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Short communication

Determination of magnesium and calcium in 30% sodium chloride by ion chromatography with on-line matrix elimination

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Abstract

Ion chromatography with on-line matrix elimination reliably determines low microgram-per-litre amounts of magnesium and calcium in brine (30% NaCl). Magnesium and calcium from 100 μl of brine were concentrated on a metal-chelating resin containing iminodiacetate functional groups. After excess sodium was rinsed away, magnesium and calcium were eluted from the metal-chelating column, separated on a cation-exchange column, and detected by suppressed conductivity. This method was reproducible at 5 μg/l magnesium and calcium in brine.

Keywords: Brine; Magnesium; Calcium; Metal cations

1. Introduction

To prevent membrane poisoning, new membrane technology in chlor-alkali cells requires feed brine that is relatively free of alkaline earth metals [1]. Membrane manufacturers recommend that saturated brines be purified to a total hardness of 50 μg/l to extend membrane life and ensure electrical current efficiency in the cell.

The direct determination of magnesium and calcium in brine is a challenging analytical problem. Jones and coworkers developed high-performance chelation ion chromatography to determine metals in brines [2–10]. In their approach, a chromatographic resin is coated with a chelating dye that contains at least one iminodiacetate group. Metals are concentrated and separated on this chelating column and then detected by absorbance at 490 nm after a postcolumn reaction with 4-(2-pyridylazo)resorcinol-zinc-ethylenediaminetetraacetic acid. Using a Xylenol Orange coated-column they determined 3 μg/l magnesium and 6 μg/l calcium in 30% NaCl [5].

Here a commercial iminodiacetate column is used to concentrate magnesium and calcium from 30% sodium chloride. This column's affinity for magnesium and calcium is greater than its affinity for sodium. The column is rinsed with 1 m*M* hydrochloric acid to remove sodium, and then magnesium and calcium are eluted with 20 m*M* methanesulfonic acid (MSA) and separated on a cation-exchange column. This cation-exchange column has the proper selectivity and enough capacity to separate low μg/l concentrations of magnesium and calcium from mg/l concentrations of sodium [11]. The cations are detected by suppressed conductivity [12]. This paper describes the development of this method and its linearity and precision at low μg/l concentrations of

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magnesium and calcium. This method can be considered an extension of earlier work at Vulcan Chemical [David Hildebrand, Vulcan Chemical, Wichita, KS, USA, personal communication].

2. Experimental[1]

2.1. Materials

Sodium hydroxide, 50% (w/w), was obtained from Fisher (Pittsburgh, PA, USA). Methanesulfonic acid (>99%) was purchased from Fluka (Buchs, Switzerland). High purity hydrochloric acid was purchased from J.T Baker (Ultrex II, 36.9%, Phillipsburg, NJ, USA). Magnesium and calcium standard solutions (1 g/l) were obtained from VWR Scientific (San Francisco, CA, USA). The high purity brine (≈5.2 *M*) was kindly provided by Vulcan Chemical. Type I reagent grade deionized water (18 MΩ cm or better) was used for all sample and eluent preparations.

2.2. Equipment

A DX-500 chromatography system (Dionex, Sunnyvale, CA, USA) consisting of a GP40 gradient pump, a CD20 conductivity detector, and a LC20 chromatography enclosure equipped with a rear-loading Rheodyne (Cotati, CA, USA) injection valve (Valve 2) was used for all chromatography. An LC10 chromatography organizer containing a rear-loading Rheodyne injection valve (Valve 1) was used for matrix elimination. Both valves contained tefzel rotor seals. A single-piston pump (DQP, Dionex) was used to rinse the metal-chelating column prior to switching it in-line with the cation-exchange column set. A cation self-regenerating suppressor (CSRS-II, Dionex) was used in the AutoSuppression mode at a power setting of 300 mA. A personal computer equipped with PEAKNET chromatography software (Dionex) was used for data acquisition and instrument control.

[1]AutoSuppression, CSRS, cation self-regenerating suppressor and IonPac, are registered trademarks of the Dionex Corporation. MetPac is a trademark of the Dionex Corporation.

2.3. Sample and standard preparation

The pH of the brine samples was adjusted for optimum magnesium and calcium recovery. We added 0.2 ml of 500 m*M* NaOH to 9.8 ml of brine. Calibration standards must be prepared in brine. Magnesium and calcium were added to brine to obtain final concentrations of 5, 25, 50, 75, 100 and 200 μg/l of each. The pH of these solutions was adjusted as above.

2.4. Chromatography

A 1 *M* MSA stock solution was prepared by diluting 65.5 ml MSA to 1 l. The 20 m*M* MSA eluent was prepared using the 1 *M* MSA and vacuum-degassed water. The MSA eluent was pressurized with helium (8 p.s.i., 55.2 kPa). The chromatography system was configured as shown in Fig. 1 [13]. A 50 ft. length of 0.02 in. I.D. tubing was installed as the waste line to provide the necessary backpressure for the sample pump (1 ft.=30.48 cm; 1 in.=2.54 cm). The chromatography method is outlined in Table 1. In Fig. 1, Valve 1 is in the load position and Valve 2 is in the inject position. At zero minute Valve 2 is switched to the load position and a 100-μl sample loop was loaded by pulling the sample into the loop using a syringe on the waste port of Valve 1. The loop was overfilled with at least three times the loop volume to ensure reproducible sampling. The sample was then injected onto the metal-chelating column (MetPac CC-1, capacity=0.4

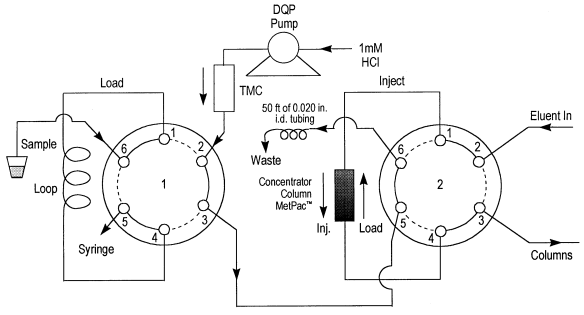

Fig. 1. Configuration of the chromatographic system for determining magnesium and calcium in 30% NaCl. In this diagram, the system is at initial conditions with Valve 1 in the load position and Valve 2 in the inject position. Table 1 describes the state of both valves at each point in the analysis.

Table 1
Chromatography method for magnesium and calcium determination in 30% NaCl

Time (min)	Valve 1 position	Valve 2 position	Remarks
Initial	Load[a]	Inject[b]	See Fig. 1
0.0	Load	Load	Fill sample loop
1.0	Inject	Load	Sample to MetPac and MetPac rinsing
20.0	Load	Inject	Begin sampling[c]
35.0	Load	Inject	Finish sampling

[a] In the load position, ports 1–6, 2–3, and 4–5 are connected.
[b] In the inject position, ports 1–2, 3–4, and 5–6 are connected.
[c] Begin sampling refers to data collection (the MetPac column is switched in line with the IonPac CS12A analytical columns).

mequiv., Dionex). The column was rinsed with 1 m*M* HCl at a flow-rate of 2 ml/min using the DQP pump. A trap column (TMC-1, Dionex) was used between the DQP pump and the MetPac to remove magnesium and calcium from the 1 m*M* HCl rinse solution. A system blank should be run periodically to determine if the capacity of the TMC-1 has been exhausted. After a 20-min rinse, Valve 2 was switched to the inject position. This placed the MetPac in line with the cation-exchange guard (5× 0.4 cm) and separator (25×0.4 cm) columns (IonPac CS12A, Dionex). Magnesium and calcium were eluted from the MetPac column in the opposite direction of sample loading and separated on the CS12A column set using 20 m*M* MSA at a flow-rate of 1 ml/min.

3. Results and discussion

To determine the low concentrations of magnesium and calcium in the high-purity brines used for chlor-alkali production, a method that does not require dilution is preferred due to the possible contribution of magnesium and calcium in the diluent to the final result. Here we concentrate the magnesium and calcium in 100 μl of brine on a iminodiacetate column (MetPac). Prior to analysis the pH of the brine is adjusted to 11.5 with NaOH. At high pH the MetPac column has an increased selectivity for magnesium and calcium over sodium. We found that magnesium and calcium recovery was maximized at pH 11.5 and not improved at higher pH values (data not shown). Without pH adjustment there was incomplete recovery of magnesium and calcium. At lower pH values the MetPac column has a greater affinity for sodium and the high concentration of sodium in brine exhausts the capacity of the MetPac column. This leads to an incomplete recovery of magnesium and calcium. Handley et al. found that magnesium and calcium uptake by their Xylenol Orange column was highest at pH 10.8 [2]. Magnesium and calcium could not be detected in the NaOH used for pH adjustment.

After loading the MetPac with 100 μl of pH-adjusted brine, the column was rinsed with 40 ml of 1 m*M* HCl (20 min at 2 ml/min) to remove excess sodium. Smaller rinse volumes resulted in sodium peaks that were too large to reliably quantify low concentrations of magnesium and calcium. A stronger rinse solution (2 m*M* HCl) caused incomplete recovery of magnesium and calcium. This loss is presumably due to partial elution of magnesium and calcium during the rinse step.

After rinsing, magnesium and calcium were eluted from the MetPac with 20 m*M* MSA, separated on an cation-exchange column, and detected by suppressed conductivity. Fig. 2A shows an analysis of high-purity brine. This brine contains less than 5 μg/l magnesium and calcium. Fig. 2B shows the same

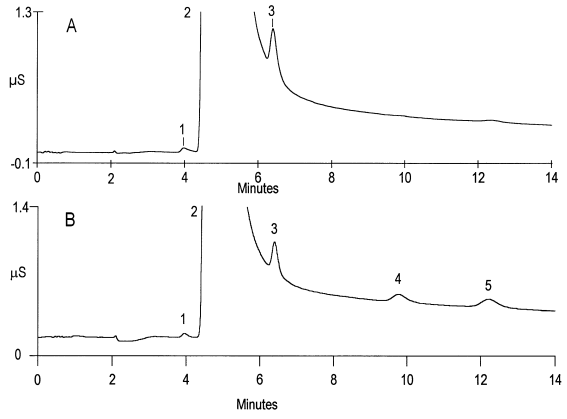

Fig. 2. Determination of magnesium and calcium in 30% NaCl. Panel A shows the analysis of 100 μl of high-purity brine. Panel B shows the analysis of 100 μl of high-purity brine to which 25 μg/l of magnesium and calcium were added. Peaks 1, 2, 3, 4, and 5 are lithium, sodium, potassium, magnesium and calcium, respectively. The chromatographic conditions are described in Section 2.

brine to which we added 25 μg/l magnesium and calcium. Even after rinsing the MetPac column a large amount of sodium remains, but not enough to interfere with the separation and quantification of magnesium and calcium. This method was linear for both magnesium and calcium in brine (r^2=0.9999 for each) over the range tested (0–200 μg/l).

Using the method described here we could reproducibly determine 5 μg/l magnesium and calcium in brine. For seven replicate injections, the area R.S.D.s were 1.9 and 2.5% for magnesium and calcium, respectively. Determination of magnesium and calcium concentrations below 5 μg/l is difficult. Larger injection volumes may be possible, but the method was nonlinear between 25 and 200 μg/l magnesium and calcium with a 200 μl injection volume due to incomplete analyte recoveries at the higher concentrations. It may be possible to reduce the run time of this method by increasing the flow-rate of the rinsing step to 4.0 ml/min and decreasing the rinse time to 10 min. In a brief study, we found that barium and strontium can be determined by extending the chromatographic run time 10 min, though with detection limits about four times higher than found for magnesium and calcium.

In conclusion, low concentrations of magnesium and calcium in brine can be reliably determined by first concentrating the cations on an iminodiacetate column. After rinsing to remove excess sodium, magnesium and calcium are separated from the remaining sodium on a cation-exchange column and detected by suppressed conductivity.

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