12.2.5 Method Blank (MB1)

The method blank should not contain any target compounds at or above the reporting limit. If non-compliant, then the method blank should be reanalyzed to determine if instrument contamination was the cause. If the method blank is still non-compliant and the samples are within the extraction holding time, then request re-extraction using an SDR and reanalyze all associated samples containing target compounds at < 10x amount found in the method blank. If a sample contains target compounds at ≥ 10x amount found in the method blank, or if target compounds are not detected in the sample, then that sample does not require re-extraction and the results may be reported without qualification. If the samples our outside the extraction holding time, then contact the project manager using an SDR. Unless directed otherwise, samples will not be extracted outside the holding time and the data will be submitted with appropriate narration.

12.2.6 Matrix Spike

The recoveries for the spiked compounds should be within the advisory limits. If non-compliant, check calculations and spike preparation for documentable errors. If no errors are found, and the associated blank spikes are within advisory limits, then sample matrix effects are the most likely cause.

12.2.7 Matrix Spike Duplicate

See Matrix Spike for recoveries. RPD's should be within the advisory limits. If non-compliant, check calculations for documentable errors. Check unspiked sample results and surrogate recoveries for indications of matrix effects. If significant differences exist between the MS and MSD, reanalysis of the sample spikes may be necessary.

12.2.8 Surrogate Spike

The recoveries for the surrogate(s) should be within advisory limits. If non-compliant, check calculations and spike preparation for documentable errors. If no errors are found, and the surrogate recoveries in the method blank and blank spikes are within the advisory limits, then sample matrix effects are the most likely cause. However, any samples with surrogate recoveries significantly below the advisory limits with, no visible chromatographic cause,

should be reanalyzed to determine if an injection error was the cause for the low recovery. If the surrogate recoveries in the associated method blank and blank spike are not within advisory limits, and the samples are within the extraction holding time, then re-extract and reanalyze all associated samples. If the samples are outside the extraction holding time, then contact the project manager using and SDR. Unless otherwise directed, samples will not be re-extracted out of hold time and data will be submitted with appropriate narration.

12.2.9 Continuing Calibration Verification (CCV)

The response factors of the initial calibration check standard should not vary from the response factors of the corresponding standard from the calibration curve by more than ± 15% on at least one column for each target compound, and on both columns for any compound reported positive. If more than 10% of the target compounds fail this criteria, then the standard is considered to be non-compliant. If the standard is non-compliant, then reanalyze the standard. If the standard is still non-compliant, then remove 1 meter from the guard column of the GC. If the standard is still non-compliant, then prepare a new standard. If the new standard is non-compliant, then recalibrate the instrument with a new curve. All target compounds which fail this criteria should be narrated as showing increased sensitivity, and how this might bias data. Notify the project manager of any non-compliance using the SDR. Unless directed otherwise, samples will not be analyzed outside of holding time and the data will be submitted with appropriate narration.

12.2.10 Retention Time Windows

Initial retention time windows must be established following the procedure described in Section 6.5. Daily windows are then established as in Section 6.6.4 at the beginning of each analytical sequence. If a continuing standard has any analytes which are outside of their daily windows, corrective actions must be taken before continuing. Check the purge-and-trap for leaks, or check the carrier gas flow to see that it has not been changed. Evaluate the data for usability based on a comparison with the standards run during the analytical sequence. Also, consider the retention times for the surrogates and spiked compounds analyzed before and after the sample in question.

13.0 HEALTH AND SAFETY

Care should always be taken when working with samples of unknown composition. For specific hazards associated with the solvents used or any of the standard materials see the specific MSDS.

Table 1

Purgeable Halocarbons Determined by SW846 Method 8010

Compound	Reporting Limit	
	ug/L	ug/kg
Bromodichloromethane	0.80	0.80
Bromoform	0.80	0.80
Bromomethane	0.80	0.80
Carbon Tetrachloride	0.80	0.80
Chlorobenzene	0.80	0.80
Chloroethane	0.80	0.80
2-Chloroethylvinyl ether	0.80	0.80
Chloroform	0.80	0.80
Chloromethane	0.80	0.80
Dibromochloromethane	0.80	0.80
1,2-Dichlorobenzene	0.80	0.80
1,3-Dichlorobenzene	0.80	0.80
1,4-Dichlorobenzene	0.80	0.80
Dichlorodifluoromethane	0.80	0.80
1,1-Dichloroethane	0.80	0.80
1,2-Dichloroethane	0.80	0.80
1,1-Dichloroethene	0.80	0.80
trans-1,2-Dichloroethene	0.80	0.80
1,2-Dichloropropane	0.80	0.80
trans-1,3-Dichloropropene	0.80	0.80
Methylene Chloride	0.80	0.80
1,1,2,2-Tetrachloroethane	0.80	0.80
Tetrachloroethene	0.80	0.80
1,1,1-Trichloroethane	0.80	0.80
1,1,2-Trichloroethane	0.80	0.80
Trichloroethene	0.80	0.80
Trichlorofluoromethane	0.80	0.80
Vinyl Chloride	0.80	0.80

RELEASED
2019-007454
July 27, 2020 - TJW

ORGANIC ANALYSIS PROTOCOL
Analysis of Purgeable Halocarbons by Gas Chromatography (GC)

These Approval Signatures Are Kept on File
with WESTON®'s Analytics Division
QA Standard Practice Records

REVISION NUMBER: 04

	Printed Name:	Signature/Date:
Written By:	Janet L. Smaga Unit Leader, GC Volatiles	Janet L Smaga 7-15-93
Approved By:	Linda S. Mackley Section Manager, Organics Department	Linda S Mackley 7-15-93

Historical File:
Revision 00: 08/29/90
Revision 01: 02/05/91
Revision 02: 03/11/93
Revision 03: 05/06/93
Revision 04: 07/14/93

Reason for Change; Revision 04:

- Updated the instrument listing and the corrective action section.

RELEASED
2019-007454
July 27, 2020 - TJW

INORGANIC ANALYSIS PROTOCOL
Nitrate-Nitrogen by Lachat QuikChem AE: Cadmium Reduction of Nitrate to Nitrite

CONTROLLED DISTRIBUTION
COPY # : Uncontrolled
ISSUED TO : Techallov QAP - (VAL)
Full Signature Approvals Are Kept on File
with WESTON®'s Analytics Division
QA Standard Practice Records

REVISION NUMBER: 00

1.0 PURPOSE

This method was used to determine the amount of nitrogen as nitrate-nitrite in a given sample. Nitrate-nitrogen alone can be determined by subtracting the nitrite-nitrogen amount determined by a separate procedure.

2.0 REFERENCES

This SOP was written using EPA 600/4-79-020 Method 353.2. Instrument specific instructions are taken from Lachat Method 10-107-04-01-C.

The Lachat QuikChem AE Auto Analyzer is used in place of the Technicon Auto Analyzer described in the method.

3.0 METHOD SUMMARY

A clear sample is passed through a column containing granulated copper-cadmium to reduce nitrate-nitrogen to nitrite-nitrogen. The nitrite-nitrogen (that originally was present plus reduced nitrate-nitrogen) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically.

4.0 INTERFERENCES

4.1 Residual chlorine can oxidize the cadmium column and reduce its efficiency.

4.2 Low results may be obtained from samples containing high amounts of iron, copper or other metals. The addition of EDTA in the buffer helps reduce this interference.

4.3 Samples containing high amounts of organics, including oil and grease, will coat the cadmium granules. Pre-extraction with an organic solvent should be performed on these samples.

4.4 Turbidity should be removed by filtration through a 0.45 um pore diameter membrane prior to analysis.

5.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Sample containers, preservation techniques, and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Samples should be preserved to a pH < 2. Listed below are the holding times and the references which include container and preservation requirements for compliance with the Clean Water Act (CWA) and the Safe Drinking Water Act (SDWA).

Regulation	Holding Time	Reference
CWA	28 days	40 CFR, Part 136.3
SDWA	28 days	EPA 600/4-79-020

6.0 INSTRUMENTATION AND EQUIPMENT

6.1 Lachat QuikChem AE System

Wavelength: 520 cm
Cell Path Length: 1.0 cm
Sample Loop Size: 17 cm
Cycle Period: 40 sec*
Inject to Start Period: 19 sec*

*These conditions can be adjusted to optimize instrument conditions.

6.2 Glassware/Miscellaneous

- disposable test tubes
- disposable 5 cc syringes
- 0.45 um filters (syringe or membrane)
- 100 mL volumetric flasks
- eppendorf pipets and tips

7.0 PREVENTATIVE MAINTENANCE

7.1 Change all pump tubing, manifold tubing, O-rings, and transmission tubing monthly.

7.2 Clean the surface of the instrument daily and wipe up all spills immediately.

7.3 Download the files to a disk on a monthly basis.

7.4 Check diagnostic when instrument is turned on for valve function, sample function, and detector function. Response to problems immediately.

7.5 Consult Lachat manuals for instructions on how to diagnose problems.

8.0 STANDARD AND REAGENTS

All standards and reagents are prepared with Type II Deionized Water, unless otherwise stated, in Class A volumetric flasks.

8.1 Sulfanilamide Color Reagent

To 600 mL DI water in a 1.0 L volumetric flask, add 100 mL 85% phosphoric acid, 40 g sulfanilamide, and 1 g N-(1-naphthyl)ethylenediamine dihydrochloride. Dissolve the mixture by stirring on a stir plate for 30 minutes. Dilute to volume and mix again.

- Life of Reagent: one month
- Storage Requirements: store in the dark

8.2 Ammonium Chloride Buffer

To 800 mL DI water contained in a 1.0 L volumetric flask, dissolve 85 g ammonium chloride (NH_4Cl) and 1.0 g disodium ethylenediamine tetracetic acid dihydrate ($Na_2EDTA \cdot 2H_2O$). Adjust pH to 8.5 with 15 N sodium hydroxide and dilute to volume.

- Life of Reagent: one year
- Storage Requirements: none

8.3 15 N Sodium Hydroxide

Slowly dissolve 150 g sodium hydroxide in 250 mL DI water. Cool.

- Life of Reagent: one year
- Storage Requirements: Store in a plastic bottle.

8.4 2% Copper Sulfate

In a 1.0 L volumetric flask, add 20 g copper sulfate ($CuSO_4 \cdot 5H_2O$) to ~800 mL DI water. Mix and then dilute to volume with DI water.

- Life of Reagent: one year
- Storage Requirments: none

8.5 Acetone

Purchased from a chemical vendor.

- Life of Reagent: manufacturers recommendation
- Storage Requirements: store in a flammables cabinet

8.6 1 M Hydrochloric Acid

To a 100 mL volumetric flask containing approximately 80 mL DI water, add 8 mL hydrochloric acid (HCl). Mix and dilute to volume with DI water.

- Life of Reagent: one year
- Storage Requirment: none

8.7 Nitrate Stock Solution I, 100 mg N/L

To a 1.0 L volumetric flask containing approximately 800 mL DI water, add 0.722 g potassium nitrate (KNO_3) and 2 mL chloroform ($CHCl_3$). Mix and dilute to volume with DI water.

- Life of Reagent: six months
- Storage Requirements: keep refrigerated

8.8 Nitrate Stock Solution II, 100 mg N/L

Prepare as Reagent 8.7 using an alternate source of potassium nitrate.

- Life of Reagent: six months
- Storage Requirements: keep refrigerated

8.9 Nitrite Stock Solution III, 100 mg N/L

To a 1.0 L volumetric flask containing approximately 800 mL DI water, dissolve 0.4926 g potassium nitrite (KNO_2). Preserve with 2 mL chloroform ($CHCl_3$). Mix and dilute to volume with DI water.

- Life of Reagent: six months
- Storage Requirements: keep refrigerated

8.10 Cadmium Granules, 0.3 - 15 Mesh

Purchased from a chemical vendor. CAUTION: Extremely Toxic.

- Life of Reagent: manufacturers recommendation
- Storage Requirements: none

9.0 PROCEDURE

9.1 Reporting Limit

Waters..... 0.1 mg N/L
Wastes..... 1 mg N/kg

9.2 Sample Size

Waste samples:	10 g/100 mLs DI water
Sludge & Oil Samples:	*10 g/100 mLs DI water
Water samples:	10 mLs

*More sample may be used for sludges high in water content when a low dry weight reporting limit is required.

9.3 Cadmium Column Preparation

9.3.1 Weigh 10 g of cadmium granules into a 250 mL beaker. WEAR GLOVES since cadmium is extremely toxic.

9.3.2 Wash the cadmium with several 50 mL aliquots of DI water. Save the washings for proper disposal!

9.3.3 Wash the cadmium with a 50 mL portion of acetone followed by two DI washings. Save the washings for proper disposal!

9.3.4 Wash the cadmium twice with 50 mL portions of 1 M hydrochloric acid (HCl). The cadmium should have a silver sheen. Rinse it several times with DI water. Save all the rinses for proper disposal!

9.3.5 Add 100 mL 20% copper sulfate to the cadmium and swirl. Allow to sit at least 5 minutes. If the copper sulfate has lost its blue color, repeat the rinse with fresh copper sulfate. If not and the cadmium appears to be dark grey/black, rinse several times with ammonium chloride buffer (Rgt. 8.2). Store the cadmium covered with ammonia chloride buffer.

9.4 Packing the Cadmium Column

WEAR GLOVES!

9.4.1 Unpack any cadmium currently present in the column. Reserve the foam ends for further use and properly dispose of the used cadmium.

9.4.2 Set up green pump tubing with transmission tubing, tubing converter, a union fitting, and 0.032 ID tubing. Place the assembled tubing into the pump.

Place the transmission tubing into the container of ammonia chloride buffer. Turn the pump on and fill the tubing with buffer. Turn the pump off. Attach the empty cadmium column to the buret stand. Place one foam plug into the bottom of the empty column. Attach one end fitting union connector and a small piece of 0.032 ID tubing to the column. Plug the small amount of tubing into the union connector which is attached to the reagent line. Turn the pump back on and fill the whole system. Turn the pump off. Check to see that the meniscus of the ammonium chloride rises above the column.

9.4.3 Using a small scoop, carefully add treated cadmium to the empty column. Tap the column with the handle of a screw driver to pack the cadmium tightly. When the level of cadmium reaches about 5 mm from the top, insert the second foam plug and attach the other end fitting. Turn on the pump and fill the added tubing. Check the flow through the column by setting the speed of the pump to 35 and collecting the fluid coming from the column. The rate should be greater than 4 mL/min. Shut the pump off and carefully attach the end fitting together at the union. Take care not to entrap air into the system. The filled cadmium column should weigh 36 - 36.5 g.

9.5 Manifold Preparation

Place the manifold on the proper Lachat channels. Attach all the tubing as shown in the manifold diagram. Turn the main instrument and the pump on. Check the main instrument display for proper functioning. Turn on the Master Computer and download the proper method. Insert the transmission tubing into the respective solutions. When all tubing is filled and you are certain there are no leaks, attach the prepared cadmium column. Great care needs to be taken so that air does not enter the column. Follow these directions:

9.5.1 Make sure all reagents are pumped into the manifold and no air is present.

9.5.2 Turn the pump off.

9.5.3 On the column, disconnect the center tubing from one of the union connectors and immediately connect it to the outlet tubing of the buffer mixing coil.

9.5.4 Connect the open tubing on the column to the tee fitting where the coloring reagent is added.

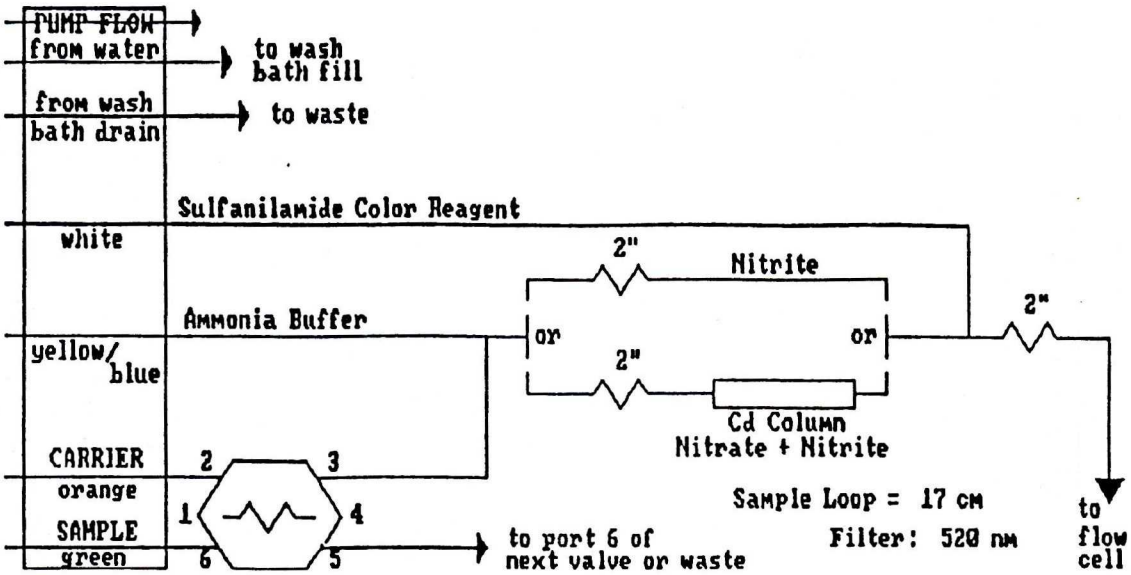
9.5.5 Turn the pump on at normal speed.

9.5.6 Direction of flow through the column is irrelevant.

If air enters the column, it can lower the efficiency of the column. Small bubbles may not interfere, but if reduction is not adequate, this is quite often the problem.

Manifold Diagram

Manifold Diagram:



CARRIER is water.

2" is 135 cm of tubing on a 2 in coil support

APPARATUS: Standard valve, flow cell, and detector head modules are used.

All manifold tubing is **0.8 mm (0.032 in)** i.d. This is 5.2 uL/cm.

MANIFOLD DIAGRAM REVISION DATE: 30 December 1986

Reference: QuikChem Method 10-107-04-1-C

9.6 Calibration Procedure

Instrument calibration consists of two types: Initial Calibration and Continuing Calibration.

9.6.1 Initial Calibration

Establishes the calibration range of the instrument and determines the instrument response over that range.

The autoanalyzer will be calibrated prior to each day of use. The calibration standards will be prepared from reference materials appropriate to the analyses being performed, and working standards will include five (5) concentraations which cover the anticipated range of measurement. One of the calibration standards will be at the desired detection limit. Additionally, a calibration blank will be analyzed. The requirement for an acceptable initial calibration will be a correlation coefficient equal to or greater than 0.995 in order to consider the response linear over the measured range.

If the correlation coefficient criteria of 0.995 is not met, the instrument will be recalibrated prior to analysis of samples. Calibration data, to include the correlation coefficient, will be entered into the laboratory notebook with the sample data to maintain a permanent record of instrument calibrations.

Before sample analysis, an Initial Calibration Verification (ICV) Standard is analyzed. The response calculated as percent recovery of this standard must be within +/- 10% of the true vaue or the instrument is recalibrated. The response of the Initial Calibration Blank (ICB) must be less than the reporting limit.

9.6.2 Continuing Calibration

Used within an analytical sequence to verify stable calibration throughout the sequence, and/or to demonstrate that instrument response did not drift during a period of non-use of instrument.

A Continuing Calibration Verification (CCV) and Blank (CCB) will be analyzed at a frequency of 10% and at the end of the analysis sequence. The response, calculated as a percent recovery of the true value, must be +/- 10%

of the true value. The response of the CCB must be less than the detection limit.

9.7 Analytical Sequence

Calibration Controls	Sequence	Control Limit
Standards	prior to samples	+/-10%
Corr. Coeff.	prior to samples	≥ 0.995
Column Efficiency Std.	prior to samples/prior to ICV/ICB	90 - 110%
Init. Cal. Ver. (ICV)	prior to samples/after calibration	90 - 110%
Init. Cal. Blk. (ICB)	prior to samples/after calibration	< Reporting Limit
Cont. Cal. Ver. (CCV)	every 10 readings	90 - 110%
Cont. Cal. Blk. (CCB)	every 10 readings	< Reporting Limit

Quality Controls	*Frequency	Control Limit
Prep. Blk. (PB)	1 in 20 samples	< Reporting Limit
Lab. Control Std. (LCS)	1 in 20 samples	80 - 120%
LCS Duplicate (LCSD)	1 in 20 samples	80 - 120%
Matrix Duplicate	1 in 20 samples	≤ 20% RPD
Matrix Spike	1 in 20 samples	75 - 125%

*Drinking Water samples are analyzed in sets of 10 with a duplicate and spike performed on the drinking water matrix. Control limits are ≤ 20% RPD for duplicates and +/- 15% for spikes.

9.8 Standards Preparation

(Use volumetric flasks to prepare the following standards.)

Daily Standard ID	Concentration (ppm)	Volume of Standard I (Rgt. 8.7)
A	2.0	2 mLs diluted to 100 mLs
B	1.5	1.5 mLs "
C	1.0	1 mLs "
D	0.5	0.5 mLs "
E	0.2	0.2 mLs "
F	0.1	0.1 mLs "
G	0.0	0.0 mLs "

9.9 Quality Control Standards

Quality Control	Volume of Standard II (Rgt. 8.8)	Concentration
Lab. Control Std. (LCS)	1.0 mLs / 100 mLs DI Water	1.0 ppm
LCS Duplicate	1.0 mLs / 100 mLs DI Water	1.0 ppm
ICV/CCV	1.0 mLs / 100 mLs DI Water	1.0 ppm
Matrix Spike	1.0 mLs / 100 mLs DI Water	1.0 ppm

9.9.1 1.0 ppm Nitrite Standard for Column Efficiency

Dilute 1.0 mL of Nitrite Stock Solution III (Rgt. 8.9) to volume with DI water in a 100 mL volumetric flask. Analyze in sequence (See Section 9.7.) The recovery acceptance limit is 90 - 110%. When the column efficiency standard recovery is calculated against the ICV concentration, the acceptance limit of 90 - 110% must be met as well.

9.10 Sample Preparation and Analysis

9.10.1 Water Samples

9.10.1.1 Pour approximately 10 mL of sample into a test tube. Adjust the pH to neutral with 15 N sodium hydroxide and place in the rack.

9.10.1.2 If turbidity is present, filter the sample through a 0.45 um membrane filter prior to analysis.

9.10.1.3 If oil & grease is present, extract the sample with freon prior to analysis.

9.10.2 Waste/Soil Samples

9.10.2.1 Weigh 10 g of sample, to the nearest 1.0 g, into a 250 mL beaker. Add 100 mL of DI waters and stir on a stir plate for approximately 30 minutes.

9.10.2.2 Filter the sample through a glass fiber filter, then through a 0.45 um membrane filter.

9.10.2.3 If oil & grease is present, extract the filtrate with freon prior to analysis.

9.10.3 Colorimetric Analysis

9.10.3.1 Double check the order of samples on the rack with the tray identification.

9.10.3.2 Submit the tray for analysis.

10.0 CALCULATIONS

Terminology:

N_3N_2 Total nitrogen in the form of nitrate-nitrogen and nitrite-nitrogen obtained directly from the auto analyzer.

NO_3 Nitrogen in the nitrate-nitrogen form.

NO_2 Nitrogen in the nitrite-nitrogen form obtained from EPA Methods 354.1 or 300.0.

10.1 Nitrate

N_3N_2 mg/L = N_3N_2 (mg N/L curve) x dilution factor

NO_3 mg/L = N_3N_2 (mg N/L) - NO_2 (mg/L)

$$N_3N_2 \text{ mg/kg} = \frac{N_3N_2 \text{ (mg N/L curve)}}{\text{sample wt. (g)}} \times \text{final volume (mLs)} \times \text{dilution factor}$$

$$N_3N_2 \text{ mg/kg (dry weight)} = \frac{N_3N_2 \text{ (mg/kg wet wt.)}}{\text{\% solids (as decimal)}}$$

10.2 Column Efficiency

$$\frac{\text{1.0 mg N/L } N_3N_2 \text{ observed}}{\text{1.0 mg N/L } NO_2 \text{ observed}} \times 100$$

10.3 Matrix Spike Recovery

$$\frac{\text{(matrix spike result - sample result)}}{\text{known concentration}} \times 100$$

10.4 % Relative Percent Difference

$$\frac{|\text{sample result - duplicate result}|}{\text{(sample result + duplicate result/2)}} \times 100$$

10.5 Reporting Results

Without rounding, enter the raw data on the appropriate LOTUS Spreadsheet. Carefully print, review and approve the spreadsheet before creating a print file and transferring the data to LIMS.

11.0 QUALITY CONTROL

11.1 One method blank and two Lab Control Standards (LCS) will be included in each laboratory lot of 20 samples. Regardless of the matrix being processed, the LCS and method blanks will be in an aqueous media.

11.2 The method blank will be examined to determine if contamination is being introduced in the laboratory.

11.3 The LCS's will be examined to determine both precision and accuracy.

11.4 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

11.5 Precision will be measured by the reproducibility of both LCS's and will be calculated as relative percent difference (%RPD). Results must agree within in-house control limits or statistical control limits in order to be considered acceptable.

11.6 One matrix spike and matrix duplicate is performed per matrix per 20 sample analytical set. Results must agree within the in-house precision/accuracy limits or statistical control limits in order to be considered acceptable.

12.0 CORRECTIVE ACTIONS

When an out of control situation occurs, the analysts must use their best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of their immediate supervisor, QA personnel, or other experienced staff if they are uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, QA personnel or the lab manager.

12.1 Listed below are steps to be taken when an out of control situation occurs. The analyst must:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on a corrective action report form;
- document on the corrective action report that an in control has been achieved; and
- receive approval (signature) of the Section Manager, Unit Leader, QA personnel, or the Laboratory Manager prior to the release of any analytical data associated with the problem.

12.2 Suggested Actions to specific out of control situations:

12.2.1 Calibration Curve

- reanalyze the standard curve;
- prepare new stock and/or working standards;
- check reagents/solutions and prepare fresh if necessary.

12.2.2 Initial Calibration Verification (ICV)

- repeat ICV to verify proper preparation;
- prepare new ICV from original stock;
- check for instrument base-line drift;
- restandardize with existing standards, reanalyze;
- check reagents/solutions and prepare fresh if necessary;
- prepare new stock and/or working standards and recalibrate;

12.2.3 Initial Calibration Blank (ICB)

- prepare a new ICB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis or reagent contamination are two common sources).

12.2.4 Laboratory Control Standards (LCS)

If either LCS1 or LCS2 exceeds acceptance limits:
- reanalyze LCS to verify that an out of control situation exists;
- determine the source of error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be either the reagents, the LCS stock solution, or the preparation area.)

Precision: LCS1 and LCS2 must meet the control limits of $\leq$ 20% RPD. If this criteria is not met, and both LCS's meet the % Recovery control limits, then see your Section Manager or Unit Leader for proper corrective action.

12.2.5 Preparation Blank (PB)

- reanalyze PB to verify contamination at a level > Reporting Limit;
- determine the source of contamination and correct the problem;
- all samples whose concentration is <10 times the PB level must be reprocessed and reanalyzed; any sample which is >10 times the PB level need not be reanalyzed. However, a corrective action report must be filled out and approval obtained.

12.2.6 Matrix Duplicate (DUP)

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies;
- if the reanalysis is within the control limits, the second value is reported;
- if the reanalysis is still outside of the control limits, a CAR must be written and then approved by your Section Manager or Unit Leader.

12.2.7 Matrix Spike (MS)

- the sample must then be reprocessed and reanalyzed unless the sample concentration exceeds the spike concentration by a factor of 4 times;
- the original spike results must be entered onto the spreadsheet with the "S" code even though the control limits were exceeded;
- the reanalysis result must be entered onto the spreadsheet using the "T" code regardless of whether it is within the control limits. There is no need to write a corrective action if both the "S" and "T" codes were entered into LIMS.

12.2.8 Continuing Calibration Verification (CCV)

- repeat CCV to verify proper preparation;
- prepare new CCV from original stock;
- check for instrument base-line drift;
- check reagents/solutions and prepare fresh if necessary;
- recalibrate with a new standard curve and repeat all samples since the previous in control CCV;
- never dispose of any samples until you are sure that all QC are within their designated control limits.

12.2.9 Continuing Calibration Blank (CCB)

- prepare a new CCB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis or reagent contamination

are two common sources).

- never dispose of any samples until you are sure that all QC are within their designated control limits.

13.0 HEALTH AND SAFETY

As always, general laboratory safety practices should always be followed. Waste samples should be handled with care due to the uncertainty of the properties and contents involved. Refer to the specific MSDS for the hazardous properties of any chemical or reagent involved in this procedure.

Proper disposal procedures for cadmium need to be followed due its extreme toxicity.

RELEASED
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INORGANIC ANALYSIS PROTOCOL
Nitrate-Nitrogen by Lachat QuikChem AE: Cadmium Reduction of Nitrate to Nitrite

These Approval Signatures Are Kept on File
with WESTON®'s Analytics Division
QA Standard Practice Records

REVISION NUMBER: 00

	Printed Name:	Signature/Date:
Written By:	Charlene J. Troyer Wet Chemistry Analyst	Charlene J. Troyer 1/15/93
Contributor:	Donna J. McClure Wet Chemistry Unit Leader	Donna J. McClure 1/15/93
Approved By:	Diane L. Harper Wet Chemistry Section Manager	Diane L. Harper 1/15/93

Historical File: Revision 00: 01/15/93

Reasons for Change, Revision 00:

- formalize the procedures used to determine Nitrate-Nitrogen by the Lachat.

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INORGANIC ANALYSIS PROTOCOL
Turbidimetric Analysis of Sulfate and Sulfur

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REVISION NUMBER: 01

1.0 PURPOSE

To determine the sulfate concentration in drinking, surface, and ground waters; and solid matrices (includes modifications for soil preparation).

2.0 REFERENCE

This SOP was written using the following references:

2.1 EPA 600/04-79-020, Method 375.4.

2.2 SW-846, 3rd Ed., November 1986, Method 9038 as a secondary reference. (There are no appreciable differences between the two methods.)

2.3 Standard Methods, 17th Ed., Method 4500-SO_4^{2-} is also a turbidimetric method, but uses significantly different buffers and timing. The timing from this method has been incorporated into this SOP.

2.4 ASTM Method D-129, is used as the reference for sulfur analysis. The analysis of the bomb washings is by EPA Method 375.4.

3.0 METHOD SUMMARY

The turbidimetric sulfate test is used to determine the amount of sulfate ion converted to a barium sulfate suspension under controlled conditions. Sulfate

ion is precipitated in a Hydrochloric Acid medium with Barium Chloride so as to form barium sulfate crystals of uniform size. The resulting turbidity is determined by a spectrophotometer and compared to a curve prepared from standard sulfate solution.

4.0 INTERFERENCES

4.1 Suspended matter, color, and turbidity are positive interferences that may be corrected for by routinely running color blanks on all samples prior to the addition of barium chloride. Some samples will require pre-filtering as well.

4.2 Silica in concentrations of > 500 mg/L will interfere.

5.0 SAMPLE CONTAINER, PRESERVATION AND HANDLING

Sample container, preservation techniques and hold times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times and the references which include container and preservation requirements for compliance with the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

Regulation	Holding Time	Reference
CWA	28 days	CFR 40 Part 136.3
SDWA	28 days	EPA-570/9-82-002

6.0 INSTRUMENTATION AND EQUIPMENT

6.1 Spectrophotometer

Wavelength of 420 nm and a light path of 1 cm

6.2 Miscellaneous

- an electric timer or a clock with a second hand
- measuring spoon, capacity 0.2 to 0.3 mL
- magnetic stir plate used at a constant speed
- stir bars of identical shape and size
- stir bar retriever

- 250 mL beakers
- 5 mL dispenser containing conditioning reagent
- 100 mL volumetric flasks (standard preparations)
- pipettes, eppendorfs and serological
- small test tubes

7.0 PREVENTIVE MAINTENANCE

7.1 The cuvette and spectrophotometer cell must be kept clean. The cuvette must be rinsed with DI prior to analysis. The spectrophotometer cell should be visually examined for any sample spillage or build-up of barium sulfate.

7.2 Spectrophotometer must be kept clean at all times. Yearly professional maintenance must be done. Manufacturers recommended calibration procedures must be followed.

NOTE: Do not use the sipper attachments on the spectrophotometer. The Barium Chloride may build up in the flow-through cell.

8.0 STANDARDS AND QC SOLUTIONS

All reagents are prepared with Type II DI Water, unless otherwise stated, in Class A volumetric flasks.

8.1 Conditioning Reagent

In a 2000 mL beaker, add 1200 mL DI Water, 120 mL concentration hydrochloric acid, and 400 mL 95% ethanol or isopropanol making sure the graduated cylinder is rinsed thoroughly after each measurement. Weigh out 300 g of sodium chloride on a top loading balance and add to the above mixture. Add 200 mL of glycerol, a clean stir bar, and place the mixture on a stir plate until all of the sodium chloride dissolves. Transfer the solution to a clean labeled bottle.

- Life of Reagent: one year
- Storage Requirements: store at room temperature

8.2 Calcium Chloride Leaching Solution, 0.15%

To a 1.0 L volumetric flask partially filled with DI water, add 1.5 g calcium chloride (oven dried in a 105°C oven) and fill. Add a clean stir bar and place on a stir plate until all of the calcium chloride is dissolved. Transfer the solution to a clean labeled bottle.

- Life of Reagent: one year
- Storage Requirements: room temperature

8.3 Stock Solution I, 1000 mg SO_4/L

Dry about 3 g of anhydrous Sodium Sulfate (Na_2SO_4) in the oven at 105°C for at least 2 hours. Cool in a desiccator to room temperature. Using an analytical balance capable of measuring 0.1 mg, weigh out 1.4786 g of the dried crystals and add it to a 1.0 L volumetric flask. Dissolve in DI water and dilute to volume. Transfer the solution to a clean and properly labeled bottle.

- Life of Reagent: one year
- Storage Requirements: store at room temperature

8.4 Stock Solution II, 4000 mg SO_4/L

Dry approximately 7 g of anhydrous Sodium Sulfate, from a different manufacturer than Rgt. 8.3, in a 105°C oven for at least two hours. Cool in a desiccator to room temperature. Using an analytical balance capable of measuring 0.1 mg, weigh out 5.9144 g of dried crystals and place in a 1.0 L volumetric flask, dissolve in DI water and dilute to volume. Transfer the solution to a clean and properly labeled bottle.

- Life of Reagent: one year
- Storage Requirements: room temperature

8.5 Barium Chloride Crystals, 20 to 30 mesh

Purchased from a chemical vendor.

- Life of Reagent: three years or manufacturer's recommendation
- Storage Requirements: room temperature

9.0 PROCEDURE

All sulfate analysis is done on non-preserved (general) samples.

9.1 Reporting Limits

Waters.....5 mg/L
Soils/Wastes.....50 mg/kg

9.2 Sample Size

Waters.....100 mLs
Soils/Wastes.....10 grams

9.3 Sample Preparation

9.3.1 Preliminary Testing

To pre-test, place 8-10 mL of sample in a small test tube with a small scoop of barium chloride and a few drops of conditioning reagent. Shake well and visually compare the resulting turbidity to that of a similarly treated high standard.

9.3.2 Soil/Waste Preparation

9.3.2.1 Weigh out 10 g of sample, to the nearest 0.1 g, in a 250 mL beaker.

9.3.2.2 Add 100 mLs of 0.15% Calcium Chloride Leach Solution to the beaker.

9.3.2.3 Stir the mixture on a stir plate for 60 minutes.

NOTE: Alternatively, weigh the sample into a 250 mL plastic sample bottle, add 100 mL of water and shake for 30 minutes on the wrist-action shaker.

9.3.2.4 Filter the mixture through a Whatman 541 or GF/C filter.

9.3.2.5 Pre-test the filtrate as stated in Section 9.3.1.

9.3.3 Sulfur analysis is done by sulfate analysis of the washings from the firing of a portion of a sample in a Parr oxygen bomb. Pre-test as in Section 9.3.1 and treat the bomb washings as a water sample until calculating the % sulfur result.

9.4 Analysis

9.4.1 Allow 30 minutes for the spectrophotometer to warm up at 420 nm wavelength. Zero the instrument with DI water.

9.4.2 Place 100 mL of standards, blanks, and prepared samples in properly labeled 250 mL beakers. Record the RFW#'s, weight, dilutions, etc., in the date book.

9.4.3 To calibrate, first add 5.0 mL of conditioning reagent (Rgt. 8.1) to the blank and each standard of the curve and to the ICV and ICB only. These must be read and in control before color blanks or sample absorbances can be read.

9.4.4 Stir each standard or sample for exactly 1.0 minute at constant speed. Set aside the sample and continue with the next standard or blank.

9.4.5 Six minutes after the addition of the $BaCl_2$ to the first beaker, begin reading the standards on the spectrophotometer (wavelength 420 nm). Timing is important. Each sample must be stirred for 1 minute with the $BaCl_2$ and then allowed to sit for 5 additional minutes prior to reading. Practice will allow a continuous cycle of stirring and reading so that a set of samples may be read efficiently.

9.4.6 Stop reading after the curve, ICV and ICB are read. Calculate the correlation coefficient of the curve and the ICV/ICB to insure that they are within control limits (See Section 9.5).

9.4.7 Add 5.0 mL of conditioning reagent to each sample aliquot and the QC beakers.

9.4.8 Read each sample or sample dilution on the spectrophotometer **without adding Barium Chloride** to correct for color or turbidity that filtering may not have removed. CCVs and CCBs with Barium Chloride must be stirred for 1.0 minute and read after 5 minutes between every ten readings. See Analytical Sequence (Section 9.5).

NOTE: All positive color blank absorbances are subtracted from the sample absorbances prior to the mg/L calculation. Negative color blanks are not subtracted. If a color blank absorbance is higher than the sample absorbance, a note must be made the in the data book. If the color blank of an undiluted or lesser diluted sample is zero or negative, a color blank is not needed on a greater dilution of the same sample.

9.4.9 Once all of the color blanks are read, beginning reading each sample as described in Sections 9.4.3 - 9.4.5.

9.5 Analytical Sequence

Calibration Controls	Sequence	Control Limit
Standards	prior to samples	y-int < MDL abs.
Corr. Coeff.	prior to samples	≥ 0.995
Init. Cal. Ver. (ICV)	after calibration	90 - 110% Recovery
Init. Cal. Blk. (ICB)	after ICV	< MDL
Cont. Cal. Ver. (CCV)	every 10 readings	90 - 110% Recovery
Cont. Cal. Blk. (CCB)	after every CCV	< Reporting Limit

Quality Controls	Frequency	Control Limit
Prep Blank (PB)	1 in 20 samples	< Reporting Limit
Lab Control Std. (LCS)	1 in 20 samples	+/- 20% Recovery
Lab Control Std. Dup. (LCSD)	1 in 20 samples	≤ 20% Recovery
Matrix Spike (MS)	1 in 20 samples	+/- 25% Recovery
Matrix Spike Dup. (MSD)	1 in 20 samples	≤ 20% RPD

All acronyms are defined in Section 12 of this procedure.

Drinking water samples must be done in sets of 10 or fewer samples. The control limits for drinking waters are 90 - 110% recovery for LCSs; RPDs of ≤ 10%; and matrix spike recoveries must be 85 - 115% recovery.

9.6 Calibration Procedure

Before any instrument is used as a measurement device, the instrumental response to known reference materials must be determined. The manner in which various instruments are calibrated is dependent upon the particular type of instrument and its intended use. All sample measurements are made within the calibrated range of the instrument. Preparation of all reference materials used for the calibration will be documented.

9.6.1 Instrument calibration consists of the two types: Initial Calibration and Continuing Calibration

9.6.1.1 Initial Calibration

Establishes the calibration range of the instrument and determines the instruments response over that range.

9.6.1.2 Continuing Calibration

Used within an analytical sequence to verify stable calibration throughout the sequence, and/or to demonstrate that the instrument response did not drift during a period of non-use of the instrument.

9.6.2 Standards Preparation

Standards	Volume of Standard I (Use Eppendorf and/or volumetric pipettes)
0.0 mg/L	100 mL DI Water
5.0 mg/l	500 uL diluted to 100 mL in a vol. flask
7.5 mg/L	750 uL diluted to 100 mL in a vol. flask
10.0 mg/L	1000 uL diluted to 100 mL in a vol. flask
15.0 mg/L	1500 uL diluted to 100 mL in a vol. flask
20.0 mg/L	2000 uL diluted to 100 mL in a vol. flask
25.0 mg/L	2500 uL diluted to 100 mL in a vol. flask
30.0 mg/L	3000 uL diluted to 100 mL in a vol. flask
40.0 mg/L	4000 uL diluted to 100 mL in a vol. flask

Class A Volumetric Flasks are used to prepare the above standards.

9.6.3 Quality Control Preparation

Quality Control Standard	Volume of Standard II (Use Eppendorf and/or volumetric pipettes)
Init. and Cont. Cal. Blank (ICB/CCB)	100 mL DI Water
Init. and Cont. Cal. Ver. (ICV/CCV), 20 mg/L	500 uL diluted to 100 mL in a vol. flask
LCS/LCSD, 20 mg/L	500 uL diluted to 100 mL in a vol. flask
Matrix Spike, 20 mg/L undiluted sample	500 uL diluted to 100 mL in a vol. flask

10.0 CALCULATIONS

10.1 Water samples

mg/L SO_4 = mg/L (curve) x dilution

10.2 mg/kg as received = $\frac{\text{mg/L (curve) x dilution x final volume}}{\text{sample size (g)}}$

10.3 mg/kg dry weight = $\frac{\text{mg/kg as received}}{\text{\% solids as decimal}}$

10.4 % Sulfur

mg/kg as SO_4 = $\frac{\text{mg/L (curve) x dilution x volume from bomb}}{\text{bombed sample size (g)}}$

% Sulfur = $\frac{\text{mg/kg}}{30{,}000}$

10.5 Accuracy

10.5.1 ICV/CCV, LCS/LCSD % Recoveries:

% R = $\frac{\text{observed concentration}}{\text{actual concentration}}$ x 100

10.5.2 Matrix Spike % Recovery

$$\% R = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

10.6 Precision

Matrix Dup. and LCS Dup. Relative Percent Difference (RPD)

$$RPD = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

10.7 Reporting Results

Without rounding, enter the raw data on the appropriate Lotus spreadsheet. Carefully print, review and approve the spreadsheet. Have the data book and spreadsheet approved and signed by the designated reviewer before creating a print file and transferring the data to LIMS.

11.0 QUALITY CONTROL

11.1 One method blank and two Lab Control Standards (LCS) will be included in each laboratory lot of 20 samples. Regardless of the matrix being processed, the LCS and method blanks will be in an aqueous media.

11.2 The method blank will be examined to determine if contamination is being introduced in the laboratory.

11.3 The LCS's will be examined to determine both precision and accuracy.

11.4 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

11.5 Precision will be measured by the reproducibility of both LCS's and will be calculated as relative percent difference (%RPD). Results must agree within in-house control limits or statistical control limits in order to be considered acceptable.

11.6 One matrix spike and matrix duplicate is performed per matrix per 20 sample analytical set. Results must agree within the in-house precision/accuracy limits or statistical control limits in order to be considered acceptable.

12.0 CORRECTIVE ACTIONS

When an out of control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, QA personnel or the lab manager.

12.1 Listed below are steps to be taken when an out of control situation occurs. The analyst must:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on a corrective action report form;
- document on the corrective action report that an in control has been achieved; and
- receive approval (signature) of the Section Manager, Unit Leader, QA personnel, or the Laboratory Manager prior to the release of any analytical data associated with the problem.

12.2 Suggested Actions to specific out of control situations:

12.2.1 Calibration Curve

- reanalyze the standard curve;
- prepare new stock and/or working standards;
- check reagents/solutions and prepare fresh if necessary.

12.2.2 Initial Calibration Verification (ICV)

- repeat ICV to verify proper preparation;
- prepare new ICV from original stock;
- check for instrument base-line drift;
- restandardize with existing standards, reanalyze;
- check reagents/solutions and prepare fresh if necessary;
- prepare new stock and/or working standards and recalibrate;

12.2.3 Initial Calibration Blank (ICB)

- prepare a new ICB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis or reagent contamination are two common sources).

12.2.4 Laboratory Control Standards (LCS)

If either LCS1 or LCS2 exceeds acceptance limits:
- reanalyze LCS to verify that an out of control situation exists;
- determine the source of error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be either the reagents, the LCS stock solution, or the preparation area.)

Precision: LCS1 and LCS2 must meet the control limits of $\leq$ 20% RPD. If this criteria is not met, and both LCS's meet the % Recovery control limits, then see your Section Manager or Unit Leader for proper corrective action.

12.2.5 Preparation Blank (PB)

- reanalyze PB to verify contamination at a level > Reporting Limit;
- determine the source of contamination and correct the problem;
- all samples whose concentration is <10 times the PB level must be reprocessed and reanalyzed; any sample which is >10 times the PB level need not be reanalyzed. However, a corrective action report must be filled out and approval obtained.

12.2.6 Matrix Duplicate (DUP)

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies;
- if the reanalysis is within the control limits, the second value is reported;
- if the reanalysis is still outside of the control limits, a CAR must be written and then approved by your Section Manager or Unit Leader.

12.2.7 Matrix Spike (MS)

- the sample must then be reprocessed and reanalyzed unless the sample concentration exceeds the spike concentration by a factor of 4 times;
- the original spike results must be entered onto the spreadsheet with the "S" code even though the control limits were exceeded;
- the reanalysis result must be entered onto the spreadsheet using the "T" code regardless of whether it is within the control limits. There is no need to write a corrective action if both the "S" and "T" codes were entered into LIMS.

12.2.8 Continuing Calibration Verification (CCV)

- repeat CCV to verify proper preparation;
- prepare new CCV from original stock;
- check for instrument base-line drift;
- check reagents/solutions and prepare fresh if necessary;
- recalibrate with a new standard curve and repeat all samples since the previous in control CCV;
- never dispose of any samples until you are sure that all QC are within their designated control limits.

12.2.9 Continuing Calibration Blank (CCB)

- prepare a new CCB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;

- determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis or reagent contamination are two common sources).
- never dispose of any samples until you are sure that all QC are within their designated control limits.

13.0 HEALTH AND SAFETY

As always, general laboratory safety practices should always be followed. Waste samples should be handled with care due to the uncertainty of the properties and contents involved. Refer to the specific MSDSs for the hazardous properties of any chemical or reagent involved in the procedure.

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INORGANIC ANALYSIS PROTOCOL
Turbidimetric Analysis of Sulfate and Sulfur

These Approval Signatures Are Kept on File
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REVISION NUMBER: 01

	Printed Name:	Signature/Date:
Updated By:	Diane L. Harper Wet Chemistry Section Manager	Diane L Harper 3-11-93
Contributor:	Daniel A. Knieriemen Wet Chemistry Analyst	Daniel A. Knieriemen 3/11/93
Approved By:	Diane L. Harper Wet Chemistry Section Manager	Diane L. Harper 3-11-93

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Reasons for Change, Revision 01:

- Additions to Section 6.0 and Clarification of Section 9.0.

RELEASED
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INORGANIC ANALYSIS PROTOCOL
Total and Volatile Suspended Solids
(Non-Filterable Residue)

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REVISION NUMBER: 01

1.0 PURPOSE

To determine the total non-filterable residue content in drinking, surface, and ground waters, domestic and industrial liquid wastes.

2.0 REFERENCE

This SOP was written using the following methods as references:

For Total Suspended Solids (TSS), EPA 600/4-79-020, Method 160.2 and Standard Methods, 17th Ed., Method 2540D.

For Volatile Suspended Solids (VSS), EPA 600/4-79-020, Method 160.4 and Standard Methods, 17th Ed., Method 2540E.

3.0 METHOD SUMMARY

3.1 Suspended solid matter in natural or man-made water bodies is of environmental importance because the presence of such material decreases the amount and depth of light penetration to the water body. The decrease in light penetration then decreases the potential for productivity of zooplankton and photoplankton of the water body, limiting the available food sources to higher vertebrates and invertebrates that are necessary to keep the ecosystem in balance.

3.2 Wastewater treatment plant operators use this information as a guide to pump performance within the plant and can often troubleshoot potential future problems. Final effluents are monitored to evaluate overall plant performance as well as to provide estimations of the suspended solids loading to the receiving stream.

3.3 Suspended solids material occurs naturally as silt, leaves, etc., and is caused by a variety of naturally occurring processes such as rain, decay, animal activities, etc. Litter and industrial effluents are sources of manmade suspended solids pollutants. Suspended solids materials are easily removed by filtration.

3.4 A sample may contain two types of solids, dissolved solids, and suspended solids. The suspended solids are those particles retained by a micro-fiber filter while the dissolved solids pass through the filter. The type of filter holder, the pore size, porosity, area and thickness of the filter and the physical nature, particle size and amount of material deposited on the filter are the principal factors affecting the trapping of suspended solids materials. The residue remaining on the filter paper is dried to a constant weight at 103-105°C.

If the TSS is less than the reporting limit, then VSS will not need to be determined.

4.0 INTERFERENCES

Exclude large floating particles or submerged agglomerates of non-homogeneous materials from the sample if they are not representative of the sample. Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 200 mg of residue. For samples high in dissolved solids, thoroughly wash the filter to ensure removal of dissolved material. Prolonged filtration times resulting from filter clogging may produce high results owing to excessive solids caught on the clogged filter.

5.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times, and the references which include container and preservation requirements for compliance with the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

Regulation	Holding Time	Reference
CWA NPDES	7 days	CFR 40 pt. 36.3
SDWA	7 days	EPA-570/9-82-002

All analyses are performed on unpreserved samples.

6.0 INSTRUMENT AND EQUIPMENT

- Analytical Balance - capable of weighing to 0.1 mg
- 103-105°C oven
- desiccator
- vacuum
- 100 mL graduated cylinder
- suction flask (side armed)
- crucible holder
- gooch crucibles, 40 mL
- Whatman 934-AH glass fiber filters
- 10 mL class A pipettes

7.0 PREVENTATIVE MAINTENANCE

7.1 Calibration check of balance, daily

7.2 Calibration check of 103-105°C oven, daily

7.3 Desiccant is inspected daily by analyst

8.0 STANDARDS AND REAGENTS

All standards and reagents are prepared with Type II Deionized Water **unless otherwise stated.**

8.1 Stock Solution I; 200 mg/L

Weigh out 200 mg diatamaceous earth (DE) to the nearest 1 mg and add it to 500 ml DI water in a 1.0 L volumetric flask. Dilute to volume with DI water and mix thoroughly.

- Life of QC Solution: one day
- Storage Requirements: none

8.2 Stock Solution II; 25 mg/L

Prepare as above using 25 mg DE rather than 200 mg.

- Life of QC Solution: one day
- Storage Requirements: none

9.0 PROCEDURE

9.1 Reporting Limit.....5 mg/L (based on a 100 mL minimum sample)

9.2 Sample Size

Working sample size varies, generally 100 ml is sufficient, but it is acceptable to increase or decrease the volume to obtain a range of at least 1.0 mg of residue, not to exceed 200 mg.

9.3 Crucible Preparation

9.3.1 Assemble the filtering apparatus. Insert one filter disk into a crucible with the wrinkled side up and place the crucible in a vacuum apparatus. Wet the filter with a small volume of distilled water to seat it against the support. Turn on the vacuum and wash with three successive 20 mL volumes of DI water.

Continue suction until all traces of water are gone. Turn off the vacuum and place the crucible on the rack. When all crucibles are done, place the rack in a 103-105°C oven for a minimum of one hour.

After removing the rack from the oven, store it in a desiccator until cooled (a minimum of one hour). The moisture content will equilibrate during cooling.

9.3.2 To prepare a crucible for VSS, bring the muffle furnace up to 550 +/- 50°C. Place the prepared gooch(es) into the preheated muffle furnace for 15 minutes. Remove the gooch(es) and allow them to cool to room temperature before putting them into a desiccator. Store the gooch(es) in the desiccator for at least one hour prior to use.

9.3.3 Weigh the crucible and record the weight and crucible number.

9.4 Sample Analysis

9.4.1 Shake the sample vigorously and quantitatively transfer the sample to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after the sample has passed through.

9.4.2 With suction still on, rinse the graduated cylinder with 10 mL of DI water and add that rinsate to the filter. Apply the vacuum until all the water is drained through. Rinse the filter with 2 additional 10 mL portions of DI water, allowing complete drainage between rinses. Apply suction for about 3 minutes after filtration is complete.

9.4.3 Carefully remove the crucible from the suction apparatus. Dry at least one hour at 103-105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg, or less than 4% of the previous weight, whichever is less.)

9.4.4 If VSS is to be determined, transfer the crucibles from 9.4.3 to a muffle furnace that has been pre-heated to 550 +/- 50°C and ignite for 15-20 minutes. Cool somewhat first then cool to the balance temperature in a desiccator. Weigh to the nearest 0.1 mg. Repeat the cycle of igniting, cooling and weighing until the weight loss is less than 4$ of the previous weight.

9.5 Analytical Sequence

Quality Controls	Frequency	Control Limit
Prep. Blk. (PB)	1 in 20 samples	< Reporting Limit
Lab. Control. Std. (LCS)	1 in 20 samples	+/- 20% Recovery
Lab. Control. Std. Dup. (LCSD)	1 in 20 samples	+/- 20% Recovery
Matrix Spike (MS)	1 in 20 samples	+/- 25% Recovery
Matrix Spike Dup. (MSD)	1 in 20 samples	+/- 20 RPD

▸All acronyms are defined in Section 12 of this procedure.
▸Drinking water samples must be analyzed in sets of 10 and have a matrix spike and duplicate performed on this matrix. The control limits for LCS's are +/- 10%; Matrix Spikes are +/- 15%; and Matrix Duplicates are ≤ 10 RPD.

9.7 Calibration Procedure

Laboratory balances are calibrated and serviced annually by a factory representative. In addition, an analyst checks the balance daily with two masses: one in the gram range and one in the milligram range. A record of calibrations and daily checks will be kept in the balance log.

Class S weights are used by the analysts for daily balance checks.

Oven and refrigerator thermometers will be calibrated annually against a National Bureau of Standards (NBS) certified thermometer in the range of interest. Annual calibrations will be recorded in a calibration notebook. Daily readings will be recorded with the respective oven or refrigerator before and after the drying period.

9.7.1 Standards Preparation

9.7.1.1 Preparation Blank (PB)

300 mls DI water

9.7.1.2 Laboratory Control Standard (LCS) and LCS Duplicate; 200 mg/L

300 mLs of Stock Solution I (Rgt. 8.1).

9.7.1.3 Matrix Spike; 25 mg/L

Pour 100 mLs of Stock Solution II (Rgt. 8.2) through the same filter as the sample to be spiked. If possible (see constraints from Section 4.0), spike 100 mL of sample for a spike concentration of 25 mg/L. If other than 100 mL of sample volume was spike, calculate the spike concentration as follows:

$$\text{mg/L spike concentration} = \frac{25\ \text{mg/L} \times 100\ \text{mL}}{\text{mL sample}}$$

NOTE: There is no matrix spike or LCS for VSS. Only a preparation blank and a matrix duplicate can be analyzed.

9.7.1.4 Matrix Duplicate

Duplicate of one sample.

10.0 CALCULATIONS

10.1 Sample Calculation

10.1.1 Total Suspended Solids

$$\text{mg/L} = \frac{(A - B) \times 1{,}000{,}000}{C}$$

Where:
A = final weight (g) of crucible plus sample
B = initial weight (g) of crucible
C = sample volume (mL)

10.1.2 Volatile Suspended Solids

$$mg/L = \frac{(A - D) \times 1{,}000{,}000}{C}$$

Where:
A = weight of crucible and residue before igniting (g)
D = weight of crucible and residue after igniting (g)
C = sample volume (mL)

10.2 Accuracy

10.2.1 LCS/LCSD % Recoveries

$$\% R = \frac{\text{observed concentration}}{\text{actual concentration}} \times 100$$

10.2.2 Matrix Spike % Recovery

$$\% R = \frac{(\text{spiked sample}) - (\text{unspiked sample})}{\text{spiked concentration}} \times 100$$

10.3 Precision

10.3.1 Matrix Dup. and LCS Dup. Relative Percent Difference (RPD)

$$RPD = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

10.4 Reporting Results

Without rounding, enter the raw data on the appropriate Lotus spreadsheet. Carefully print, review and approve the spreadsheet. Have the data book and spreadsheet approved and signed by the designated reviewer before creating a print file and transferring the data to LIMS.

11.0 QUALITY CONTROL

11.1 One method blank and two Laboratory Control Standards (LCS) will be included in each laboratory lot of 20 samples. Regardless of the matrix being processed, the LCS and method blanks will be in an aqueous media.

11.2 The method blank will be examined to determine if contamination is being introduced in the laboratory.

11.3 The LCS's will be examined to determine both precision and accuracy.

11.4 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be within the laboratory's acceptance limits in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

11.5 Precision will be measured by the reproducibility of both LCS's and will be calculated as relative percent difference (%RPD). Results must agree within in-house control limits or statistical control limits in order to be considered acceptable.

11.6 One matrix spike and matrix duplicate is performed per matrix per 20 sample analytical set. Results must agree within the in-house precision/accuracy limits or statistical control limits in order to be considered acceptable.

12.0 CORRECTIVE ACTIONS

When an out of control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, QA personnel or the lab manager.

12.1 Listed below are steps to be taken when an out of control situation occurs. The analyst must:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on a corrective action report form;
- document on the corrective action report that an in control has been achieved; and
- receive approval (signature) of the Section Manager, Unit Leader, QA personnel, or the Laboratory Manager prior to the release of any analytical data associated with the problem.

12.2 Suggested Actions to specific out of control situations:

12.2.1 Laboratory Control Standards (LCS)

If either LCS1 or LCS2 exceeds acceptance limits:
- reanalyze LCS to verify that an out of control situation exists;
- determine the source of error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be either the reagents, the LCS stock solution, or the preparation area.)

Precision: LCS1 and LCS2 must meet the control limits of $\leq$ 20% RPD. If this criteria is not met, and both LCS's meet the % Recovery control limits, then see your Section Manager or Unit Leader for proper corrective action.

12.2.2 Preparation Blank (PB)

- reanalyze PB to verify contamination at a level > Reporting Limit;
- determine the source of contamination and correct the problem;
- all samples whose concentration is <10 times the PB level must be reprocessed and reanalyzed; any sample which is >10 times the PB level need not be reanalyzed. However, a corrective action report must be filled out and approval obtained.

12.2.3 Matrix Duplicate (DUP)

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies;
- if the reanalysis is within the control limits, the second value is reported;
- if the reanalysis is still outside of the control limits, a CAR must be written and then approved by your Section Manager or Unit Leader.

12.2.4 Matrix Spike (MS)

- the sample must then be reprocessed and reanalyzed unless the sample concentration exceeds the spike concentration by a factor of 4 times;
- the original spike results must be entered onto the spreadsheet with the "S" code even though the control limits were exceeded;
- the reanalysis result must be entered onto the spreadsheet using the "T" code regardless of whether it is within the control limits. There is no need to write a corrective action if both the "S" and "T" codes were entered into LIMS.

13.0 HEALTH AND SAFETY

As always, general laboratory safety practices should always be followed. Waste samples should be handled with care due to the uncertainty of the properties and contents involved. Refer to the specific MSDS for the hazardous properties of any chemical or reagent involved in this procedure.