

MEASUREMENT OF ANALYTES USING THE KONELAB ANALYZER

Approvals (Signature/Date):



March 23, 2005

Andrea Teal
Quality Assurance Manager

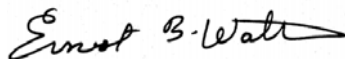
Date



March 23, 2005

Benjamin Gulizia
Laboratory Director/Lead Technical Director

Date



March 23, 2005

Ernest Walton
Health & Safety Manager / Coordinator

Date

Copyright Information:

This documentation has been prepared by TestAmerica Analytical Testing Corp. and its affiliates ("TestAmerica"), solely for their own use and the use of their customers in evaluating their qualifications and capabilities in connection with a particular project. The user of this document agrees by its acceptance to return it to TestAmerica upon request and not to reproduce, copy, lend, or otherwise disclose its contents, directly or indirectly, and not to use it for any other purpose other than that for which it was specifically provided. The user also agrees that where consultants or other outside parties are involved in the evaluation process, access to these documents shall not be given to said parties unless those parties also specifically agree to these conditions.

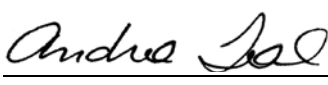
THIS DOCUMENT CONTAINS VALUABLE CONFIDENTIAL AND PROPRIETARY INFORMATION. DISCLOSURE, USE OR REPRODUCTION OF THESE MATERIALS WITHOUT THE WRITTEN AUTHORIZATION OF TESTAMERICA IS STRICTLY PROHIBITED. THIS UNPUBLISHED WORK BY TESTAMERICA IS PROTECTED BY STATE AND FEDERAL LAW OF THE UNITED STATES. IF PUBLICATION OF THIS WORK SHOULD OCCUR THE FOLLOWING NOTICE SHALL APPLY:

©COPYRIGHT 2007 TESTAMERICA ANALYTICAL TESTING CORP. ALL RIGHTS RESERVED.

Facility Distribution No. 1

Distributed To: QA Navigator

SOP REVISION / REVIEW SUMMARY

<p>SOP Number: <u>GE01:03.18.05:1</u> Review Date: <u>March 18, 2005</u> Effective Date: <u>April 18, 2005</u></p> <p>Review / Revision Type: Analytical/procedural revisions</p> <ul style="list-style-type: none">- Revision # change. Completed SOP Training Forms are required. <p>Summary of Changes:</p> <ul style="list-style-type: none">- Complete re-write.- Added several new analyses to be analyzed by this method: nitrate, nitrite, total phosphorus, TKN, hydrazine, tannin & lignin, and hexavalent chromium- Revised the SOP title- Revised format to be consistent with current STL Savannah SOP format and NELAC requirements- Revised safety information- Added quality control, method performance, preventative maintenance, and waste management information	
<p>SOP Number: <u>GE01:03.18.05:1A</u> Review Date: <u>August 5, 2005</u> Effective Date: <u>August 5, 2005</u></p> <p>Review / Revision Type: Minor text, grammatical, and/or formatting changes</p> <ul style="list-style-type: none">- Alpha character revision, notification is not required. SOP training is not required. <p>Summary of Changes:</p> <ul style="list-style-type: none">- Minor typographical changes made to Section 1.0, and 9.0. Separated method and SOP references for total cyanide and free cyanide. <p>Approval:</p> <p>Quality Assurance Manager: <u></u> Date: <u>August 5, 2005</u> Andrea Teal</p>	
<p>SOP Number: <u>GE01:03.18.05:1B</u> Review / Effective Date: <u>March 14, 2007</u></p> <p>Review / Revision Type: Minor text, grammatical, and/or formatting changes</p> <ul style="list-style-type: none">- Alpha character revision, notification is not required. SOP training is not required. <p>Summary of Changes:</p> <ul style="list-style-type: none">- Minor grammatical changes.- Revised all referenced SOP titles to be consistent with current revisions.	

Approval:

Quality Assurance Manager:



Andrea Teal

Date: March 14, 2007

SOP Number: GE01:03.18.05:1C

Review / Effective Date: March 14, 2007

Review / Revision Type:

Minor text, grammatical, and/or formatting changes

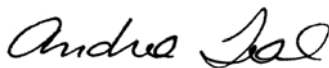
- Alpha character revision, notification is not required. SOP training is not required.

Summary of Changes:

- Updated method references for Chloride, Cyanide, Orthophosphate, and Cyanide.

Approval:

Quality Assurance Manager:



Andrea Teal

Date: February 14, 2008

SOP Number: GE01:03.18.05:1D

Review Date: December 31, 2008

Effective Date: February 19, 2009

Review / Revision Type:

Minor text, grammatical, and/or formatting changes

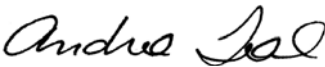
- Alpha character revision, notification is not required. SOP training is not required.

Summary of Changes:

- Included Ammonia Distillation information from SOP GE15. SOP GE15 is now obsolete.
- Removed references to cyanide and hydrazine as these are no longer performed using this procedure.
- Updated nitrate soil preparation procedures to match current lab practice.
- Removed reference to SOP AN99: *Definitions, Terms, and Acronyms*. This SOP is now obsolete. Definitions are now contained in the glossary in the Laboratory Quality Manual.
- Revised all referenced SOP titles to be consistent with current revisions.
- Removed raw data from Attachments.

Approval:

Quality Assurance Manager:



Andrea Teal

Date: December 31, 2008

1.0 SCOPE AND APPLICATION

This SOP describes the procedures used by TestAmerica Savannah to determine the concentration of various analytes in water and soil using the Konelab autoanalyzer. The following analytes may be determined:

ANALYTE	REFERENCE METHOD	APPLICATION NOTE/ SOP SUMMARY
Ferrous iron	SM3500-Fe-D	Appendix A
Chloride	EPA 325.2, EPA 9251, SM4500Cl-E	Appendix B
Sulfate	EPA 375.4, EPA 9038	Appendix C
Ortho-Phosphate	EPA 365.1, SM4500-P-F	Appendix D
Ammonia	EPA 350.1	Appendix E
Nitrate	EPA 353.2	Appendix F
Nitrite	EPA 353.2	Appendix F
Total Phosphorus	EPA 365.4	Appendix G
TKN	EPA 351.2	Appendix H
Tannin & Lignins	SM5550B	Appendix I
Hexavalent Chromium	EPA 7196A, SM3500-Cr-D	Appendix J

The routine analytes, reporting limits (RLs), method detection limits (MDLs), and precision and accuracy limits associated with these methods are listed in the LIMS Method Limit Groups (MLGs).

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 The SOP Appendices contain the method parameters required to perform the analysis. The appendices also contain a summary of the “chemistries” (reagents, procedures, wavelengths, etc.) used to measure the target analyte.

2.2 Instrument Design, Data System, and Basic Operation

2.2.2 Instrument Design

The analytical components (analyzer and autosampler) of the Konelab Model 20 Analyzer are contained in a single unit equipped with casters, which allows the unit to be moved easily. The dimensions of the analyzer are 80cm wide, 120 cm high, 79 cm deep, and it weighs 150 kg.

No plumbing is required for this instrument as there are reservoirs for both reagent water as well as a waste container. Reagents are stored on the autosampler and are kept at a temperature of approximately 10 degrees below ambient. The reagents can be loaded in 10, 20, or 60mL containers. The sampler monitors the volume of reagents and warns the analyst when the reagent is running out.

The samples and reagents are dispensed into disposable, acrylic multicell cuvettes that hold 12 separate analyses. The maximum volume of sample used is 120uL with the maximum total volume of sample and reagent of 250uL. The accuracy of the sampler is accomplished through the use of an inline GC-type syringe that is driven by micro-stepping motors. During the incubation period(s), the sample cuvettes are maintained @37°C.

The measurement system is a single channel interference filter photometer with beam splitting reference. The color wheel can be configured with up to 15 different filters. Fiber optic cabling transfers the light signal from the source to the detector. The lamp is a halogen lamp. The lamp

can be tested by the use of a water blank. This test checks the stability of the lamp at all 15 filter settings as well as testing the optical purity of all 12 positions of a cuvette. The detection step can be set up to treat all standards and samples in the same time fashion, that is, the time between reagent addition and absorbance readings will be the same for all sample and standard positions.

2.2.2 Data System

The data system is a separate unit and is placed near the analyzer on a separate desk or counter. The software system is based on the Windows NT operating system. The hardware interface can be either RS232 or an Ethernet connection and can be integrated to both transmit and receive information from a LIMS.

Programmable instrument parameters include:

Volume of sample (maximum of 125uL)	Wavelength
Type and order of reagent(s) addition	Background absorbance
Time of sample/reagent mixing	Timing of absorbance readings
Dilutions	
Track reagents lot numbers/expiration dates.	

QC checks can be programmed into the methods as needed, including initial and continuing control standards, blanks, and upper and lower limits on absorbance. If samples or standards exceed these control limits, the data are flagged.

The data may be printed on the day of analysis or archived and retrieved as needed. The data can be sorted by test or by sample ID, and the results are stored on the hard drive and can also be archived on a CD-ROM.

2.2.3 Operation:

The instrument analyzes samples in the following general order:

Sample is dispensed into the cuvettes according to the test method (maximum sample volume is 125uL)
The reagents are added to the sample and mixed
The sample is incubated
The sample absorbance is measured (if absorbance exceeds calibration range, sample is diluted as defined in the test method and reanalyzed. If the dilution exceeds the maximum range, the data are flagged and the analyst must prepare dilution for sample)

The calibration of the instrument can be linear, nonlinear, or bias correction. The calibration can be accomplished through separate calibrator samples or with a series of dilutions made automatically from an onboard standard.

Tests may be chosen individually, or groups of analyses can also be set up. For example, a test can be set up for nitrate that will automatically choose to run nitrate+nitrite and nitrite. The difference between the two tests will be calculated and the nitrate will be reported. Test methods may include multiple analyses that are analyzed on the same type of preserved sample. For example, chloride, phosphate, nitrite, and sulfate may be included in one Konelab method and analyzed from the same sample portion placed in the autosampler

Samples are loaded into racks that hold 14 samples each. Racks may be removed and replaced with more samples as the analyses are finished. The sampler holds up to 6 racks of 14 samples. The racks can be fitted to hold sample containers from 0.5mL up to 10mL. Two separate wash

stations are used to minimize sampler carryover. The probe is flow through and externally rinsed. Rush samples can be added into one of 5 stat positions.

Instrument and software maintenance tests are an integral part of the analytical system. The test programs evaluate items such as temperature, dispensing ratios, both accuracy and precision of the dispenser, and photometric noise.

2.3 Definitions

Definitions – Refer to TestAmerica Savannah's *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions.

3.0 SAFETY

Employees must abide by the policies and procedures in the analytical SOPs, TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

3.1 Specific Safety Concerns or Requirements

All samples must be treated as if they are hazardous. The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested for residue/solids may contain hazardous chemical compounds or biological organisms. The analyst must wear protective clothing (lab coat or apron), eye protection (glasses or face shield), and disposable gloves when handling these samples.

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

Potassium cyanide and sodium cyanide will give off hydrogen cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

Pyridine is flammable and will cause severe irritation to the respiratory tract. It can cause dizziness, headaches, nausea, and shortness of breath. Vapors can cause irritation of the eyes. Contact with the eyes can cause severe irritation, possible corneal burns and eye damage.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. MSDS can be found in electronic format on Oasis on the EH&S webpage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Barium Chloride	Poison Irritant	0.5 mg/m ³ TWA	May be fatal if swallowed. Harmful if inhaled. Avoid contact with eyes, skin, and clothing. Avoid breathing dust. Keep container closed and when in use adequate ventilation.
Chloramine-T	Contact Irritant	None	Harmful if swallowed or inhaled. Causes redness, irritation and pain to skin, eyes, and respiratory tract. Can cause allergic reactions. Symptoms of inhalation can include burning sensation, coughing, wheezing, laryngitis, shortness of breath, sore throat, bronchitis, pneumonitis, and pulmonary edema.
Ferric Nitrate	Oxidizer	None	Causes irritation to the respiratory tract. Causes irritation, redness, and pain to the skin and eyes.
Mercuric Thiocyanate	Poison	0.1 mg/m ³ Ceiling (Mercury Compounds)	Extremely Toxic. Causes irritation to the respiratory tract. May produce Hydrogen Cyanide gas if combined with strong acids. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Phenol	Corrosive	5 ppm-TWA	Breathing vapor, dust or mist results in digestive disturbances. Will irritate and possibly burn respiratory tract. Rapidly absorbed through the skin with systemic poisoning effects to follow. Discoloration and severe burns may occur, but may be disguised by a loss in pain sensation. Eye burns with redness, pain, blurred vision may occur. May cause severe damage and blindness.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Potassium Cyanide, Sodium Cyanide	Poison Corrosive	5 mg/m ³ TWA as CN	This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death. Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m ³	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m ³ - TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 INTERFERENCES

4.1 Ferrous Iron

The reaction is of ferrous iron with 1,10-phenanthroline is free from common interferences. Long storage times or exposure of samples to light must be avoided. Protect from light and analyze as soon as possible.

4.2 Chloride

Highly colored samples can positively interfere. Turbid samples should be filtered.

4.3 Sulfate

Silica above 500mg/L will interfere.

Color and turbidity due to the sample matrix can cause positive interferences that must be accounted for by the use sample blanks analyzed with no reagent. The absorbance or turbidity of the blank is subtracted from the absorbance or turbidity of the treated sample, and the concentration is determined from the corrected response.

4.4 Ortho-Phosphate

Blue colored components may interfere. High concentrations of arsenic may interfere.

4.5 Ammonia

Extreme sample pH values may interfere. Proper sample preservation and adjustment just prior to analysis should alleviate this problem. Turbidity and color in samples must be filtered and/or diluted prior to analysis. Residual chlorine should be removed at the time of sampling by the addition of sodium thiosulfate.

Samples that are tested against a compliance limit must be distilled, or a comparison of distilled and undistilled aliquots must be on file to demonstrate that the sample is free from interferences and that the analysis of the undistilled sample yields comparable results. Comparable results means that the results for the distilled and undistilled samples agree within 10% (percent difference less than 10%) using the distilled aliquot result as the reference.

4.6 Nitrate

Build up of suspended matter in the reduction column will restrict the sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered through a glass fiber filter or a 0.45um membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of particulate matter present in the sample.

Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.

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

4.7 Nitrite

There are very few known interferences at concentrations less than 1,000 times that of the nitrite; however, the presence of strong oxidants or reductants in the samples will readily affect the nitrite concentrations. High alkalinity (>600mg/L) will give low results due to a shift in pH.

4.8 Total Phosphorus

High iron concentrations can cause precipitation of, and subsequent loss of, phosphorus. Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus.

Sample turbidity must be removed by filtration after digestion. Sample color that absorbs in the photometric range used for analysis will also interfere.

4.9 Total Kjeldahl Nitrogen

High nitrate concentrations (10x or more than the TKN level) result in low TKN values. If interference is suspected, samples should be diluted and reanalyzed.

4.10 Tannin and Lignin

This reaction is not specific for tannins and lignins since other aromatic hydroxyl compounds and other reducing compounds also cause a reaction.

4.11 Hexavalent Chromium

Iron in concentrations of greater than 1mg/L may produce a yellow color, but this is usually not significant when measured at 540nm. Hexavalent molybdenum and mercury salts react to form colored complexes with the color reagent, but the intensities of the colors produced are much lower than for chromium at the specified pH. Mercury and molybdenum concentrations of up to 200mg/L can be tolerated. Vanadium interferes more strongly, but concentrations of up to 10 times that of chromium can be tolerated.

All samples should be adjusted to pH<2 prior to analysis with nitric acid to minimize interference and to allow proper color development.

After acidification, soil digestates should be purged with helium to eliminate excess carbon dioxide gas. Bubble formation in the cuvettes can interfere with readings.

The recovery of soluble forms of hexavalent chromium may be low where the sample matrix contains substances that are readily oxidized by hexavalent chromium (a reducing matrix_). The

measurement pH and oxidation-reduction potential may provide information about the ability of hexavalent chromium to persist in the sample.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Ferrous Iron

Samples are routinely collected in 250-mL plastic bottles with no preservative. Samples are iced at the time of collection and stored at 4°C (less than 6°C but not frozen) until the time of analysis. Protect from light and analyze the samples as soon as possible.

If the sample(s) cannot be analyzed within 24 hours of collection, filter the samples through a 0.45µm filter and adjust the pH to <2 with concentrated HCl. Store the samples at 4°C (less than 6°C but not frozen) and protect from light. Analyze as soon as possible.

5.2 Chloride

Aqueous and soil/sediment samples are routinely collected in 100-mL pre-cleaned plastic containers with no preservative. Holding time is 28 days.

5.3 Sulfate

Aqueous and soil/sediment samples are routinely collected in 120-mL plastic containers with no chemical preservative. The samples are iced at the time of collection and maintained at 4°C (less than 6°C with no frozen samples) until the time of analysis. Samples should be analyzed as soon as possible with a maximum holding time of 28 days.

5.4 Ortho-Phosphate

Aqueous samples are routinely collected in 120-mL plastic bottles and are unpreserved. The samples are iced at the time of collection and stored at 4°C (less than 6°C with no frozen samples) until the time of analysis. The holding time for orthophosphate in liquids is 48 hours.

Soil samples are routinely collected in plastic jars. The samples are iced at the time of collection and stored at 4°C (less than 6°C with no frozen sample) until the time of preparation and analysis. The hold time for soil samples is 28 days from collection.

5.5 Ammonia

Aqueous samples are routinely collected in plastic 250-mL containers. The samples are acidified to pH <2 with sulfuric acid, iced at the time of collection, and maintained at 4°C (less than 6°C with no frozen samples) until the time of preparation and analysis. Holding time is 28 days.

NOTE: The pH of each liquid sample must be checked and documented in the lab. If the pH is >2, add additional sulfuric acid until the pH is ≤2 and initiate an anomaly report. The volume of sulfuric acid must not exceed 1% of the volume of the container or sample; e.g., no more than 2.5mL of sulfuric acid per 250-mL container or sample.

Residual chlorine should be removed at the time of sampling by the addition of sodium thiosulfate.

Soil and solids samples are routinely collected in plastic containers. The samples are iced at the time of collection and maintained at 4°C (less than 6°C with no frozen samples) until the time of preparation and analysis. The holding time is 28 days.

5.6 Nitrate

Analysis should be made as soon as possible. If analysis can be made within 48 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 48 hours, they should be preserved with sulfuric acid (2mL H₂SO₄ per liter) and refrigerated.

5.7 Nitrite

Analysis should be made within 48 hours on a sample preserved by refrigeration at 4°C.

5.8 Total Phosphorus / Total Kjeldahl Nitrogen

Samples should be collected in plastic or glass bottles and must be preserved with H₂SO₄ to a pH<2 and cooled to 4°C at the time of collection. Samples should be analyzed as soon as possible after collection. If storage is required, preserved samples are maintained at 4°C and may be held for up to 28 days.

5.9 Tannin and Lginins

Liquid samples are collected in plastic containers. The samples are iced at the time of collection and maintained at 4°C (less than 6°C with no frozen samples) in the lab until the time of analysis. No holding time is listed in the reference method. The samples should be analyzed as soon as possible.

5.10 Hexavalent Chromium

Aqueous samples are routinely collected in 100-mL or 250-mL plastic containers with no preservative. Samples are stored at 4°C (less than 6°C with no frozen samples) and analyzed within 24 hours of collection.

Soil samples should be stored in plastic or glass sealed containers, field-moist, at 4°C (less than 4°C with no frozen samples) until analysis. When stored as above, Cr⁺⁶ has shown to be quantitatively stable for at least 30 days from the time of collection. The alkaline digest has also been shown to be stable for up to 168 hours after the digestion.

6.0 APPARATUS AND MATERIALS

Konelabs Model 21 Analyzer

7.0 REAGENTS

The preparation of reagents must be documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures*. See the appropriate SOP Appendix for the reagents used in each analysis.

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures*. See the appropriate SOP Appendix for the standards used in each analysis.

9.0 SAMPLE PREPARATION

ANALYTE	AQUEOUS PREP	SOIL PREP
Ferrous iron	Filter	NA
Chloride	Filter	Soil leachate
Sulfate	Filter	Soil leachate
Ortho-Phosphate	Filter	Soil leachate
Ammonia	Filter*	Soil leachate
Nitrate	Filter	Soil leachate
Nitrite	Filter	Soil leachate
TKN	SOP GE20	SOP GE20
Total Phosphorus	SOP GE20	SOP GE20
Tannin and Lignin	Filter	Soil leachate
Hexavalent Chromium	Filter	SOP ME21

*Ammonia samples may be distilled upon request.
See SOP Appendix for the LCS and MS spiking levels.

Basic solid leaching procedure:

Weigh out approximately 5g (5-5.5g) into a 100-mL screw-cap plastic bottle. Record the weight to the nearest 0.1g. Add 100mL of reagent water to each sample container and place on the extractor.

Prepare a method blank by adding 100mL of reagent water to an extraction bottle. Assume a sample weight of 5.0g. Place on extractor.

Prepare a LCS by adding the appropriate volume of spiking solution to 100mL of reagent water in an extraction bottle. Assume a sample weight of 5.0g. Place on extractor.

Weigh two additional 5g aliquots of one of the samples for the MS and MSD. Add the appropriate volume of the spiking solution to the sample. Add 100mL of reagent water to each sample container and place on the extractor.

Rotate for 2 hours for every parameter, except ammonia.

Remove the containers from the extractor and allow the leachates to settle. Filter the extract using a syringe filter with a 0.450-um pore size filter and analyze the extracts as liquid samples.

Ammonia solid leaching procedure:

Weigh out approximately 20g (20-20.4g) into a 100-mL screw-cap plastic bottle. Record the weight to the nearest 0.1g. Add 100mL of 2M potassium chloride to each sample container and place on the extractor.

Prepare a method blank by adding 100mL of reagent water to an extraction bottle. Assume a sample weight of 5.0g. Place on extractor.

Prepare a LCS by adding the appropriate volume of spiking solution to 100mL of reagent water in an extraction bottle. Assume a sample weight of 5.0g. Place on extractor.

Weigh two additional 5g aliquots of one of the samples for the MS and MSD. Add the appropriate volume of the spiking solution to the sample. Add 100mL of reagent water to each sample container and place on the extractor.

Rotate for 30 minutes for ammonia.

Remove the containers from the extractor and allow the leachates to settle. Filter the extract using a syringe filter with a 0.450-um pore size filter and analyze the extracts as liquid samples.

Ammonia distillation procedure:

10mL of 0.04N sulfuric acid is added to the receiving vessel.

The receiving vessel is positioned with the tip of the condenser under the surface of the acid in the vessel.

20mL of sample is added to the micro-distillation unit reaction chamber.

2mL of 1N sodium hydroxide is added to sample in the reaction chamber and the heated tuned on to start the distillation.

A total volume of 20mL (acid + distillate) is collected.

10.0 ANALYTICAL PROCEDURES

See the appropriate SOP Appendix for the analytical procedure.

11.0 DATA ANALYSIS AND CALCULATIONS

See the appropriate SOP Appendix for the analytical procedure.

12.0 QUALITY CONTROL AND DATA ASSESSMENT

QC data must be evaluated against the precision and accuracy criteria set forth in the Method Limit Groups in LIMS and SOP SA-QA-17: *Evaluation of Batch QC Data*. These requirements are summarized in the SOP summaries in the appendices for each analyte.

12.1 Analytical batch

SOP SA-QA-17 provides guidance for establishing and evaluating QC items to be included in an analytical batch. The minimum requirements are a method blank and a lab control standard (LCS) for each batch of twenty or fewer samples. Matrix spikes are analyzed as specified in the analytical method. These requirements are summarized in the SOP summaries in the appendices for each analyte.

12.2 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP QA05: *Preventive and Corrective Action Procedures*. QA05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures.

13.0 METHOD PERFORMANCE

The Reporting Limits (RL), the Method Detection Limits (MDL), and accuracy and precision limits associated with these methods are given in the Method Limit Groups in LIMS.

13.1 Initial and Continuing Demonstration of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures*.

13.2 Method Detection Limit

The method detection limit must be determined for each analyte in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

14.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

Refer to the manufacturer's guides for trouble-shooting items.

15.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

15.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Excess samples, reagents, and standards must be disposed in accordance with the TestAmerica Savannah Addendum to the Environmental Health and Safety Manual.
- Non-hazardous acidic and alkaline wastewater and samples must be neutralized before disposal into the sewer system.
- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.
- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.
- Waste containing pyridine must be isolated and transferred to the waste department for disposal.

16.0 REFERENCES

TestAmerica Savannah's *Quality Assurance Manual (QAM)*, current revision

Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; American Public Health Association: Washington, DC, 1989.

Water Analysis Handbook; HACH Company, 1985

Methods for Chemical Analysis of Water and Wastes; U.S. EPA Office of Research and Development: Cincinnati, OH, March, 1983.

Test Methods for Evaluating Solid Waste, Third Edition; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November 1986.

17.0 TABLES, DIAGRAMS, AND VALIDATION DATA

The appendixes to this SOP contain QC summary tables and application notes relevant to this procedure.

APPENDIX A-FERROUS IRON SOP SUMMARY AND APPLICATION NOTES

QC ITEM	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Initial Calibration	Initially and when verification standards fail to meet acceptance criteria	Minimum three point curve with correlation coefficient ≥ 0.995 and acceptable ICV	-reevaluate curve -re-prepare and re-analyze one or more standards -prepare new stock, calibration standards, and re-analyze
Initial Calibration Verification(ICV)-independent source	After initial calibration	+/-10% of true value	-reevaluate calibration curve -re-prepare and re-analyze ICV standard -re-prepare ICV stock -re-calibrate
Continuing Calibration Verification (CCV)	After every 10 absorbance readings	+/-20% of true value	-reevaluate calibration curve -re-prepare and re-analyze CCV standard -re-prepare CCV stock -re-calibrate
Initial/Continuing Calibration Blank (ICB/CCB)	After verification standards	< RL in MLG	-reevaluate calibration curve -re-prepare and re-analyze ICB/CCB standard -locate source of contamination and re-prepare and re-analyze ICB/CCB
Lab control sample (LCS)	The ICV and CCV are prepared from a source independent of the calibration standards and is reported as the LCS.		
Matrix spike/Matrix spike duplicate (MS/MSD)	Per batch of 20 or fewer samples (1 MS and 1 MSD per 20 samples)	Recovery within LQM control limits	-report recoveries and flag results as having matrix interference -spike all samples associated with the MS/MSD and evaluate for matrix interferences -dilute the samples to minimize the matrix interferences, re-spike and reanalyze -analyze samples by MSA
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	SOP SA-QA-06	SOP SA-QA-06
Method Detection Limit (MDL)	Annually	SOP SA-QA-07	SOP SA-QA-07

Ferrous Iron

Application Notes:

For the measurement of Ferrous iron in reducing conditions of ground and acid surface drainage. This analysis is based on SM3500-FeD.

Principle:

Ferrous iron is determined by reaction with phenanthroline in acid solution producing an orange color with a maximum absorbance of 510nm.

Stock Solutions:

Standard Ferrous iron solution:

Dissolve 0.7022g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ to 50mL reagent water. Acidify to pH <2 with 1:1 HCl and dilute to 100mL in volumetric glassware.

Working Solutions:

Ammonium acetate buffer

Dissolve 250g $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in 150 mL reagent water. Add 700 mL conc. (glacial) acetic acid. *Because $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ contains a significant amount of iron, new reference standards must be made with each buffer preparation.*

Color Reagent

Dissolve 100 mg $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$ (1,10-phenanthroline monohydrate) in 100 mL reagent water. Add 2 drops of conc. HCl.

Standard solutions

Prepare solutions in the required analytical range. e.g., 0, 0.050, 0.010, 0.020, 0.50, 1.0.

APPENDIX B-CHLORIDE SOP SUMMARY AND APPLICATION NOTES

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL; include zero as point	Before sample analysis, every six months, and when continuing calibration verification fail.	Regression curve with correlation coefficient ≥ 0.995 ; initial calibration verification within $\pm 10\%$ of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) – independent source	After initial calibration	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Calibration Verification (CCV)-mid range standard	After every 10 sample measurements	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL in MLG	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch of 20 or fewer samples	< RL in MLG	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS	Per batch of 20 or fewer samples	$\pm 15\%$ of the expected value	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
MS/MSD	At a frequency of 5% of samples (one MS and one MSD per twenty samples)	LQM Appendices	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	-linearity criteria -recovery of QCS within 90-110% -determination of MDL	-Reanalyze IDOC
MDL Study	Annually	-SOP SA-QA-07	-evaluate according to SA-QA-07

Chloride

Application Notes:

For the measurement of Chloride in potable, surface, saline and waste waters.

Principle:

Chloride reacts with mercuric thiocyanate forming a mercuric chloride complex. Released thiocyanate reacts with iron (III) forming a red ferric thiocyanate complex the color produced, measured at 480nm, is proportional to the chloride concentration.

Stock Solutions:

Mercuric Thiocyanate:

Thiocyanate $[\text{Hg}(\text{SCN})_2]$ dissolved in 1000ml Methanol. Mix and filter as necessary.

Ferric Nitrate:

Dissolve 202g Ferric Nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ in 800 ml distilled water. Carefully add 44.4ml of concentrated Nitric Acid. Dilute to 1000ml with distilled water. Store in an amber bottle.

Standard Chloride 1000mg/L:

Dissolve 1.6484g dried Sodium Chloride $[\text{NaCl}]$ in 1000 ml of distilled water

Working Solutions:

Color Reagent

Dissolve 75ml of stock Mercuric Thiocyanate and 75ml of stock Ferric Nitrate to 500ml with distilled water.

Standard Chloride solutions

Prepare standard solutions in the required analytical range. e.g. 0, 10, 20, 40, 60, 80, 100 mg/l.

APPENDIX C-SULFATE SOP SUMMARY AND APPLICATION NOTES

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL; include zero as point	Before sample analysis, every six months, and when continuing calibration verification fail.	Regression curve with correlation coefficient ≥ 0.995 ; initial calibration verification within $\pm 10\%$ of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) – independent source	After initial calibration	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Calibration Verification (CCV)-mid range standard	After every 3-4 sample measurements	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL in MLG	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch of 20 or fewer samples	< RL in MLG	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS	Per batch of 20 or fewer samples	$\pm 25\%$ of the expected value	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
MS/MSD	At a frequency of 5% of samples (one MS and one MSD per twenty samples)	Criteria in MLG	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	-linearity criteria -recovery of QCS within 90-110% -determination of MDL	-Reanalyze IDOC
MDL Study	Annually	-SOP SA-QA-07	-evaluate according to SA-QA-07

Sulfate

Application Notes:

For the measurement of Sulfate in potable, surface, and wastewaters.

Principle:

Sulfate ion is precipitated in a strongly acid medium with Barium Chloride. The resulting turbidity is measured photometrically at 405nm and compared with appropriate standard solutions.

Stock Solutions:

Stock Sulfate Standard – 1000 mg/L as SO_4 :

Dissolve 1.479g anhydrous Na_2SO_4 in distilled water and dilute to 1000mL.

Working Solutions:

Precipitating solution

Dissolve 10.0g of Barium Chloride [$BaCl_2$] 20g Sodium Chloride [$NaCl$] and 0.5g Gelatin in 300mL of distilled water (requires prolonged stirring to dissolve).

Carefully add 5mL of conc. Hydrochloric acid and dilute to 1000mL with distilled water.

Standard Sulfate solutions

Prepare standard solutions in the required analytical range. E.g. 0, 5, 10, 15, 20, 25, 30, 35 mg/L.

APPENDIX D-ortho-PHOSPHATE SOP SUMMARY AND APPLICATION NOTES

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL; include zero as point	Before sample analysis, every six months, and when continuing calibration verification fail.	Regression curve with correlation coefficient ≥ 0.995 ; initial calibration verification within $\pm 10\%$ of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) – independent source	After initial calibration	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Continuing Calibration Verification (CCV)-mid range standard	After every 10 sample measurements	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL in MLG	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch of 20 or fewer samples	< RL in MLG	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS	Per batch of 20 or fewer samples	$\pm 10\%$ of the expected value	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
MS/MSD	At a frequency of 5% of samples (one MS and one MSD per twenty samples)	MLG Appendices	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	-linearity criteria -recovery of QCS within 90-110% -determination of MDL	-Reanalyze IDOC
MDL Study	Annually	- SOP SA-QA-07	-evaluate according to SA-QA-07

O-Phosphate

Application Notes:

For the measurement of orthophosphate in potable, surface, saline and, wastewaters.

Principle:

Orthophosphate reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex which, when reduced with ascorbic acid, produces an intense blue color which is measured photometrically at 880nm (or at 660nm). The absorbance is proportionate to the amount of orthophosphate in the sample.

Stock Solutions:

Antimony potassium tartrate solution

Dissolve 0.3g $K(SbO)C_4H_4O_6 \cdot \frac{1}{2} H_2O$ in 50mL distilled water and dilute to 100mL. Store in a dark bottle and refrigerate.

Ammonium molybdate

Dissolve 4.0g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 100mL of distilled. Store in a plastic container.

Dilute Sulphuric acid

Very slowly add 140ml of conc H_2SO_4 to 1000mL of distilled water. Cool.

Ascorbic Acid solution

Dissolve 1.76g ascorbic acid in 100mL of distilled water. This solution is stable for 5 days when refrigerated.

Standard Phosphate Solution – 1000mg/L as P

Dissolve 4.3936g anhydrous K_2PO_4 in 1000ml of distilled water

Working Solutions:

Reagent 1

Add 75mL of stock Ammonium Molybdate to 250mL of dilute Sulphuric acid. Add 25mL of stock Antimony Potassium Tartrate to this mixture.

Reagent 2

Stock Ascorbic acid solution.

Mix 28mL of Reagent 1 with 12mL of Reagent 2 – prepare daily.

Standard solutions

Prepare standard solutions in the required analytical range. E.g. 0, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0mg/L.

APPENDIX E-AMMONIA SOP SUMMARY AND APPLICATION NOTES

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL	Before sample analysis, every six months, and when continuing calibration verification fail.	Regression curve with correlation coefficient ≥ 0.995 ; initial calibration verification within $\pm 10\%$ of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) – independent source	After initial calibration	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Continuing Calibration Verification (CCV) -mid-range point from the calibration curve	After every 10 sample measurements	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL in MLG	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Reporting limit (RL) Standard-lowest standard in initial calibration curve	Daily-optional Required for Fla. DEP samples	Detected	-reanalyze -remake and reanalyze -recalibrate
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch	< RL in MLG	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS	Per batch	Criteria in MLG	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
MS/MSD	Per batch	Criteria in MLG	-Check calculations -SA-QA-17 Decision Matrix
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	-linearity criteria -recovery of QCS within 90-110% -determination of MDL	-Reanalyze samples
MDL Study	Annually	-SOP SA-QA-07	-reanalyze samples

Ammonia-N

Application Notes:

For the measurement of Ammonia in potable, surface, saline and, waste waters.

Principle:

Ammonia reacts with hypochlorite and alkaline phenol in the presence of sodium nitroprusside to form indophenol blue. The color produced is measured at 660nm.

Working Solutions:

Sodium Phenate solution

Dissolve 93mL liquid ($\geq 89\%$) phenol in 500mL ammonia free water, slowly add 32g NaOH and mix thoroughly and dilute to 1000mL with ammonia free water. **CAUTION:** Wear gloves and eye protection when preparing this solution.

Sodium Hypochlorite solution

Dilute 250mL of 5.25% NaOCl with 250mL ammonia free water.

EDTA buffer

Dissolve 50g of disodium ethylenediamine tetraacetate and 5.5g of NaOH in 1000mL of ammonia free water.

Sodium Nitroprusside solution

Dissolve 0.5g of $\text{Na}_2(\text{NO})\text{Fe}(\text{CN})_5 \cdot 2\text{H}_2\text{O}$ in 1000mL of ammonia free water.

Standard Ammonia solutions

Dissolve 3.819g of dried Ammonium chloride $[\text{NH}_4\text{Cl}]$ in 2000mL of ammonia free water.

Prepare standard solutions in the required analytical range. E.g. 0, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0mg/L.

APPENDIX F -NITRATE/NITRITE SOP SUMMARY AND APPLICATION NOTES

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL; include zero as point	Before sample analysis, every six months, and when continuing calibration verification fail.	Regression curve with correlation coefficient ≥ 0.995 ; initial calibration verification within $\pm 10\%$ of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) – independent source	After initial calibration	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Calibration Verification (CCV)-mid range standard	After every 10 sample measurements	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL in MLG	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch of 20 or fewer samples	< RL in MLG	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS	Per batch of 20 or fewer samples	$\pm 20\%$ of the expected value	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
MS/MSD	At a frequency of 5% of samples (one MS and one MSD per twenty samples)	Criteria MLG	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	-linearity criteria -recovery of QCS within 80-120% -determination of MDL	-Reanalyze IDOC
MDL Study	Annually	-SOP SA-QA-07	-evaluate according to SA-QA-07

Nitrate / Nitrite

Application Notes:

This method is applicable to the determination of nitrite singly, or nitrite and nitrate combined in drinking water, surface and saline waters, and domestic and industrial wastes. The applicable range of this method is 0.050 to 2.0mg/L nitrate-nitrite nitrogen. The range may be extended with simple dilution.

Principle:

A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye, which is measured spectrophotometrically. Separate, rather than combine, nitrate-nitrite values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.

Stock Solutions:

Nitrate Standards (1000mg/L NO₃-N):

Dissolve 0.6068g NaNO₃ in reagent water and dilute to 100mL. For the second source standard, dissolve 0.7218g KNO₃ in reagent water and dilute to 100mL.

Nitrite Standards (1000mg/L NO₂-N):

Dissolve 0.4926g NaNO₂ in reagent water and dilute to 100mL. For the second source standard, dissolve 0.6076g KNO₂ in reagent water and dilute to 100mL.

Working Solutions:

Ammonium Chloride-EDTA

Dissolve 13g of ammonium chloride and 1.7g of disodium ethylenediamine tetraacetate in 900mL of reagent water. Adjust pH to 8.5 with concentrated ammonium hydroxide and dilute to 1000mL.

Color Reagent

Dissolve 10g sulfanilamide and 1.0g N-(1-naphthyl) ethylene diamine dihydrochloride in a mixture of 100mL concentrated phosphoric acid and 800mL DI water and dilute to 1000mL.

Standards:

Prepare a series of standards by diluting suitable volumes of stock solution to 100mL with reagent water.

APPENDIX G -TOTAL PHOSPHORUS SOP SUMMARY AND APPLICATION NOTES

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL; include zero as point	Before sample analysis, every six months, and when continuing calibration verification fail.	Regression curve with correlation coefficient ≥ 0.995 ; initial calibration verification within $\pm 10\%$ of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) – independent source	After initial calibration	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Calibration Verification (CCV)-mid range standard	After every 10 sample measurements	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL in MLG	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch of 20 or fewer samples	< RL in MLG	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS	Per batch of 20 or fewer samples	$\pm 40\%$ of the expected value	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
MS/MSD	At a frequency of 5% of samples (one MS and one MSD per twenty samples)	Criteria in MLG	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	-linearity criteria -recovery of QCS within 60-140% -determination of MDL	-Reanalyze IDOC
MDL Study	Annually	-SOP SA-QA-07	-evaluate according to SA-QA-07

TOTAL PHOSPHORUS

Application Notes:

This procedure is applicable to the measurement of total phosphorus in potable, surface waters, and domestic and industrial wastes, which are first digested by the Kjeldahl digestion method. This analysis is based on EPA Region 9 SOP #596 and EPA method 365.4.

Principle:

Total phosphorus is converted to orthophosphate ion in the digestion and the colorimetric analysis is based on the reactions that are specific for the orthophosphate ion.

Stock Solutions:

Antimony Potassium Tartrate:

Dissolve 3.0g $C_8H_4K_2O_{12}Sb_2 \cdot H_2O$ in 800mL reagent water and dilute to 1L in volumetric glassware. Store in a dark bottle and refrigerate.

Ammonium Molybdate:

Dissolve 40.0g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 800mL reagent water and dilute to 1L in volumetric glassware. Store in a plastic container.

Phosphate Standard:

Dissolve 4.3936g anhydrous K_2PO_4 in 800mL reagent water and dilute to 1L in volumetric glassware.

Working Solutions:

Color Reagent

Add 35mL concentrated sulfuric acid, 213mL stock ammonium molybdate solution, and 72mL stock antimony potassium tartrate solution to 500mL reagent water. Dilute to 1L in volumetric glassware and mix.

Ascorbic Acid

Dissolve 6.0g $C_6H_8O_6$ in 50mL reagent water and dilute to 100mL in volumetric glassware. Prepare fresh daily.

Sodium Chloride/Sodium Hydroxide

Dissolve 160g NaCl and 20g NaOH in 600mL reagent water. Let cool and dilute to 1L in volumetric glassware.

Standards:

Prepare a series of standards (e.g. 0.10, 0.30, 0.50, 1.0, 3.0, 5.0) by diluting suitable volumes of stock standard to 1L. Standards must be digested with each digest of samples before analysis.

Diluent:

In a 1-L volumetric, add 40mL concentrated sulfuric acid to 500mL DI water. Bring to volume with DI water and mix.

APPENDIX H -TKN SOP SUMMARY AND APPLICATION NOTES

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL; include zero as point	Before sample analysis, every six months, and when continuing calibration verification fail.	Regression curve with correlation coefficient ≥ 0.995 ; initial calibration verification within $\pm 10\%$ of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) – independent source	After initial calibration	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Calibration Verification (CCV)-mid range standard	After every 10 sample measurements	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL in MLG	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch of 20 or fewer samples	< RL in MLG	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS	Per batch of 20 or fewer samples	$\pm 25\%$ of the expected value	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
MS/MSD	At a frequency of 5% of samples (one MS and one MSD per twenty samples)	Criteria in MLG	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	-linearity criteria -recovery of QCS within 75-125% -determination of MDL	-Reanalyze IDOC
MDL Study	Annually	-SOP SA-QA-07	-evaluate according to SA-QA-07

TOTAL KJELDAHL NITROGEN

Application Notes:

This method covers the determination of total Kjeldahl nitrogen in drinking, ground, and surface waters as well as domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins, and peptides into ammonia, but does not convert the nitrogenous compound of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, and semicarbons and some refractory tertiary amines. The applicable range is 0.20 to 5.0mg/L TKN. The range may be extended with sample dilution.

Principle:

Total Kjeldahl nitrogen is the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate under the conditions of digestion. The sample is heated in the presence of sulfuric acid. The resulting residue is cooled, diluted, and analyzed for ammonia. This digested sample may also be used for phosphorus determination.

Working Solutions:

0.80N NaOH:

Mix 32g NaOH and 900mL reagent water in a 1-L volumetric until dissolved. Dilute to volume with reagent water.

Buffer:

Add 35.0g $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ to 500mL reagent water in a 1-L volumetric. Mix and add 20.0g disodium EDTA. Mix and add 50.0g NaOH. Mix until dissolved and bring to volume with reagent water.

Color Reagent:

Add 15.00g sodium salicylate and 0.100g sodium nitroprusside to 50mL reagent water in a 100-mL volumetric. Mix until dissolved and bring to volume with DI water. Make weekly or more often if necessary.

Hypochlorite:

Add 6.4mL commercial 5.25% sodium hypochlorite to a 100-mL volumetric. Bring to volume with DI water and mix well. Prepare fresh daily.

Diluent:

Add 40mL concentrated sulfuric acid to 500mL DI water in a 1-L volumetric. Bring to volume with DI water and mix.

APPENDIX I TANNIN AND LIGNIN SOP SUMMARY AND APPLICATION NOTES

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL; include zero as point	Before sample analysis, every three months, and when continuing calibration verification fail.	Regression curve with correlation coefficient ≥ 0.995 ; initial calibration verification within $\pm 10\%$ of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) – independent source	After initial calibration	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Calibration Verification (CCV)-mid range standard	After every 10 sample measurements	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL in MLG	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch of 20 or fewer samples	< RL in MLG	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS	Per batch of 20 or fewer samples	$\pm 20\%$ of the expected value	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
MS/MSD	At a frequency of 5% of samples (one MS and one MSD per twenty samples)	Criteria in MLG	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	-linearity criteria -recovery of QCS within 90-110% -determination of MDL	-Reanalyze IDOC
MDL Study	Annually	-SOP SA-QA-07	-evaluate according to SA-QA-07

TANNIN AND LIGNIN

Application Notes:

This procedure may be used to estimate the concentration of “tannins and lignins” in water and wastewater.

Principle:

Tannins and lignins contain aromatic hydroxyl groups which react with Folin phenol reagent to form a blue colored complex whose concentration can be measured at 700nm. The standard used in this procedure is tannic acid and all results are reported as substances reducing Folin phenol reagent in mg of tannic acid per liter. This procedure is based on guidance in Standard Methods 5550B.

Stock Solutions:

1000ppm Tannic Acid Stock:

Dissolve 0.1000g tannic acid in DI water and dilute to 100mL. Avoid strong agitation as the solution is somewhat soapy and may foam.

100ppm Intermediate Standard:

Dilute 10mL of the tannic acid stock solution to 100mL with DI water.

Working Solutions:

Hach TanniVer Tannin Reagent:

Purchase from Hach.

Hach Sodium Carbonate Solution For Tannin-Lignin:

Purchase from Hach.

Prepare an LCS/CCV by diluting 0.50mL of the intermediate standard to 50mL with DI water.

Prepare an MS/MSD by 0.10mL of the intermediate standard to each of two 10mL aliquots of the sample chosen as the matrix spike sample.

Standards:

Prepare standards in the working range, e.g. 0, 0.10, 0.30, 0.50, 1.0, 1.5, and 2.0mg/L by diluting the intermediate standard with DI water.

APPENDIX J HEXAVALAENT CHROMIUM SOP SUMMARY AND APPLICATION NOTES

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL; include zero as point	Before sample analysis, every six months, and when continuing calibration verification fail.	Regression curve with correlation coefficient ≥ 0.995 ; initial calibration verification within $\pm 10\%$ of expected value	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) – independent source	After initial calibration	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Calibration Verification (CCV)-mid range standard	After every 10 sample measurements	$\pm 10\%$ of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL in MLG	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch of 20 or fewer samples	< RL MLG	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS	Per batch of 20 or fewer samples	$\pm 15\%$ of the expected value for aqueous samples $\pm 20\%$ of the expected value for soils	-Check calculations -Reanalyze -SA-QA-17 Decision Matrix
MS/MSD	At a frequency of 5% of samples (one MS and one MSD per twenty samples)	$\pm 15\%$ of the expected value for aqueous samples $\pm 20\%$ of the expected value for soils	-Check calculations -Reanalyze -Spike or post spike all associated samples. Dilute samples as needed until MS recovery is satisfactory. Raise detection limits according to dilution. -SA-QA-17 Decision Matrix
Demonstration of Capability (DOC)	Initially per analyst, and then annually thereafter	-linearity criteria -recovery of QCS within 90-110% -determination of MDL	-Reanalyze IDOC
MDL Study	Annually	-SOP SA-QA-07	-evaluate according to SA-QA-07

HEXAVALENT CHROMIUM

Application Notes:

For the determination of hexavalent chromium in water, wastewater, and soil extracts and digestates.

Principle:

The sample is acidified to a pH<2 and a color reagent is added (1,5-diphenyl carbazide). The intensity of the purple color, measured at 540nm, is proportional to the concentration of hexavalent chromium present in the sample.

Stock Solutions:

1000ppm Hexavalent Chromium Solution:

Purchased to Aldrich.

50ppm Hexavalent Chromium Second Source Stock:

Purchased from Hach.

Working Solutions:

Color Reagent:

Transfer 0.1250g of 1,5-diphenyl-carboxide to a clean 25mL flask. Add about 10mL acetone and swirl to dissolve. Dilute to the 25mL mark and mix well. Keep tightly capped and store in the dark.

50% Nitric Acid for pH Adjustment:

Slowly add 50mL of concentrated nitric acid to 50mL DI water. Mix carefully.

Standards:

Prepare standards in the working range, e.g. 0, 0.002, 0.010, 0.025, 0.050, 0.100, 0.300, and 0.500mg/L.