Calibration must be done weekly.

10.2 **Setting Up and Running a Conductivity Calibration:**

10.2.1 Select the workplace icon.

10.2.2 Insert new line in sample data chart.

10.2.3 Select *Conductivity Cal SGS* method from the drop-down menu.

10.2.4 Enter sample position of 100µmhos/cm buffer.

10.2.5 Name sample *Conductivity Cal*.

10.2.6 Set sample size to 1.0 mL.

10.2.7 Press *Apply* and close dialogue box.

10.2.8 Press *Start* to run conductivity calibration.

10.3 **Checking a Conductivity Calibration:**

10.3.1 Pour out approximately 70-80 mL of the five conductivity standards into four different plastic 110mL tube or equivalent.

10.3.2 Insert new line in sample data chart.

10.3.3 Select *Conductivity STD Check SGS* method from drop down menu.

10.3.4 Enter sample position of 5 µmhos/cm buffer.

10.3.5 Name sample the true value of the buffer.

10.3.6 Set sample size to 50.0 mL.

10.3.7 Press the arrow that points to the right, immediately beside the *Line* number near the bottom of the dialogue box.

10.3.8 Repeat steps 10.3.3-10.3.7 for the remaining conductivity standards.

10.3.9 Press *Start* to run conductivity calibration check.

10.3.10 Press the Database icon to review the calibration check data. The QC recovery should be within ±10% of the true value for the standards >5.0 µmhos/cm. The 5.0 µmhos/cm should be within ±50% of the true value. The 10 µmhos/cm and 1000 µmhos/cm are posted into LIMS as the LCS and CVS, respectively. The remaining standards are verified that they meet QC criteria before continuing with analyzing samples, but they are not posted.

10.4 A three-point calibration is performed for pH using buffers with pH values 4, 7, and 10. Calibration must be done weekly.

10.5 **Setting Up and Running a pH Calibration:**

10.5.1 Insert new line in sample data chart.

10.5.2 Select *pH Cal – 3buffers SGS* method from the drop-down menu.

10.5.3 Input sample position as 1.

10.5.4 Name sample *pH Cal*.

10.5.5 Set sample size to 1.0mL.

10.5.6 Press *Apply* and close dialogue box.

10.5.7 Fill three 110mL sample tubes with ph 4, 7, and 10 buffers. Set these buffers into positions 55, 56, and 57 respectively. (*Note: Buffers MUST be placed in these positions, no matter what position is set as the sample position.)*

10.5.8 Press *Start* to run pH calibration.

10.6 **Checking a pH Calibration:**

10.6.1 Fill three different plastic 110 mL tubes approximately ¾ of the way with the three pH buffers.

10.6.2 Insert new line in sample data chart.

10.6.3 Select *pH SGS* method from drop down menu.

10.6.4 Enter sample position of pH 4 buffer.

10.6.5 Name sample the true value of the buffer.

10.6.6 Set sample size to 50.0mL.

10.6.7 Press the arrow that points to the right, immediately beside the *Line* number near the bottom of the dialogue box.

10.6.8 Repeat steps 10.6.3-10.6.7 for the other two pH standards.

10.6.9 Press *Start* to run pH calibration check.

10.6.10 Press the *Database* icon to review the data. The passing criterion is ± 0.05 pH points from the true standard value.

11.0. ANALYSIS:

11.1 **Setting Up the Instrument:**

11.1.1 Inspect all reagent containers to assure that the levels are appropriate *(**Note:** This is the area that is most prone to mistakes)*. Empty waste container if necessary, make sure both water tanks are filled with DI H_2O and make sure there are appropriate levels of titrant.

11.1.2 Prepare samples for analysis. All samples are analyzed at room temperature. Shake the sample to homogenize and pour sample out filling the 110mL tubes approximately ¾ of the way full.

11.1.3 Put two containers of DI H_2O in the last two positions. These will be the rinses.

11.1.4 Ensure stopper on pH probe is removed.

11.2 **Setting Up the Software:**

11.2.1 Open the Tiamo software and open the *Workplace* tab.

11.2.2 Insert new line in the *Sample data* chart.

11.2.3 Select appropriate method(s) for what the particular sample needs to be analyzed for.

11.2.4 Enter the sample position for the current sample.

11.2.5 Label with appropriate HSN.

11.2.6 Enter sample size of 50.0mL. (***Note:** Limited volume samples may not have a high enough volume for the full 50.0mL. In these cases, assign a sample size that is 10.0mL less than what is in the tube. This is to make sure the titrator does not draw up air.)*

11.2.7 Press the arrow that points to the right, immediately beside the Line number near the bottom of the dialogue box.

11.2.8 Repeat steps 11.2.3 – 11.2.7 for the remainder of the samples.

11.2.9 The maximum number of samples that can be analyzed at a time is 54. The last five sample positions are reserved for the rinses and pH calibration.

11.2.10 It may be necessary to flush the titrant lines before analysis if a new titrant is used in the cartridge or if bubbles develop in the titrant line. In Tiamo click the *Manual* icon. Choose the appropriate dosing device, click the *Prepare* tab and press *Start*.

11.3 Starting the instrument – press the *Start* icon.

11.4 The instrument will stop when the *Sample data* chart is complete. New samples can be added at any time during the process. The instrument will analyze the samples in the order of the *Sample data* chart and NOT in order of sample positions.

12.0. QUALITY CONTROL:

12.1 Precision Measurements – Run one sample duplicate for every ten samples.

12.1.1 **Conductivity:** Duplicate should have a Relative Percent Difference (RPD) of ≤ 20% or a difference of less than 1.0 µmhos/cm for low-level samples. Low level samples are samples with a conductivity result below 10 µmhos/cm. If duplicate fails re-homogenize the sample by thorough agitation, rinse cell and repeat analysis.

12.1.2 **pH:** Duplicate readings must agree within 0.1 pH units. If duplicate fails re-analyze sample. Samples that fail this criterion should be flagged as non-homogeneous.

12.1.3 **Alkalinity:** Duplicate should have a RPD of ≤25%. If the RPD fails, shake the sample well to ensure that the sample is well mixed. Reanalyze the sample and duplicate.

12.1.4 **Acidity:** Duplicate should have a RPD of ≤25%. If the RPD fails, shake the sample well to ensure that the sample is well mixed. Reanalyze the sample and duplicate.

12.2 Accuracy Measurements – Run a QC sample for every twenty samples.

12.2.1 **Conductivity:** Run the 10 µmhos/cm and 1000 µmhos/cm standards as calibration checks. The QC recovery should be within ±10% of true value. If QC sample is not within criteria, recheck once. If it is still outside QC criteria, then re-calibrate and repeat analysis. This applies to waters and soils.

12.2.2 **pH:** Measure the pH of the 7 buffer solution. The pH buffer must be within 0.05 pH units. If QC sample is not within 0.05 pH units, re-calibrate and repeat analysis.

12.2.3 **Alkalinity:** Run a 250 mg/L Laboratory Control Sample (LCS) that has been prepared in the lab (section 8.5). Control limits for QC recovery are ± 15%. If the QC sample recovers outside control limits, check the accuracy of the titrant concentration and reanalyze.

12.2.4 **Acidity:** Run a 37 mg/L LCS that has been prepared in the lab (section 8.7). Control limits for QC recovery are ±15%. If the QC sample recovers outside control limits, check the accuracy of the titrant concentration and reanalyze.

12.3 Calibration Criteria – Calibration checks are needed for both conductivity and pH readings.

12.3.1 **Conductivity:** Calibrate the titrator with the 100 µmhos/cm standard (***Note:*** *Be sure that the true value of the standard is the one that is entered into the* Conductivity Cal SGS *method).* The EPA

Manual for the Certification of Drinking Water Laboratories (5th edition) states that conductivity probes are to be calibrated monthly. SGS North America, Inc. – Alaska Division performs the calibration weekly. A calibration check is then performed using 5 µmhos/cm, 10µmhos/cm, 100µmhos/cm, and 1000µmhos/cm. The QC recovery should be within ±10% of true value for the standards >5.0 µmhos/cm. The 5.0 µmhos/cm should be within ±50% of the true value. If QC sample is not within QC criteria, re-calibrate and repeat analysis.

12.3.2. **pH:** A three-point calibration is used with pH 4, 7, and 10 buffers. A calibration check is then done with pH 4, 7, and 10 buffers. The pH buffer readings must be within 0.05 pH units of the true value. If QC sample is not within 0.05 pH units, re-calibrate and repeat analysis. pH calibrations are to be performed weekly.

12.3.3. Conductivity, Alkalinity, & Acidity, Blank Criteria – Run a method blank (MB) (DI water) at the beginning of each run of 20 samples. For soils, add 60 mL of DI water to 60 g of Teflon chips, prepare as in section 9.1-9.2 and analyze. The acceptable range for blanks is less than the LOQ. If the blank value is outside acceptable control limits, the quality of deionized water should be examined. Samples having concentration greater than 10 times the blank value may be reported with comments. Samples having less than 10 times the blank value must be reanalyzed.

12.3.3.1. Alkalinity Blanks for DOD clients and drinking water samples must be evaluated at ½ the LOQ.

12.4. Alkalinity analysis, (drinking water): an additional QC sample (LLQ): low level quantitation) must be analyzed at the LOQ.

12.5. 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 QA Office or Technical Department.

13. CALCULATIONS, REVIEW AND REPORTING:

13.1 Units/Significant Figure:

13.1.1 **Conductivity:** Units are µmho/cm reported to two decimal places.

13.1.2 **pH:** Units are pH and are reported to one decimal place for samples and two decimal places for calibration.

13.1.3 **Alkalinity:** Units are mg/L and are reported to two decimal places.

13.1.4 **Acidity:** Units are mg/L and are reported to two decimal places.

13.2 Equations:

13.2.1 **Resistivity:**

13.2.1.1 Resistivity is calculated using the measured conductivity as follows:

$$\text{Resistivity (ohm-m)} = \frac{1}{(A/10{,}000)}$$

Where: A = Conductivity, µmho/cm

13.2.2 **Alkalinity:**

13.2.2.1 Alkalinity can be reported as four different types, depending on the pH values and amount of titrant used to obtain the different pH endpoints. The most common form is alkalinity as $CaCO_3$ (Total alkalinity) and it is calculated as follows:

$$\text{Alkalinity (mg/L } CaCO_3) = \frac{A*B*50{,}000}{C}$$

Where: A = mL of titrant to pH 4.5
B = H_2SO_4 normality, N
C = Sample volume, mL

13.2.2.2 If the initial pH is greater than 8.3, the auto titrator will titrate to pH 8.3 and record the volume of titrant used (expressed as P). The titrator will then continue titrating to a pH of 4.5 (The total volume is expressed as T). Use equation described in 13.2.2.1 and Table listed in 13.2.2.3 to determine the alkalinity relationships.

13.2.2.2 Types of Alkalinity

P & T Relationship	OH^- Alkalinity	CO_3 Alkalinity	HCO_3 Alkalinity
P=0	0	0	T
P < ½ T	0	2P	T – 2P
P = ½ T	0	2P	0
P > ½ T	2P - T	2(T – P)	0
P = T	T	0	0

P = Phenolphthalein alkalinity (calculated from volume of titrant to pH 8.3)
T = Total alkalinity (calculated from volume of titrant to pH 4.5)

13.2.2.3 If the calculated total alkalinity value is less than 20 mg/L, the auto-titrator will titrate the sample to a pH of 4.2. **Low-level alkalinity is posted in place of total alkalinity, except for the method blank**. Low-level alkalinity is calculated as follows:

$$\text{Low Level Alkalinity (mg/L, } CaCO_3) = \frac{(2A - D)*B*50{,}000}{C}$$

Where: A = Titrant volume to pH 4.5, mL
B = H_2SO_4 normality, N
C = Sample volume, mL
D = Titrant volume to pH 4.2, mL

13.2.3 **Acidity:**

13.2.3.1 The Acidity of a sample is calculated as follows:

$$\text{Acidity (mg/L)} = \frac{A*B*50{,}000}{C}$$

Where: A = Titrant volume to pH 8.3, mL
B = NaOH normality, N

C = Sample volume, mL

13.2.4. **Free Carbon Dioxide using 4500-CO_2: Nomograph for evaluation (See Attachment F):**

13.2.4.1. Aline temperature (scale 1) & Total Dissolved solids (scale 3) which determines Point **P1**

13.2.4.2. Aline pH (scale 4) & bicarbonate Alkalinity (scale 7) which determines Point **P2**

13.2.4.3. Aline **P1 & P2** to determine **free CO_2 (scale 5)**

Note: Temperature data found in the auto sampler instrument runlog
TDS, pH, and alkalinity are found in LIMs. (Inquiry by sample number -Show results tab)

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 own at all times. Proper PPE when handling samples includes a lab coat, gloves, and safety glasses. In addition, when handling concentrated acids or bases, a face shield and apron must be worn

15.0. POLLUTION PREVENTION:

15.1. 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).

15.2. Pollution prevention techniques utilized in this method are smaller sample sizes to reduce the amount of waste and titrant. The conductivity calibration has been changed from a four-point calibration to a one-point calibration. Because the calibration check is only needed at the high and low levels, we have been able to eliminate the use of two conductivity standards.

16.0. METHOD PERFORMANCE:

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

17.0. DETECTION LIMIT (DL) STUDY:

17.1 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. Further guidance on performing a DL study can be found in SOP 116.

17.1.1 **Conductivity:** DL studies are not applicable to conductivity analysis.

17.1.2 **pH:** DL studies are not applicable to pH analysis.

17.1.3 **Alkalinity:** Per ADEC drinking water requirements DL studies are verified annually at a minimum. DL studies are performed when a new operator is trained, when a new instrument is purchased for analysis, or when a major modification to the methodology is made. The suggested DL spiking level for alkalinity is 2.0 mg/L.

17.1.4 **Acidity:** A DL study is performed initially, when a new instrument is purchased for analysis or when a major modification to the methodology is made. The suggested spiking level for acidity is 3.7 mg/L.

18.0. LIMIT OF DETECTION (LOD):

Refer to SOP 116 for further guidance.

19.0. LIMIT OF QUANTITATION(LOQ):

19.1 **Conductivity:** The current LOQ for this method is 5.0 µmho/cm.

19.2 **pH:** There is no LOQ available for this method.

19.3 **Alkalinity:** The current LOQ for this method is 10 mg/L.

19.4 **Acidity:** The current LOQ for this method is 10 mg/L. An LOD/LOQ verification needs to be performed quarterly for acidity.

19.5 *Note: LOQs are subject to change. A change to the LOQ does not necessitate a revision to this SOP.*

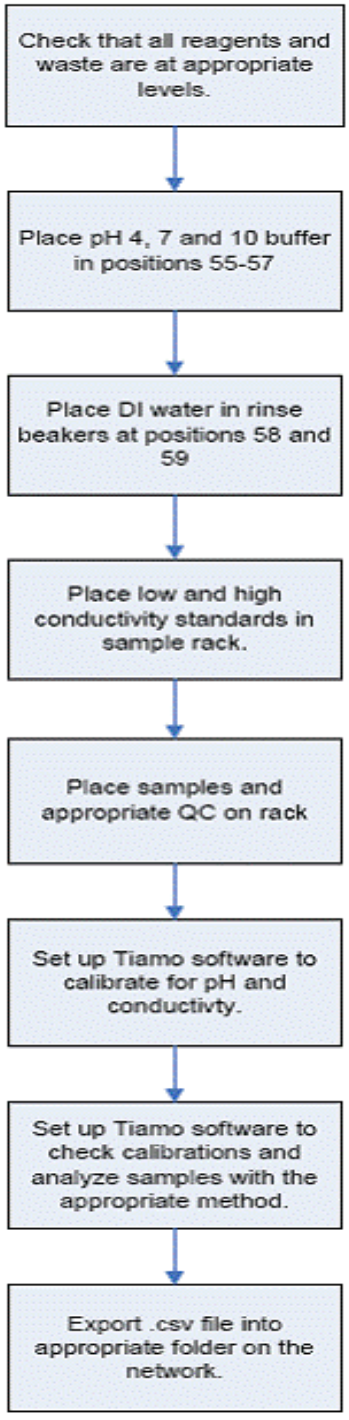
20.0. REFERENCES:

20.1 Standard Methods for the Examination of Water and Wastewater, 23rd edition online.

21.0. ATTACHMENTS:

Attachment A: Flow Chart
Attachment B: Corrective Action Table – Conductivity
Attachment C: Corrective Action Table – pH
Attachment D: Corrective Action Table – Alkalinity
Attachment E: Corrective Action Table – Acidity
Attachment F: pH Best Practices
Attachment G: Free Carbon Dioxide Nomograph

ATTACHMENT A – Flow Chart



ATTACHMENT B: Corrective Action Table – Conductivity

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM 2510 A,B	Calibration: Confirm all points 5, 10, 100, and 1000	Weekly	± 50% for low point ± 10% for all other points	1. Find source of problem and correct. 2. Repeat calibration.
	LCS, CVS (two point calibration verification)	1 per batch ≤ 20 samples	± 10%	1. Take a new homogenous portion of standard, rinse the cell and reanalyze. 2. Check instrument calibration or recalibrate.
	Duplicate (DUP) Sample	1 per ≤ 10 samples	RPD ≤ 20% or a difference of <1.0 µmho/cm for low-level samples	1. Take a new homogenous portion of sample, rinse the cell and reanalyze.
	Method Blank (MB)	One per batch of ≤ 20 samples	< LOQ	1. Re-rinse sample cell and reanalyze blank. 2. Check quality of DI system and operation.

ATTACHMENT C: Corrective Action Table – pH

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM4500H-B	Calibration: Three-point calibration	Weekly	Calibration Verification must pass	3. Find source of problem and correct. 4. Repeat calibration.
	Calibration Verification (read back buffers 4, 7, and 10). Buffer 7 is used for the LCS.	After calibration	Readback must be within 0.05 pH units of the known pH	1. Find source of problem and correct. 2. Repeat calibration.
	QC Sample (LCS) Buffer 7	1 per batch of ≤ 20 samples	Result must agree within 0.05 pH units of known pH	Recalibrate
	Matrix DUP	Minimum of 1 per batch, or 1 per ≤ 10 samples	Result must agree within 0.1 pH units	1. Reanalyze sample. 2. Samples that fail this criterion should be flagged.

ATTACHMENT D: Corrective Action Table – Alkalinity

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM 2320B	Calibration: Three-point calibration	Weekly	Calibration Verification must pass	1. Find source of problem and correct. 2. Repeat calibration.
	Calibration Verification (read back buffers 4, 7, and 10)	After calibration	Read back must be within 0.05 pH units of the known pH	1. Find source of problem and correct. 2. Repeat calibration.
	MB **MB for Drinking Water Samples**	1 per batch of ≤ 20 samples	Less than the LOQ **Evaluate at ½ LOQ**	1. Evaluate samples. Samples having a concentration of greater than 10 times the blank value may be reported. Samples having a concentration of less than 10 times the LOQ must be reanalyzed. 2. Evaluate the DI water. 3. Recalibrate and reanalyze all affected samples.
	LCS	1 per batch of ≤ 20 samples	Recovery ± 15%	1. Check accuracy of titrant concentration. 2. Reanalyze.
	DUP sample	1 per ≤ 10 samples	RPD ≤ 25%	1. Ensure that sample is well mixed 2. Reanalyze.

ATTACHMENT E: Corrective Action Table – Acidity

Analytical Method	QC Check	Frequency	Acceptance Criteria	Corrective Action
SM 2310B	Calibration: Three point calibration	Weekly	Calibration Verification must pass	1. Find source of problem and correct. 2. Repeat calibration.
	Calibration Verification (read back buffers 4, 7, and 10)	After calibration	Readback must be within 0.05 pH units of the known pH	1. Find source of problem and correct. 2. Repeat calibration.
	MB	1 per batch of ≤ 20 samples	Less than the LOQ	1. Evaluate samples. Samples having a concentration of greater than 10 times the blank value may be reported. Samples having a concentration of less than 10 times the LOQ must be reanalyzed. 2. Evaluate the DI water. 3. Recalibrate and reanalyze all affected samples.
	LCS	1 per batch of ≤ 20 samples	Recovery ± 15%	1. Check accuracy of titrant concentration. 2. Reanalyze.
	DUP sample	1 per ≤ 10 samples	RPD ≤ 25%	1. Ensure that sample is well mixed 2. Reanalyze.

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: Alkalinity, Acidity, pH, Free CO_2 & Conductivity by Auto-titrator	**Revision Date**: January 2021
Method No: SM2320B, SM2310B, SM4500H-B, 4500-CO_2, SM2510A and B	**SOP No**: 394r09
Page: 21 of 22	**Supersedes:** 394r08

Attachment F: pH Best Practices

Keep the electrode hydrated

Why – Drying out the electrode leads to drifting pH values, slow response times and incorrect measurements.

Fix – 'Revive' a dry electrode by submerging the bulb and junction in pH storage solution for at least one hour.

Rinse, do not wipe your electrode

Why – Wiping the pH glass can produce a static charge which interferes with the pH reading of the electrode.

Fix – Simply rinse the electrode with tap water. Blot (do not rub) with a lint-free paper towel (e.g. Kimwipes®) to remove excess moisture.

Store your electrode in storage solution

Why – Storing in deionized water (DI) causes ions to leach from the glass membrane and reference electrolyte, resulting in a slow and sluggish response.

Fix – Store your electrode in storage solution.

Clean your electrode regularly

Why – Deposits can form on the electrode during use, coating the sensing glass. This can lead to erroneous calibrations and readings.

Fix – Clean the electrode using a specially formulated cleaning solution for pH electrodes - ideally one that is designed for your application.

Calibrate often

Why – All pH electrodes need to be calibrated often for best accuracy.

Fix – The frequency of calibration depends on how accurate you want to be - daily calibration is ideal.

Pick the right electrode for your sample

Why – General purpose electrodes are functional for a wide variety of applications but not ideal for all samples.

Fix – Based on your sample, you may require an electrode designed for food, viscous, semi, non-aqueous, or other types of samples.

Open or loosen the fill hole cap

Why – A closed electrode fill hole may lead to slower stabilization times.

Fix – Loosen or remove the fill hole cap. Remember to put it back when storing the electrode. (Not applicable for non-refillable electrodes)

Keep the electrolyte level full

Why – Electrolyte flows out from the reference junction over time. Low electrolyte levels may cause erratic readings.
(Not applicable for non-refillable electrodes)

Fix – Ensure that your electrode fill solution level is no less than one-half inch from the fill hole cap.

Properly submerge your electrode

Why – Both the pH sensing glass and reference junction need to be completely immersed in order to function properly.

Fix – Add enough sample to submerge both the junction and sensing glass.

Inspect your electrode

Why – Over time, the sensing portion of the glass becomes less responsive and will eventually fail. Damage from use is also possible. This will cause erroneous readings.

Fix – Check your electrode for damage and perform a slope and offset calculation. Reference blog for instructions.

Attachment G: Free Carbon Dioxide Nomograph

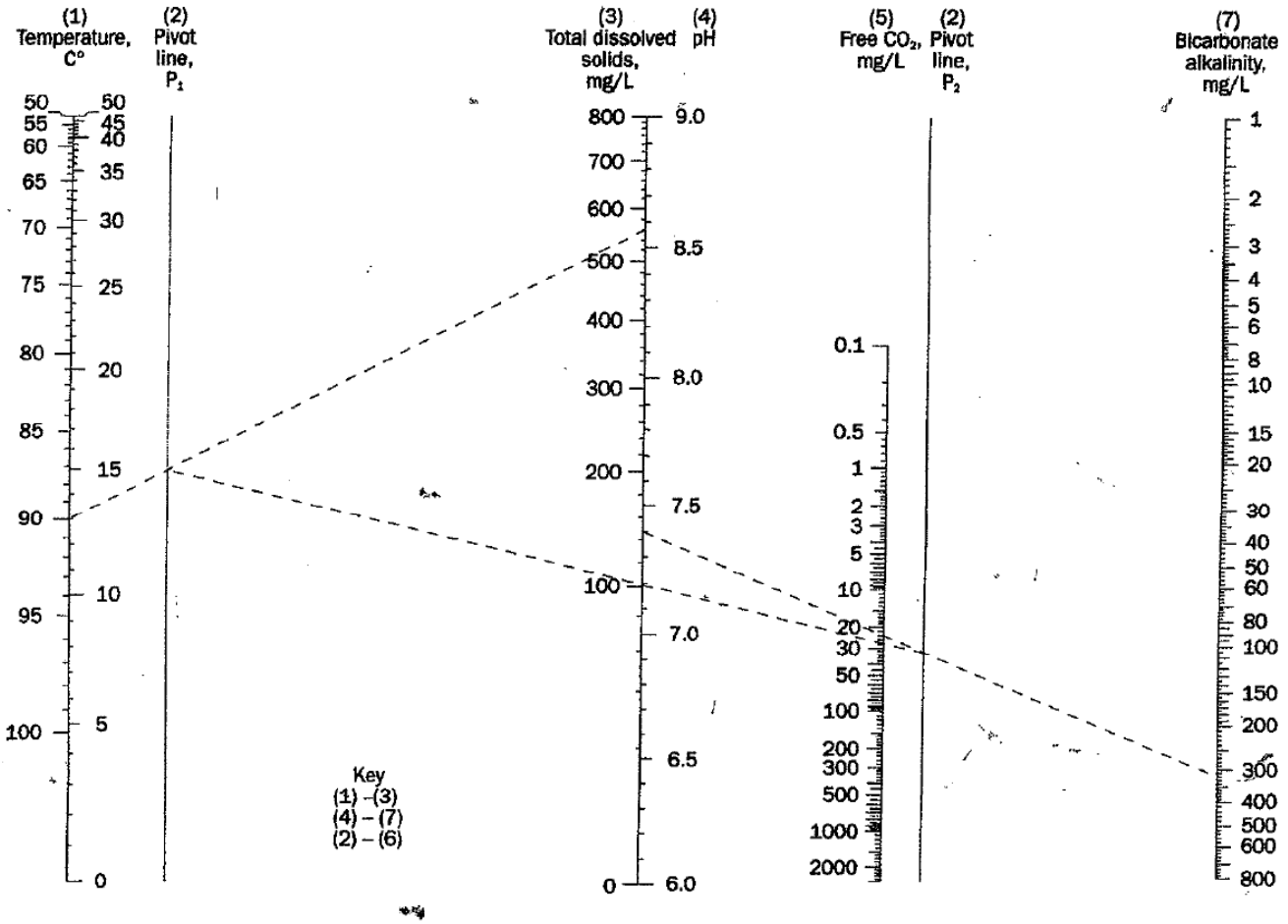


Figure 4500-CO_2:4. Nomograph for evaluation of free carbon dioxide content. To use: Align temperature (Scale 1) and total dissolved solids (Scale 3), which determines Point P_1 on Line 2; align pH (Scale 4) and bicarbonate alkalinity (Scale 7), which determines Point P_2 on Line 6; align P_1 and P_2 and read free carbon dioxide on Scale 5. (Example: For 13°C temperature, 560 mg total dissolved solids/L, pH 7.4, and 320 mg alkalinity/L, the free carbon dioxide content is found to be 28 mg/L.)

LAB MANAGER: _____

QA MANAGER: Joseph Rennie

EFFECTIVE DATE: 9/27/2017

TITLE: HEXAVALENT CHROMIUM (SOILS)

REFERENCES: SW846 3060A (Revision 1, Dec. 1996) - for digestion; SW846 7196A (Revision 1, July 1992) - for analysis

REVISEDSECTIONS: 9.8, 9.15, 9.16, 10.0, 10.4, 10.7, 12.1

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of hexavalent chromium in soils, sludges, brick, concrete, and other solid matrices. The solid sample is digested in an alkaline digestion solution to solubilize both water soluble and water insoluble hexavalent chromium compounds. Magnesium chloride in a phosphate buffer is added to suppress oxidation of Cr (III). The hexavalent chromium is determined in the digestate by reaction with diphenylcarbazide in acid solution. The diphenylcarbazide complex produces a characteristic pink color which can be measured spectrophotometrically at 540 nm.

2.0 SUMMARY

2.1 This method uses an alkaline digestion to solubilize both water-insoluble (with the exception of partial solubility of barium chromate in some soil matrices, and water soluble Cr(VI) compounds in solid waste samples. The pH of the digestate must be carefully adjusted during the digestion procedure. Failure to meet the pH specifications will necessitate redigestion of the samples.

2.2 The sample is digested using 0.28M Na2CO3 /0.5M NaOH solution and heating at 90- 95°C for 60 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

2.3 The Cr(VI) reaction with diphenylcarbazide is the most common and reliable method for analysis of Cr(VI) solubilized in the alkaline digestate. The use of diphenylcarbazide has been well established in the colorimetric procedure, in rapid-test field kits, and in the ion chromatographic method for Cr(VI). It is highly selective for Cr(VI) and few interferences are encountered when it is used on alkaline digestates.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at 0.40 mg/kg for soils, based on the low standard of 0.010 mg/l x 100 ml volume with a sample weight of 2.5 g.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's) For most methods, the mid-level calibration check standard criteria is ± 10 percent of the true value. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the detection limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the

results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: hexavalent chromium.

5.4 For weighing out hexavalent chromium samples and standards, put clean paper towels around weighing area; front and both sides of analytical balance. These will be used to capture possible spills or dust. Place an additional clean paper towel to the side for cleaned items after weighing such as spatula, weighing dish and similar.

5.5 Before weighing, put on a dust mask. After taking a dust mask, reseal the plastic bag of dust masks for the next person. Hands must be clean.

5.6 Keep all standards in a secondary container while in use to contain in case of spills. Place the secondary container so that it will not interfere with using the balance.

5.7 Put on nitrile gloves and carefully weigh out samples and standards, putting lids on immediately after use. For the solid LCS (NIST), make sure to mix the standard in the fume hood by stirring. This LCS should not be shaken to mix. Standard must be in a closed container when outside the fume hood except for when you are weighing out your aliquot. Take out the aliquot and immediately reclose the container.

5.8 Rinse all spatulas and weighing dishes with 10% nitric after use. A final rinse with DI water will follow. Place cleaned items on the clean paper towel.

5.9 All rinse must be captured in a properly labeled poly container. Paper towels and gloves to be disposed in lab waste receptacles.

5.10 Put a small amount of 10% nitric on the capture paper towels. Fold paper towels at least once and use to wipe down the area, including the balance to leave it clean for the next person. Then wet paper towels with DI water and wipe off the acid residue.

5.11 Remove nitrile gloves inside out and replace with a clean pair. Return cleaned items and utensils to their appropriate storage bag for the next person.

5.12 Store all items in a labeled cabinet.

6.0 PRESERVATION & HOLDING TIME

6.1 Soil samples should be kept under refrigeration at $\leq 6^0$ C until time of digestion.

6.2 All samples that are analyzed following this method must be analyzed within 30 days of sample collection. The alkaline digestate is stable for up to 168 hours after extraction from soil.

7.0 INTERFERENCES

7.1 Waste material suspected of containing soluble Cr(III) concentrations greater than 4 times the laboratory Cr(VI) reporting limit may have Cr(VI) results that are biased high due to method induced oxidation. The addition of Mg (II) salts, in a phosphate buffer, is added to suppress this oxidation.

7.2 During the analysis of the alkaline digest for hexavalent chromium using diphenylcarbazide, high concentrations of molybdenum and mercury (> 200 mg/l) can interfere. Concentrations of vanadium greater than 10 times the level of hexavalent chromium may also cause interferences.

8.0 APPARATUS

8.1 Volumetric flasks and pipets and graduated cylinders, class A. All glassware should be washed with soap and tap water and then well rinsed with deionized water.

8.2 50 and 250 ml glass beakers with watch glasses. All glassware should be washed with soap and tap water and then well rinsed with deionized water.

8.3 Filter paper, 0.45 um. Acceptable filter papers include the following: MSI cellulostic white grid filters, 0.45 um, 47 mm (catalog number E04WG047S1).

8.4 Filter pump and vacuum filtration apparatus.

8.5 pH meter.

8.6 Hot plate, capable of maintaining the digestion solutions at 90 to 95 C, with constant stirring ability.

8.7 Four place analytical balance.

8.8 Thermometer, calibrated to an NIST certified thermometer a minimum of once per year.

8.9 Graduated plastic beakers.

8.10 One or two place balance.

8.11 Spectrophotometer measuring at 540 nm and having a light path of 1-cm or longer. Model: Thermo Scientific GENESYS 20 UV-VIS Spectrophotometer, or similar.

9.0 REAGENTS

9.1 All reagents should be made from ACS grade reagents unless otherwise noted. Deionized water should be used whenever water is needed. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Nitric acid, HNO_3, concentrated, trace metals grade.

9.3 Nitric acid, HNO_3, 5.0 M, trace metals grade. Add 32 ml of concentrated nitric acid to approximately 50 ml of DI water. Dilute to a final volume of 100 ml with DI water and mix well. Store at 20-25°C in the dark. Do not use concentrated nitric acid to make up the 5.0 M solution if it has a yellow tinge. The yellow color is indicative of a photo reduction of nitrate to nitrite, a reducing agent for Cr(VI).

9.4 Sodium Carbonate, Na_2CO_3, anhydrous.

9.5 Sodium Hydroxide, NaOH.

9.6 Magnesium Chloride, $MgCl_2$ (anhydrous). Note: 392.18 mg of $MgCl_2$ is equivalent to 100 mg of Mg^{2+}.

9.7 Phosphate Buffer Solution (0.5 M K_2HPO_4/0.5 M KH_2PO_4 buffer at pH 7): Dissolve 87.09 g of K2HPO4 and 68.04 g of KH_2PO_4 into 700 ml of distilled deionized water. Transfer to a 1 liter volumetric flask and dilute to volume.

9.8 Digestion Solution: Dissolve 20.0 g of NaOH and 30.0 g of Na_2CO_3 in distilled deionized water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20 to 25°C and prepare fresh monthly. The pH of this digestion solution must be checked and recorded before using. If the pH is not greater than or equal to 11.5, then the digestion solution should be discarded and a new solution should be made up.

9.9 Insoluble hexavalent chromium spike, lead chromate, $PbCrO_4$. The insoluble matrix spike is prepared by adding 10 to 20 mg of $PbCrO_4$ to the insoluble matrix spike aliquot.

9.10 Soluble hexavalent chromium spiking solution stock. A 1000 mg/l stock solution of potassium dichromate can be used as the stock solution for the spiking solution. (Available as 1000 mg/l chromium solution, AAS grade from Fisher or equivalent).

9.11 Soluble hexavalent chromium spiking solution, 100 mg/l. Add 10.0 ml of the 1000 mg/l hexavalent chromium to a 100 ml volumetric flask and dilute to volume with DI water. Mix well. One (1.00) ml of this spiking solution can be used to spike the soluble matrix spike aliquot. The approximate level of the spike in the spiked sample will be 40 mg/kg.

9.12 Sulfuric acid, 10 percent (v/v). Add 10 ml of concentrated sulfuric acid to approximately 70 ml of DI water. Mix well and let cool. Dilute to a final volume of 100 ml with DI water.

9.13 Acetone. Do not use acetone that comes in a container with a metal or metal lined cap.

9.14 Diphenylcarbazide solution. Dissolve 0.250 g of 1,5 diphenylcarbazide in 50 ml of acetone. Store in a brown or a foil covered bottle to minimize exposure to light. Discard when the solution becomes discolored or monthly, whichever comes first. (Note: Be sure to check the quality of the diphenylcarbazide solution before adding it to the sample.

9.15 Hexavalent Chromium Calibration Standard Solutions. The calibration standards must be prepared fresh daily before digestion, but may be associated with multiple digestion batches from the same day. For instrument calibration, prepare the standards from the stocks as shown below. For all standards, add 50 ml of digestion solution to a labeled plastic beaker and then pipet in the appropriate amount of a stock solution. Do not dilute these standards to the final volume at this time. All calibration standards must go through the entire digestion process, starting at step 10.4.

9.15.1 Hexavalent Chromium, 10 mg/l stock solution. Add 1.00 ml of 1000 mg/l hexavalent chromium to a 100 ml volumetric flask and dilute to volume with DI water. Mix well.

9.15.2 Hexavalent Chromium, 1.0 mg/l stock solution. Add 10 ml of 10 mg/l hexavalent chromium to a 100 ml volumetric flask and dilute to volume with DI water. Mix well.

9.15.3 Add the amount of stock specified below to the 50 ml of digestion solution.

Blank: No spike is added to the blank.
0.010 mg/l. Add 1.0 ml of 1.00 mg/l
0.050 mg/l: Add 0.50 ml of 10.0 mg/l.
0.100 mg/l: Add 1.00 ml of 10.0 mg/l.
0.300 mg/l: Add 3.00 ml of 10.0 mg/l.
0.500 mg/l: Add 5.00 ml of 10.0 mg/l.
0.800 mg/l: Add 8.00 ml of 10.0 mg/l.
1.00 mg/l: Add 10.0 ml of 10.0 mg/l.

9.16 Hexavalent Chromium CCV (Continuing Calibration Verification) Solutions. The check standards must be prepared fresh daily before digestion. Prepare the standards from the stocks as shown below. All check standards must go through the entire digestion process, starting at step 10.4. A minimum of 4 check standards should be made for a batch of 20 samples. Note: The check standards must be made from a different source than the calibration standards.

9.16.1 Hexavalent Chromium 10.0 mg/l stock solution. Add 2.00 ml of 1000 mg/l hexavalent chromium to a 200 ml volumetric flask and dilute to volume with DI water. Mix well.

9.16.2 For initial calibration curves that have the 1.00 mg/l standard as the upper limit, a calibration check at 0.500 mg/l must be used. Therefore, add the amount of stock solution specified below to 50 ml of digestion solution. Do not dilute to a final volume. This entire solution should be digested.

0.500 mg/l: Add 5.00 ml of the 10.0 mg/l stock solution

10.0 DIGESTION PROCEDURE

Below is a step-by-step procedure for the digestion of samples for the determination of hexavalent chromium.

10.1 For each sample to be analyzed, weight out 2.5 $\pm$ 0.10 g of the sample into a clean, labeled glass beaker. A one or two place balance may be used for this weighing. The sample should be well mixed before the aliquot is removed as described in OQA-042, the representative sample aliquot SOP.

10.1.1 For the sample that is to be used for the quality control sample, weigh out six 2.5 $\pm$ 0.10 g aliquots from the well mixed sample. . One aliquot will be for the soluble Cr(VI) matrix spike, one aliquot will be for the insoluble Cr(VI) matrix spike, one aliquot will be for the original sample analysis, one aliquot will be for the duplicate sample analysis, and the remaining two aliquots will be used to complete the procedures required if the initial post-digest spike does not meet the $\pm$ 15 criteria.

10.2 Add the spikes to the matrix spikes and the spike blanks.

10.2.1 Spike the soluble Cr(VI) matrix spike with 1.0 ml of the 100 mg/l Cr(VI) spiking solution. (Check with the area supervisor or manger before starting to see if an additional spike level will be needed.)

10.2.2 Spike the soluble Cr(VI) spike blank with 1.0 ml of the 100 mg/l Cr(VI) spiking solution.

10.2.3 Using an analytical balance, weigh out 0.010 to 0.020 g of $PbCrO_4$ onto a clean piece of weighing paper and carefully add the spike into the insoluble matrix spike sample. Make sure to record the weight used.

10.2.4 Note: This second spike blank is optional. Using an analytical balance, weigh out 0.010 to 0.020 g of $PbCrO_4$ onto a clean piece of weighing paper and carefully add the spike into the insoluble spike blank sample. Make sure to record the weight used.

10.3 Add 50 ml of digestion solution to each sample. Also add approximately 0.4 g of $MgCl_2$ (from 0.38 to 0.42 g) using two digits analytical balance. After that, using a repipetter, add 0.5 ml of the 1.0 M phosphate buffer. In addition to the samples, 3 extra beakers should be prepared for the method blank, the soluble Cr(VI) spike blank, and the insoluble Cr(VI) spike blank.

10.4 In addition to the samples, the CCV (continuing calibration check) standards and calibration standards should also be digested. Add the entire CCV solution (refer to step 9.16) into a clean, labeled glass beaker. Also add approximately 0.4 g of $MgCl_2$ and 0.5 ml of the 1.0 M phosphate buffer.

10.5 Cover all samples and quality control (including the calibration check samples) with watch glasses. Add a stirring bar to each sample and stir the samples for at least 5 minutes without heating.

10.6 Place the samples on a stirring hot plate. Heat the samples up to 90 - 95°C with constant stirring for 60 minutes, maintaining a temperature range of 90 to 95°C. The temperature should be measured by placing a calibrated thermometer in an extra beaker containing digestion reagent on the hot plate. The temperature must be recorded at 30 minutes and 60 minutes during the digestion process. Both the start and the stop time of the digestion must be recorded.

10.7 Allow digestates to cool to room temperature, while continuing to stir or agitate the samples. Filter them through 0.45 um filter paper. Rinse the filter and filtration apparatus with DI water and transfer the filtrate into labeled graduated plastic beakers.

10.7.1 If the filters become clogged using the 0.45 um filter paper, a larger size filter paper (Whatman GFB or GFF) may be used to pre-filter the samples. However, the final filtration must be through the 0.45 um filters. If a pre-filtration is required, it should be recorded on the digestion log.

10.7.2 The solids and the filter remaining after the filtration of the matrix spikes may need to be saved in a labeled plastic beaker and stored in the refrigerator. If low recoveries are obtained on the matrix spikes, these solids may be needed for additional analyses. Check with the area supervisor or manager for further instructions.

10.7.3 At this point, the digestates are stable and may be held for up to 168 hours before proceeding with step 10.8.

10.8 Do not start this step unless the analysis will be started within one hour after this step has been completed. The calibration standards should also be taken through this process.

10.8.1 Place a stirring bar in the sample and place it on a stirring plate. Adjust the pH of the solution between 7.00 and 8.00 by carefully adding 5.0 M nitric acid to the digestate while constantly measuring the pH. Do **not** let the pH of the solution go below 7.00. If the pH goes below 7.00, then the digestate must be discarded and a new digestate prepared. Make sure to record the final pH.

10.8.2 If the pH is changing too rapidly with 5.0 M nitric acid, then a more dilute solution of nitric acid may be used for the pH adjustment.

10.8.3 Carbon dioxide and nitric acid fumes will be evolved during this process. Therefore, this step must be performed in a hood or well ventilated area.

10.9 Quantitatively transfer the contents of the beaker to a 100 ml volumetric flask or class A graduated cylinder and adjust the sample volume to the mark with DI water. Mix well. At this point, a brief description of each sample (color, turbidity, etc.) can be added to the digestion log.

10.9.1 If the same cylinder is used for multiple samples, it must be rinsed with deionized water at least 3 times between samples.

11.0 ANALYSIS PROCEDURE

11.1 Turn on the spectrophotometer and let it warm up for at least 30 minutes. Set the wavelength to 540 nm and adjust the zero.

11.2 Using a class A graduated cylinder, transfer quantitatively 45.0 ml of the sample or standard to be analyzed to a labeled plastic beaker.

11.3 Add 1.0 ml of diphenylcarbazide solution and mix well.

11.4 Slowly add 10 percent sulfuric acid to each sample, mixing well after each addition. Adjust the pH to a range of 1.5 to 2.5. Test the pH of each sample with a pH meter when the effervescence is minimal and record this reading. (On some samples, a small amount of effervescence has been observed several hours after the pH adjustment was completed.)

11.4.1 A background correction point must also be prepared for each sample with 10 ml of sample adjusted to a pH of 1.5 to 2.5 with sulfuric acid. The background correction point should not contain diphenylcarbazide. Make sure to record the adjusted pH of the background correction point.

11.5 If the samples are turbid at this point, filter them through a 0.45 um filter. If the sample aliquot is filtered, the background aliquot must also be filtered.

11.6 Transfer the samples to 50 ml volumetric flasks or class A graduated cylinders and dilute to a final volume of 50 ml with DI water. Let the samples stand for 5 to 10 minutes after the reagents are added for full color development.

11.6.1 If the same cylinder is used for multiple samples, it must be rinsed with deionized water at least 3 times between samples.

11.7 Read the standard calibration curve first, and then a calibration check standard and a reagent blank, making sure to record all results on the strip chart recorder. The correlation coefficient for the curve must be greater than or equal to 0.995, the check standard must be within 10 percent of the true value, and the reagent blank must be less than the reporting detection limit before the analysis can be continued.

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

11.8 After the curve and the initial quality control are completed, the samples may be analyzed. First read the sample result. If the result is over the highest point in the calibration curve, do not read the background correction point. If the result is within the calibration curve, the background correction point must be read immediately after the sample analysis is complete and before starting the next sample.

11.9 After every 10 samples or every 20 readings (10 samples plus 10 background correction points), a digested CCV and a reagent blank will be analyzed. The reagent blank must be less than the reporting limit, and the CCV must be within 10% of the true value. If they are outside of this range, do not proceed. Check with the laboratory supervisor or manager for further directions.

11.10 After the quality control sample analysis is completed, prepare a post-digest spike on this sample. The sample should be spiked at 2 times the concentration found in the original sample aliquot or 40 mg Cr(VI)/kg, whichever is greater. Then proceed through steps 11.3 to 11.6 and analyze the spiked sample. Calculate the recovery immediately. If the recovery is not within 85 to 115 percent, proceed to steps 11.11 and 11.12.

11.10.1 The 40 mg/kg spike can be made by spiking a 45 ml aliquot of digestate containing 1.125 g of digested sample with 0.45 ml of 100 mg/l Cr(VI) standard (Section 9.10).

11.10.2 This spiking level requirement is taken from method 3060a. A lower level spiking requirement is given in the NJDEP 7196A method, but guidance from the state suggested using the 3060A spiking levels when following the 3060a digestion.

11.11 Dilute by a factor of 1:5 a fraction of the quality control sample. Place 45 ml of the diluted sample into a plastic beaker. Then proceed through steps 11.3 to 11.6 and analyze the sample. Also prepare a background correction point at this dilution and analyze it immediately following the analysis of the diluted sample.

11.12 Take an additional 45 ml aliquot of the sample and adjust the pH to between 8.0 and 8.5 using 1.0 N NaOH. Record the final pH. Then spike the sample at 2 times the concentration found in the original sample aliquot or 40 mg Cr(VI)/kg, whichever is greater. After the sample is spiked, proceed with steps 11.3 through 11.6, and analyze the pH adjusted post-digest spike.

11.13 Before completion of the analysis, a second analyst must verify that all pH adjustments are present and documented in the paperwork.

11.14 The calculations should be done as shown below. Values less than the IDL should be treated as zero for all calculations.

11.14.1 Calculation of the sample result.

Conc. Cr(VI) in the sample in mg/kg =

$$\frac{\text{(conc. in digestate in ug/ml) x (final volume in ml) x DF}}{\text{(initial sample weight in g) x (\%solids/100}}$$

11.14.1.1 For samples requiring trivalent chromium results, the following equation must be used:

Conc. Total chromium (mg/kg) – Conc. Hexavalent chromium (mg/kg)

11.14.2 Calculation of amount spiked.

Spike amount (SA) in mg/kg =

$$\frac{\text{(conc. of spiking solution, ug/ml) x (vol. of spike, ml)}}{\text{(initial sample weight in g) x (\%solids/100)}}$$

11.14.3 Calculation of matrix spike recovery.

$$\text{MS Rec.} = \frac{\text{(SSR - SR) x 100}}{\text{SA}}$$

where SSR = Spiked sample result
SR = Sample result and
SA = Spike added.

11.14.4 Calculation of duplicate rpd.

$$\text{Dup RPD.} = \frac{\text{(SR - DR) x 100}}{\text{\{(SR + DR)/2\}}}$$

where SR = Sample result and
DR = Duplicate result.

12.0 QUALITY CONTROL

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements as taken from these methods. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.1 A new 5 point calibration curve must be analyzed on each analysis day. The calibration curve must have a correlation coefficient greater than or equal to 0.995 percent. The calibration curve must be digested in the same manner as the samples.

12.2 All samples should initially be analyzed undiluted. If the sample concentration is higher than the highest standard, then the sample should be diluted and reanalyzed. The dilution should be made so that, if possible, the sample is in the mid-range of the calibration curve.

12.3 One preparation blank is required for each set of 20 samples or less or with each batch, whichever is most frequent. The preparation blank must contain all of the reagents in the sample volumes as used in the preparation of the samples. (The preparation blank should never be used to blank correct the samples.) The preparation blank must be less than the reporting limit. If the preparation blank does not meet the criteria, then the entire batch must be redigested.

12.4 A continuing calibration verification (CCV) standard at approximately the mid-point of the curve must be analyzed after every 10 samples or every 20 readings (10 sample readings plus 10 background readings). The CCV standard must be prepared from a different stock than the calibration curve and should be taken through the digestion process as outlined in the procedure section of this SOP. A CCV standard must be analyzed at the beginning of the analysis immediately after the analysis of the calibration curve. All CCV standards must be within 10 percent of the true value for that standard. If they are outside of this range, do not proceed. Check with the laboratory supervisor or manager for further directions.

12.5 A reagent blank (or CCB) must be analyzed after each CCV. The reagent blank must be less than the reporting detection limit. If this criteria is not met do not proceed. Check with the laboratory supervisor or manager for further directions.

12.6 A duplicate sample must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. An acceptance criteria of 20 percent relative percent difference should be applied if the original and duplicate sample values are greater than or equal to 4 times the reporting detection limit. If the values are less than 4 times the reporting detection limit, then a control limit of $\pm$ the reporting detection limit should be applied.

12.7 Both a soluble and an insoluble hexavalent chromium matrix spike must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. The acceptance range for matrix spike recoveries is 75 to 125 percent recovery. If the matrix spike recoveries for either the soluble or the insoluble spikes are not within these recovery limits, then the lab supervisor or manager must be immediately notified. The client services department will then be notified to contact the client. The method requires additional testing as listed below, but the lab should not proceed with this testing until client approval is obtained and the testing is logged into the LIMS system.

12.7.1 All samples and quality control must be re-homogenized, re-digested and reanalyzed to verify the original sample results.

12.7.2 Additional tests, such as oxidation-reduction potential, pH, sulfide, ferrous iron, etc., may be requested to help quantify the reducing nature of the sample. For some projects, eH and pH analysis may be specified for all samples at the start of the project. Eh and pH data plots must be provided in the data deliverable if this analysis is specified

12.7.3 A mass balance study for total chromium may be done, using the digested solids remaining after the alkaline digestion and filtration of the matrix spike and from a unspiked aliquot of the sample.

12.8 A post-digest spike must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller. The acceptance range for post digest spike recoveries is 85 to 115 percent recovery.

12.9 A spike blank or lab control sample must be prepared and analyzed for each set of 20 samples of a similar matrix or with each batch, whichever is smaller The spike blank or lab control can be prepared using either soluble or insoluble hexavalent chromium as the spike. The acceptance range for the spike blanks is 80 to 120 percent recovery. If the spike blanks are not within that range, then the entire batch must be redigested and reanalyzed.

12.10 Spike Witnessing. Addition of insoluble and soluble spike amounts must be verified by a spike witness at the time spike additions occur. These include all spiked blanks, matrix spikes, and if applicable, solid lab control standards. The spike witness must verify the correct solutions and amounts of those solutions are being added to the correct samples (or containers, if spiked blanks). The spike witness must document (by initialing and dating) on the preparation log that they have observed and confirmed proper spike additions.

13.0 DOCUMENTATION REQUIREMENTS

13.1 The analyst should document all relevant information, including all sample weights and volumes, digestion times and temperatures, all intermediate and final pH values, all times relevant to the pH adjustment process, all sample and background analysis results, and any relevant comments for any section of the digestion or analysis. Sample digestion and analysis sheets are provided.

13.2 Analyses are done using an automated analysis spreadsheet where the sample absorbances are recorded electronically. If this electronic recording option is not available, then the analyst must verify all recorded absorbances. All reagent identification numbers should be recorded on the sample worksheets. In addition, all reagent information such as lot numbers should also be recorded in the reagent logbook.

14.0 DATA REVIEW AND REPORTING

14.1 All samples should be updated to analysis (GN) batches in the LIMS system. The analyst should calculate all matrix spike, duplicate, external, and CCV recoveries and review the results of all blanks.

14.2 All documentation must be completed, including reagent references and spike amounts and spiking solution references.

14.3 A data file should be exported to the LIMS system and the spike amounts should be entered into the file at the GNAPP process step.

14.4 A final data package, consisting of the prep and analysis raw data, the LIMS cover page, the reagent reference pages, and the QC summary pages must be turned into the area supervisor or other senior reviewer for review.

14.5 After review by the supervisor, the data is released in the LIMS for access to the clients. Review includes verifying the spike amounts, recoveries, and RPD's as well as the sample results and document such as all pH values.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment

must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes
15.2.2 Hazardous aqueous wastes
15.2.3 Chlorinated organic solvents
15.2.4 Non-chlorinated organic solvents
15.2.5 Hazardous solid wastes
15.2.6 Non-hazardous solid wastes

16.0 ADDITIONAL REFERENCES

16.1 No additional references are required for this SOP.

LAB SUPERVISOR: Dan Lyons

QA OFFICER: Olga G. Gaidan

EFFECTIVE DATE: 1-31-2020

TITLE: METALS BY INDUCTIVELYCOUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP) USING SOLIDS STATE ICP
REFERENCE: SW846 6010D
REVISED SECTIONS: 12.3.1,12.8
ADDED SECTIONS: 12.20

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of metals in water, wipes, sludges, sediments, and soils. Sample matrices are pretreated following SW846 methods for digestion of soil, sediment, sludge, wipe or water samples. Refer to specific digestion SOP's for more information on digestion techniques.

1.2 A variety of metals can be analyzed by ICAP. These include, but are not limited to, Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Si, Ag, Na, Sr, Tl, Sn, Ti, V, Zn, Li P and Pd W S Bi Zr

2.0 SUMMARY

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This SOP describes operation of the ICAP 6500 and ICAP 7000 Spectrometer following method SW846 6010D.

2.2.1 This inductively coupled argon plasma optical emission spectrometers (ICP-OES) uses an Echelle optical design and a Charge Injection Device (CID) solid-state detector to provide elemental analysis. Control of the spectrometer is provided by PC based iTEVA software.

2.2.2 In the instrument, samples are nebulized, and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a spectrometer, and the intensities of the emission lines are monitored the solid-state detector.

2.2.3 Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used must be as free as possible from spectral interference and must reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. Interferences which cannot be addressed with background correction must be corrected using the appropriate interelement correction factors.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The normal reporting limits for this method have been established at the concentrations listed in Table 1. Reporting limits may vary depending on client needs and lab protocols, but the reporting limits must always be verified with a low check which meets the criteria outlined in this SOP. In addition, the reporting limits must always be greater than the MDL. Refer to the scheduling sheets and check with the metal's supervisor for further information.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method. Refer to SGS SOP EQA075

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed, and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards.

SPIKE BLANK SAMPLE. Digest and analyze a laboratory control sample (Soil LC) or spike blank with each set of samples.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX SPIKE DUPLICATE: A matrix spike duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the matrix spike duplicate and the matrix spike must be assessed.

$$\frac{(|\text{Matrix Spike Result} - \text{Matrix Spike Duplicate Result}|) \times 100}{(\text{Matrix Spike Result} + \text{Matrix Spike Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in each matrix containing the analyte. Refer to SGS SOP EQA075 for further details.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for

contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.)

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards must be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analysis.

LOW LEVEL CALIBRATION VERIFICATION (CRI or LLCCV). The LLCCV or CRI standard is a check standard containing the elements of interest at (or below) the reporting level for each element.

HIGH STANDARD/LINEAR RANGE: The high standard is a check standard containing elements of the interest at the instrument linear range. The linear range establishes the highest concentration that may be reported without diluting the sample. The acceptance criteria are +/-10 of the true value.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the SGS Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All water samples must be preserved with nitric acid to a pH of 2 or less. All solid samples must be stored in a refrigerator at 4 degrees C.

6.2 All samples must be analyzed within 6 months of the date of collection.

7.0 INTERFERENCES

7.1 Several types of interferences can cause inaccuracies in trace metals determinations by ICP. These interferences are discussed below.

7.2 Spectral interferences are caused by overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. Corrections

for these interferences can be made by using interfering element corrections, by choosing an alternate analytical line, and/or by applying background correction points.

7.3 Physical interferences can be caused by changes in sample viscosity or surface tension, by high acid content in a sample, or by high dissolved solids in a sample. These interferences can be reduced by using an internal standard, by making sample dilutions or by analyzing a sample using the method of standard additions.

7.4 Chemical interferences are not pronounced with ICAP due to the high temperature of the plasma, however if they are present, they can be reduced by optimizing the analytical conditions (i.e. power level, torch height, etc.).

8.0 EQUIPMENT AND SUPPLIES

8.1 Currently there are five solid state ICPs available for use in the lab. They are Thermo 6500 and 7000 ICP units. These units have been optimized to obtain low detection limits for a wide range of elements. Since they are solid state systems, different lines may be included for elements to obtain the best analytical results. However, the lines which are normally included in the normal analysis program are shown in Table 2.

8.2 Instrument auto-samplers. For random access during sample analysis.

8.3 Class A volumetric glassware and pipets.

8.3.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for a minimum of 2 hours. It must then be rinsed at least 3 times with deionized water.

8.4 Glass autosampler tubes

8.4.1 Autosampler tubes must be washed with soap and tap water and then soaked in a 10% nitric acid bath for a minimum of 2 hours. They must then be rinsed at least 3 times with deionized water.

8.5 Autopipettes with tips. These must be calibrated and checked as outlined in the autopipette SOP, EQA004.
8.6 ASXPRESS PLUS Valve system from CETAC
8.7 Argon humidifier

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Hydrochloric acid, trace metals grade.

9.3 Nitric Acid, Baker instra-analyzed or equivalent.

9.4 Standard stock solutions available from Absolute, Inorganic Ventures, CPI, Ultra Scientific or equivalent.
Note: All standards must be ICP quality standards.
Calibration Standards: These are made up by diluting the stock solutions to the appropriate concentrations. Fresh calibration standards must be prepared every day.

9.4.1 Standards must be approximately matrix matched to the samples. For most samples, a 5 percent nitric acid and 5 percent hydrochloric acid will approximate the acid matrix of the sample and limit nebulization problems. If it is known that the samples contain a significantly different acid matrix,

then the matrix of the standards must be modified, or the samples must be diluted so that they are in a similar matrix to the curve.

9.4.2 Standards must be prepared so that there is minimal spectral interference between analytes. See Table 10 for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP. The standard curve consists of a blank and 1 non-zero standard at the levels shown in Table 10.

9.5 Calibration/Rinse Blank. The calibration blank is prepared by diluting a mixture of 50 ml of concentrated nitric acid and 50 ml of concentrated hydrochloric acid to a final volume of 1 liter with deionized water.

9.6 Analytical Quality Control Solutions. All the solutions below are prepared by adding either mixed or single element metals solutions to a solution containing 5 percent nitric acid and 5 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. These solutions must be placed in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.

9.7.1 Initial Calibration Verification solution (ICV). This standard solution must be made from a different source than the calibration curve. The values for each element must be near the midpoint of the calibration curve. This solution is used to verify the accuracy of the initial calibration. See Table 4 for suggested ICV concentrations.

9.7.2 Continuing Calibration Verification solution (CCV): The metals concentrations for this standard must be at approximately the mid-point of the calibration curve for each element. This standard must be prepared from the same source that is used for the calibration curve. See Table 4 for suggested CCV concentrations.

9.7.3 Interference Element Check Solutions. These solutions must be used on a periodic basis to check the interfering element corrections on the instruments and interfering element solutions may be modified. Two acceptable solutions are outlined below.

9.6.1.1 ICSA Solution (Interference Check Standard) This is a QC standard used to verify the accuracy of the interferents (Al, Ca, Fe, and Mg) and the accuracy of the inter-element correction factors applied in the absence of analyte. The recommended concentrations are shown below. If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements.

Al	500 mg/L
Ca	400 mg/L
Fe	200 mg/L
Mg	500 mg/L

9.6.1.2 ICSAB Solution (Interference Check Standard with analytes): The ICSAB solution contains both the interferents and the analytes of interest. The recommended concentrations are shown below. If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements

Ag	1.0 mg/L	Zn	1.0 mg/L
Ba	0.50 mg/L	As	1.0 mg/L
Be	0.50 mg/L	Se	1.0 mg/L
Cd	1.0 mg/L	Sb	1.0 mg/L
Co	0.50 mg/L	Tl	1.0 mg/L
Cr	0.50 mg/L	Mo	0.5 mg/L
Cu	0.50 mg/L	P	0.5 mg/L
Mn	0.50 mg/L	Al	500 mg/L
Ni	1.0 mg/L	Ca	400 mg/L

Pb	1.0 mg/L	Fe	200 mg/L
V	0.50 mg/L	Mg	500 mg/L
W	0.50 mg/L	Zr	0.50 mg/L
Li	0.50 mg/l	Sr	0.5 mg/l
Bi	0.50 mg/l	Ti	0.5 mg/l
B	0.50 mg/l	S	0.5 mg/l
Sn	0.50 mg/l	Si	0.5 mg/l

9.6.2 CRI Standards (also referred to as LLCCV). The CRI standard must contain the elements of interest at (or below) the reporting limit for each element. The CRI level is at the reporting limit as shown in Table 1. This solution is to be prepared at the reporting limit level for each element. They must be made in the same matrix as the calibration standards. Note: The CRI must be verified at the RL before any dilutions are applied

9.7 Matrix Spike and Spike Blank Solution: The final concentrations suggested for the matrix spike and spike blank solutions are shown in Table 5. Refer to METALS SPIKING SOLUTION AND STANDARDS PREPARATION SOP EMP 202 Table 1,1A, and 3 for preparation/concentration and amount of spiking solutions. Appropriate amount of the resulting stock solution is added to the matrix spike and blank spike samples before they are digested.

9.8 Matrix Spike and Spike blank (For aqueous samples and TCLP leachates).

9.8.1 The final concentrations suggested for the matrix spike are shown in Table 5. Spiking solutions, they are prepared by adding either mixed or single element metals solution. Refer to METALS SPIKING SOLUTION AND STANDARDS PREPARATION SOP EMP 202 Table 1,1A, and 3 for preparation/concentration and amount of spiking solutions. Resulting stock solution is added to the matrix spike and blank spike samples before they are digested.

9.8.2 The Spike blank sample must be digested and analyzed for every batch of 20 samples or less. The Blank spike prepared by adding either mixed or single element metals solutions to DI water and bringing up to a fixed final volume. For TCLP samples, the blank spike must be made using blank leachate solution rather than DI water. 50 ml of this solution is digested and brought to a final volume of 50 ml.

9.9 Liquid Argon or Argon Gas. Argon is provided by Air Products in the large outdoor tank. No lab monitoring of the tank is normally necessary

9.10 Internal Standard Solution (with matrix modifier). To a 2-liter flask containing approximately 1500 ml of DI water, add 40 ml of 10,000 mg/l Cesium solution, 10 ml of 10000 mg/l indium, and 2 ml of 10000 mg/l yttrium. Add 100 ml concentrated nitric acid and 100 ml concentrated hydrochloric acid and bring to a final volume of 2000 ml and mix well. This solution is added to all samples and standards as the instrument is running using a split line on the peristaltic pump.

10.0 PROCEDURE

10.1 General procedure on how to operate the SS Trace is described below. Refer to the Thermo 6500-7000 operation manual for further details.

10.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, the dehumidifier is filled with DI water up to the level between Minimum and Maximum, and that there are no leaks in the torch area.

10.3 Turn on the recirculating cooler. Verify that the liquid argon is turned on.

10.4 Set up the pump tubing and engage the peristaltic pump.

10.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.) If internal standard is being used, make sure that sufficient internal standard solution is prepared.

10.6 Start up the instrument following the sequence shown below.

10.6.1 Double click the **iTEVA Control Center** Icon on desktop. Type ***admin*** in User Name field, and then click OK.

10.6.2 Once the iTEVA Control Center window is opened, click on **Plasma** Icon at status bar area. Then click on **Instrument Status** to check the interlock indicators (torch compartment, purge gas supply, plasma gas supply, water flow and exhaust must be in green; drain flow and busy must be in gray) and the Optics Temperature. (It needs to be around 38°C.) Click on the Close box.

10.6.3 Click **Plasma On**. After the plasma is on, close the Status window and let the instrument warm to up for 15 to 20 minutes before starting the analysis. New tubing may take an hour to stabilize.

10.7 Torch Alignment and Auto Peak

10.7.1 If the torch has been cleaned, then it must be realigned after it is replaced

10.7.1.1 Open the method and then click on **Sequence** tab, and then click on List View Icon until you reach rack display.

10.7.1.2 Send probe to the cup which is filled with 2 ppm Zn solution in Autosampler program. eg. Go to S-6 position (you can assign any position in the rack for torch alignment) which is filled with 2 ppm Zn solution.

10.7.1.3 Click on **Analysis** tab and then select **Torch Alignment** from **Instrument** drop down menu. There will be a popup dialog box present. Click RUN. Then there will be another dialog box pop up (This is a reminder for Torch Alignment Solution (2 ppm Zn)), let the solution to pass through the plasma and click Ok. Now, the instrument is initiating an automated torch alignment. It takes about 7 minutes to complete this step. Progress is indicated in the progress bar.

10.7.1.4 After Torch Alignment is done, click Close. Click on **Sequence** tab and then follow by **List View** Icon.

10.7.1.5 Go to Rinse position at rack display, right click to select Go to rinse and let it rinse for 2 minutes.

10.7.2 Perform Auto Peak.

10.7.2.1 It is recommended that the Auto Peak Adjust procedure be performed monthly or whenever the peak shape has shifted for any element. A standard that contains all of the lines of interest is used and the system automatically makes the appropriate fine adjustment. (CCV solution is used for this process.)

10.7.2.1.1 A shift in peak shape can be defined as when the peak is no longer in the middle of the defined viewing window. The window must be set so that the peak is approximately centered and there is a sufficient area measured so that reproducible, consistent data can be obtained at reporting limit levels. This is

done as part of the automatic process, but the window size can be adjusted manually in the method based on the shape of the peak to obtain the best fit for the peak. A wider peak may need a broader integration window for the best analysis. In general, the window must cover at least the top 1/3 of the peak.

10.7.2.2 Click **Sequence** tab and then click on **List View** Icon till the rack is displayed.

10.7.2.3 Send the probe to the cup which is filled with CCV solutions using Autosampler program (you can assign any position in the rack which has CCV solution filled for auto peak adjust) then click on **Analysis** tab. All elements' result is showed in the display area. From **Instrument** drop down menu, select **Perform Auto Peak**. There will be a popup dialog box present. Highlight _All Elements, then click RUN. Then there will be another dialog box pop up (This is a reminder for Perform Auto Peak Solution), click Ok. Now, the instrument is performing auto peak adjust. It takes about 5 minutes to complete this process. The Auto Peak dialog box will show a green " √" in front of All Elements, which indicates Auto Peak is completed.

10.8 Open the method and start up the run.

10.8.1 Click on **Analyst** Icon at the workspace. Go the Method and choose Open from the drop-down menu. Select the method with a Revision (usually select the last revision used).

10.8.2 Go to **Method** tab at the bottom of left-hand corner to click on **Automated Output** at the workspace area. Type a filename in Filename field in the data display area (i.e.: SA073107M1: starts with SA, then follow by MM-DD, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs).

10.8.3 Click on **Sequence** tab at the bottom of left-hand corner. From **Auto-Session** drop down menu bar, click on **New Autosampler** to create a sequence. This will pop up a dialog box, then click on **New** and fill number of samples (i.e.: 100) in the Number of Samples field and the sample ID (usually leave this field empty) in Sample Name field. Type a sequence name (i.e.: SEQ073107M1: starts with SEQ, then MM-DD-YY, then M1; M1 indicates the first analytical run for that day, then follow by M2, M3 and so on for the second and third runs) in the Sequence Name field. Click OK, then put in "0" on Settle Time between the Sequences box, click OK.

10.8.4 Right click on **Untitled** (CETAC ASX-520 Enviro 5 Named Rack is the rack that currently using) at the workspace area, click on **Auto-Locate ALL** to locate all samples.

10.8.5 Double click on **Untitled** again, then click on the sequence name (i.e.: SEQ073107M1), on the data display area, type the sequence in Sample name column, dilution factor (if needed) in CorrFact column, check the box in front of Check column, and select an appropriate check table.

10.8.6 Once done with creating sequence, go to **Method** drop down menu and save all changes as **Save As**. There will be a Save a Method dialog box present, go to Save Option to check on "Overwrite Method and bump revision number" box, then click OK.

10.8.7 Go to **Sequence** tab, click on **List View** Icon from tool bar, then click on **Connect Autosampler to PC and Initialize** Icon. (Now, the autosampler tip is up and sits on the top of the rinse cup.)

10.8.8 The sequence includes the calibration and run quality control.

10.8.8.1 Calibrate the instrument as outlined below using the standards shown in Table 3. This calibration procedure is done a minimum of once every 24 hours. The calibration standards may be included in the autosampler program or they may be run separately.

10.8.8.2 Analyze ICV and ICB after the calibration is completed and before any samples are analyzed.

10.8.8.3 For mixed runs (EPA 200.7 and SW846 6010D), the first CCV is designated the ICCV. For samples and quality control, insert the list pointer after a space after the sample. Check with the metal's supervisors for additional information on the use of list pointers. In general, list pointer 7 refers to the SW846 6010D method and list pointer 1 refers to EPA 200.7 method.

10.8.8.4 Low Level Calibration Verification (Low checks or LLCCV) Run low checks at reporting limit levels after ICCV and CCB. The low checks are named as CRI (or CRIB for DOD run), CRID and CRIA. The levels for each low check are listed in Table 6, Table 7 and Table 8.

10.8.8.4.1 Muti-level low check solutions must be analyzed for default reporting limits and special client reporting limits.

10.8.8.4.2 Method limits of 80 to 120% are applied to the CRI low check standard.

10.8.8.5 Before analyzing any real samples, an interference check solution (ICSA-ICSAB) must be checked. For all spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solutions must contain **less than** the absolute value of the reporting limit for each element.

10.8.8.6 If the interfering element solution is not within specifications and that element must be reported, then new interfering element correction (IEC) factors will need to be generated following the procedure outlined in Section 11 below. If new IEC's are generated, then the run must be restarted from the ICSA, ICSAB quality control samples and new CCV checks must be run before any samples can be reported.

10.8.8.7 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control must be analyzed. Each sample including calibration standards and QC needs at least 3 replicates using at least 5 seconds integration time, this time can be modified. For samples containing levels of elements greater than approximately 5 times the reporting limits, the relative standard deviations for the replicates must be less than 5%. If not, reanalyze the sample. Upon reanalysis, the RSDs are acceptable then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element must be evaluated by the data reviewer and footnoted if necessary. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

10.8.8.8 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for 60-120 seconds to ensure that analyte memory effects are not occurring. A time of 60-120 seconds is recommended for most analyses. When using Sprint valve and ASX EXPRESS Plus unit the uptake and rinse timing are being controlled by the valve configurator, Follow the manufacturer guide line. Normal timing for the valve configurator is as follow.

Loop Evacuation Delay: 1-3 Sec
Loop Load: 5-11 Sec
Time to Evacuate: 1-3 Sec
Rinse Station Fill: 5-10 Sec
Rinse Evacuation Delay: 1-3 sec
Equalization Delay: 1-3 Sec
Probe Rinse: 5-10 Sec

10.8.8.9 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth samples during an analysis run, whichever is more frequent, and at the end of the sample run.

10.8.8.10 If the CCV solution is not within 10 percent of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element. Additionally, for the elements with a CCV greater than 5 times the reporting limit, the relative standard deviation for the replicates must be less than 5 percent.

10.8.8.11 The CCB results must be less than the reporting limit or limit of quantitation for each desired target analyte. If these criteria are not met, then no samples can be reported in the area bracketed by the failing CCB for the failing element and all samples must be submitted for reanalysis.

10.8.8.11.1 However, if the samples are high relative to the CCB (> 10 X the CCB level) and a higher reporting limit is acceptable for the final end use of the data, then the samples may be evaluated using a higher reporting limit to meet the CCB criteria. This must be clearly documented on the run if a higher reporting limit is applied.

10.8.8.11.2 In addition, at the reviewer's discretion, samples that are < RL may be reported when the CCB is biased high. Analysts must assume that samples bracketed by a failing CCB must be reanalyzed unless instructed otherwise.

10.8.8.11.3 If a CCB fails, if possible, the analyst must stop the run and run a new CCV, CCB pair before proceeding with the analysis of any additional samples.

10.8.8.12 For one sample per preparation batch a serial dilution must be prepared. Normally the sample used for the serial dilution is the sample that is used for the matrix spike and matrix spike duplicate. For the serial dilution, a 1:5 dilution must be made on the sample.

10.8.8.13 When matrix spike or matrix spike duplicate is out of acceptable limits, then post-digest spikes be prepared to determine potential interferences.

10.8.8.14 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. The verifications may be necessary by rinsing the lines with an acid solution and then rereading the sample. A limit check table may be built into the autosampler file so that samples exceeding the linear range are flagged on the raw data.

10.8.8.15 For the interelement spectral interference corrections to remain valid during sample analysis, the interferent concentration must not exceed its linear range. If the interferent exceeds its linear range or its correction factor is big enough to affect the element of interest even at a lower concentration, sample dilution with reagent blank and reanalysis is required. In these circumstance analyte detection limits are raised.

10.8.8.16 Anytime that the interference is large relative to the sample, dilution may be required.

10.8.8.17 For any readings where the internal standard is outside of the range of 70 to 130% of the internal standard level in the calibration blank, then the sample must be diluted until the internal standard is within that range. See Table 11 for the assigned Internal Standard for each element.

10.8.9 This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required to meet other method and/or client requirements. Run the

ICSA and ICSAB solutions as instructed by the metals lab supervisor or manager or as noted in the program code instructions.

10.8.10 After the instrument is optimized, click **Run Auto-Session** Icon to start the run.

10.8.11 If you need to add or delete samples once the run is started, follow the steps shown below.

10.8.11.1 Adding Samples.

10.8.11.1.1 Click on **Sequence** tab, then click on **List View** Icon at the tool bar. There is the sequence table on the data display area.

10.8.11.1.2 Click on **Add Samples** Icon. This will pop up the dialog box, then fill number of samples that need to add in field. Click OK. By doing this, samples will be added at the end of sequence without a location the rack.

10.8.11.1.3 Go to the added samples, on the To position ID column, assign a number for each sample. This number will be the position in the rack. On the Samplename column, type in sample IDs, fill in Corr Fact (if needed) and Check Table.

10.8.11.1.4 The added samples will be analyzed at the end of the original sequence run order unless you assign them to run under different order.

10.8.11.2 Deleting Samples.

10.8.11.2.1 Click on **Sequence** tab, then click on **List View** Icon under the sequence display area.

10.8.11.2.2 To the sample that need to be deleted, on the to position ID column, change the number to "0". By doing this, that sample will be unlocated in the rack and the autosampler tip will go to the next sample.

10.9 When the analysis is completed export the data to LIMS following the procedure outlined below.

10.9.1 Double click on **ePrint** Icon on desktop. There will be a LEADTOOLS ePRINT dialog box pop up, then click **Finish Jobs** and **OK** boxes.

10.9.2 Double click the **PDF** Icon on desktop, the PDF file will present as Document_#. Right click on that file, select **Rename** to change the file name to an assigned analytical run ID. (i.e.: MA8324). This is the raw data for MA8324.

10.9.3 Drop the raw data to LIMS.

10.9.4 By completing above steps, the raw data (i.e.: MA8324) can be pulled up in the Raw Data Search function.

10.9.5 For any Thallium hit found during the data review or analysis, the sample will be rerun to confirm. If the hit is confirmed, check the thallium spectrum of that sample to determine if the hit is caused by the matrix interference or true. If the spectrum indicates any matrix interference, then the sample will be rerun on dilutions to bring the thallium result to <RL

10.10 The data must be reviewed in the LIMS as outlined in the inorganic data review SOP, EQA034. Calculations for water samples are done automatically in the LIMS using the equation shown below.

original sample concentration of metal (μg/l) =

(conc. in the digestate (μg/l)) x (final digestate volume (ml))

(Initial sample volume (ml))

10.11 Aft the end of the analysis day, the ICP must be brought down using the following sequence:

10.11.1 Place the autosampler tip in rinse cup and rinse in a mixed solution of 5% nitric acid and 5% hydrochloric acid for 10 minutes and in DI water for 20 minutes. **Note**: A stronger acid may be needed depending on the matrix of the samples that were analyzed.

10.11.2 Turn off the plasma by click on the **Plasma** Icon and click on **Plasma Off**.

10.11.3 Close all iTEVA programs/ windows.

10.11.4 Release the tension on the sample pump platen.

10.11.5 Switch off recirculating chiller.

11.0 PROCEDURE FOR GENERATION OF INTERFERING ELEMENT CORRECTION FACTORS

11.1 All IEC's must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly. It is recommended that elements with frequent high concentrations or with large IEC's must be checked more frequently.

11.2 Calculate the IEC correction factors and enter them into the method. Verify that the recalculated sample results are within QC limits. Calculate the correction factor using the equation shown below. This correction factor must be added to the correction factor already in place in the method for a given element.

$$\text{IEC} = \frac{\text{Concentration Result of the element with the interference}}{\text{Concentration result of the interfering element}}$$

11.3 Analyze the ICSA/ICSAB solutions and/or SIE solutions and verify that the combined standards are within QC limits. If they are not, make additional changes to the IEC factors and then re-verify both the individual and combined solution values.

11.4 Save and update the method.

11.5 Interfering element correction factors saved as raw data along with the run printouts daily so that the IEC's for a given run are traceable.

12.0 QC REQUIREMENTS

12.1 This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements for method SW846 6010D.

12.2 Method Detection Limits (MDLs). Refer to SGS SOP EQA075 Initial MDLs are determined by preparing and analyzing seven method blank samples and seven spiked samples of the matrix to be measured. The spiking level is typically at 2-10 times the estimated MDL. Spiking levels in excess of 10 times the estimated detection limit may be required for analytes with very poor recovery. The samples must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates. The mean and standard deviation of the data set is calculated from the replicates, from which the MDL is calculated based on the formula in section 7.4.SGS SOP EQA075

12.3 Instrument Detection Limits (IDLs). Instrument Detection Limits (IDLs). It is required that IDL's be completed **ANNUALLY** or after major instrument maintenance or by project specifications. The Instrument Detection Limits (in ug/L) are determined by analyzing 10 replicates of a reagent blank

solution. The IDL is defined as 3 times the standard deviation of 10 reps added to the mean of the replicates; as long as it is 0 or positive (Use zero for the mean if the mean is negative.). IDLs shall be determined and reported for each wavelength used in the analysis of the samples.

12.4 Linear Calibration range: The linear range establishes the highest concentration that may be reported without diluting the sample. Following calibration, analyze a standard at a higher concentration than the high standard in the calibration. The standard must recover within 10% of the true value, and if successful, establishes the linear range. The linear range standards must be 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.

12.5 Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB). After every new calibration, an ICV must be analyzed. The analysis of the ICV may be followed by the analysis of the ICB,

12.5.1 For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates that exceed 5 times the reporting limit must have a relative standard deviation of less than 5 percent. The ICV must be from a different source than the calibration standards and must be near the mid-point of the calibration curve. If the ICV does not meet criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria.

12.5.2 If an ICB is analyzed, then all elements to be reported must be less than ½ of the RL (LLOQ). If the ICB is outside of criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria.

12.6 Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB). Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run.

12.6.1 For the CCV, all elements to be reported must be within 10 percent of the true value and the replicates that are greater than 5 times the reporting limit must have a relative standard deviation of less than 5 percent. The CCV must be made from the same source as the calibration standards at a concentration near the mid-level of the calibration curve. If an element does not meet the recovery criteria of the CCV (90 to 110%), then no samples can be reported for that element in the area bracketed by the CCV. Relative Error (%RE) must be 10% for CCV (See section 12.20 for calculation)

12.6.1.1 If the replicate RSD is high, but all replicates are within the recovery limits, then the results can be accepted at the discretion of the reviewer.

12.6.2 For the CCB, all elements to be reported must be less than the reporting limit (LLOQ). If an element does not meet this criterion then no samples can be reported for that element in the area bracketed by the CCB.

12.7 Interference Check Standard (ICSA-ICSAB). An interference check standard must be analyzed at the beginning of each analytical run. For all spiked elements, the analyzed results must be within 20 percent of the true values. For unspiked elements, the interfering element solutions must contain less than the absolute value of the reporting limit for each element. If these criteria are not met, then no samples containing the elements in question can be reported in the area bracketed by this QC unless the samples contain no significant interferents.

12.8 Low Level Calibration Verification (CRI, CRIB, CRID, CRIA or LLCCV). These are the low- level calibration verification standards containing the elements of interest at (or below) the reporting level for

each element. A low-level check standard at or below the RL/LOQ must be analyzed at the beginning of each calibration (analysis) batch. The acceptance criterion for these checks is 80 to 120% recovery. Relative Error (%RE) must be 20% for LLCCV (See section 12.20 for calculation)

12.8.1 The low-level calibration verification is initially verified by the analysis of at least 7 replicate samples, spiked at the RL/LOQ and processed through all preparation and analysis steps of the method. The mean recovery and relative standard deviation of these samples provide an initial statement on precision and accuracy at the LLOQ. In most cases the mean recovery must be +/- 35% of the true value and RSD must be < 20%. Ongoing quarterly verification is required.

12.8.2 More frequent LLCCV checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed low check at the end of a run.

12.9 Method Blank: The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. All elements to be reported must be less than ½ of the RL (LLOQ). if the samples are high relative to the Method blank (> 10 X of the level), then the samples may be reported. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank is considered acceptable.

12.9.1 The default 6010D method limit for the method blank is that is must be less than one half of the reporting limit.

12.9.2 If the method blank does not meet criteria, then it can be reanalyzed along with any associated samples. If it is still unacceptable, then all associated samples must be redigested and reanalyzed along with the other appropriate batch QC samples

12.10 Spike Blank: The laboratory must digest and analyze a spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. The laboratory must assess laboratory performance of the spike blank against recovery limits of 80 to 120 percent. In house spike blank limits may also be generated to support these default limits. If the spike blank is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element.

12.10.1 If solid lab controls are used, then the manufacturer's QC Performance Acceptance Limits must be applied.

12.11 Matrix Spike: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Recoveries must be assessed against default limits of 75 to 125 percent. In house limits may be generated for this method for informational purposes only Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result) / Amount Spiked) x 100 = matrix spike recovery

12.11.1 Post-digest spike must be performed when matrix spike is out of the limits of 75 to 125 percent.

12.12 Matrix Spike Duplicate (MSD) or Matrix Duplicate DUP). The laboratory must digest a matrix spike duplicate or matrix duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (RPD) between the MSD and the MS or between the DUP and the sample must be assessed. The RPD is calculated as shown below. The control limit for the duplicate RPD is method defined as 20%. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the

reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

12.12.1 If a MSD or duplicate is out of control, then the data must be checked carefully to confirm that the high rpd for a given element is not a result of an analytical problem. If an analytical problem is suspected, the MSD or duplicate must be reanalyzed for confirmation. If the initial and reanalysis are in agreement (within 20%), then the high rpd is a result of preparation or sample issues and further analysis of the initial preparation is not required. If the initial and reanalysis are not in agreement due to an analytical problem, then any affected samples in the associated batch must also be reanalyzed for that element.

12.12.2 If more than 50% of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high RPD, then the MSD or duplicate must be redigested for confirmation, unless the sample matrix is such that the non-homogeneity of the sample is visually apparent. If the results confirm, the results from the original MSD or duplicate must be flagged as indicative of possible sample non-homogeneity. If the results do not confirm, then the whole batch must be digested and reanalyzed.

12.12.3 If 50% or less of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high rpd, then the high rpd(s) must be footnoted as indicating possible sample non-homogeneity unless other problems are suspected. If problems are suspected, the reviewer will initiate redigestion and reanalysis of the batch.

12.12.4 The calculations used to calculate RPD are shown below.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

12.13 Serial Dilution. A serial dilution is required on a frequency of one in 20 samples. For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution must be prepared. Normally the sample used for the serial dilution is the sample that is used for the matrix spike and matrix spike duplicate. For the serial dilution, a 1:5 dilution must be made on the sample. The results of the 1:5 dilution must agree within 20 percent of the true value as long as the sample is greater than 25 times the reporting limit for that element before dilution and the sample results are within the linear range. If not, an interference effect must be suspected, and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown below.

$$\frac{100 \times ((\text{Sample result} - \text{Serial dilution result}))}{\text{Sample result}} = \text{Serial dilution percent difference}$$

12.14 Post Digestion Spike: Post-digest spikes used to determine potential interferences. The test only needs to be performed for the specific elements that failed original matrix spike limits, and only if the spike concentration added was greater than the concentration determined in the unspiked sample.
Using unspiked QC sample, spike with a known quantity of target elements. Post spike concentration is at matrix spike concentration. See TABLE 5 for suggested concentrations of Metals in the Post digestion spike and Table 18 for preparation of post spike. The recovery of the post-digestion Spike must fall within 75 to 125 % acceptance range, relative to the known true value. If the post-digestion MS recovery fails to meet the acceptance criteria, the sample results must be reported as estimated values.
((Post spiked Sample Result - Sample Result) / Amount Spiked) x 100 = Post spike recovery

12.15 For TCLP samples, a post-digest spike for any element where the matrix spike recovery is less than 50% and the sample concentration for that element is within 20% of the appropriate regulatory level and not over the regulatory level. If the post-digest spike passes within limits of 75 to 125% recovery, the low recovery will be attributed to a sample matrix effect at digestion and no further analyses will be required. If the post-digest spike fails, then a second post-digest spike will be prepared on a sample dilution. If this spike passes, all samples will be rerun at this dilution level to confirm the sample results. If the post-digest spike fails again on the diluted sample, then Method of Standard Additions (MSA) will be performed for this sample.

12.16 IEC Correction Factor Generation. All interfering element correction factors (IEC's), must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly. The result of <2 times RL (LLOQ) is required on IEC.

12.17 Lower Limit of Quantitation check sample (LLQC). The LLQC is a sample at the reporting limit that is taken through the entire preparation and analytical process. This standard must be analyzed when reporting limits are initial established and on an as needed basis after that. The LLQC is equivalent to the LOQ (Limit of quantitation) standard which must be analyzed quarterly for the DOD QSM program. The limits of quantitation are verified when all analytes in the LLQC sample are detected within 20% of their true value. If the limits cannot be verified at the spiked level, then the quantitation limit must be adjusted to a level where verification is successful.

12.18 Calibration Curve. The calibration curve must be prepared daily using a minimum of a calibration blank and one non-zero. The calibration must be verified with LLCCV/CRI and an ICV before any samples can be analyzed. If the curve is not verified as described in section 12.5 or 12.8, then no results can be reported for those elements which did not meet quality control criteria.

12.19 HIGH STANDARD: The high standard is required in run and acceptance criteria are +/-10 of the true value. See HSTD table 14 for preparation and true value.

12.20 Measurement the Relative Error (%RE):
Relative error is calculated using the following equation:

$$\% \text{ Relative Error} = \frac{x'i - xi}{xi} \times 100$$

xi = True value for the standard
x'i = Measured concentration of the standard
The Relative Error for the CCV is 10% and for LLCCV (CRI) is 20%

13.0 CALCULATIONS

13.1 For water samples, the following calculations must be used. Refer to the QC section for the calculations to be used for the QC samples.

original sample concentration of metal (μg/l) =

$$\frac{\text{(conc. in the digestate (μg/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

13.2 For soil samples, the following calculations must be used.

concentration of the metal in the dry sample (mg/kg) =

$$\frac{\text{(conc. in the digestate (mg/l) x final digestate volume(L))}}{\text{(sample wt. (kg)) x (\% solids/100)}}$$

14.0 DOCUMENTATION REQUIREMENTS

14.1 If any samples or QC checks require reanalysis, a brief explanation of the reason must be documented in the raw data. All instrument data must be exported to the LIMS system and a copy of the run log must be included in the logbook by the instrument.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed. The SGS Lot Number must be cross-referenced on the standard vial.

14.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. A copy of any outside maintenance reports must also be kept in the log. In addition to the maintenance, the maintenance log must also contain daily information on such items as the profile intensity. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error and a reason for the correction. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information must also be verified during this review.

15.0 INSTRUMENT MAINTENANCE

15.1 Recommended periodic maintenance includes the items outlined below.

15.1.1 Change the pump tubing weekly or as needed.

15.1.2 Clean the filter on the recirculating pump approximately once a month and dust off the power supply vents every one to two weeks.

15.1.3 Clean the radial view quartz surface weekly or more often if needed.

15.1.4 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

15.1.5 Change the sampler tip as needed (every one to two months).

15.1.6 Clean the recirculating pump lines every 3 months or more often if needed.

15.1.7 Clean the slides on the autosampler with methanol and wipe them with a Kim Wipe saturated with Teflon spray a minimum of once per day.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Nonhazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes
16.2.3 Chlorinated organic solvents
16.2.4 Non-chlorinated organic solvents
16.2.5 Hazardous solid wastes
16.2.6 Non-hazardous solid wastes

17.0 ADDITIONAL REFERENCES

17.1 Refer to other SOP's for ICP analysis (CLP, and EPA 200.7 for both DW and WW).

TABLE 1: NORMAL REPORTING LIMITS BY ELEMENT				
ANALYTE	WATER & WIPE REPORTING LIMIT(µg/l)	SOIL REPORTING LIMIT (mg/kg)	SOIL REPORTING LIMIT (ug/l)	TCLP REPORTING LIMIT
Aluminum	200	50	500	
Antimony	6	2	20	
Arsenic	3	2	20	0.50
Barium	200	20	200	1.0
Beryllium	1	0.2	2	
Cadmium	3	0.5	5	0.025
Calcium	5000	500	5000	
Chromium	10	1	10	0.05
Cobalt	50	5	50	
Copper	10	2.5	25	
Iron	100	50	500	
Lead	3	2	20	0.50
Magnesium	5000	500	5000	
Manganese	15	1.5	15	
Nickel	10	4.0	40	
Potassium	10000	1000	10000	
Selenium	10	2	20	0.50
Silver	10	0.5	5	0.05
Sodium	10000	1000	10000	
Thallium	10	1	10	
Vanadium	50	5	50	
Zinc	20	5	50	
Boron	100	10	100	
Molybdenu	20	1	10	
Palladium	50	5.0	50	
Sulfur	50	10	100	
Silicon	200	20	200	
Strontium	10	5	50	
Tin	10	10	200	
Titanium	10	1	10	
Tungsten	50	5	50	
Zirconium	10	2	20	
Bismuth	20	2	20	
Lithium	50	5	50	
Phosphorus	50	10	100	
Cerium	100	10	100	

Cerium is being calibrated to monitor IEC factor only.

TABLE 2: ANALYTICAL LINES ON THE SSTRACE			
ELEMENT	WAVELENGTH	PLASMA VIEW	WAVELENGTH RANGE SELECTION
Al	396.1	Radial	High
As	189.0	Axial	Low
Ca	317.9	Radial	High
Fe	259.9	Radial	High
Mg	279.0	Radial	High
Mn	257.610	Axial	High
Pb	220.3	Axial	Low
Se	196.0	Axial	Low
Tl	190.8	Axial	Low
V	292.4	Axial	High
Ag	328.0	Axial	High
Ba	455.4	Radial	High
Be	313.0	Radial	High
Cd	228.8	Axial	Low
Co	228.6	Axial	Low
Cr	267.7	Axial	High
Cu	324.7	Axial	High
K	766.4	Radial	High
Na	589.5	Radial	High
Ni	231.6	Axial	Low
Sb	206.8	Axial	Low
Zn	206.2	Axial	Low
B	208.9	Axial	Low
Mo	202.0	Axial	Low
P	177.4	Axial	Low
S	182.0	Axial	Low
Sr	407.7	Radial	High
Sn	189.9	Axial	Low
Ti	334.9	Axial	High
Si	212.4	Axial	Low
W	207.9	Axial	Low
Zr	339.1	Axial	High
Bi	223.0	Axial	Low
Li	670.7	Radial	High
Ce	404.0	Axial	High

TABLE 3: CALIBRATION STANDARD LEVELS in ug/l		
Element	**STD A (Blank)**	**STD B**
Aluminum	0	80000
Antimony	0	4000
Arsenic	0	4000
Barium	0	4000
Beryllium	0	4000
Cadmium	0	4000
Calcium	0	80000
Chromium	0	4000
Cobalt	0	4000
Copper	0	4000
Iron	0	80000
Lead	0	4000
Magnesium	0	80000
Manganese	0	4000
Nickel	0	4000
Potassium	0	80000
Selenium	0	4000
Silver	0	500
Sodium	0	80000
Thallium	0	4000
Vanadium	0	4000
Zinc	0	4000
Boron	0	4000
Molybdenum	0	4000
Phosphorus	0	4000
Sulfur	0	4000
Silicon	0	**10000**
Strontium	0	4000
Tin	0	4000
Titanium	0	4000
Tungsten	0	4000
Zirconium	0	4000
Bismuth	0	4000
Lithium	0	4000
Cerium	0	4000

TABLE 4: ICV, and CCV LEVELS		
Element	**ICV Suggested Level in ug/l**	**CCV Suggested Level in ug/l**
Aluminum	40000	40000
Antimony	2000	2000
Arsenic	2000	2000
Barium	2000	2000
Beryllium	2000	2000
Cadmium	2000	2000
Calcium	40000	40000
Chromium	2000	2000
Cobalt	2000	2000
Copper	2000	2000
Iron	40000	40000
Lead	2000	2000
Magnesium	40000	40000
Manganese	2000	2000
Nickel	2000	2000
Potassium	40000	40000
Selenium	2000	2000
Silver	250	250
Sodium	40000	40000
Thallium	2000	2000
Vanadium	2000	2000
Zinc	2000	2000
Boron	2000	2000
Molybdenum	2000	2000
Phosphorus	2000	2000
Sulfur	2000	2000
Silicon	5000	5000
Strontium	2000	2000
Tin	2000	2000
Titanium	2000	2000
Tungsten	2000	2000
Zirconium	2000	2000
Bismuth	2000	2000
Lithium	2000	2000
Cerium	N/A	2000

TABLE 5: SUGGESTED CONCENTRATIONS OF METALS IN THE MATRIX SPIKE, SPIKE BLANK AND POST SPIKE FOR AQ, SOIL AND TCLP MATRIX			
ELEMENT	**SOILS FINAL CONCENTRATION IN mg/kg**	**AQUEOUS/SOIL FINAL CONCENTRATION IN µg/l**	
Aluminum	2500	25000	
Antimony	200	2000	
Arsenic	200	2000	
Barium	200	2000	
Beryllium	200	2000	
Cadmium	200	2000	
Calcium	2500	25000	
Chromium	200	2000	
Cobalt	200	2000	
Copper	200	2000	
Iron	2500	25000	
Lead	200	2000	
Magnesium	2500	25000	
Manganese	200	2000	
Nickel	200	2000	
Potassium	2500	25000	
Selenium	200	2000	
Silver	25	250	
Sodium	2500	25000	
Thallium	200	2000	
Vanadium	200	2000	
Zinc	200	2000	
Boron	200	2000	
Molybdenum	200	2000	
Phosphorus	200	2000	
Sulfur	200	2000	
Silicon	500	5000	
Strontium	200	2000	
Tin	200	2000	
Titanium	200	2000	
Tungsten	200	2000	
Zirconium	200	2000	
Bismuth	200	2000	
Lithium	200	2000	
Cerium	N/A	N/A	

TABLE 6: SUGGESTED CONCENTRATIONS OF METALS IN THE QUALITY CONTROL SAMPLE LOW CHECK (CRI or CRIB) SOLUTION	
ELEMENT	**FINAL CONCENTRATION IN µg/l**
Sb	6
As	8
Ba	200
Be	2
Cd	3
Cr	10
Co	50
Cu	10
Pb	3
Mn	15
Ni	10
Se	10
Tl	10
V	50
Zn	20
B	100
Bi	20
Li	50
Mo	20
P	50
Sr	10
S	50
Sn	10
Ti	10
W	50
Zr	10
Ag	5
Si	200
Al	200
Ca	5000
Fe	100
Mg	5000
K	5000
Na	5000
Ce	N/A

TABLE 7: SUGGESTED CONCENTRATIONS OF METALS IN THE QUALITY CONTROL SAMPLE LOW CHECK (CRID) SOLUTION	
Element	**Final Concentration in µg/l**
Sb	
As	3
Ba	4
Be	1
Cd	1
Cr	2
Co	3
Cu	
Pb	
Mn	3
Ni	4
Se	5
Tl	
V	2
Zn	10
B	
Bi	
Li	
Mo	
Pd	
Sr	
S	
Sn	
Ti	
W	
Zr	
Ag	
Si	
Al	100
Ca	1000
Fe	
Mg	100
K	2000
Na	1000
Ce	N/A

TABLE 8: SUGGESTED CONCENTRATIONS OF METALS IN THE QUALITY CONTROL SAMPLE LOW CHECK (CRIA) SOLUTION	
ELEMENT	**FINAL CONCENTRATION IN µg/l**
Sb	20
As	20
Ba	
Be	
Cd	
Cr	
Co	
Cu	
Pb	20
Mn	
Ni	
Se	20
Tl	
V	
Zn	
B	
Bi	
Li	
Mo	
Pd	
Sr	
S	
Sn	200
Ti	
W	
Zr	
Ag	
Si	
Al	500
Ca	2000
Fe	500
Mg	2000
K	
Na	
Ce	

Solution shown in Table 8 is not the part of the routine run but can be used as needed for higher detection limit.

TABLE 9: INTERNAL STANDARDS				
ELEMENTS	**Y 3600**	**Y 3710**	**Y 2243**	**In 2306**
Sb			X	
As			X	
Ba		X		
Be		X		
Cd			X	
Cr	X			
Co				X
Cu	X			
Pb				X
Mn	X			
Ni				X
Se			X	
Tl				X
V	X			
Zn			X	
B			X	
Bi			X	
Li		X		
Mo			X	
P			X	
Sr		X		
S			X	
Sn			X	
Ti	X			
W			X	
Zr	X			
Ag	X			
Si			X	
Al		X		
Ca		X		
Fe		X		
Mg		X		
K		X		
Na		X		
Ce	X			

TABLE 10: PREPARATION AND CONCENTRATION OF ICP DAILY CALIBRATION AND INTERNAL STANDARD

Standard Name	Elements	Vendor Name	Item Name (for multi-elements)	Stock Lot #	Expira-tion Date	Acid Matrix	Acid Manu-facturer	Acid Lot #	Stock Conc. (mg/l)	Vol. Added (ml)	Total Vol. (ml)	Std Conc. (mg/l)	Exp. Date	Date	Analyst (Initials)
MA-__________ STDA	None	N/A		N/A	N/A	__% HNO3 __% HCl			0.000	0.000	1000	0.000			
MA-__________ STDA	None	N/A		N/A	N/A	__% HNO3 __% HCl			0.000	0.000	1000	0.000			
MA-__________ STDA	None	N/A		N/A	N/A	__% HNO3 __% HCl			0.000	0.000	1000	0.000			
MA-__________ STDA	None	N/A		N/A	N/A	__% HNO3 __% HCl			0.000	0.000	1000	0.000			
MA-__________ STDA	None	N/A		N/A	N/A	__% HNO3 __% HCl			0.000	0.000	1000	0.000			
MA-__________ - STDB	B,Ba,Be,Cd,Co, Cr3,Cu,Mn,Ni,P, Pb,Se,Sr,TL,V, Zn	Inorganic Ventures	Accutest-13 REV1			__% HNO3 __% HCl			1000	0.80	200	4.00			
	As,Mo,Sb,Sn,Ti, W,Zr	Inorganic Ventures	Accutest-14 REV1						1000	0.80		4.00			
	Ag	In house							125	0.80		0.50			
	Bi								1000	0.80		4.00			
	Li								1000	0.80		4.00			
	S								1000	0.80		4.00			
	Si								1000	2.00		10.00			
	Al.Na,K,Fe,Mg, Ca	Inorganic Ventures	Metals Mix						5000	3.20		80.00			
	Ce								1000	0.80		4.00			
MA-__________ - IS	Y					__% HNO3 __% HCl			10000	2.00	2000	10.00			
	Cs								10000	40.00		200.00			
	In								10000	10.00		50.00			
MA-__________ - IS	Y					__% HNO3 __% HCl			10000	2.00	2000	10.00			
	Cs								10000	40.00		200.00			
	In								10000	10.00		50.00			

TABLE 11: PREPARATION AND CONCENTRATION OF CCV

Standard Name	Elements	Vendor Name	Item Name (for multi-elements)	Stock Lot #	Expira-tion Date	Acid Matrix	Acid Manu-facturer	Acid Lot #	Stock Conc. (mg/l)	Vol. Added (ml)	Total Vol. (ml)	Std Conc. (mg/l)	Exp. Date	Date	Analyst (Initials)
MA-_____-CCV	B,Ba,Be,Cd,Co,Cr3,Cu,Mn,Ni,P,Pb,Se,Sr,TL,V,Zn	Inorganic Ventures				__% HNO3 __% HCl			1000	2.00		2.00			
	As,Mo,Sb,Sn,Ti,W,Zr	Inorganic Ventures							1000	2.00		2.00			
	Ag	In house							125	2.00		0.25			
	Bi								1000	2.00		2.00			
	Li								1000	2.00		2.00			
	S								1000	2.00		2.00			
	Si								1000	5.00		5.00			
	Al,Na,K,Fe,Mg,Ca	Inorganic Ventures	Mineral Mix						5000	8.00		40.00			
	Ce								1000	2.00		2.00			

TABLE 12: PREPARATION AND CONCENTRATION OF ICV

Standard Name	Elements	Vendor Name	Name (for multi-elements)	Stock Lot #	Exp. Date	Acid Matrix	Acid Manu-facturer	Acid Lot #	Stock Conc. (mg/l)	Vol. Added (ml)	Total Vol. (ml)	Std Conc (mg/l)	Exp. Date	Analyst (Initials)	Date
	Ba								1000	2.0	1000	2.00			
	Be								1000	2.0		2.00			
	Cd								1000	2.0		2.00			
	Co								1000	2.0		2.00			
	Cr								1000	2.0		2.00			
	Cu								1000	2.0		2.00			
	Mn								1000	2.0		2.00			
	Ni								1000	2.0		2.00			
	V								1000	2.0		2.00			
	Zn								1000	2.0		2.00			
	As								1000	2.0		2.00			
	TL								1000	2.0		2.00			
	Pb								1000	2.0		2.00			
	Se								1000	2.0		2.00			
	Sb								1000	2.0		2.00			
	B								1000	2.0		2.00			
	Mo								1000	2.0		2.00			
	Sn								1000	2.0		2.00			
	Sr								1000	2.0		2.00			
	Ti								1000	2.0		2.00			
	W								1000	2.0		2.00			
	Zr								1000	2.0		2.00			
	S								1000	2.0		2.00			
	Bi								1000	2.0		2.00			
	Li								1000	2.0		2.00			
	P								1000	2.0		2.00			
	Ag								1000	0.250		0.25			
	Si								1000	5.00		5.00			
	Al								10000	4.0		40.00			
	Ca								10000	4.0		40.00			
	Fe								10000	4.0		40.00			
	Mg								10000	4.0		40.00			
	K								10000	4.0		40.00			
	Na								10000	4.0		40.00			

TABLE 13: PREPARATION AND CONCENTRATION OF ICSA AND ICSAB SOLUTIONS.

ICSA:

Standard Name	Elements	Vendor Name	Item Name (for multi-elements)	Stock Lot #	Expiration Date	Acid Matrix	Acid Manufacturer	Acid Lot #	Stock Conc. (mg/l)	Vol. Added (ml)	Total Vol. (ml)	Std Conc. (mg/l)	Expiration Date	Analyst (Initials)	Date
MA-___-___ - ICSA	Mg		N/A			___% Nitric ___% HCl			10000	50.0	1000	500			
	Al		N/A						10000	50.0	1000	500			
	Ca		N/A						10000	40.0	1000	400			
	Fe		N/A						10000	20.0	1000	200			

ICSAB:

Standard Name	Elements	Vendor Name	Item Name (for multi-elements)	Stock Lot #	Expiration Date	Acid Matrix	Acid Manufacturer	Acid Lot #	Stock Conc. (mg/l)	Vol. Added (ml)	Total Vol. (ml)	Std Conc. (mg/l)	Expiration Date	Analyst (Initials)	Date
MA-___-___ - ICSAB	Ag,Cd,Ni,Pb,Zn		CLP ILM 03.0 Analytes B			___% HNO3 ___% HCl			100	10	1000	1.00			
	Ba,Be,Cr, Co,Cu,Mn,V								50	10	1000	0.50			
	Al								10000	50.0	1000	500			
	Ca								10000	40.0	1000	400			
	Fe								10000	20.0	1000	200			
	Mg								10000	50.0	1000	500			
	Sb								1000	1.0	1000	1.00			
	As								1000	1.0	1000	1.00			
	Se								1000	1.0	1000	1.00			
	Tl								1000	1.0	1000	1.00			
	Mo								1000	0.5	1000	0.50			
	W								1000	0.5	1000	0.50			
	Zr								1000	0.5	1000	0.50			
	B								1000	0.5	1000	0.50			
	Sr								1000	0.5	1000	0.50			
	Sn								1000	0.5	1000	0.50			
	Ti								1000	0.5	1000	0.50			
	Si								1000	0.5	1000	0.50			
	S								1000	0.5	1000	0.50			
	Bi								1000	0.5	1000	0.50			
	Li								1000	0.5	1000	0.50			
	P								1000	0.5	1000	0.50			

TABLE 14: PREPARATION AND CONCENTRATION OF HIGH STANDARD

Standard Name	Elements	Vendor Name	Item Name (for multi-elements)	Stock Lot #	Expira-tion Date	Acid Matrix	Acid Manu-facturer	Acid Lot #	Stock Conc. (mg/l)	Vol. Added (ml)	Total Vol. (ml)	Std Conc. (mg/l)	Exp. Date	Date	Analyst (Initials)
MA-_____ - HSTD (Regular)	B,Ba,Be,Cd,Co, Cr3,Cu,Mn,Ni,P, Pb,Se,Sr,TL,V, Zn	Inorganic Ventures	Accutest-13 REV1			__% HNO3 __% HCl			1000	8.00	1000	8.00			
	As,Mo,Sb,Sn,Ti, W,Zr	Inorganic Ventures	Accutest-14 REV1						1000	8.00		8.00			
	Ag	In house							125	5.00		0.625			
	Bi								1000	8.00		8.00			
	Li								1000	8.00		8.00			
	S								10000	10.00		100.00			
	Si								10000	2.50		25.00			

Standard Name	Elements	Vendor Name	Item Name (for multi-elements)	Stock Lot #	Expira-tion Date	Acid Matrix	Acid Manu-facturer	Acid Lot #	Stock Conc. (mg/l)	Vol. Added (ml)	Total Vol. (ml)	Std Conc. (mg/l)	Exp. Date	Date	Analyst (Initials)
MA-_____ - HSTD (Minerals)	Al					__% HNO3 __% HCl			10000	30.00	1000	300.00			
	Mg								10000	30.00		300.00			
	K								10000	20.00		200.000			
	Na								10000	20.00		200.00			
	Ca								10000	20.00		200.00			
	Fe								10000	20.00		200.00			

TABLE 15: PREPARATON AND CONCENTRATION OF CRI SOLUTION

Standard Name	Elements	Vendor Name	Item Name (for multi-elements)	Stock Lot #	Expira-tion Date	Acid Matrix	Acid Manu-facturer	Acid Lot #	Stock Conc. (mg/l)	Vol. Added (ml)	Total Vol. (ml)	Std Conc. (mg/l)	Expira-tion Date	Analyst (Initials)	Date
	Sb					___% HNO3			6.00			0.006			
	Mo	Inorganic Ventures	ACCUTEST-20A			___% HCl			20.00			0.020			
	Sn								10.00	**1.00**		0.010			
	Ti								10.00			0.010			
	W								50.00			0.050			
	Zr								10.00			0.010			
	Al								200.00			0.200			
	As								8.00			0.008			
	Ba								200			0.200			
	Be	Inorganic Ventures	ACCUTEST-20B						2.00			0.002			
	B								100.00			0.100			
	Cd								3.00			0.003			
	Ca								5000			5.000			
	Cr								10.0	**1.00**	**1000**	0.010			
	Co								50.00			0.050			
	Cu								10.0			0.010			
	Fe								100.0			0.100			
MA-_____ - CRI	Pb								3.0			0.003			
	Mg								5000			5.000			
	Mn								15.0			0.015			
	Ni								10.0			0.010			
	P								50.0			0.050			
	K								5000			5.000			
	Se								10.0			0.010			
	Na								5000.0			5.000			
	Sr								10			0.010			
	TL								10			0.010			
	V								50			0.050			
	Zn								20			0.020			
	Bi	In house	Intermediate						20	1.00		0.020			
	Li	In house	Intermediate						50	1.00		0.05			
	S	In house	Intermediate						50	1.00		0.05			
	Zr	In house	Intermediate						10	1.00		0.01			
	Si								1000	0.20		0.20			
	Ag	In house	Intermediate						10	0.50		0.005			

TABLE 16: PREPARATION AND CONCENTRATION OF CRID SOLUTION

Standard Name	Elements	Vendor Name	Item Name (for multi-elements)	Stock Lot #	Expiration Date	Acid Matrix	Acid Manufacturer	Acid Lot #	Stock Conc. (mg/l)	Vol. Added (ml)	Total Vol. (ml)	Std Conc. (mg/l)	Expiration Date	Analyst (Initials)	Date
	Al					___% HNO3			100.00			0.100			
	As	Inorganic Ventures	ACCUTEST-21			___% HCl			3.00			0.003			
	BA								4.00	1.00	1000	0.004			
	Be								1.00			0.001			
	Cd								1.00			0.001			
MA-_____ - CRID	Ca								1000.00			1.000			
	Cr								2.00			0.002			
	Co								3.00			0.003			
	Mg								100			0.100			
	Mn								3.00			0.003			
	Ni								4.00			0.004			
	K								2000.00			2.000			
	Se								5			0.005			
	Na								1000.0			1.000			
	TL								2.00			0.002			
	V								2.0			0.002			
	ZN								10.0			0.010			

TABLE 17: PREPARATION AND CONCENTRATION OF POST SPIKE SOLUTION

					Date		Analyst		MP #	
Post spike for ICP Method 6010D					**QC sample #**					
Spiking solution	Elements	Spike added (Y/N)	Vendor	Intermediate Lot #	Exp. Date	Conc. (mg/l)	Amt of Spike added (ml)	Digestate sample volume (ml)	Final Digestate volume in ml (Spike+ Sample)	Final Conc at the instrument (mg/l)
Mixed ICP intermediate Metals Solution (ACCUTEST-13A-REV1)	Ba,Be,B Cd,Cr,Co,Cu,Pb ,Mn,Ni,P,Se,Sr, TL,V,Zn					200	0.2			2
Mixed ICP intermediate Metals Solution (ACCUTEST-14A-REV1)	Sb,As,Mo,Sn,Ti, W,Zr					200	0.2		20	2
Ag Spike Intermediate	Ag					20	0.25			0.25
Metals Mix	Ca,Al,Fe,Mg,K, Na					5000	0.1			25
S spike	S					200	0.2			2
Bi Spike	Bi					200	0.2			2
Li Spike	Li					200	0.2			2
Si spike	Si					1000	0.1			5

For preparations of post spike Intermediate solutions follow the ICP Intermediate preparation book.

Current Version Revision Information

Changes / Edits made (this should include added or deleted information within a sentence or paragraph only):

Section / Subsection	Detailed description of what was revised
12.6.1	Added RE criteria
12.8	Added RE criteria

Sections or Subsections deleted:

Section / Subsection	Reason section or subsection was removed

Sections or Subsections added:

Section / Subsection	Reason section or subsection was added
12.20	Added calculation for %RE

History of Revisions

Version #	Date of Revision	Revised By

END OF DOCUMENT

LAB SUPERVISOR: Robert Smith

QA OFFICER: Olga L. Gomez

EFFECTIVE DATE: 1-4-2021

TITLE: DIGESTION OF SOILS FOR ICP AND ICP-MS ANALYSIS
REFERENCES: SW846 3050B (Revision 2, December 1996)
REVISED SECTIONS: 4.0 (MDL), 8.1, 9.5, 10.5, 10.11
ADDED SECTIONS: 8.13

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the digestion of sediments, soils, sludges, solid wastes, and wipes. After digestion, the samples can be analyzed by ICAP or by ICP-MS (or by graphite furnace AA for antimony). This digestion method is based upon SW846 method 3050B, Revision 2, 12/96.

2.0 SUMMARY

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) of sample is
digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Then hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals, this digestate is filtered and the filter paper and residues are rinsed, first with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 Ml.

2.2 In method 3050B, the final HCl addition is not included for ICP-MS digestates as chloride is interference for several elements on ICP-MS. However, the HCl is necessary for good solubility of many elements. HCl interferences at the ICP-MS can normally be addressed with corrections at the ICP-MS. Therefor it is recommended that HCl be added for ICP-MS digestions by this method unless otherwise directed by the lab supervisor or manager.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 See determinative method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed, and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits must also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent must be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent must be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intra laboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

METHOD BLANK: The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method

blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is distinguishable form method blank results.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the SGS Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 Non-aqueous samples must be refrigerated at the time of receipt.

6.2 All samples must be digested and analyzed within 6 months of the time of collection.

7.0 INTERFERENCES

7.1 Sludge and soil samples can contain diverse matrix types, which may contain a variety of interferences. Spiked samples can be used to determine if these interferences are adequately

treated in the digestion process. For a discussion of other interferences, refer to specific analytical methods.

8.0 APPARATUS

8.1 The apparatus needed for this digestion procedure are listed below

8.2 Digestion block. Temperature adjustable and designed to hold sample digestion tubes and capable of maintaining temperatures from 90 to 95°C.

8.3 Thermometers calibrated with NIST traceable thermometers. To be used to monitor digestion temperatures.

8.4 Sample digestion tubes and ribbed watch glasses.

8.5 Automatic pipeter bottles.

8.6 100 ml volumetric flasks.

8.7 Glass funnels.

8.8 Fisher Q8 filter paper.

8.9 Top loader balance.

8.10 Volumetric Pipets, class A.

8.11 Disposable Wood Spatulas

8.12 Ceramic Mixing Bowl.

8.13 Auto pipet

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required.

9.2 Hydrochloric acid. Baker Instra-analyzed or equivalent.

9.3 Nitric Acid. Baker Instra-analyzed or equivalent.

9.4 Hydrogen Peroxide, 30 %.

9.5 Metals Spiking Solutions. All metals spiking solutions must be made up in a solution of 2 % nitric acid as described in Table 1. Mixture of Spike solution can be purchased from the outside vendor (eg. Inorganic ventures/Agilent, Absolute etc.). Use volumetric glassware and pipets or autopipets. Check with the metal's supervisor for additional information. Different levels of spiking solutions may be used as specified by the area supervisor.

9.5.1 The expiration date for the spiking solution is defined as the earliest date of any element or compound in that solution.

9.6 Teflon Chips

9.7 Solid Lab Control (Mixture of Metals analytes in Soil Matrix). This would be commercially purchased.

10.0 PROCEDURE: Using Q8 (or equivalent) Filter paper

10.1 Weigh out an amount of wet sample equivalent to 1 g of dry sample into a numbered digestion tube. Label each digestion tube with the complete sample number, the MP number, Date, and the number corresponding to the flask used for filtration (see section 10.11). The sample must be weighed out using a top loader balance and the weights must be recorded to two places past the decimal. Make sure that the sample identification is accurately recorded with the digestion tube numbers on the sample digestion log.

10.1.1 Make sure that the sample has been thoroughly mixed before weighing out the representative sample. Discard rocks, sticks, etc. from the sample. (Refer to the SOP EQA042 for proper sample aliquot procedures). All homogenization and sample handling must be done with wooden spatulas and ceramic (or other non-metal) bowls.

10.1.2 If the sample has low percent solids, a larger sample size may be used to obtain a weight approximately equivalent to 1 g of dry sample. Check with the metals supervisor for additional direction with sampled with low percent solids or unusual matrices.

10.1.3 If the sample is a wipe, weighing is not necessary. Transfer the entire wipe into the labeled digestion tube and proceed with the digestion following steps 10.2 through 10.10. Extra wipes must be supplied by the client for the matrix spike or duplicate.

10.1.4 If the sample is leachate oil, measure 1ml of the sample and follow the steps starting at section 10.4. Leachate oil samples are handled using soil procedure on a volume basis.

10.2 In addition to the samples, a spike blank or a lab control and a method blank must be set up with each batch of 20 samples or less. A matrix spike, a matrix spike duplicate or a duplicate must be set up with each batch of 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. Refer to Table 1 for spiking levels to use for each MS and Spike Blank.

10.2.1 For the method blank and spike blank, instead of weighing out soil add approximately 1 g of Teflon chips to the digestion tube. Add the spiking solution to the blank spike after the chips are in the tube.

10.2.2 For some clients, a solid lab control is required rather than a blank spike. In that case, the solid lab control must be weighed out in the same manner as a sample.

10.2.3 For the matrix spike and matrix spike duplicate, refer to the metals spiking SOP, EMP202, for information on the preparation and amount of spiking solution require to be added to the sample in the digestion tube.

10.2.4 For additional details on spiking solutions and preparation, refer to the metals spiking sop, EMP202.

10.2.5 For leachate oil QC samples use 1ml of leachate and follow the steps starting at section 10.4

10.3 For samples to be tested for sulfur, where sulfide is suspected to be, add 2.0 ml of 30% hydrogen peroxide and let the samples sit for 30 minutes. All associated quality control (method blank, spike blank or lab control, matrix spike, and matrix spike duplicate) must be treated in the same manner. The spikes must be added before the addition of the hydrogen peroxide and acid. Record these steps on the digestion log. Proceed to step 10.5

10.4 Add 10 ml of 1:1 nitric acid to all Quality Control and samples.

10.5 Place the numbered tubes into a digestion block and cover with watch glasses. Heat the samples at 90 to 95°C until they come to a gentle reflux and then continue to heat the samples for an additional 10 to 15 minutes. Do not allow the samples to boil. After the heating is complete, allow the samples to cool.

10.6 Add an additional 5ml of concentrated nitric acid to all quality control and samples. Heat the samples at a gentle reflux for an additional 30 minutes. Do not allow the volume to be reduced to below 5 ml. Cool.

10.6.1 If brown fumes are generated during this digestion, add an additional 5ml aliquot of concentrated nitric acid and heat for 30 more minutes. Repeat this process until no more brown fumes are generated.

10.7 Continue the digestion at 90 to 95ºC until the volume is reduced to 5 ml or for a period of 2 hours. Do not let the samples boil at any point during the digestion process.

10.8 Add 2 ml of water and 3 ml of 30 % hydrogen peroxide to each sample and reflux until the effervescence subsides. Cool.

10.8.1 The 30% hydrogen peroxide may be added in smaller or larger initial aliquots depending on the sample characteristics. If sample effervescence is suspected to be a problem, smaller aliquots must be used.

10.9 Continue to add 30 % hydrogen peroxide in 1ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. NOTE: Do not add more than a total of 10 ml of 30 % hydrogen peroxide. Continue the digestion at 90 to 95ºC until the volume is reduced to 5 ml or for a period of 2 hours.

10.9.1 For the batch that needs total sulfur, do not add more than a total of 8 ml of 30% hydrogen peroxide at this stage of the digestion because 2 ml is added prior to the digestion.

10.10 Add 10 ml of concentrated HCl and reflux for an additional 15 minutes.

10.10.1 HCl may be omitted for some ICP-MS digestions for limited elements (As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, and Tl) at the discretion of the area supervisor or manager. However, in normal circumstances it must be added. Refer to section 2.2.

10.11 Filter the digestate through Fisher Brand Q8 filter paper (or equivalent) into 100 ml volumetric flasks and be sure to label all the flasks with the numerical value assigned to the digestion tube containing the corresponding sample (ex. 1,2,3). Make sure to rinse the digestion tubes and the filter paper well with deionized water. Dilute to volume of 100 ml with deionized water and mix well. The sample is now ready for analysis.

10.11.1 For ICP-MS analysis, the digestate must be further diluted at the instrument before analysis (normally at least by a factor of 2 to 5) and the dilution factor must be added to the instrument file.

11.0 QUALITY ASSURANCE

11.1 For each digestion batch of 20 samples or less, a lab control or a spike blank and a method blank must be prepared. Solid lab controls are required for some clients. Check with the metals supervisor for additional information.

11.2 For every 20 samples, a matrix spike, a matrix spike duplicate or a duplicate must be prepared. Matrix spike duplicates are normally used unless otherwise specified by the client requirements.

11.3 If a batch is a running batch, samples can be added to the batch (along with a method blank and spike blank or lab control) up to a maximum of 2 weeks.

11.3.1 Running batches are not allowed for all clients. Check with the metals supervisor for additional information.

11.4 Refer to the analytical methods SOPs for additional information on method quality control.

12.0 DOCUMENTATION

12.1 All digestion information must be entered on a digestion log. The information required includes the sample identification, the initial sample weight, the final sample volume, the acids used (including both amount and lot number), the spikes used, and the digestion times, temperatures, and the thermometer identification. Both the corrected and uncorrected temperature must be recorded.

12.2 The analyst must write additional information such as unusual sample characteristics in the Comments section. All spiking solution information must be entered in the metals spiking solution notebook.

12.3 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

12.4 Certificates of analysis for all primary stocks must be kept on file. If a certificate is received in the lab, give the original to the area supervisor for submission for filing with the QA department.

13.0 DATA REVIEW & REPORTING

13.1 The prep analyst is responsible for updating the samples to SCH status in the LIMS system and for entering the prep information into the LIMS. This may be done manually or electronically. When the prep information is in the LIMS, the completed paperwork must be turned into the metals supervisor for review.

13.2 The supervisor or a metals analyst reviews the preparation information and approves the data in the LIMS system.

13.3 The original paperwork is submitted to the report generation department for filing.

13.4 Supervisory (or peer) personnel will review and sign all reagent documentation a minimum of once per month.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2.

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non-hazardous aqueous wastes.

14.2.2 Hazardous aqueous wastes.

14.2.3 Chlorinated organic solvents.

14.2.4 Non-chlorinated organic solvents.

14.2.5 Hazardous solid wastes.

14.2.6 Non-hazardous solid wastes.

15.0 ADDITIONAL REFERENCES

15.1 Refer to the ICP and ICPMS analytical SOP’s and the spiking procedure SOP (EMP202).

Current Version Revision Information

Changes / Edits made (this should include added or deleted information within a sentence or paragraph only):

Section / Subsection	Detailed description of what was revised
	SGS current format
4.0	Updated MDL definition
8.1	Deleted reference to beakers
9.5	Added vendor
10.5	Deleted reference to beakers
10.11	Added requirement for mixing well

Sections or Subsections deleted:

Section / Subsection	Reason section or subsection was removed

Sections or Subsections added:

Section / Subsection	Reason section or subsection was added
8.13	Auto-pipet added

History of Revisions

Version #	Date of Revision	Revised By
21	8/22/19	Maria Ruschke
22	01/04/21	Rakesh Pathak

END OF DOCUMENT

Appendix D
Donlin Gold Laboratory Data Validation Forms and Information

FIELD DATA REVIEW AND VALIDATION CHECKLIST – DONLIN GOLD PROJECT

Sample Point(s):	Date Collected:			
	Date Shipped to Lab:			
	Collected By:			
Category	**Yes**	**No**	**N/A**	**Comments**
Reported Data				
1. Are all appropriate data fields filled out?				
2. Are water level data measurements calculated and recorded correctly?				
3. Are flow measurements calculated and recorded correctly?				
General				
1. Are sample results for field measurements consistent with historical data for specific sample point(s)?				
2. Note additional comments/observations (use back of sheet if necessary):				
Reviewed by: **Date:**				

LAB DATA REVIEW AND VALIDATION CHECKLIST (QAR)– DONLIN GOLD PROJECT

Lab Work Order:

Lab ID Client ID	Date Collected	Date Lab Received

Donlin Gold Project – (Page:)

Parameter	Method	Blank	Matrix Spike	Duplicate	LCS	MSD
Alkalinity	SM20 2320B					
pH	SM20 4500 HB					
Conductivity	SM20 2510B					
TDS	SM20 2540C					
TSS	SM20 2540D					
Chloride	EPA 300.0					
Sulfate	EPA 300.0					
Fluoride	EPA 300.0					
Nitrate/Nitrite	SM20 4500NO-3F					
Ammonia	SM20 4500NH3-G					
Total Cyanide	SM20 4500-CN C,E					
WAD Cyanide	SM20 4500-CN I					
Metals, ICP (Ca, Mg, B, Fe)	EPA 200.8					
Metals, ICP-MS (Na, K, Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Li, Mn, Mo, Ni, Se, Ag, Tl, V, Zn)	EPA 200.8					
Mercury (Low Level)	EPA 1631E					

Reported Data		Yes	No	Comments
1. COC & other field documents included?				
2. All reporting requirements satisfied? (Section 4.4, items 1, 3, and 4)				
3. Parameters reported match parameters requested?				
4. Methods reported match methods requested?				
5. Reporting limits and units as requested?				
6. Electronic file matches hard copy?				
1. Analysis holding times met?				
1. Blanks	Proper frequency?			
	Acceptance criteria met?			
2. LCSs	Proper frequency?			
	Acceptance criteria met?			
3. Matrix Spikes	Proper frequency?			
	Acceptance criteria met?			
4. Duplicates	Proper frequency?			
	Acceptance criteria met?			
1. Are sample results consistent with historical data for specific sample point(s)?				
Reviewed by:			Date:	

CORRECTIVE ACTION FORM – DONLIN GOLD PROJECT

Sample I.D.(s)_____ **Date Sampled** _____

Laboratory Job Number(s)_____ **Date Analyzed** _____

Reviewed By_____

Describe the deficiency:

Document all correspondence involved:
(Include date and time of the communication(s), as well as the name and position of all individuals contacted. Also include a synopsis of each communication, attach extra pages as necessary)

Define a corrective action:

Explain the resolution:

Acid Based Accounting Analysis Protocol

The ratio of neutralization potential from carbonate materials (NP_{CO3}) to acid generating potential (AP) is determined as follows (SRK 2011):

Total sulfur content of the material will be measured in the onsite laboratory using a LECO® analyzer. AP is then calculated from the total sulfur concentration where:

AP = 31.25 x total sulfur (weight percent)

NP would be measured in the onsite laboratory using the Sobek method (Sobek et al., 1978). The rock is digested with boiling hydrochloric acid, and then the base equivalent amount of acid consumed is determined by titrating the acid solution to a pH of 7 and converting the measured quantities to NP expressed as kilograms (kg) calcium carbonate per tonne ($CaCO_3$/t). Once NP is calculated, a correction factor is applied to account for the presence of carbonates that do not contribute to the actual neutralizing potential of the material. NP_{CO3} would be estimated from the following equations:

$NP_{CO3} = NP$ *(for* $NP \leq 22.7$ *kg* $CaCO_3$*/t)*

$NP_{CO3} = 0.85 \cdot NP + 3.4$ *(for* $NP > 22.7$ *kg* $CaCO_3$*/t)*

Variables that were incorporated in the block model to aid with the geochemical classification of waste rock at the proposed Donlin Gold project include NP from carbonate minerals (NP_{CO3}), and AP.

NP from carbonate minerals (NP_{CO3}) was estimated from:

$NP_{CO_3} = 0.76 \cdot NP + 4.8$

To avoid a bias at low NP values, the calculated NP_{CO3} should not exceed analytical NP when NP is below 50 lb. (22.7 kg) $CaCO_3$/t. Therefore, the following rules are applied to the calculation of NP:

If $NP \leq 22.7$ *kg* $CaCO_3$*/t:* $NP_{CO3} = NP$

If $NP > 22.7$ *kg* $CaCO_3$*/t:* $NP_{CO3} = 0.85 \cdot NP + 3.4$

Appendix B
Wildlife Mortality Reporting Forms

MINE SITE WILDLIFE MORTALITY REPORT FORM

DONLIN GOLD PROJECT

DATE: _____

WAD CYANIDE - RESULT OF ANALYSIS: _____

Number and Species Identification

RAPTORS_____

SONGBIRD_____

UPLAND GAME_____

WATERFOWL_____

SHOREBIRD_____

MAMMAL_____

OTHER_____

Reporter: _____

Title:_____ Phone:_____

MAIL TO:

US Fish & Wildlife Service
Ecological Service
101-12th Avenue
Fairbanks, Alaska 99701

Alaska Department of Fish & Game
Habitat Division
1300 College Road
Fairbanks, Alaska 99701-1599

Observer Comments (Include maps showing location of find, date, and other information):

_____

_____

_____

_____

_____

_____

_____

_____

SEMI-ANNUAL MINE SITE MORTALITY REPORT

DONLIN GOLD PROJECT

REPORTING PERIOD:_____

YEAR: _____

MORTALITIES

Number and Species Identification

	CYANIDE	NON-CYANIDE
RAPTORS	_____	_____
SONGBIRD	_____	_____
UPLAND GAME	_____	_____
WATERFOWL	_____	_____
SHOREBIRD	_____	_____
MAMMAL	_____	_____
OTHER	_____	_____

Reporter: _____

Title:_____ Phone:_____

MAIL TO:

US Fish & Wildlife Service
Ecological Service
101-12th Avenue
Fairbanks, Alaska 99701

Alaska Department of Fish & Game
Habitat Division
1300 College Road
Fairbanks, Alaska 99701-1599

Observer Comments (Include maps showing location of find, date, and other information):

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