Standard Operating Procedure for the Analysis of Cations in Fresh Waters by Flame Atomic Absorption Spectrometry

CCAL 60B.3

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1.0 Scope and Application

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

	Wavelength	MDL (mg/L)	Flame Gases
Calcium	422.7	0.06	A-Ac
Iron	248.3	0.06	A-Ac
Magnesium	285.2	0.02	A-Ac
Manganese	279.5	0.02	A-Ac
Potassium	766.5	0.03	A-Ac
Sodium	589.0	0.01	A-Ac

A-Ac = air-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.

$$\mathrm{MDL} = ts$$

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 Shimadzu AA-7000F FAAS

6.1.1 Shimadzu ASC-7000 Autosampler
6.1.2 Instrument Controller
6.1.3 WizAArd Data Collection Software
6.1.4 Burner Heads for Air-C_2H_2 and N_2O/Air-C_2H_2
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

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

6.12 Gas Purifier and Flashback Arrestor

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 #	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L
0	0	0	0	0	0	0
1	1.50	1.00	0.25	0.50	0.50	0.50
2	3.00	2.00	0.50	1.00	1.00	1.00
3	5.00	3.00	1.00	1.50	2.00	2.00
4	6.00		1.50	2.00		3.00
5	8.50		2.50	3.00		5.00
6	10.00		3.00			6.00

7.2.2 *Check Standard:*
Standards are prepared by serial dilution of single element standards purchased from vendors that provide traceability to NIST standards. A check standard is analyzed every ten samples.

Standard #	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L
Check 1	1.50	0.50	0.25	0.25	0.25	0.50
Check 2	5.00	1.50	1.00	1.25	0.75	2.00
Check 3	8.50	2.50	2.50	2.50	1.50	5.00

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 more than 30 days prior to analysis, they are stored frozen at -15ºC.

8.2 CCAL does not use the addition of chemical stabilizers, unless specifically requested, except in analysis of iron. For samples requiring iron analysis, 100uL ultrapure hydrochloric acid is added to 50 mL of sample.

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 between samples as a rinse, and after check standards to monitor baseline signal.

9.3 Check Standard: Run every ten samples. The check standard is from a source or lot other than that of the calibration standard.

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 QCCS results are used to create control charts, and 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 1% of theoretical weight of aliquot volume.

10.3 The FAAS is calibrated every analysis run. The WizAArd software is setup to use second order curve fit of three or more 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 Shimadzu AA-7000 Instrument Operating Parameters

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	60 psi

11.2 Method Settings

	Support/ Fuel	Wave length (nm)	Slit, nm	Lamp Current (mA)	Fuel Rate (L/min)	CCAL MDL	Additive	Comment
Ca	Air/ C2H2	422.7	0.7	3	2	0.06	La2O3	
Mg	Air/ C2H2	285.2	0.7	5	1.8	0.02	La2O3	
Na	Air/ C2H2	589	0.2	10	1.8	0.01	none	
K	Air/ C2H2	766.5	0.7	10	2	0.03	none	
Mn	Air/ C2H2	279.5	0.2	4	2	0.02	none	
Fe	Air/ C2H2	248.3	0.2	6	2.2	0.06	none	
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 verify 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 head 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.
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 an absorbance of approximately 0.2.
11.3.7 Run the calibration using second order 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 WizAArd 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.

12.3 To determine total hardness using concentrations of calcium and magnesium in mg/L:

Total Hardness = (Ca x 2.497) + (Mg x 4.118), final units as equivalents $CaCO_3$

13.0 Method Performance

13.1 This method was validated through inter-laboratory studies. The CCAL Water Analysis Laboratory participates in the USGS Standard Reference Water QA Proficiency Testing (PT) 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: Guide to Minimizing Waste in Laboratories*, available from the American Chemical Society at www.acs.org.

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 *Less is Better: Guide to Minimizing Waste in Laboratories*, available from the American Chemical Society at www.acs.org, and *Environmental Management Guide For Small Laboratories* (233B00001) from the US Environmental Protection Agency at https://nepis.epa.gov.

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 Shimadzu Instrument Users Manuals. Shimadzu Corp. http://shimadzu.com.

16.5 US EPA, January 1998, Revision 2. "Flame Atomic Absorption Spectrometry", Method 7000B, SW-846, US Environmental Protection Agency, Office of Solid Wate 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

18.0 Document Revision History

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Address update
Section 13.1: add Environment Canada Proficiency Testing Program participation.

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Section 8.1: add hold time
Section 9.2 edit blank run frequency
Section 11.2: update method settings
General editing throughout

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New Version: 60B.3
Section 1, 7 & 11: remove strontium, barium and associated references
Section 7: update magnesium calibration standard concentrations
Section 8: add preservation for iron samples
Section 12: add hardness calculation
Section 13: remove NWRI participation
General editing throughout