

Determination of Cation and Anion Concentrations in Water Samples by Ion Chromatography

1. Introduction

Ion Chromatography is a method used to measure major cation and anion concentrations in aqueous samples. These concentrations are useful in determining the water type from the producing water source. Major ion concentrations may also be used as tracers to evaluate contamination, flow, or mixing in a system. Additional information on ion chromatography can be found in the USGS publication edited by Fishman and Friedman (1989).

2. Interfaces with Other Methods

Balance Calibration (EGL Method 29)

Sample Control, Labeling, and Disposition (EGL Method 25)

3. Materials and Equipment

- Ion chromatograph and accessories (pump, detector, columns, suppressor, etc.)
- Nitrogen and/or helium gas
- Gas reducing valves and pressure regulators associated with external gas use
- Type 1 (18 megohms-cm) deionized water (DI water)
- Eluent cartridge or reagents to prepare eluent manually
- Reagents to prepare calibration standards or certified standard solutions. The certified standard solutions may include 1000 mg/L single element standards of calcium, magnesium, sodium, potassium, ammonium, chloride, fluoride, sulfate, and nitrate; or other cation and anion standards, as necessary
- USGS Standard Reference Samples or comparable reference standards
- Analytical balance capable of weighing up to 150 grams to the nearest 0.001-gram (if using standard reagents to make in-house standard solutions)
- Syringes or auto sampler
- Digital pipettes and pipette tips
- Refrigerator
- 0.45 μm pore size or smaller filters
- Vials and caps

4. Procedure

Check the Eluent Reservoir and fill, if necessary.

Start the instrument either manually from the interface or use the STARTUP program on the control panel. Allow the instrument to warm up for a period of about one hour.

Set up the sequence for the run. Include standards and samples to be analyzed. Label the samples as standard, validation or unknown. Can use the last sequence or an earlier sequence which is setup in a similar fashion and uses the same program and methods, and rename it.

Prior to running unknown samples, check the instrument calibration using a calibration standard. The analytes in the calibration check standard must be within $\pm 15\%$ of the accepted values for the standard. If one or more of the values exceed the $\pm 15\%$ acceptance criteria, a fresh calibration standard may be prepared from the stock standard and analyzed. If the freshly prepared standard still exceeds the 15% acceptance criteria for one or more of the analytes, the instrument will need to be recalibrated per Section 5.

Check for analytical accuracy by analyzing commercially prepared standard solutions traceable to NIST or other nationally recognized standard reference samples (SRS). The analyzed values of the standards should be within 3σ of the most probable values for the standard. The most probable values for the Standard Reference Samples prepared by the USGS Branch of Quality Systems can be found at bqs.usgs.gov/srs/.

Filter samples containing particulates through a prewashed 0.45 μm or smaller disposable filter prior to analysis to avoid clogging or fouling the resin column.

Dilute unknown samples to a specific conductance of 300 $\mu\text{s}/\text{cm}$ or less. Unknown samples may also be reanalyzed at additional sample dilutions to measure low-concentration analytes, but the specific conductance of the reanalyzed sample should not exceed 4,000 $\mu\text{s}/\text{cm}$ to avoid fouling of the resin column.

If injecting the samples manually, flush the sampling system thoroughly with each new sample using a rinse volume of at least ten times the loop volume if adequate sample volume is available and then inject the sample. If using an auto sampler, the auto sampler will perform both a flush of the sample system and sample injection automatically.

5. Calibration and Quality Control Samples

Annual calibration of the digital pipettes will be required if the pipettes are used to prepare volumetric dilutions of the standards or unknown sample solutions. When using an IC equipped with an eluent generator, calibration of the IC is required every two months or whenever the criteria in Paragraph 4 indicate recalibration is necessary. If the eluent is prepared manually, the IC will be calibrated each use.

Digital Pipette Calibration

The digital pipettes will be calibrated by pipetting a known volume of DI water into a beaker and measuring the weight using a balance. A minimum of

three measurements will be performed at both the minimum and maximum volumes of a variable volume pipette. Three measurements of the weights will be performed on a fixed volume pipette.

The calibration will be acceptable if the measured weights are within 1% of the full-scale volume of the pipette. If the weights are outside of the acceptance criteria, the volume may be adjusted using the calibration tool provided with the pipette and rechecking the calibration. If the pipette cannot be adjusted to meet the acceptance criteria, the pipette should be replaced.

Ion Chromatograph Calibration

When using identical eluent programs (either gradient or isocratic), multiple calibration curves may be combined to extend the analytical calibration range or to add additional analytes to the calibration.

Prepare calibration standards containing a single analyte or a mixture of analytes at a minimum of three concentration levels by adding accurately measured volumes of one or more stock standards to a volumetric flask and diluting to volume with DI water. Alternately, the weights of the standards may be measured on a balance to prepare the standards gravimetrically. The larger the possible range in concentration of analytes in your samples the more calibration and reference standards you need.

Flush the sampling system with the calibration standard using rinse volume of at least ten times the loop size.

Inject standards and determine approximate retention times. Inject at least three different concentrations for each analyte of interest and view the calibration curves.

For calibrations that are approximately one order of magnitude from the low standard to the high standard, linear calibration curves can be used. For calibrations that exceed two orders of magnitude from the low standard to the high standard, quadratic calibration curves will be used. In both cases, the calibration is acceptable if the correlation coefficient of the regression is 0.995 or greater.

To test for instrument drift, standards shall be analyzed on each IC run and after at least every 12 unknown samples.

For every 10 samples or fraction thereof, duplicate analyses of the unknown samples shall be performed for QC purposes.

Reference blanks shall be analyzed on each IC run and after at least every 20 unknown samples to check for instrument contamination.

Standard Reference Samples are procured from the USGS Branch of Quality Systems. The most probable values for the Standard Reference Samples can be found at bqs.usgs.gov/srs/.

6. Limits, Precautions, and Interferences

Interferences can be caused by ions with retention times that are similar to and thus overlap the analytes of interest. Unresolved peaks will also result when the concentration of one of the analytes is much higher than the concentration of an analyte in an adjacent peak. Changing the eluent concentration or the flow rate may improve the peak resolution.

Stock standards and working standards should be refrigerated after preparation to reduce microbial degradation of the standards.

Small sample volume, whether it is due to a small volume sample or a small sample loop, decreases the sensitivity of the instrument at lower concentrations. A small volume sample limits your ability to rerun the sample if needed.

Samples preserved with acids should not be analyzed for anions because the high concentration of the anionic component of the acid may overload the anion column.

Detection limits will be determined for each eluent program (gradient or isocratic) by analyzing 10 replicate samples of the lowest-level calibration standard. The detection limits will then be calculated by multiplying the standard deviation of the replicate analyses by a factor of three. Detection limits will be measured at least once per year.

7. Acceptance of Data

The satisfactory performance of this procedure will be judged by the analysis of quality control samples which include calibration standards, Standard Reference Samples, and duplicate samples. As a goal, the error of IC analyses should be $\leq \pm 15\%$ and $\leq \pm 20\%$ for bicarbonate. For low-level concentrations (less than 1 mg/L), the acceptance criteria is ± 0.15 mg/L of the accepted value. If the results are found to be outside these acceptance limits, the samples will be reanalyzed. If there is insufficient sample volume for reanalysis, the larger errors will be assigned to the sample and the results reported as estimated.

Precision of the results are expected to be better than $\pm 5\%$ of the reported values. For low-level concentrations (less than 1 mg/L), the precision is ± 0.15 mg/L of the reported values.

8. Data Handling and Transfer

Data from the IC are stored on a personal computer attached to the instrument. The data can be exported to an Excel™ spreadsheet using the Batch Report function on the File menu.

The spreadsheet will be used to transfer the data from the instrument into the LIMS. The results will then be checked by the Analyst and accepted by the Inorganic Lead.

9. References

5–A1. Methods for determination of inorganic substances in water and fluvial sediments, by M.J. Fishman and L. C. Friedman, editors: USGS—TWRI Book 5, Chapter A1. 1989. 545 pages.

10. Attachments

Attachment 1: Detailed analyte list

11. History of Changes

Revision 0: initial issue.

Detailed Analyte List

The following ions can be measured using ion chromatography:

Cations:

Ammonium
Calcium
Magnesium
Potassium
Sodium

Anions:

Bicarbonate
Bromide
Chloride
Fluoride
Nitrate
Sulfate