USGS New York Water Science Center
Soil and Low Ionic Strength Water Quality Laboratory

Inductively Coupled Plasma – Optical Emission Spectrometry

Standard Operating Procedure

1. Scope and Application

Analytes

Calcium, Magnesium, Aluminum, Silicon, Sodium, and Potassium

1.2 Reporting limit

2.0 μmol Ca^{2+}/L
1.0 μmol Mg^{2+}/L
1.0 μmol Al^{3+}/L
6.0 μmol Si^{4+}/L
1.0 μmol Na^{+}/L
1.0 μmol K^{+}/L

1.3 Applicable matrices

This method is used to determine the concentrations of Ca, Mg, Al, Si, Na, and K in precipitation, dilute surface waters and soil waters.

1.4 Dynamic range

The analytical range for the determination of calcium is from 1.0 µmol Ca^{2+}/L to 200.2 µmol Ca^{2+}/L. The analytical range for the determination of magnesium is from 0.5 µmol Mg^{2+}/L to 82.3 µmol Mg^{2+}/L. The analytical range for the determination of aluminum is from 0.5 µmol Al^{3+}/L to 7.40 µmol Al^{3+}/L. The analytical range for the determination of silicon is from 3.0 µmol Si^{4+}/L to 142.4 µmol Si^{4+}/L. The analytical range for the determination of sodium is from 0.5 µmol Na^{+}/L to 217.5 µmol Na^{+}/L. The analytical range for the determination of potassium is from 0.5 µmol K^{+}/L to 51.6 µmol K^{+}/L. Sample concentrations that exceed these ranges must be diluted and reanalyzed.

2. Summary of Procedure

This analysis is performed by inductively coupled plasma – optical emission spectrometry. Samples are aspirated through a nebulizer and carried to the plasma. The concentration of the element is proportional to the intensity of light emitted as excited electrons return to ground state.

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 Material Safety Data Sheets (MSDS).

3.2 Miscellaneous

In case of malfunction, push the red emergency shut off button located on the front of the instrument.

4. Sample Preservation, Containers, Processing and Analysis Times

4.1 Sample Preservation

Unfiltered and filtered samples are preserved with 0.3 mL ultrapure nitric acid.

4.2 Containers

Samples are stored in either 60-mL acid washed polyethylene bottles or 30-mL acid washed polyethylene bottles (samples which are analyzed for aluminum only).

4.3 Processing and Analysis Times

Sample processing: one week
Lab analysis: six months
LIMS entry: one week

5. Reagents and Standards

5.1 General Information

All reagents are commercially purchased 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. Liquid Argon

Commercially purchased liquid argon in an XL-45 tank.

B. Nitric Acid

Use commercially purchased ultrapure nitric acid (HNO_3).

C. 1% Nitric Acid

1. In a 2,000 mL Erlenmeyer flask add 20 mL of ultrapure HNO_3 to 1,000 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. Prepare as needed.

5.3 Standards

A. Calcium, Magnesium, Aluminum, Silicon, Sodium, and Potassium Stock Solutions, 1,000 mg Ca^{2+}/L, 1,000 mg Mg^{2+}/L, 1,000 mg Al^{3+}/L, 1,000 mg Si^{4+}/L, 1,000 mg Na^{+}/L, 1,000 mg K^{+}/L

1. All stock solutions are purchased commercially.
2. The stock solutions are valid until the expiration date listed on the bottle.

3. To avoid contamination, aliquots of standards must not be withdrawn directly from bottle.

B. Blank Standard
1. Fill a 500-mL volumetric flask with approximately 250 mL of Milli-Q water.
2. Add 0.5 mL ultrapure HNO_3.
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 monthly.

C. Calcium, Magnesium, Aluminum, Silicon, Sodium, and Potassium Working Standard
1. Pipet desired amount of stock solutions into a 500-mL volumetric flask containing 250 mL Milli-Q water.
2. Add 0.5 mL ultrapure HNO_3.
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 monthly.

Stock Solution	Stock Added (mL)	Analyte Concentration
Calcium	4.0	200.2 μmol/L (8.0 mg/L)
Magnesium	1.0	82.3 μmol/L (2.0 mg/L)
Silicon	2.0	142.4 μmol/L (4.0 mg/L)
Aluminum	0.1	7.40 μmol/L (0.20 mg/L)
Sodium	2.5	217.5 μmol/L (5.0 mg/L)
Potassium	1.0	51.16 μmol/L (2.0 mg/L)

D. Calcium, Magnesium, Aluminum, Silicon, Sodium, and Potassium Quality-Control (QC) Stock Solutions, 1,000 mg Ca^{2+}/L, 1,000 mg Mg^{2+}/L, 1,000 mg Al^{3+}/L, 1,000 mg Si^{4+}/L, 1,000 mg Na^{+}/L, 1,000 mg K^{+}/L
1. All stock solutions are purchased commercially. This stock must be from a manufacturer or lot different from the standard stock.
2. The stock solutions are valid until the expiration date listed on the bottle.
3. To avoid contamination, aliquots of standards must not be withdrawn directly from bottle.

E. Calcium, Magnesium, Aluminum, Silicon, Sodium, and Potassium QC Samples
1. Pipet desired amount of QC stock solutions into a 1,000-mL volumetric flask containing 500 mL Milli-Q water.

2. Add 1.0 mL ultrapure HNO_3.
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 monthly.

QC-high Sample

Stock Solution	Stock Added (mL)	Analyte Concentration
Calcium	4.0	99.8 μmol/L (4.0 mg/L)
Magnesium	1.0	41.14 μmol/L (1.0 mg/L)
Silicon	3.0	106.8 μmol/L (3.0 mg/L)
Aluminum	0.3	11.15 μmol/L (0.30 mg/L)
Sodium	1.0	43.5 μmol/L (1.0 mg/L)
Potassium	1.0	25.58 μmol/L (1.0mg/L)

QC-low Sample

Stock Solution	Stock Added (mL)	Analyte Concentration
Calcium	1.0	24.95 μmol/L (1.0 mg/L)
Magnesium	0.25	10.3 μmol/L (0.25 mg/L)
Silicon	1.0	35.6 μmol/L (1.0 mg/L)
Aluminum	0.04	1.49 μmol/L (0.04 mg/L)
Sodium	0.25	10.9 μmol/L (0.25 mg/L)
Potassium	0.25	6.4 μmol/L (0.25mg/L)

6. QC Procedure

A. The standard curve is a linear plot of intensity vs. concentration using the blank and high standard.
B. Quality-control samples are analyzed at the start of a 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 sample‘s known value.
D. If one of the QC samples fails the acceptance criteria, the QC sample is re-run. If the QC sample fails again the run is stopped, the QC sample is remade from the substock, and/or the instrument is re-calibrated. Samples associated with the failed QC sample are re-analyzed.

7. Chemical Analysis Procedure

7.1 Instrumentation

PerkinElmer – Optima 2100 inductively coupled plasma – optical emission spectrometer

WinLab32 for ICP software v 3.1.0.0107
WinLab32 Data Management software v 3.1.0.0107

7.2 Start-Up

A. Check the waste water container and empty if nearing capacity.
B. Make sure that the torch is correctly installed and the torch compartment door is shut.
C. Make sure the argon pressure to the instrument is set at 100 PSI (between 80-120 PSI).
D. Make sure the shear gas is set at 100 PSI (between 80-120 PSI).
E. Fill 2,000 mL plastic rinse bottle with 1% nitric acid, and put in the rinse tube.
F. Engage pump tube windings.
G. Turn on the chiller.
H. Turn the hood on high power.
I. Open **WinLab32** software by clicking on the **Winlab32** icon on the desktop.
J. Click on the **Workspace** icon and open desired workspace.
K. Make sure the sample probe is in the rinse. The **F11** key will raise or lower the probe.
L. Click the **On** button on the plasma control window.
M. Let the instrument warm up for about 20 minutes or until initialize optics has completed (this will happen automatically after about 20 minutes and is optional to do). Close the Spectrometer Control pop-up window.
N. In the automated analysis control window, click **Open** Results Data Set Name box. Click on **Browse** to choose a database library folder to store the results of the analysis. Highlight a blank row at the bottom of the list. At the top of the window, enter the date (MM_DD_YY) in the Name box and the element symbols in the Description box. Click **OK**.
O. To create a new sample information file (SIF) click on the **Sample Information** icon. Enter Batch ID (MM_DD_YY), Sample IDs and the A/S locations (autosampler location 9 is the starting sample). Enter any desired sample descriptions in the Trip, Blank, Blind column. Click **File-> Save As-> Sample Information File**. Enter filename (MM_DD_YY) and click **Save**. Click **File-> Print-> Active Window** to print a bench sheet. Close or minimize the sample information editor window.
P. In the automated analysis control window, click on the **Analyze** tab. If the current SIF does not appear click **Rebuild List**.
Q. Load blank, standard, QC's, and samples in tray.

7.3 Calibrations and Analysis

A. In the automated analysis control window, click on an **Analyze** button.
B. If the QC samples pass, then the autosampler will go to the first sample and start the run. If either QC sample fails twice, the instrument will

automatically recalibrate and continue with the run even if the QC's fail again. The run will need to be stopped manually by clicking on an **Analyze** button.

C. If the QC samples fail after the recalibration, try initializing optics again by going to **Tools -> Spectrometer Control** then clicking **Initialize Optics**, refill the standard tubes or prepare new standards.
D. The QC locations during the run are preset in the method. If either QC sample fails twice, the instrument will automatically recalibrate and rerun the previous 10 samples.
E. Sample data that show saturation error codes during the run must be diluted and reanalyzed.

7.4 Shutdown

A. To stop the analysis prior to the end of the run, click on an **Analyze** button. In the pop-up window choose **Stop Immediately** and then click **OK**.
B. Leave the sipper in the rinse water for about 5 minutes to rinse the spray chamber. Then raise the sample probe (**F11 Key**) from the rinse for a few minutes until the spray chamber is relatively dry.
C. Click the **OFF** button in the plasma control window.
D. Release the pump tube windings.
E. Turn off the chiller.
F. Turn the hood down to low power.
G. Exit WinLab32.

7.5 Maintenance

A. Clean injector tube daily and let it dry overnight.
B. Pump tube windings must be changed after about 2 weeks of analyzing or when they appear to be worn.
C. Empty the waste water container when full.
D. Make sure coolant reservoir in the chiller is full (check monthly). Fill with circulation fluid (Poly-Clear).
E. Periodically, the torch, spray chamber, and nebulizer may need to be cleaned.

7.6 Data Processing and LIMS entry

A. Open **Data Manager**.
B. Click on **Select Library**, open desired dataset file.
C. Highlight the desired dataset.
D. To print the report click **Report** icon.
E. Choose **Use Existing Design**.
F. Click on **Browse**, open **Regular Report**, then click **Next**.
G. Click on **Enable/Disable** to choose the samples to report.
H. Click **Preview** button then click **Print**.
I. Close the preview window and the data reporting wizard window.

J. To export the data click on the **Export** icon.
K. Choose **Use Existing Design**.
L. Click **Browse**, open **Export Default Text Tab**, and then click **Next**.
M. Click **Finish** then **Export Data**.
N. Click on the **Finish** button.
O. The text file will be exported to X:\ICPData\Optima 2100\H2O
P. Open and edit text file if necessary.
Q. Double click **Watershed LIMS** icon.
R. Click **Import Data** icon.
S. Under the **Import** drop down, choose **Perkin Elmer ICP**.
T. Choose and open the desired file.
U. Choose **Client**, **Units**, type in **Test Date**, and choose **Analyst**.
V. Exclude and/or edit any data necessary.
W. Click **Client ID to Sample No**.
X. Click **Check Analysis**
Y. Click **Set Data**.
Z. Investigate problems for data that did not transfer or are duplicated.

8. Archiving requirements

8.1 Data

Data files are backed-up daily by an automatic back-up program. Hard copies of the runs are filed and kept indefinitely. The laboratory LIMS system is backed up daily by an automatic back-up program.

8.2 Samples

Samples are stored at room temperature until data can be verified. Sample bottles are cleaned and reused for new samples.

9. References

Perkin Elmer, 2000, AS-93 plus Autosampler for Atomic Spectrometry: User's Guide 0993-5278.

Perkin Elmer, 2004, Optima 2000: Hardware Guide 0993-6730.

Polyscience, 2004, Refrigerated Recirculating Chillers Operation Manual.

U.S.G.S. National Water Quality Laboratory, Format for SOP – Laboratory Analytical Method.

WinLab32 for ICP software v 3.1.0.0107

WinLab32 Data Management software v 3.1.0.0107

10. Key words

Inductively coupled plasma, optical emission spectrometry, water samples, calcium, magnesium, aluminum, silicon, sodium, potassium.