Abstracted from Laboratory Operations, Pg. 82, Section 4.5.8. Calcium, Magnesium, Sodium, and Potassium by Inductively Coupled Plasma-Atomic Emission Spectroscopy
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Calcium, Magnesium, Sodium and Potassium by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

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Table 4.29. Typical wavelength selection for ICP-AES

Analyte	Typical Wavelength (nm)	Concentration Range (mg L^{-1})	Typical Wavelength (nm)	Concentration Range (mgL^{-1})
Calcium	393.366	<1.000	315.887	> 1.000
Magnesium	279.553	All		
Potassium	766.491	<0.500	769.897	>0.500
Sodium	589.592	<0.500	588.995	>0.500

Reagents and Solutions

i. The purity of water used for dilution is highly important. Use only filtered DI water (resistivity >18.0 MΩ).
ii. liquid argon
iii. nitric acid at various concentrations for cleaning the torch
iv. Triton-X 100 for cleaning the spray chamber

Calibration

Stock standard solutions generally are purchased commercially:

i. yttrium (1000 mg L^{-1}, 250 mL in 2% HNO3)
ii. cesium chloride (100 g)
iii. calcium (1000 mg L^{-1}, 250 mL in 2% HNO3)
iv. magnesium (1000 mg L^{-1}, 250 mL in 2% HNO3)
v. sodium (1000 mg L^{-1} ppm, 250 mL in 2% HNO3)
vi. potassium (1000 mg L^{-1}, 250 mL in 2% HNO3)

Stock standard solutions must come with a certificate of analysis. Each solution must be pre-tested to ensure purity. For example, magnesium stock standard solution must not contain calcium, sodium or potassium. The presence of any of these other elements will contaminate the intermediate stock solution, where all the elements are combined from measured portions of stock standard solutions.

Prepare a dilution of the new stock standard solution and analyze it as an unknown by using old calibration standards to calibrate the instrument.

i. Into a rinsed weigh boat dispense 1 gm of new stock standard solution.
ii. Pour this solution into a clean, rinsed and calibrated 1 L volumetric flask. See Appendix C for details concerning calibration of glassware.
iii. Using Type I DI water, rinse weigh boat into the flask and fill the flask to the 1 L mark.
iv. Mix well and allow solution to equilibrate for at least one hour.

v. Analyze this diluted new stock standard solution using the old calibration set.
vi. Measurements should fall within the expected range of precision around 1.000 mg L^{-1}. There must be no other alkali or alkaline earth metals evident in each stock standard solution.
vii. If this diluted stock standard solution fails to meet the 1.000 mg L^{-1} QC specification, discard the solution and start the preparation again. Ensure that the solution has rested for one hour before analysis. If a second preparation fails or if other elements are present, do not use this stock standard solution. Discard it or, if possible, return it to the vendor.

Intermediate Stock Solutions

New flasks and bottles used as containers for intermediate stock solutions must be conditioned. This is done by soaking them in DI water over night, then rinsing them three times with DI water and drying them in a warm oven. This conditioning only needs to be done the first time that new containers are put into service. See Appendix C for calibration procedures for flasks and procedures for storing glassware. Also see Appendix C for analytical balance calibration details.

1) Start with a 1 L volumetric flask that has been calibrated and is to be used for this purpose only. Calibrate this flask by dispensing DI water by weight into the flask and then marking the flask at the fluid line.

2) Next, weigh a stock standard solution in the amount listed in Table 4.30 (to the 4th decimal place) in a weigh boat that has been rinsed with DI water. Transfer the weighed stock standard solution from the weigh boat into the calibrated 1 L volumetric flask.

3) Rinse the weigh boat three times with DI water and transfer each of the three rinses into the volumetric flask.

4) Repeat this procedure for each of the four stock standard solutions, combining the solutions into the same calibrated 1 L volumetric flask.

5) Record the exact weights of stock solutions used in the ICP-AES Intermediate Stock and Calibration Standards logbook. Add DI water to dilute the contents of the flask to the 1 L fluid line.

Table 4.30. ICP Intermediate Stock Requirements and Final Concentrations in a 1 L flask (CAPMoN, 2013)

Analyte	Required Stock Volume (mL)	Examples of Actual Volume used (mL)	Concentrations in final 1 L solution (mg L^{-1})
Mg^{2+}	50	50.0009	50.0009
Ca^{2+}	50	50.0005	50.0005
Na^{+}	50	50.0007	50.0007
K^{+}	50	50.0004	50.0004

Calibration Standards

1) Weigh all volumes using an analytical balance. Rinse all weigh boats thoroughly. Use conditioned HDPE bottles that are dedicated for use in storing calibration standards. Do not use bottles from other procedures.

2) Starting with Standard 9 in Table 4.31, prepare the calibration standards by diluting the required volumes listed in the table to 500 mL with DI water. Weigh the required volumes as close as possible to the amounts listed in the table. Record the exact weights in the ICP-AES Intermediate Stock and Calibration Standards Logbook.

3) Prepare fresh calibration standards every four months or as required.

Table 4.31. ICP Calibration Standards Prepared by Diluting the Required Volumes to 500 mL for each standard (CAPMoN, 2013)

Standard	Concentration (mg L^{-1})	Required Volume (mL)	Stock Used
Standard 9	5.000	50	Intermediate stock
Standard 8	3.000	30	Intermediate stock
Standard 7	1.500	15	Intermediate stock
Standard 6	1.000	10	Intermediate stock
Standard 5	0.500	5	Intermediate stock
Standard 4	0.250	2.5	Intermediate stock
Standard 3	0.100	1	Intermediate stock
Standard 2	0.050	25	Standard 6
Standard 1	0.015	7.5	Standard 6

Table 4.32. ICP Range of Operation

Analyte	Concentration Range (mg L^{-1})
Calcium	0.005 to 5.000
Magnesium	0.005 to 3.000*
Potassium	0.005 to 3.000*
Sodium	0.005 to 5.000

*Magnesium and potassium standard curves may be extended to 5.000 ppm. These two analytes tend to have low concentrations in precipitation. Magnesium concentrations may be high in marine locations due to sea salt and potassium concentrations may be high at some continental locations due to organic matter. Adding the 5.000 ppm standards for magnesium or potassium may result in greater imprecision at lower concentrations. Most software will allow the user to select which standards are needed for the calibration curve.

Yttrium (Y) and Cesium Chloride (CsCl) Solutions (CAPMoN, 2013)

1) Weigh out 10.1 g of CsCl powder and transfer it into a calibrated 1 L volumetric flask that is not used for any other purpose. Note the exact weight of CsCl to the first decimal place in the ICP-AES Intermediate Stock and Calibration Standards Logbook. Rinse the weigh boat three times with DI water and transfer the rinse into the flask. Note the lot number of CsCl in the logbook.

2) Weigh out 8.8000 g of Y solution and transfer it into the <u>same</u> volumetric flask that contains the CsCl powder. Note the exact weight of Y solution to the 4th decimal place in the logbook. Rinse the weigh boat three times with DI water and transfer each rinse into the flask. Note the lot number of Y stock solution in the logbook.

3) Mix the solution until all CsCl is dissolved. Bring the final volume to the calibration line while swirling the flask. Stopper the flask and mix by inversion.

4) Transfer the solution into a 1 L HDPE bottle reserved for this solution. The solution is kept at room temperature and is stable for six months.

Quality Control

Prepare a minimum of three QC solutions to test the calibration curve and validate sample results. It is best if one of these solutions is in the low end of the concentration range, one in the middle of the range, and one in the high end of the range. When possible, it is best to use a natural precipitation matrix; however, stock standard solutions also may be used.

QC Solutions – Precipitation Matrix

1) Save low-concentration precipitation samples that have been analyzed and the results reported. Pool this "excess precipitation" in one 10 L HDPE container.

2) Save mid-concentration precipitation samples that have been analyzed and the results reported. Pool this "excess precipitation" in one 10 L HDPE container.

3) Save high-concentration precipitation samples that have been analyzed and the results reported. Pool this "excess precipitation" in one 10 L HDPE container.

4) Analyze the pooled samples to determine the initial alkali and alkaline earth metal concentrations.

5) Adjust the concentrations of the mid- and high-concentration pooled samples, if necessary, to ensure that the concentrations are approximately in the mid to high range of the calibration curve. Adjustments can be made by adding measured portions of the 1000 mg L^{-1} stock standard solutions. Similarly, it may be necessary to dilute the low-concentration pooled sample with DI water to achieve the low range of the calibration curve.

6) See Appendix C for sterilization of QC solutions and additional details.

Run QC solutions promptly after completing calibration of the ICP-AES and every ten samples thereafter. Plot the results on a control chart.

Procedures

1) Turn on the sample changer, the pump and the ICP-AES. Turn on the personal computer and open the software for the instrument and for the sample changer.

2) Perform daily maintenance. Check the argon levels and ensure there is enough for a full run. Check the yttrium/cesium solution levels. Change the DI flush water in the sample changer daily.

3) Turn on the Radio Frequency (RF) Oscillator Circulator.

4) Ensure that the coolant gas, auxiliary (Aux) gas, nebulizer gas, pump speed and RF parameters are set according to the manufacturer's recommendations. Here are some suggested settings:

   a. coolant gas: 19 LPM
   b. Aux gas: 0.3 LPM for ignition, Aux gas 0.00 for analysis
   c. nebulizer gas: 1.2 LPM
   d. pump speed: 1.2 mL min^{-1}
   e. plasma control: 0.9 kW

5) Check that all interlocks and safety features are met and secure.

6) Light the plasma. The instrument must stabilize for 20 minutes (or to manufacturer recommendations) with the plasma on.

7) Run a sequence of water blanks until the response for Y, the internal standard, has stabilized. If the Y response does not stabilize, the Y solution (internal standard) may need to be replaced. Another corrective action to stabilize the Y response is to rinse and drain the peristaltic pump tubing.

8) Run a complete calibration sequence followed by all three QCSs. Continue with precipitation samples only after the instrument is stable and it has been successfully calibrated.

9) Pour 4 to 5 mL aliquots of all QC and precipitation samples into sample tubes and fill in the sampler racks. Determine the minimum volume the system needs for a successful analysis and ensure that the volume in each tube meets this minimum.

10) After all standards have been run, re-cap respective lids on all standards.

11) Following the run, check all calibration curves and QC results before reporting, collating or tabulating results.

12) Check all raw data individually for correct integration and output. Comment on all anomalies in the laboratory notebook and flag data accordingly.

13) Calculate results against the appropriate calibration curve and apply detection limits and correct decimal places as required. Mark all samples that exceed upper calibration ranges for dilution and repeat analysis. Ensure missing samples are accounted for and contamination codes are applied as needed.

14) Export data from the ICP-AES system software and archive all parameters associated with the analysis, including calibration data, raw data, and instrument audit trails. Audit trails include instrument performance throughout the analytical run and any information that may be useful in diagnosing a problem, such as a drifting baseline. It may be necessary to repeat the analysis at the point where the problem began.

Troubleshooting

Problem 1: Output and results are unstable.
Solution 1: Increase the plasma stabilization time. Also, check for fluctuations in room temperature. The instrumental response of the ICP-AES is affected by swings in room temperature. The ICP-AES laboratory may need supplemental air conditioning to stabilize the room temperature.

Problem 2: Contamination of the sample and/or signal
Solution 2: ICP-AES is much more sensitive than flame atomic absorption spectrophotometry, thus laboratory cleanliness is very important. Be aware of possible contamination from overhead ventilation or dirt from shoes or clothing. The instrument operator must wear a lab coat and shoes that are worn only in the ICP-AES lab. If the operator also performs other analyses, e.g., flow injection analyses, the lab coat worn for other analyses must not be worn to perform ICP-AES analysis. Also, it is important to clean the torch and spray chamber regularly.

Problem 3: The quality of the results declines throughout the analytical run.
Solution 3: The tubing in systems equipped with a peristaltic pump is susceptible to wear. Consider purchasing a FAST^{TM} system if this is a recurring problem. FAST^{TM} systems use a vacuum to move the sample from the sample tube into the injection loop. Several generic models of the FAST^{TM} system are available but make sure the system is compatible with the instrumentation and software.

Problem 4: Sudden drop in concentration or poor agreement with duplicate or triplicate measurements
Solution 4: Check the sample lines for blockage.

Problem 5: Deterioration of internal standard readings
Solution 5: Check the peristaltic pump tubing for wear. Change the tubing. Establish a maintenance program that prevents problems due to excess wear from ever occurring.

Tips to Improve Performance

1) Keep a log book that documents maintenance procedures.
2) Maintain a record of the preparation of calibration solutions. Record details, such as the dates of preparation, weights, volumes, calculations, and the person who prepared the solutions.
3) Use only dedicated glassware and containers for calibration solutions. Do not use these containers for any other purpose.
4) Clean the ICP-AES spray chamber and torch weekly or according to the workload.
5) Track the potential impact of instrument maintenance, changes in calibration solutions or the use of new reagents by specially marking these events on quality control charts.
6) Do not operate other instruments in the ICP-AES area. ICs that have KOH and carbonate eluents can be sources of contamination. Flow injection analysis systems must be kept in a room completely separate from the ICP-AES.
7) Keep the area clean. Dust and residue are serious contaminants for this analysis. Make sure the ICP-AES is installed in an area where there is minimal foot traffic.
8) Place tack mats on the floor in the doorway to the ICP-AES laboratory. Keep dirt from other areas out of the ICP-AES lab space.
9) Wear a lab coat and don't wear the lab coat used in the ICP-AES laboratory in other laboratories.
10) Wear a pair of shoes that have not been worn outside. Be careful not to track soil into the ICP-AES laboratory.
11) During an analytical run, cover the sample tray with a dust shield.
12) Do not run other samples, such as hard water samples or lake or stream water samples, before running precipitation samples without thoroughly cleaning the system.
13) If the ambient laboratory temperature is not stable, use a dedicated air conditioner to stabilize the temperature in the ICP-AES laboratory; however, be sure to avoid drafts near the instrument.
14) Avoid finger contact with the rims of test tubes. Wear clean, pre-tested gloves if necessary.
15) Use liquid argon. Two tanks can be set up side by side. Install an inline switch so that when one tank is empty, the next tank is ready.

References

CAPMoN. (2013, July). Dissolved Calcium, Magnesium, Sodium and Potassium in Precipitation and on Teflon® Membranes using Inductively Coupled Plasma-Atomic Emission Spectroscopy. *Canadian Air and Precipitation Monitoring Network National Laboratory Standard Operating Procedure SOP 5*. Toronto, ON, Canada.