

Determination of Calcium and Magnesium in Brine

INTRODUCTION

To prevent membrane poisoning, new membrane technology in chlor-alkali cells requires feed brine that is relatively free of alkaline earth metals. Membrane manufacturers recommend that saturated brines be purified to a total hardness below 50 µg/L (ppb) to extend membrane life and ensure electrical current efficiency in the cell.

Industrial laboratories have been concerned with the determination of calcium and magnesium in brine for a number of years. For example, investigators at Vulcan Chemical developed an IC method for the determination of alkaline earth metals in high-purity brine in the 1980s. The method in this Application Note can be considered an extension of previous work at Vulcan Chemical.¹

This Application Note describes a method for determining low µg/L amounts of calcium and magnesium in a 30% sodium chloride brine by ion chromatography. A MetPac™ column, which selectively retains calcium and magnesium and has a low affinity for sodium, is used to concentrate calcium and magnesium from the brine. The concentrated calcium and magnesium are separated on an IonPac® CS12A cation-exchange column and detected by suppressed conductivity detection.

EQUIPMENT

Dionex DX-500 Ion Chromatography system consisting of:

- GP40 Gradient Pump
- CD20 Conductivity Detector
- LC20 Chromatography Enclosure equipped with a rear-loading Rheodyne injection valve
- Rinsing Pump, DQP (P/N 35250)
- LC10 Chromatography Organizer equipped with a rear-loading Rheodyne injection valve

4-L Plastic bottle (for 1 mM hydrochloric acid rinsing solution)

PeakNet Chromatography Workstation

REAGENTS AND STANDARDS

Deionized water (DI H₂O), Type I reagent grade, 18 MΩ-cm resistance or better

> 99% Methanesulfonic acid (Fluka or equivalent)

Hydrochloric acid, ultrapure reagent (J.T. Baker ULTREX® II, 36.9% or equivalent)

Sodium hydroxide, 50% (w/w) aqueous solution (Fisher Scientific or equivalent)

Brine (30% sodium chloride solution, kindly provided by Dr. David Hildebrand, Vulcan Chemical, Wichita, Kansas, USA)

CONDITIONS

Trap Column (for contaminants in the rinse solution): TMC-1 Concentrator Column (P/N 49000)

Concentrator Column: MetPac CC-1 Concentrator Column (P/N 39567)

Analytical Columns: IonPac CS12A Analytical, 4 x 250 mm (P/N 46073)
IonPac CG12A Guard, 4 x 50 mm (P/N 46074)

Eluent: A: 20 mM Methanesulfonic acid

Eluent Flow Rate: 1 mL/min

Rinsing Reagent: 1 mM Hydrochloric acid

Rinsing Flow Rate: 2 mL/min
 Rinse Time: 20 min
 Total Run Time: 35 min
 Sample Volume: 100 µL
 Detection: Suppressed conductivity, CSRS®-II (4 mm), AutoSuppression® recycle mode
 System Backpressure: 1000–1500 psi (6.9–10.3 MPa)
 Background: 0.3–3 µS

Time Functions Program

Time (min)	A(%)	Valve 1 ¹	Valve 2 ²	Remarks
Initial	100	load	inject	
0.0	100	load	load	Fill sample loop
1.0	100	inject	load	Sample to MetPac
20.0	100	load	inject	Begin sampling ³
35.0	100	load	inject	Finish sampling

¹ Valve 1 is used for loading the concentrator column (MetPac).

² Valve 2 is used for eluting and separating compounds of interest on the CS12A analytical column.

³ Begin sampling refers to data collection (the MetPac column is switched in-line with the CG12A and CS12A columns.)

PREPARATION OF SOLUTIONS AND REAGENTS

Standard Solutions

Stock magnesium standard solution (1000 mg/L)
 (VWR Scientific)

Stock calcium standard solution (1000 mg/L)
 (VWR Scientific)

Calibration Standard Solutions

Appropriate calibration standards are prepared from 1000 mg/L standards specified above. Select a range similar to the expected analyte concentrations in the samples. All standards should be prepared in brine.

Eluent Solutions

Stock eluent solution: 1 M Methanesulfonic acid

Weigh 934.5 g of deionized water (Type I reagent grade, 18 MΩ-cm resistance or better) into an eluent bottle. Degas for approximately 5 minutes. Tare the bottle and carefully add 65.5 mL of > 99% methanesulfonic acid directly to the bottle.

Working eluent solution: 20 mM Methanesulfonic acid

Weigh 980.0 g of deionized water (Type I reagent grade, 18 MΩ-cm resistance or better) into an eluent bottle. Degas for approximately 5 minutes. Add 20 mL of 1 M methanesulfonic acid to the bottle.

Stock rinsing solution: 1 M Hydrochloric acid

Weigh 909.70 g of deionized water (Type I reagent grade, 18 MΩ-cm resistance or better) into an eluent bottle. Degas for approximately 5 minutes. Tare the bottle and carefully add 90.3 mL of ultrapure reagent grade hydrochloric acid directly to the bottle.

Working rinse solution: 1 mM Hydrochloric acid

Weigh 999.0 g of deionized water (Type I reagent grade, 18 MΩ-cm resistance or better) into an eluent bottle. Degas for approximately 5 minutes. Add 1 mL of 1 M hydrochloric acid directly to the bottle.

Stock sample pH adjustment solution: 500 mM Sodium hydroxide

Weigh 960.0 g of deionized water (Type I reagent grade, 18 MΩ-cm resistance or better) into an eluent bottle. Degas for approximately 5 minutes. Tare the bottle and carefully add 40.0 g of 50% sodium hydroxide directly to the bottle.

Standards and Sample Preparation

Add 0.2 mL of 500 mM sodium hydroxide solution to 9.8 mL of sample (brine).

The final concentration of sodium hydroxide is 10 mM.

SYSTEM OPERATION

System configuration and operation parameters for this application are outlined in previously published documents.^{2,3}

The sensitive analysis of calcium and magnesium in brine is accomplished in four steps:

1. Fill the sample loop
2. Load the concentrator column
3. Eliminate the sodium matrix
4. Separate calcium and magnesium

Figure 1 shows how the system performs these tasks. In Figure 1A, the system is in the standby mode, ready for sample analysis. In Figure 1B, Valve 2 is switched to the LOAD position and the sample is loaded into the 100 μL sample loop on Valve 1.

Sample Handling

The black rubber plunger in disposable plastic syringes can be a source of contamination. To minimize the introduction of contamination, pull rather than push the

sample into the loop, as shown in Figure 1B. Be sure to pull slowly so that bubbles are not introduced. The loop should be overfilled by at least 3 times its capacity ($> 300 \mu\text{L}$) to ensure reproducible results. It is important to have the TMC column in line between the DQP pump and Rheodyne Valve 1 (Figure 1A) to remove the significant amount of calcium and magnesium present in the 1 mM hydrochloric acid solution. The contamination level of calcium and magnesium in the 1 mM hydrochloric acid solution depends on the reagent purity and grade of DI water. A water blank should be run before analyzing

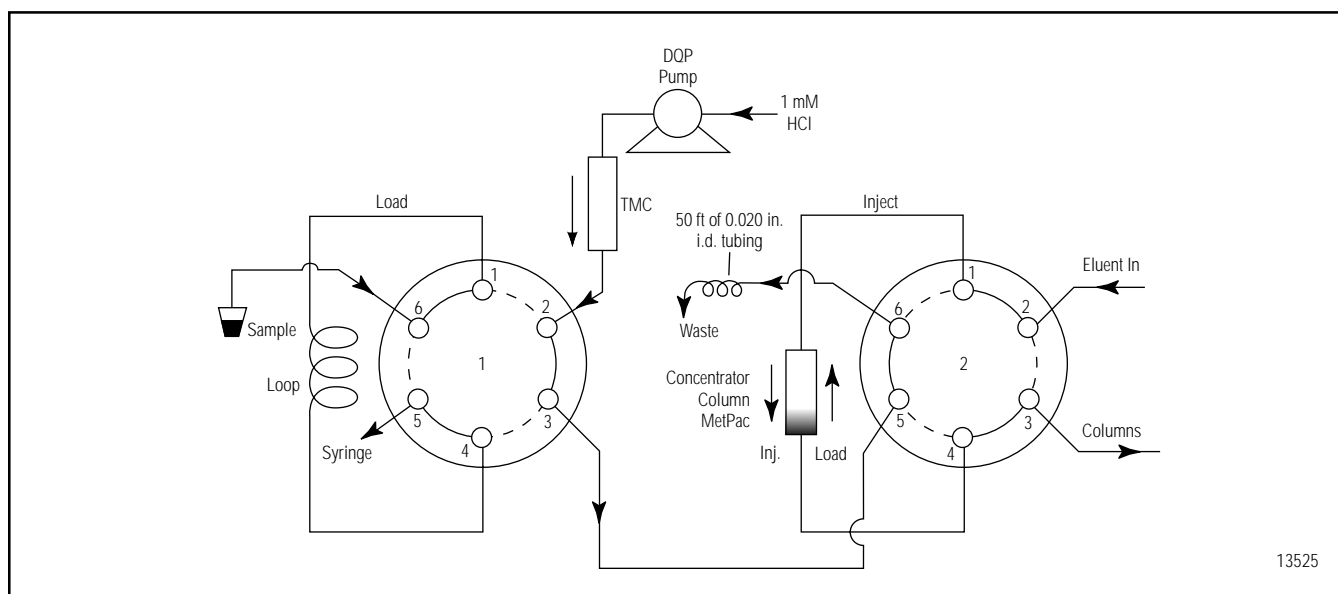


Figure 1A Initial conditions

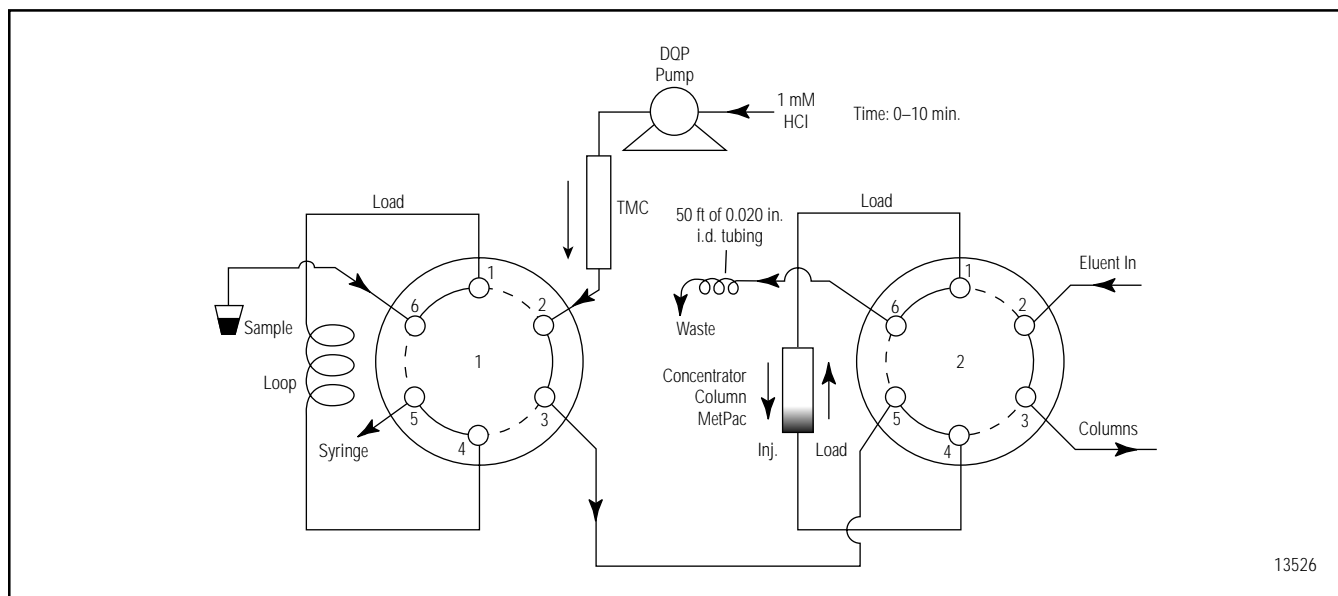


Figure 1B Loading the sample loop

samples. If there has been a significant increase in magnesium and calcium, the capacity of the TMC is exhausted. To clean the TMC, flush with approximately 25–30 mL of 1.5 M hydrochloric acid.

Matrix Elimination

After the sample loop is filled, 1 mM hydrochloric acid from the DQP transfers the sample out of the loop and onto the MetPac column in the opposite direction of the

eluent (Figure 1C). Calcium and magnesium are retained on the concentrator column. The sodium matrix is removed from the MetPac column with 1 mM hydrochloric acid from the DQP flowing at 2 mL/min for 20 minutes (DQP head pressure should be at least 100 psi). Finally, activating Valve 2 to the INJECT position switches the MetPac column in-line with the eluent stream and the analytical columns (Figure 1D). Calcium and magnesium are then eluted from the MetPac column in the reverse

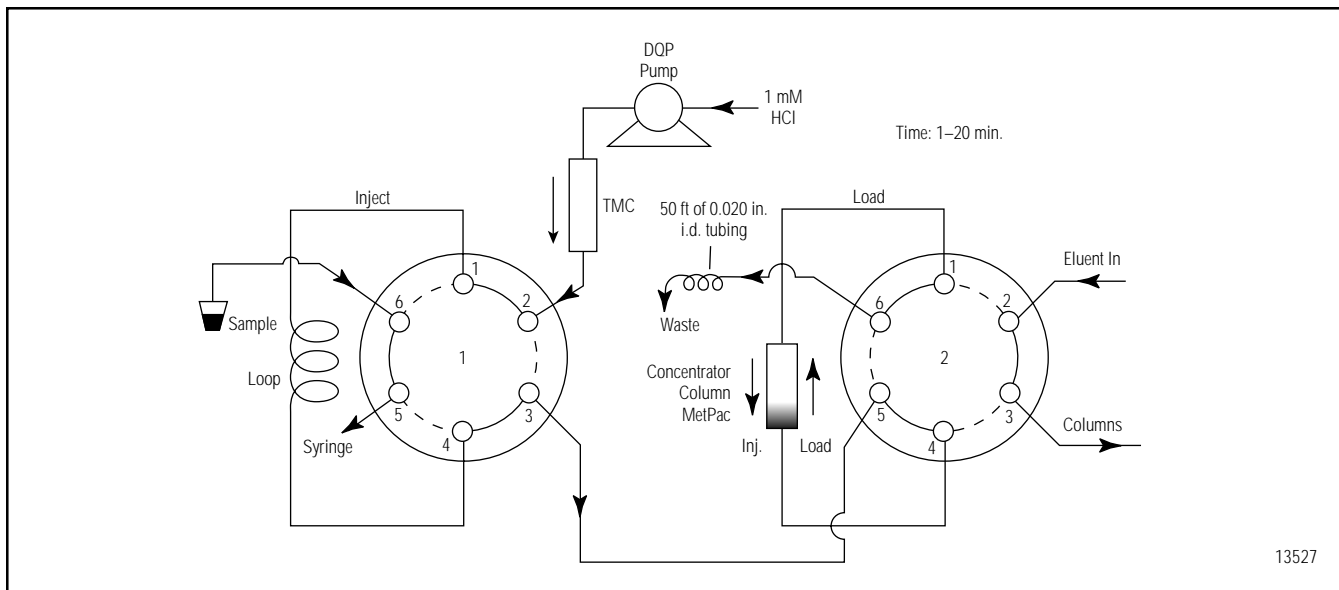


Figure 1C Loading the concentrator column and eliminating the matrix

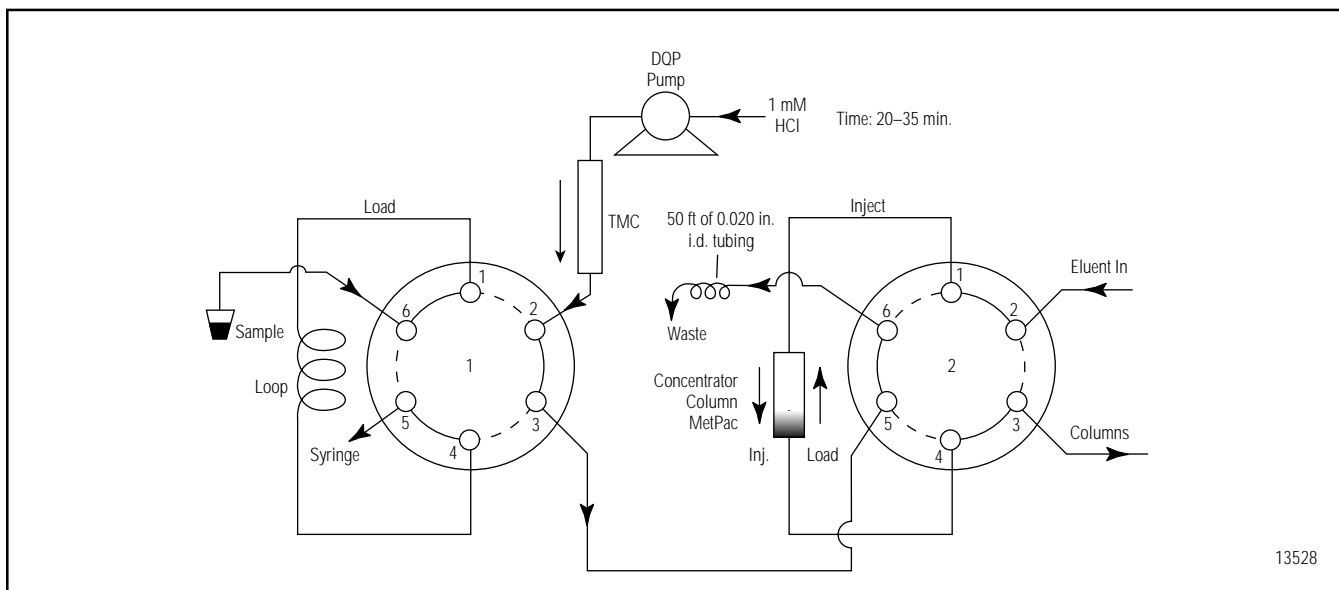


Figure 1D Chromatography of retained Calcium and Magnesium

direction of the concentration step and separated on the CG12A and CS12A columns. Special care should be taken to minimize contamination. The deionized water used for preparing the rinse solution, eluent, and sodium hydroxide solution should be free of measurable levels of ionic impurities, organics, microorganisms, and particulate matter larger than 0.2 μm in diameter.

RESULTS AND DISCUSSION

For the best performance at low $\mu\text{g/L}$ levels, it is critical that baseline noise be kept to a minimum. An equilibrated system will demonstrate a conductivity background between 0.3–3 μS . Peak-to-peak noise is typically 10 nS and system backpressure is 1000–1500 psi (6.9–10.3 MPa). A system blank is determined by using deionized water as the sample. This blank establishes the baseline and confirms the lack of contamination in the system. A small amount of sodium contamination in the system does not interfere with calcium and magnesium detection.

In these experiments, purified brine from a major chlor-alkali producer was used. Brine prepared with commercially available sodium chloride (VWR, reagent grade) contained over 100 $\mu\text{g/L}$ of calcium and magnesium. All standards must be prepared in brine. In the method described here, trace levels of magnesium and calcium in brine are concentrated on a MetPac column, which is more selective for divalent than monovalent cations. For optimum calcium and magnesium recovery, the sample pH must be adjusted to 11.5. At high pH values, the MetPac selectivity for divalent over monovalent cations is increased. At lower pH values, calcium and magnesium recoveries are poor and are not linear within the concentration range used for this analysis. Calcium and magnesium recoveries were not increased with sample pH values higher than 11.5. Figures 2 and 3 show that the detection of calcium and magnesium is linear in the low $\mu\text{g/L}$ range. Even at pH 11.5, the MetPac column binds some sodium. To remove sodium, the MetPac is rinsed with 1 mM hydrochloric acid. Higher concentrations of hydrochloric acid cause a reduction in calcium and magnesium recovery, while lower hydrochloric acid concentrations increase the rinse time required for rugged chromatography. Despite washing the MetPac column for 20 minutes to eliminate the matrix, detectable levels of sodium elute from the MetPac to the CS12A column (see Figure 4). However, this level of sodium does not interfere with the detection of low concentrations of calcium and magnesium (see Figure 5). Shorter wash times (less than

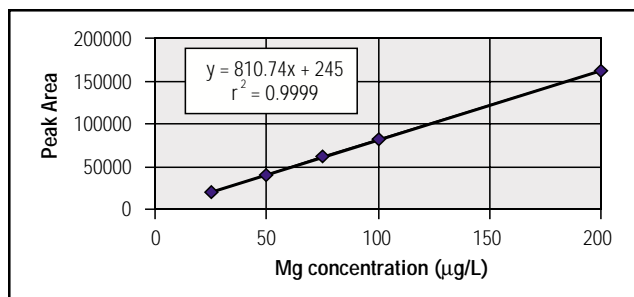


Figure 2 Magnesium calibration in brine

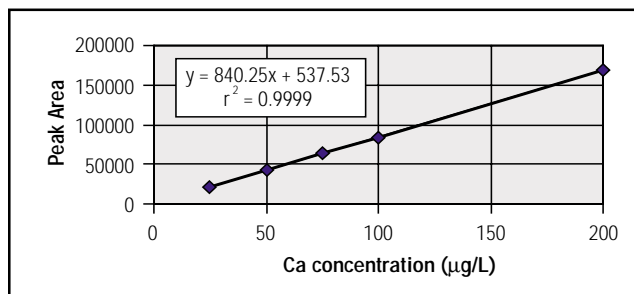


Figure 3 Calcium calibration in brine

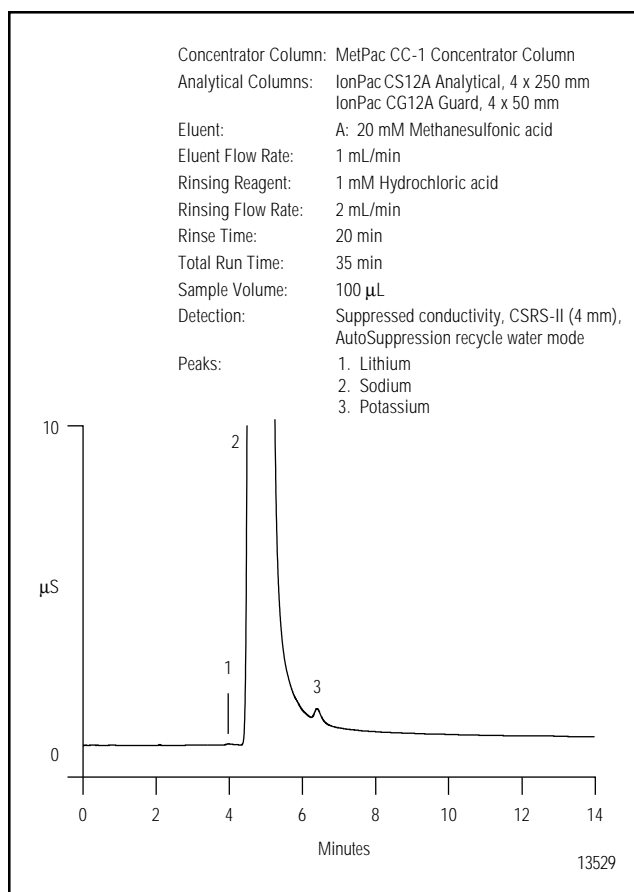


Figure 4 Brine blank

20 minutes) were investigated and did not adequately eliminate the sodium interference. The injection volume was optimized at 100 μ L. A larger injection volume may exceed the MetPac column capacity and cause irreproducible results. The data in Table 1 show that 5 μ g/L of calcium and magnesium can be easily quantified in brine.

SUMMARY

The method outlined in this Application Note accurately quantifies low μ g/L amounts of calcium and magnesium in brine by using an on-line matrix elimination technique.

REFERENCES

1. Personal communication, Dr. David Hildebrand, Vulcan Chemical, Wichita, Kansas, USA.
2. Dionex Corporation, "Determination of Trace Anions in Isopropyl Alcohol", Application Note 85.
3. Kaiser, E.; Wojtusik, M. J. *J. Chromatogr. A.* **1994**, *671*, 253–258.

LIST OF SUPPLIERS

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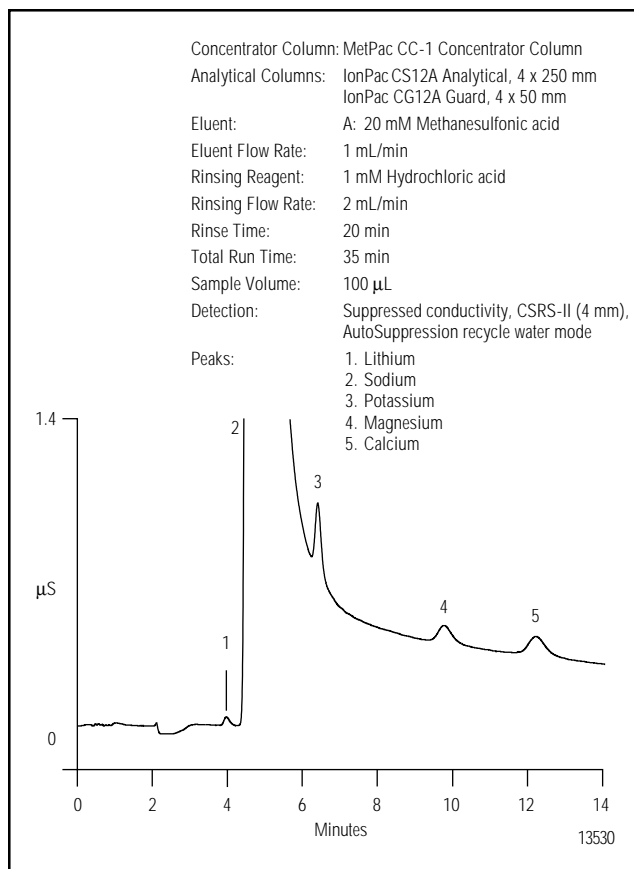


Figure 5 25 ppb of Calcium and Magnesium in brine

Table 1 Area counts and RSD of 5 ppb calcium and magnesium in brine

Injection #	5 ppb Magnesium (area count)	5 ppb Calcium (area count)
1	3748	4309
2	3773	4355
3	3709	4368
4	3817	4410
5	3856	4588
6	3826	4471
7	3921	4572
Average	3807	4439
RSD	1.86	2.46

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