Abstracted from Laboratory Operations, Pg. 53, Section 4.5.9. Calcium, Magnesium, Sodium, Potassium, and Ammonium by Ion Chromatography
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# Calcium, Magnesium, Sodium, Potassium, and Ammonium by Ion Chromatography

**Go To: Calibration, Quality Control, Procedures, Troubleshooting**

*Table 4.33. IC Operating Range for Cations in Precipitation.*

| Analyte | Concentration Range (mg $L^{-1}$) |
|---|---|
| Sodium | 0.005 to 5.00 |
| Potassium | 0.010 to 3.00 |
| Calcium | 0.020 to 5.00 |
| Magnesium | 0.010 to 3.00 |
| Ammonium | 0.010 to 5.00 |

### Calibration

### Reagents and Solutions

i. Ultra-pure Type I DI water (resistivity >18MΩ).
ii. Eluent Generator Cartridge Methanesulfonic Acid (MSA)

### Stock standard solutions

Stock standard solutions containing 1000 mg $L^{-1}$ of each sodium, potassium and ammonium ion may be purchased as certified solutions from different manufacturers or prepared from high purity salts that are dried at 105ºC for an hour, dissolved and diluted to 1000 mL as listed in Table 4.34.

Calcium and magnesium 1000 mg $L^{-1}$ solutions are available in 2% nitric acid. See ICP-AES section 4.5.8 for details.

New flasks and bottles for storing stock standard solution must first be conditioned by soaking in DI water over night, then rinsed with DI water three times and dried in a warm oven. Conditioning of flasks and bottles only needs to be done once when the containers are new and before putting them into service. See Appendix C for calibration of flasks and balances and for glassware storage conditions.

1) It is highly recommended that standard solutions be prepared by dispensing the volumes by weight and calibrating all receiving flasks. Flasks may be calibrated by dispensing DI water by weight into the flask and then marking the flask at the fluid line.

2) Weigh all volumes using an analytical balance. Rinse all weigh boats thoroughly. Use conditioned HDPE bottles to store stock standard solutions. Use glassware and bottles that are dedicated solely to standard solution preparation and storage.

3) Make three stock standard solutions: NaCl, $(NH_4)_2SO_4$ and $KNO_3$, each with a concentration of 1000 mg $L^{-1}$. Table 4.34 lists the required salt masses. Weigh each salt carefully into a calibrated and conditioned 1 L volumetric flask. Mix and store in designated, conditioned HDPE flasks. Solutions are stable for one year.

4) To ensure consistency between old and new stock standard solutions, prepare a dilution of the new stock standard solution and analyze it as an unknown by using old calibration standards as calibrators. Here is a step-by-step procedure:

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.
iii. Using Type I DI water, rinse the 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 stock standard solution but use the old standard solutions to calibrate the instrument.
vi. Measurements should fall within the expected range of precision around 1.00 mg $L^{-1}$. If so, transfer the full strength 1000 mg $L^{-1}$ stock standard solution into an HDPE flask and store at 4°C. If this QC specification is not met, discard this stock standard solution and begin the preparation again. Be sure to allow the solution to equilibrate for an hour before analysis.

*Dispensing large volumes of stock solution to make working calibration standards is a more accurate procedure than dispensing more concentrated stock solutions in small volumes.*

*Table 4.34. Cation Stock Standard Solutions. The salt masses specified result in 1000 mg $L^{-1}$ of $Na^{+}$, $K^{+}$ and $NH_4^{+}$). Final volume is 1 L.*

| Salt | Weight (g) |
|---|---|
| **NaCl** | 2.542 |
| **KNO3** | 2.586 |
| **$(NH_4)_2SO_4$** | 3.663 |

**Low Working Standard1**

1) Prepare Low Working Standard 1 (L-Std 1) by dispensing each stock standard solution by weight into a calibrated, conditioned 1 L volumetric flask. The volumes are specified in table 4.35. Dilute to 1 L with DI water.

*Table 4.35. Preparation of L-Std 1*

| Low Std. # | Solution | $Na^{+}$ (mL) | $K^{+}$ (mL) | $NH_4^{+}$ (mL) | $Ca^{2+}$ (mL) | $Mg^{2+}$ (mL) | Final Volume (mL) |
|---|---|---|---|---|---|---|---|
| 1 | Each stock standard | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 1000 |

2) Use L-Std 1 to prepare low-range working standards 2 through 5 (Table 4.37). Flasks must be conditioned, calibrated and designated for L-Std 1.

**High Working Standard1**

1) Prepare High Working Standard 1 (H-Std 1) by dispensing each stock standard solution by weight into a calibrated, conditioned 1 L volumetric flask. The volumes are specified in table 4.36. Dilute to 1 L with DI water.

*Table 4.36. Preparation of H-Std 1*

| High Std. # | Solution | $Na^{+}$ (mL) | $K^{+}$ (mL) | $NH_4^{+}$ (mL) | $Ca^{2+}$ (mL) | $Mg^{2+}$ (mL) | Final Volume (mL) |
|---|---|---|---|---|---|---|---|
| 1 | Each stock standard | 5.000 | 3.000 | 5.000 | 5.000 | 3.000 | 1000 |

2) Use H-Std 1 to prepare high-range working standards 2 through 5 (Table 4.38). Flasks must be conditioned, calibrated and designated for H-Std 1.

*Table 4.37. Low-Range Cation Working Calibration Standards*

| Low Std. # | Solution | Volume (mL) | Final Volume (mL) | $Na^{+}$ (mg $L^{-1}$) | $K^{+}$ (mg $L^{-1}$) | $NH_4^{+}$ (mg $L^{-1}$) | $Ca^{2+}$ (mg $L^{-1}$) | $Mg^{2+}$ (mg $L^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 | stock | | | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 |
| 2 | L Std. 1 | 125 | 250 | 0.250 | 0.250 | 0.250 | 0.250 | 0.250 |
| 3 | L Std. 1 | 50 | 250 | 0.100 | 0.100 | 0.100 | 0.100 | 0.100 |
| 4 | L Std. 1 | 25 | 250 | 0.050 | 0.050 | 0.050 | 0.050 | 0.050 |
| 5 | L Std. 1 | 10 | 250 | 0.020 | 0.020 | 0.020 | 0.020 | 0.020 |

*Table 4.38. High-Range Cation Working Calibration Standards*

| High Std. # | Solution | Volume (mL) | Final Volume (mL) | $Na^{+}$ (mg $L^{-1}$) | $K^{+}$ (mg $L^{-1}$) | $NH_4^{+}$ (mg $L^{-1}$) | $Ca^{2+}$ (mg $L^{-1}$) | $Mg^{2+}$ (mg $L^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 | Stock | | | 5.000 | 3.000 | 5.000 | 5.000 | 3.000 |
| 2 | H Std. 1 | 200 | 250 | 4.000 | 2.400 | 4.000 | 4.000 | 2.400 |
| 3 | H Std. 1 | 100 | 250 | 2.000 | 1.200 | 2.000 | 2.000 | 1.200 |
| 4 | H Std. 1 | 50 | 250 | 1.000 | 0.600 | 1.000 | 1.000 | 0.600 |
| 5 | H Std. 1 | 25 | 250 | 0.500 | 0.300 | 0.500 | 0.500 | 0.300 |

*IC system software should be capable of addressing low and high calibration ranges in one analytical run.*

*Run all samples in the low calibration range and for values above the low range, use the high calibration range. Dilute only those samples that have values above the high range.*

**Working Standard Solutions**

A minimum of five working calibration standard solutions per curve is recommended. IC curves are not linear and often do not go through zero. Most IC workstations allow for an unlimited number of standards. By preparing low calibration (Table 4.37) and high calibration (Table 4.38) IC curves, the potential for biases due to this non-linearity is minimized. See Figure 4.35 for calibration curves for sodium.

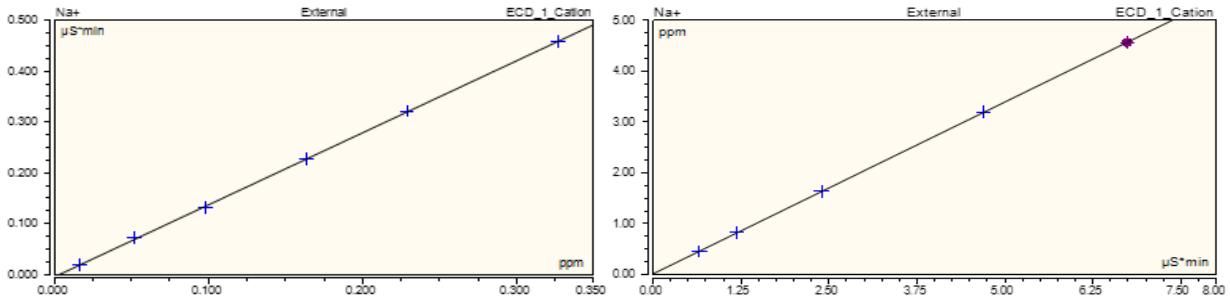


*Figure 4.35. Calibration curves for low- and high-level sodium, resp. Linearity is good in both ranges.*

Standard operating procedures call for first measuring all samples against the low calibration standards. Results above this range are read using the high calibration range. Concentrations that exceed the high-calibration limits must be diluted and reanalyzed. Never extrapolate the calibration curve to estimate results.

The two ranges of working standards illustrated in Tables 4.37 and 4.38 are typical; however, these ranges may not be best for every laboratory. In practice, ranges must be established by each laboratory and may vary over time.

Working calibration standards may be stored in clean HDPE containers at room temperature and are stable up to six weeks.

### Quality Control

### Preparing QC Solutions

Prepare two QC solutions, one for the low calibration range and one for the high calibration range. Analyze a low QC sample immediately after the IC is calibrated in the low range. Do the same in the high calibration range using the high QC solution. See Appendix C for details on sterilization and preparation of QC solutions.

#### Low QC Solutions – Precipitation Matrix

1) Save the excess volume from low-concentration precipitation samples that have been analyzed and reported. Pool the excess from some of these samples in a 10 L HDPE container and the excess from other low-concentration samples in a second 10 L HDPE container.

2) Analyze the pooled samples from each container. Designate the pooled sample with the lower concentrations as QC-A and the other as QC-B. QC-A will generally have the lowest concentration of each analyte.

3) Add DI water as needed to bring the cation concentrations of QC-A near the detection limit. Add stock standard solution as needed to bring the cation concentrations of QC-B to the mid to high range of the low calibration curve.

4) See Appendix C for sterilization and further details.

#### High QC Solutions – Precipitation Matrix

1) Save the excess volume from high-concentration precipitation samples that have been analyzed and reported. Pool the excess from some of these samples in a 10 L HDPE container and the excess from other high-concentration samples in a second 10 L HDPE container.

2) Analyze the pooled samples from each container. Designate the pooled sample with the lower concentrations as QC-C and the other as QC-D.

3) Adjust concentrations using stock standard solution, as needed, so that QC-C concentrations are near the low to mid-range of the high calibration curve and QC-D concentrations are near the mid to high range of the high calibration curve.

4) See Appendix C for sterilization and further details.

**Analytical Procedures**

1) Do not power down an IC system when not in use. Always leave the power on.

2) Check reagent levels. Check the eluent cartridge and ensure there is enough for a full run. Change the DI water in the flush reservoir and sample changer every day. Inline filters may be used to minimize particulate introduction into the system. Change inline filters daily.

3) Run DI water samples until the system is stable and equilibrated.

4) Label each tube. Prepare a schedule of analysis in the workstation software. Enter sample identification numbers into the software in the same order as the tubes will be installed in the sample changer rack.

5) Prepare samples for analysis. Ensure that each tube has a minimum volume. Minimum volumes will vary according to the size of the injection loop and loop rinse. Cover each tube opening with a pierceable cap or use Parafilm®. Place the tubes in order in the sample changer rack.

6) Check for a stable pump pressure and conductivity.

7) Check the DI water chromatogram for the correct shape. See Figure 4.36.

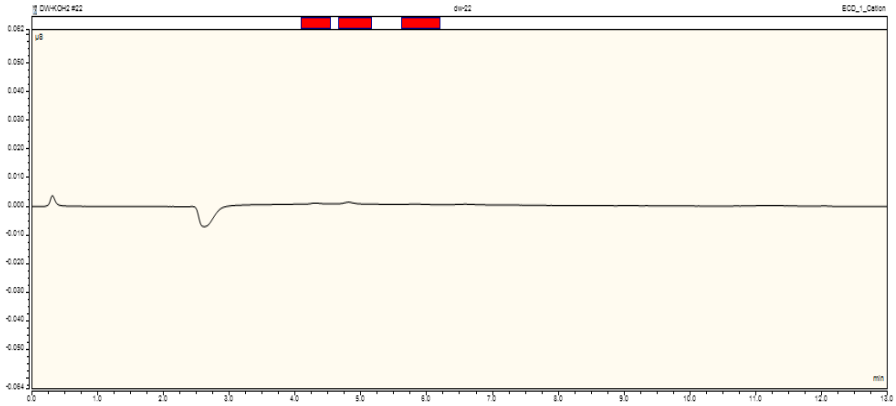

*Figure 4.36. DI water chromatogram using MSA as eluent. Note the small water dip and small peak that marks a slight increase in pump pressure at the point of sample injection.*

8) Initiate the run. Run calibration standards first. The injection should start with the highest concentration standard followed by decreasing concentrations.

9) Run a low QCS directly after completing the low calibration curve and a high QCS after completing the high calibration curve. Inject a QCS, selected at random, every ten samples thereafter. Plot the QCS results on control charts.

10) Calibrate every 30 to 50 samples.

11) Following the run, check all calibration curves and QC results before reporting, collating, or tabulating sample results. Use only the peak area, not the peak height, for calculating results.

12) Check each chromatogram individually for correct shape and integration. See Figure 4.37. Comment on all anomalies and flag data accordingly.

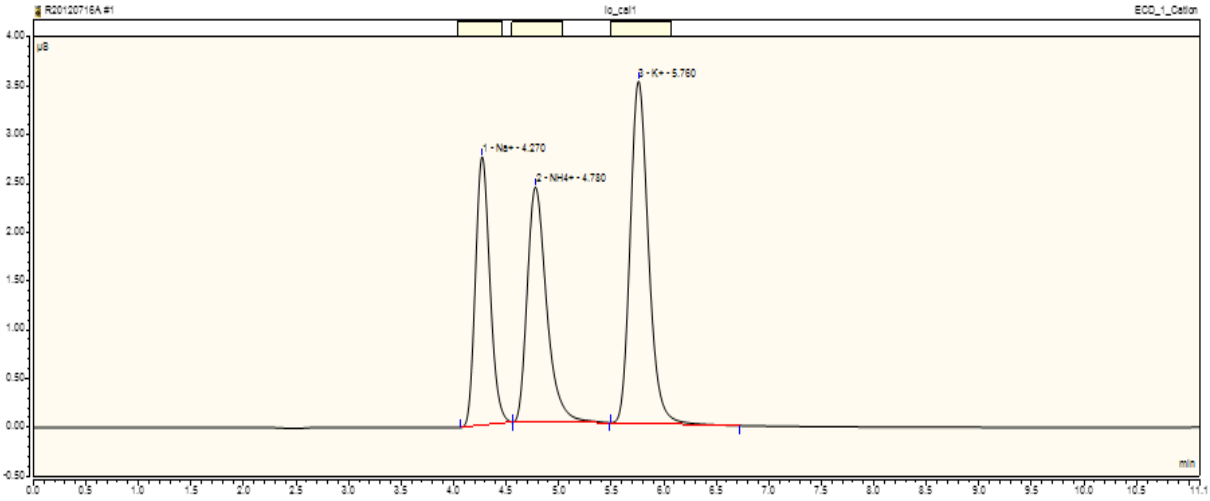


*Figure 4.37. Typical cation chromatogram using MSA as eluent.*

13) Calculate final results against the appropriate calibration curve. Use the correct decimal places. Apply detection limit notations as needed. Mark all samples that exceed upper calibration ranges for dilution and repeat analysis. Account for missing samples and ensure that contamination codes are applied as needed.

14) Export the data from the IC system and archive all parameters associated with the analysis, including calibration data, integration data, and instrument audit trails. Audit trails include instrument parameters that may be useful in diagnosing a problem, such as a chromatogram that exhibits a drifting baseline. It may be necessary to repeat the analysis at the point where a problem started.

**Troubleshooting**

**Problem 1:** Pump loses pressure or prime.
**Solution 1:** Check the EluGen® cartridge for leaks. Change the cartridge if required. Prime the pump. Check the system for leakage. Re-prime the pump and run DI water to check the system. If the pump is still unstable, disconnect the column and pump methanol through the system. Flush with water. If these steps do not eliminate the problem, change the piston seals (provided the operator has been trained to do so). Soak the piston seals in methanol for a few minutes. This ensures a better seal around the piston.

**Problem 2:** Precision not meeting QC specifications.
**Solution 2:** Check the injection valve for leaks or blocks. Make sure the sample loop is filling with each injection. Check the probe and sample lines for plugs or leaks. Change the sample loop and clean the injection valve. A plug can be found by disconnecting each length of tubing one section at a time. Pump pressure will increase significantly if the bed supports or guard column are fouled.

**Problem 3:** Ammonium curve drops below zero at low concentrations but other cation curves are linear and go through zero and behave as expected.
**Solution 3:** Prepare new standards and repeat the calibration. If this does not improve, change the suppressor.

**Problem 4:** Retention times shorten and resolution between ammonium and sodium is poor.
**Solution 4:** Clean or change the guard column. If there is no improvement clean or change the separator column.

**Problem 5:** Ammonium peak is very high and crowds the potassium peak into a 'rider' position. See Figure 4.38 for example.
**Solution 5:** Dilute the sample to reduce the ammonium peak and rerun the sample for potassium.

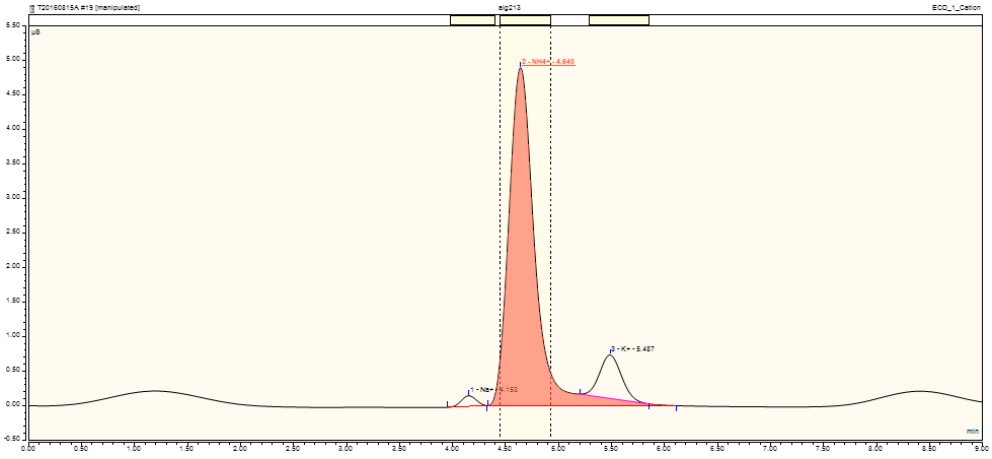


*Figure 4.38. Potassium peak riding on the tail of a high ammonium peak. This chromatogram shows magnesium cut off from the chromatogram and the calcium from the previous sample eluting first (see Problem 6.).*

**Problem 6:** Calcium and magnesium elute very late and are seen eluting in the following chromatogram (See peak at the beginning of Figure 4.38.).
**Solution 6:** Extend the run time. Sometimes run times and retention times can lengthen significantly when new columns are put into service. It is important to test the system with calibration standards to identify the retention times and adjust the run times accordingly.