

Standard Operating Procedure for the
Analysis of Cations in Fresh Waters by Flame
Atomic Absorption Spectrometry
CCAL 60A.0

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1.0 Scope and Application

- 1.1 This method covers the direct determination of sodium, potassium, calcium, magnesium, iron, manganese, strontium and barium in fresh waters. Detection limits at element specific wavelengths are reported in the table below.

	Wavelength	MDL (mg/L)	Flame Gases
Barium	553.6	0.2*	N-Ac
Calcium	422.7	0.06*	N-Ac
Iron	248.3	0.06	A-Ac
Potassium	766.5	0.03	A-Ac
Magnesium	285.2	0.02	A-Ac
Manganese	279.5	0.02	A-Ac
Sodium	589	0.01	A-Ac
Strontium	460.7	0.02*	N-Ac

A-Ac = air-acetylene; N-Ac = nitrous oxide-acetylene

2.0 Summary of Method

- 2.1 In flame atomic absorption spectrometry, water is atomized by aspiration into a flame. A light beam is directed through the flame to a monochromator, and then to a detector that measures the amount of light absorbed by the sample at a specific wavelength, determined by the element of interest. Absorbance of samples is compared with that of known standard concentrations to determine sample concentration.

3.0 Definitions

- 3.1 DI water: Water that has been through a deionization system to produce water similar to ASTM Type I reagent with 16.7 Mohms resistivity (ASTM) (Reference 16.3).
- 3.2 Method Detection Limit (MDL): The minimum concentration of an analyte that can be measured and reported with 99% confidence, based on

a one-sided 99% confidence interval (t -value at a significance level of 0.01 and $n-1$ degrees of freedom) from at least seven repeated measurements of a low concentration standard measured within an analysis run.

$$\text{MDL} = ts$$

Where,

t = Student's t value at a significance level of 0.01 and $n-1$ degrees of freedom

s = standard deviation of at least seven repeated measurements of a low level standard

3.3 FAAS: Flame Atomic Absorption Spectrometer

4.0 Interferences

4.1 Chemical Interference

4.1.1 Lack of dissociation of the molecules, or dissociation to a molecule that will not dissociate further at the flame temperature. This effect may be reduced by addition of lanthanum, or by using the higher-temperature nitrous oxide-acetylene flame. The nitrous oxide-acetylene flame may also minimize some chemical interferences encountered in air-acetylene flame (e.g. phosphate interference in the determination of calcium).

4.1.2 Ionization may reduce the ground state (potentially absorbing) population. Addition of potassium (or other lower ionization potential cation) will overcome the problem.

4.2 Molecular absorption and light scattering by solid particles in the flame can result in erroneously high absorption. Continuum-source background correction may be used to overcome the effect.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent has not been precisely determined; however, each chemical should be regarded as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Cautions are included for known extremely hazardous materials.

5.2 The following chemicals have the potential to be highly toxic or hazardous. For detailed explanations, consult the MSDS.

- 5.2.1 Nitric acid
 - 5.2.2 Hydrochloric acid
 - 5.2.3 Lanthanum Oxide
 - 5.2.4 Nitrous Oxide
 - 5.2.5 Acetylene
- 5.3 Hazards associated with compressed gases may include asphyxiation, toxic exposure, fire and explosion, in addition to the physical hazards related to working with high pressure systems. Storage, use and handling precautions are required.

6.0 Equipment and Supplies

Note: *Brand names, suppliers and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

- 6.1 Varian SpectrAA 220 System
 - 6.1.1 Varian SPS 5 Autosampler
 - 6.1.2 Instrument Controller
 - 6.1.3 SpectrAA Data Collection Software
 - 6.1.4 MK7 Burner Heads for Air-C₂H₂ and N₂O/Air-C₂H₂
 - 6.1.5 Ion Specific Lamps
- 6.2 Acetylene gas (PrePure Grade) and dual-stage regulator
- 6.3 Nitrous Oxide gas and heated dual-stage regulator
- 6.4 Compressed Air supply (compressor with dual-stage regulator and moisture traps; minimum 40 psi)
- 6.4 Laboratory glassware and pipettes
- 6.5 Balance
- 6.6 Safety glasses
- 6.7 Nitrile gloves
- 6.8 Lab coat or apron
- 6.9 Laboratory exhaust fume hood
- 6.10 High Density Polyethylene (HDPE) bottles
- 6.11 Autosampler vials

7.0 Reagents and Standards

7.1 Preparation of Reagents

7.1.1 *Lanthanum Solution, 50 g La/L*

Add 58.64 g reagent grade lanthanum oxide to a 1-L volumetric flask. Wet with approximately 50 mL DI water.

Caution: Violent Reaction

Very slowly, and in small increments, add 250 mL concentrated hydrochloric acid to the flask and swirl gently to dissolve. Once dissolution is complete, slowly add DI water and fill to the mark. Add 1 mL of lanthanum solution to 10 mL of sample.

7.1.2 *Potassium Solution, 131 g K/L*

Add 250 g reagent grade potassium chloride to a 1-L volumetric flask and dilute to the mark with DI water. Add 2 mL of potassium solution to 100 mL of sample.

7.1.3 *Nitric Acid Rinse Solution, 5% v/v HNO₃*

To approximately 800 mL of DI water in a 1-L volumetric flask, add 50 mL concentrated nitric acid. Fill to the mark with DI water.

7.2 Preparation of Standards

7.2.1 *Calibration Standards:*

Standards are prepared by serial dilution of single element standards purchased from vendors that provide traceability to National Institute of Standards and Technology (NIST) standards.

Standard #	Ba mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L	Sr mg/L
1	5.0	3.00	0.50	0.50	0.50	0.50	1.00	0.05
2	10.0	6.00	1.00	1.50	1.00	1.00	3.00	0.10
3	15.0	10.00	2.00	3.00	1.50	2.00	6.00	0.15

7.2.2 *Check Standard:*

Standards are prepared by serial dilution of single element standards purchased from vendors that provide traceability to NIST standards. Standards are run at the beginning (check 1), middle (check 2) and end (check 3) of each analysis.

Standard #	Ba mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L	Sr mg/L
Check 1	5.0	1.50	0.25	0.25	0.25	0.25	0.50	0.03
Check 2	10.0	5.00	0.75	1.00	0.80	0.75	2.00	0.06
Check 3	15.0	8.50	1.50	2.50	1.20	1.50	5.00	0.12

8.0 Sample Handling and Storage

- 8.1 If required, unfiltered samples are filtered upon receipt through glass fiber filters into clean HDPE bottles and stored at 4°C in the dark. If samples must be held prior to analysis, they are stored frozen at -18°C.
- 8.2 CCAL does not use the addition of chemical stabilizers, unless specifically requested.

9.0 Quality Control

- 9.1 Preparation of stock standards is recorded on worksheets and documented by weight of standard added to a given flask before dilution to volume with DI water. All records of certification are kept on file at CCAL Laboratory.
- 9.2 Blank: DI water run before and after the calibration, and after every check standard.
- 9.3 Check Standard: Run beginning, middle and end of run to monitor drift and calibration.
- 9.4 Method Detection Limit (MDL): Established for each analyte. Based on a one-sided 99% confidence interval (t-value) from at least seven repeated measurements of a low concentration standard. The t-distribution value is multiplied by the standard deviation of the population (n-1) to obtain the MDL.
- 9.5 Analytical Duplicate: Separate analysis from the same sample aliquot. One per ten samples.
- 9.6 Quality Control Check Sample (QCCS); filtered bulk sample, run once every analysis batch.
- 9.7 Standard recoveries and QCCS results are tracked over time to monitor overall performance.
- 9.8 Samples with concentration greater than the highest calibration standard are diluted and reanalyzed.

10.0 Calibration and Standardization

- 10.1 Balances: calibrated yearly by external vendor.
- 10.2 Pipette delivery checked daily by weight to within 2% of theoretical weight of aliquot volume.

10.3 The FAAS is calibrated every analysis run. The SpectrAA software is setup to use new rational curve fit of three working standards (see section 7.2). The r^2 value of each calibration curve should be greater than 0.995.

10.4 Check standard recoveries must be within 10% of theoretical value.

11.0 Procedure

11.1 Varian SpectrAA 220 Instrument Operating Parameters

Table 11.1

Acetylene Gas Pressure:	
tank pressure	>100 psi
flow pressure	12.5 psi
Nitrous Gas Pressure:	
tank pressure	Enough to maintain flow
flow pressure	50 psi
Air Supply:	
compressor	40 psi

11.2 Method Settings

	Support/ Fuel	Wave length (nm)	Slit, nm	Lamp Current (mA)	CCAL MDL	Additive	Comment
Ca	N2O/ C2H2	422.7	0.5	10	0.06	La2O3	
Mg	Air/ C2H2	285.2	0.5	4	0.02	none	
Na	Air/ C2H2	589	0.5	10	0.01	none	
K	Air/ C2H2	766.5	1	10	0.03	none	
Mn	Air/ C2H2	279.5	0.2	10	0.02	none	
Fe	Air/ C2H2	248.3	0.2	10	0.06	none	
Ba	N2O/ C2H2	553.6	0.5	20	0.2	KCl	
Sr	N2O/ C2H2	460.7	0.5	10	0.02	KCl	
Mg	N2O/ C2H2	285.2	0.5	4	0.02	KCl	rarely used
Ca	N2O/ C2H2	422.7	0.5	10	0.06	KCl	rarely used

11.3 Procedure

- 11.3.1 Turn on the instrument, computer and ventilation.
- 11.3.2 Open the software and start the method or set up a new method using the parameters listed in tables 11.1, 11.2 and standard values in table 7.2.1.
- 11.3.3 Install correct burner hear for the method and turn on the lamp. Check positioning of the burner head.
- 11.3.4 Turn on the gases and light the flame; aspirate DI water when flame is on.
- 11.3.5 Let the instrument and lamp warm up for 20 – 30 minutes.
- 11.3.6 Zero the instrument with DI water, and optimize operating variables for maximum response while aspirating standard #1 (lowest concentration calibration standard). Then turn the burner head to obtain approximately 0.2 absorbance.
- 11.3.7 Run the calibration using New Rational fit. Recalibrate if $r < 0.995$.
- 11.3.8 Analyze samples. Verify that check standards and duplicates are within acceptance limits.
- 11.3.9 When analyses are complete for the day, aspirate Nitric Acid Rinse Solution for 5 minutes.

11.4 System Notes

- 11.4.1 Yearly preventative maintenance as suggested by the manufacturer is required for optimum performance.
- 11.4.2 The nitrous oxide-acetylene burner head needs to be cleaned every day. Build up of residue on the burner head may require sonication, nitric acid soak, and treatment with metal cleaner (e.g Brasso).

12.0 Data Analysis and Calculations

- 12.1 The SpectrAA software prepares a standard curve by plotting standard response against known concentration. Sample response is compared to the standard curve to determine concentration.
- 12.2 Samples with concentration greater than the highest calibration standard are diluted and reanalyzed.

13.0 Method Performance

- 13.1 This method was validated through inter-laboratory studies. The CCAL participates in the USGS Standard Reference Water QA program.

14.0 Pollution Prevention

- 14.1 The chemicals used in this method pose little threat to the environment when properly managed.
- 14.2 All standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of disposable waste.
- 14.3 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

15.0 Waste Management

- 15.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, and to protect the environment by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required.
- 15.2 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington DC, 20036.

16.0 References

- 16.1 Standard Methods For The Examination of Water and Wastewater, Method 3111; Metals By Flame Atomic Absorption Spectrometry. American Public Health Association. 21st Edition, 2005.
- 16.2 Code of Federal Regulations. Protection of Environment. Section 40, Appendix B to Part 136. Definition and procedure for the determination of the method detection limit. Revision 1.11. Revised July 1, 1990. Office of the Federal Register, National Archives and Records.
- 16.3 ASTM. American Society for Testing and Materials. Standard Specifications for Reagent Water. D1193-77 (Reapproved 1983). Annual Book of ASTM Standards, Vol. 11.01. ASTM: Philadelphia, PA, 1991.
- 16.4 Varian Instrument Users Manuals. Varian, Inc. www.varianinc.com.

- 16.5 US EPA, January 1998, Revision 2. "Flame Atomic Absorption Spectrometry", Method 7000B, SW-846, US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.
- 16.6 D.T.E. Hunt and A.L. Wilson. "The Chemical Analysis of Water; General Principles and Techniques"; Royal Society of Chemistry; Burlington House, London; Second Edition, 1986.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

- 17.1 NA