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| USGS Troy WSC Laboratory 425 Jordan Road Troy, NY 12180 | Speciated Aluminum SOP | |
| | SOP No. 8 | Rev. No. 1.5 |
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USGS Water Science Center Laboratory, Troy, NY
Flow Injection Analysis - Speciated Aluminum
Standard Operating Procedure

1. Scope and Application

1.1 Analytes

Total Monomeric Aluminum and Organic Monomeric Aluminum

1.2 Reporting Limit

1.5 $\mu\text{mol Al/L}$

1.3 Applicable Matrices

This method is used to determine total monomeric aluminum and organic monomeric aluminum concentrations in precipitation, dilute surface waters and soil waters.

1.4 Dynamic Range

The analytical range for this determination is 0.1 to 37.06 $\mu\text{mol Al/L}$. Sample concentrations that exceed this range must be diluted and reanalyzed. Sample concentrations below the reporting limit are flagged "<" in the Laboratory Information Management System (LIMS).

2. Summary of Procedure

This analysis is an automated colorimetric reaction on a dual channel flow injection analyzer (FIA). Both channels are identical except for the addition of a cation-exchange column in the organic monomeric aluminum manifold. Each sample is systematically introduced into both FIA reaction manifolds. In the organic monomeric aluminum manifold, the sample is initially passed through the resin column, which removes inorganic aluminum. In both manifolds, the sample is then mixed with a phenanthroline/hydroxylamine hydrochloride reagent, which eliminates the interference of iron. The sample subsequently reacts with a pyrocatechol violet (PCV) solution that turns blue-gray in the presence of monomeric aluminum. Aluminum polymers and strongly complexed Al monomers will not react with PCV. A buffer is added to adjust the pH to about 6.2. The absorbance of the color complex is measured at a wavelength of 580 nm. Inorganic aluminum is subsequently calculated by subtracting the organic monomeric aluminum concentration from the total monomeric aluminum concentration for each sample.

3. Safety Issues

3.1 Chemical Hazards

- A. All strong acids and bases should be mixed in a fume hood.
- B. Gloves, safety glasses, and lab coats should be worn when preparing and performing this analysis.
- C. For proper handling techniques for specific chemicals, consult the appropriate Safety Data Sheets (SDS).

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4. Sample Preservation, Containers, Processing and Analysis Times

4.1 Sample Preservation

Samples are stored unfiltered at 4°C.

4.2 Containers

Samples are stored in 250-mL polyethylene bottles. The bottles are new or have been recycled and cleaned using the laboratory dishwasher.

4.3 Processing and Analysis Times

Sample processing: one week

Lab analysis: one month

LIMS entry: one week

5. Reagents and Standards

5.1 General Information

All reagents are commercially purchased, reagent grade or higher quality, and should be stored in the original container. Date the reagent bottles when received and when opened. Note expiration date, if any. No verification of the reagents is necessary.

5.2 Reagents

A. Degassed Deionized (DI) water

1. Degas Milli-Q water by bubbling with commercial-grade helium for about 2 minutes.
2. Degassed Milli-Q water is used for carrier water and for preparation of all reagents.
3. Prepare daily.

B. 1,10-Phenanthroline/Hydroxylamine Hydrochloride

1. Use 99+% purity hydroxylamine hydrochloride ($\text{H}_2\text{NOH}\cdot\text{HCl}$) and 99+% purity anhydrous 1,10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2$).
2. Add 7.6 g hydroxylamine hydrochloride and 0.56 g anhydrous 1,10-phenanthroline to a 1,000-mL volumetric flask containing about 500 mL Milli-Q water.
3. Fill close to final volume with Milli-Q water and mix thoroughly with stir bar until dissolved (about 20 minutes).
4. Remove stir bar, fill to final volume, and mix again.
5. Store in a polyethylene bottle at 4°C; label and date.
6. Prepare every other day.

C. Pyrocatechol Violet (PCV)

1. Use PCV that is about 90% pure.
2. Add 0.386 g PCV to a 1,000-mL volumetric flask containing about 500 mL Milli-Q water.
3. Swirl until the PCV has dissolved.
4. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
5. Store in a polyethylene bottle at 4°C; label and date.

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6. Prepare every other day.
- D. Hexamethylenetetramine Buffer
 1. Use 99+% hexamethylenetetramine $[(CH_2)_6N_4]$.
 2. Due to the aromatic nature of this chemical, this reagent should be prepared in a chemical safety hood.
 3. Add 168.0 g hexamethylenetetramine to a 2,000-mL volumetric flask containing about 1,000 mL Milli-Q water.
 4. Mix until all solid is dissolved.
 5. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
 6. Store in a polyethylene bottle at 4°C; label and date.
 7. Prepare every other day.
- E. 0.1 M Hydrochloric Acid
 1. Use commercially purchased 0.1 M hydrochloric acid (HCl).
 2. The solution is valid until the expiration date listed on the bottle.
- F. 1 mM Sodium Chloride
 1. Add 0.058 g sodium chloride (NaCl) to a 1,000-mL volumetric flask containing about 500 mL Milli-Q water.
 2. Swirl to dissolve solid.
 3. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
 4. Store in a polyethylene bottle; label and date.
 5. Prepare yearly.
- G. Cation-Exchange Resin (pH about 5.0)
 1. Add 100 mL Milli-Q water to a 250-mL beaker containing 100 g Amberlite IR (plus) ion-exchange resin-sodium form and 1.00 g Amberlite IR (plus) ion-exchange resin-acidic form.
 2. Mix thoroughly and decant the liquid.
 3. Wash again with Milli-Q water and then twice with 100 mL portions of 1 mM NaCl.
 4. Add 100 mL of 1 mM NaCl to the beaker.
 5. Store in a wide mouth container at 4°C; label and date.
 6. Prepare yearly.
- H. Cation-Exchange Column
 1. Remove the fittings and foam plugs at both ends of the glass column and rinse the column with Milli-Q water.
 2. Replace the foam plug at one end using forceps.
 3. Draw about 10 cc resin and supernatant into a 20-cc syringe.
 4. With the plugged side down, inject the resin into the top of the column in one motion without allowing air into the column. Once the column is full, cover the bottom end with a gloved finger and plug the top end with foam. Replace the fitting on the top end, then turn the column over and replace the fitting on the other end.

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5. Keep the column closed until the system is ready for the column addition. If the liquid drains out or air is introduced into the column, the column must be rinsed and repacked.
6. The column is repacked daily, and the resin is not recycled.
- I. Cleaning Solution
 1. Add 65 g sodium hydroxide (NaOH) to a 1,000-mL volumetric flask containing about 800 mL Milli-Q water.
 2. Swirl the flask until the pellets have dissolved.
 3. Add 6 g disodium ethylenediaminetetraacetic acid dihydrate ($\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$) to the flask.
 4. Allow to cool.
 5. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
 6. Store in a polyethylene bottle; label and date.
 7. Prepare as needed.

5.3 Standards

- A. Aluminum Standard Stock Solution, 1,000 mg Al/L
 1. The stock solution is purchased commercially.
 2. The stock solution is valid until the expiration date listed on the bottle.
 3. To avoid contamination, aliquots of stock solution must not be withdrawn directly from the bottle.
 4. The solution comes with a certificate of analysis from the provider.
- B. Aluminum Standard Substock Solution, 50 mg Al/L
 1. Pipet 25.0 mL aluminum standard into a 500-mL volumetric flask containing about 250 mL of Milli-Q water.
 2. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
 3. Store in a polyethylene bottle; label and date.
 4. Record preparation date, lot number, and expiration date of stock solutions in the instrument notebook.
 5. Prepare every 6 months.
- C. Aluminum Working Standards
 1. Pipet desired amount of standard substock into a designated 100-mL polyethylene volumetric flask containing about 50 mL Milli-Q water.
 2. Add 1.0 mL 0.1 M HCl.
 3. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
 4. Label and date.
 5. Prepare every six months or as needed.

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| Working Standard | Aluminum Concentration | Standard Substock Added (mL) |
|------------------|-------------------------------------|------------------------------|
| A | 37.06 $\mu\text{mol/L}$ (1.00 mg/L) | 2.0 |
| B | 27.80 $\mu\text{mol/L}$ (0.75 mg/L) | 1.5 |
| C | 18.53 $\mu\text{mol/L}$ (0.50 mg/L) | 1.0 |
| D | 11.12 $\mu\text{mol/L}$ (0.30 mg/L) | 0.6 |
| E | 7.41 $\mu\text{mol/L}$ (0.20 mg/L) | 0.4 |
| F | 3.71 $\mu\text{mol/L}$ (0.10 mg/L) | 0.2 |
| G | 1.85 $\mu\text{mol/L}$ (0.05 mg/L) | 0.1 |
| H | 0.00 $\mu\text{mol/L}$ (0.00 mg/L) | 0.0 |

- D. Aluminum Quality Control (QC) Stock Solution, 1,000 mg Al/L
1. The stock solution is purchased commercially. This stock must be from a manufacturer or lot different from the standard stock.
 2. The stock solution is valid until the expiration date listed on the bottle.
 3. To avoid contamination, aliquots of stock solution must not be withdrawn directly from the bottle.
 4. The solution comes with a certificate of analysis from the provider.
- E. Aluminum QC Substock Solution, 50 mg Al/L
1. Pipet 25.0 mL aluminum standard into a 500-mL volumetric flask containing about 250 mL of Milli-Q water.
 2. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
 3. Store in a polyethylene bottle; label and date.
 4. Record preparation date, lot number, and expiration date of stock solutions in the instrument notebook.
 5. Prepare every 6 months.
- F. Aluminum QC Samples
1. Pipet desired amount of QC substock into a designated 250-mL polyethylene volumetric flask containing about 100 mL Milli-Q water.
 2. Add 2.5 mL 0.1 M HCl.
 3. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
 4. Label and date.
 5. Prepare every 6 months.

| QC Sample | Aluminum Concentration | QC Substock Added (mL) |
|-----------|-------------------------------------|------------------------|
| QC-high | 18.53 $\mu\text{mol/L}$ (0.50 mg/L) | 2.5 |
| QC-low | 7.41 $\mu\text{mol/L}$ (0.20 mg/L) | 1.0 |

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6. Laboratory Performance

- A. A Laboratory Reagent Blank (LRB) comprised of Milli-Q water is analyzed directly after the first set of QCs.
- B. A laboratory duplicate is analyzed once per run. Laboratory duplicates should be no more than 10 percent different between the samples. Only the first sample value of the duplicate is entered into the database.

7. QC Procedure

- A. The standard curve is a third order curve obtained by plotting standard concentration vs. peak area. Eight standards are used for calibration. The best-fit line is drawn and the curve is accepted if the correlation coefficient is 0.998 or greater.
- B. Quality-control samples are analyzed at the start of the run, after every 10 samples during the run, and at the end of the run.
- C. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC-high known value and 15 percent of the QC-low known value.
- D. If one of the QC samples fails the acceptance criteria, the run is stopped and the QC sample is re-run. If the QC sample fails again the run is stopped and the QC sample is remade or the instrument is re-calibrated. Samples associated with the failed QC samples are re-analyzed.
- E. QC samples are not currently available for the organic monomeric aluminum analysis. The QC sample is a check of column efficiency. The resin column should remove all aluminum from the QC sample. If the QC produces a peak, the column should be repacked.

8. Chemical Analysis Procedure

8.1 Instrumentation

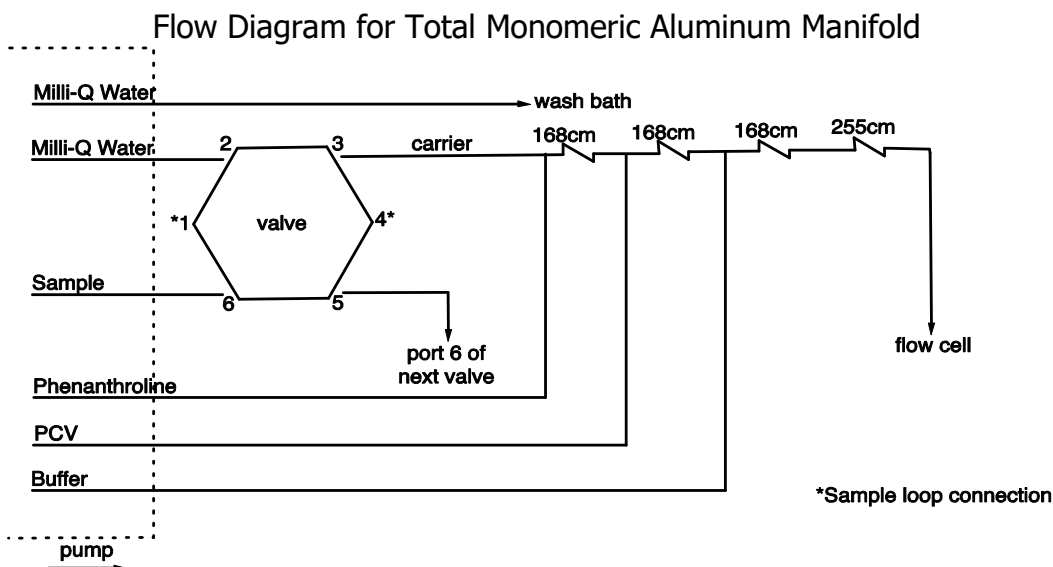
Lachat QuickChem 8500 Series 2 Dual Channel Flow Injection Analyzer
Omnion Software v. 4.0.15

8.2 Timing

Method Cycle Period - 56 seconds
Sample Period - 23 seconds
Minimum Probe in Wash Period - 24 seconds

| Setting | Total Monomeric Al Channel (seconds) | Organic Monomeric Al Channel(seconds) |
|-------------------------------|--------------------------------------|---------------------------------------|
| Load Period | 17 | 19 |
| Inject Period | 38 | 37 |
| Time to Valve | 17 | 20 |
| Expected Inject to Peak Start | 20 | 30 |
| Expected Peak Base Width | 40 | 40 |

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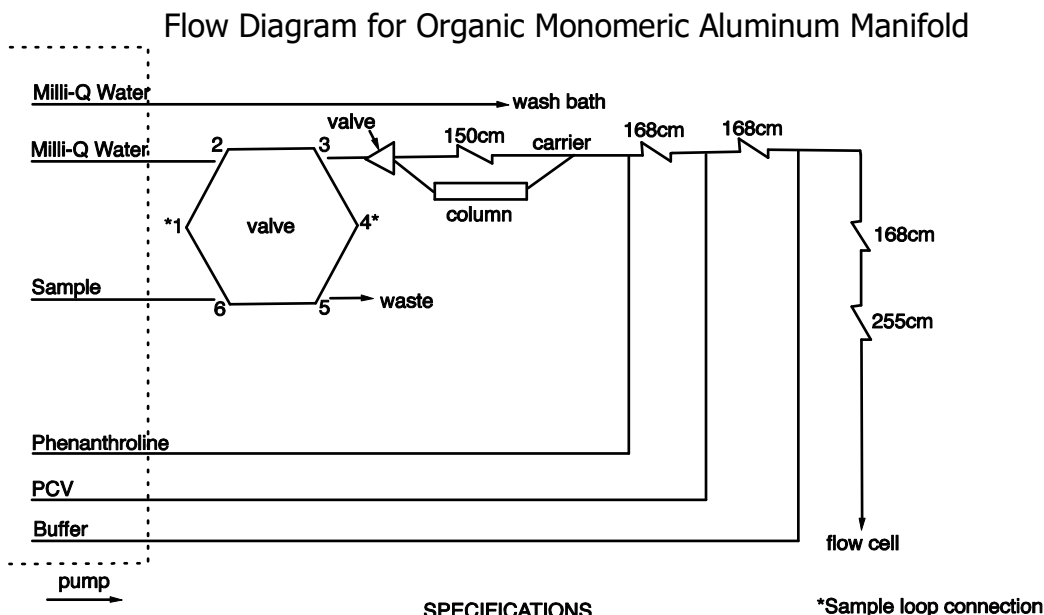


SPECIFICATIONS

Manifold tubing: 0.8 mm i.d.
Sample loop: 150 cm (780 μ L)
Flow cell: 10 mm
Interference filter: 580 nm
Pump setting: 35

Pump tubes:
Milli-Q Water/wash bath: 2.00 mL/min (green)
Milli-Q/carrier: 1.60 mL/min (blue)
Sample: 2.00 mL/min (green)

Phenanthroline: 0.32 mL/min (black)
PCV: 0.32 mL/min (black)
Buffer: 0.80 mL/min (red)



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Phenanthroline: 0.32 mL/min (black)
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8.3 Start-Up

- A. Turn the surge protector power on.
- B. On the computer desktop, double click the **Omnion** icon.
- C. Check the DI waste container daily and empty if nearing capacity.
- D. Fill the DI carrier bottle with degassed Milli-Q water.
- E. When the Omnion data system screen appears, click on **Configuration** and choose **Autosamplers**. Click on the **Initialize Autosampler** button; then close the pop-up window.
- F. Place pump tubes in appropriate reagent containers- see flow diagrams. Cover reagent bottle openings with Parafilm.
- G. Push down cartridges on pump until they click into place. Pull tighteners on pump cartridges all the way to the left.
- H. Pump should be set at remote and speed setting of 35. Turn pump on.
- I. Allow reagents and Milli-Q water to pass through system for at least 10 minutes.
- J. Turn manifold valve to allow flow through resin column. Put resin column in-line. Allow the carrier to flow through the column for a few minutes, and then turn the valve to bypass the column.
- K. Observe manifold for any leaks, clogs and/or bubbles in the lines.

8.4 Calibration

- A. Click **Open**. Double click on the **speciated aluminum calibration only.omn** file.
- B. At the top of the screen, the heading should read Omnion 4.0– Run 1 (speciated aluminum calibration only.omn).
- C. Fill tubes in calibration rack on autosampler with standards (position 1-8) and QC samples (position 9-10).
- D. Click green **Start** arrow.
- E. If the calibration is within acceptance criteria, the instrument will analyze the QC samples. If the calibration fails, a message will pop up, with options to proceed. In most cases choose **Recalibrate**.
- F. If the calibration and QC samples pass, set up a sample tray.

8.5 Analysis

- A. Take samples out of the refrigerator and let warm to room temperature.
- B. Turn manifold valve to allow flow through the resin column.
- C. Click **Open**. Double click the **speciated aluminum.omn** file.
- D. Recalibrate if necessary or delete the calibration standard rows from the run worksheet.
- E. Enter the sample serial numbers (SSNs) into the run worksheet. Use the Auto Sample ID feature if the SSNs are consecutive. A laboratory reagent blank (LRB) should be in position 1. Analyze one sample in duplicate once during each run.
- F. From menu bar select **Run**. Click **Export Worksheet Data**. Note date on run worksheet printout.

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- G. Fill the autosampler tubes with appropriate samples.
- H. Click on green **Start** arrow.
- I. Refill QC tubes and Milli-Q DI carrier bottle as needed.
- J. QC samples will be run automatically every 10 samples and at the end of the run. If all QC samples pass, the run will proceed until the tray is finished.
- K. If a QC sample fails, a message will pop up and analysis will cease. Click the **Stop Now** option. Remove SSNs that have been analyzed from the run worksheet.
- L. Click green **Start** arrow.
- M. If QC samples pass, the run will continue. If QC samples fail, reanalyze. If the QC sample fails again, remake QC samples and/or recalibrate and re-run the last 10 samples.
- N. Review the sample peaks and analysis data as the run progresses. Note any air bubbles, bad peaks, samples requiring dilutions, or re-runs.

8.6 Shut Down

- A. Turn the manifold valve to bypass the resin column.
- B. Change the pump setting to override standby.
- C. Remove pump tubes from reagent bottles and rinse lines and weights with Milli-Q water. Place lines in a beaker of Milli-Q water.
- D. After several minutes, place the PCV pump tube lines in the cleaning solution. Allow to pump about 15 seconds.
- E. Rinse PCV pump tube reagent lines with Milli-Q water and place in beaker of Milli-Q water again. Allow to pump several more minutes.
- F. Remove lines from beaker and pump air until no more water is moving through manifold.
- G. Release tension of cartridges by pushing holders on side of pump and push tension regulators on top of the cartridges all the way to the right.
- H. Exit Omnion.
- I. Turn the surge protector off.
- J. Rinse sample tubes and soak in DI water overnight. Rinse again and oven dry or air dry.

8.7 Maintenance

- A. All pump tubes should be replaced as they become worn or stretched; the frequency depends upon the number of samples analyzed. The sample and wash bath tubes should be changed as they become discolored or clogged. Note dates in instrument notebook.
- B. Interference filters should be cleaned with lens paper twice a year or whenever they become dusty or soiled.
- C. Manifold tubing should be replaced as it becomes discolored or clogged
- D. Buildup and clogging in the waste lines may require periodic replacement of the lines.

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8.8 Data Processing and LIMS Entry

- A. In Excel, open all files for the run date. Files are stored in \LAB_DATA\Lachat- speciated Al\20XX.
- B. Edit files as needed and copy/paste them into the same file.
- C. Save as a .csv file using the format mmddyyyy.
- D. Print a copy, write the filename on the copy, and close the file.
- E. Double click **Watershed LIMS** icon.
- F. Click **Import Data**.
- G. Under the Import drop down, choose **Water Monomeric Aluminum**.
- H. Choose and open the desired file.
- I. Choose **Client**, type in **Test Date**, and choose **Analyst**.
- J. Exclude and/or edit any data necessary.
- K. Click **Client ID to Sample No**.
- L. Click **Check RL Flag**.
- M. Click **Set Data**.
- N. Investigate problems for data that did not transfer or are duplicated.

9. Calculations and Data Reporting

- A. Data are output from the instrument in units of micromoles per liter and stored in the same units in the LIMS. No conversions or computations are required before the data are stored.
- B. This method has been assigned USGS National Water Information System (NWIS) method code CL162.
- C. Data that are uploaded to NWIS must be converted to mass units. Multiply by the conversion factors and store under the parameter codes listed below.

| Analyte | NWIS Parameter Code | Conversion Factor (to µg/L) |
|----------------------------|---------------------|-----------------------------|
| Total Monomeric Aluminum | 49287 | 26.98154 |
| Organic Monomeric Aluminum | 49288 | 26.98154 |

10. Archiving

- A. Data files are backed-up daily by an automated back-up program. Hard copies of the runs are filed and retained indefinitely. The laboratory LIMS system is backed up daily by automated back-up program.
- B. Samples are stored at room temperature until data can be verified.

11. References

Lachat Instruments, 1997, Methods manual for the QuikChem automated ion analyzer – Method no. 10-113-33-1-A: Milwaukee, Wisc., Lachat Instruments (variously paged).

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Lachat Instruments, 1997, Methods manual for the QuikChem automated ion analyzer Method no. 10-113-34-1-B: Milwaukee, Wisc., Lachat Instruments (variously paged).

Peden, M.E. and others, 1989, Evaluation of aluminum speciation using synthetic and natural samples – final report: Champaign, Ill., Illinois State Water Survey Contract Report 463.

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies – laboratory analysis for surface water chemistry, Washington, D.C., U.S. Environmental Protection Agency, EPA 600-4-87/026 (variously paged).

12. Key Words

Flow injection analysis, total monomeric aluminum, organic monomeric aluminum, water analysis, chemical analysis, water, soil water.

13. Revision Record

The SOP will be revised and approved as changes are required. A review will be performed no later than every two years from the last approval date and the SOP revised if necessary.

| Revision | Date | Responsible Person | Description of Change |
|----------|----------------|--------------------|---|
| 1.0-1.3 | Pre 03/05/2021 | Tricia Lincoln | All released prior to the addition of the revision record table. |
| 1.4 | 03/05/2021 | Tricia Lincoln | Updated to reflect the addition of a blank and duplicate for each run. Also some housekeeping and incidental edits. |
| 1.5 | 01/25/2022 | Tricia Lincoln | Updated to correct typo errors, calibration information, and new QA officer. |