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Determination of Manganese in Brine ($\geq 30\%$ NaCl)

INTRODUCTION

Sodium chloride brines are used in chlor-alkali cells and must have low concentrations of alkali and alkaline earth metals to prevent membrane poisoning. As discussed in Dionex Application Note 120 (AN 120), manufacturers usually focus on determining single digit $\mu\text{g/L}$ (ppb) concentrations of magnesium and calcium.¹ However, these brines are also used to produce crystalline NaCl. When the brines are prepared from seawater, the manganese concentration is also a concern because the presence of Mn limits the size of NaCl crystals.

This application update uses the same separation conditions as AN 120, but alters the online sample preparation with the MetPac™ column to effectively concentrate manganese from 10 times more sample than used in AN 120. This allows accurate determination of 10 ppb manganese in brine. These altered sample preparation conditions do not allow quantification of calcium and magnesium in brine due to the presence of calcium and magnesium in the ammonium acetate and/or acetic acid used for sample preparation.

An eluent generator produces the methanesulfonic acid eluent for the cation separation to ensure accurate eluent production, improve retention time precision, simplify operation, and deliver the other recognized benefits of an RFIC™ system.

EQUIPMENT

Dionex ICS-3000 system consisting of

- DP Dual Pump
- DC Detector/Chromatography module
- EG Eluent Generator
- AS Autosampler
- AM Automation Manager equipped with a 10-port valve
- Chromeleon® 6.8 Chromatography Workstation

Reagents and Standards

- Deionized water (DI), Type I reagent grade, 18 M Ω -cm resistivity
- Lithium hydroxide (LiOH)
- Sodium chloride (NaCl)
- Ammonium acetate ($\text{CH}_3\text{COONH}_4$)
(See Chelation Ion Chromatography, below.)
- Potassium chloride (KCl)
- Magnesium sulfate (MgSO_4)
- Calcium chloride (CaCl_2)
- Manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$)
- Ammonia solution 20% (NH_4OH)
- Glacial acetic acid (CH_3COOH)

All compounds were ACS reagent grade or better and from reliable sources.

CONDITIONS

Guard Column: IonPac® CG12A 4 × 50 mm
(P/N 46074)

Analytical Column: IonPac CS12A 4 × 250 mm
(P/N 46073)

Flow Rate: 1.00 mL/min

Eluent Source: EluGen® II EGC-MSA
(P/N 58902)

Eluent: 20 mM methanesulfonic acid

Detection: Suppressed conductivity
CSRS® ULTRA II 4 mm, recycle
mode

Suppressor Current: 70 mA

Column
Temperature: 30 °C

Noise: <1 nS

CHELATION ION CHROMATOGRAPHY

Column: MetPac CC-1, 4 × 50 mm
(P/N 42156)

Sample Loop: 1 mL

Eluents: 2M Ammonium acetate
(P/N 33440)
100 mM Acetic acid

Preconcentration
Step: See Table 1 and Figure 1.

PREPARATION OF SOLUTIONS AND REAGENTS

Eluent Solution

Automatically generate 20 mM MSA eluent on-line by pumping DI water through the EluGen II EGC-MSA using DP Pump 1.

2M ammonium acetate, pH 5.4 ± 0.1

This reagent can be purchased from Dionex or prepared as follows. Place 600 mL of deionized or high purity water into a clean 1-L glass container. Tare the bottle. Add 121 g (115 mL) of ultrapure glacial acetic acid and mix thoroughly. In a fume hood, slowly add 133 g (148 mL) of 20% ultrapure ammonium hydroxide and mix thoroughly. Agitate the bottle to thoroughly mix

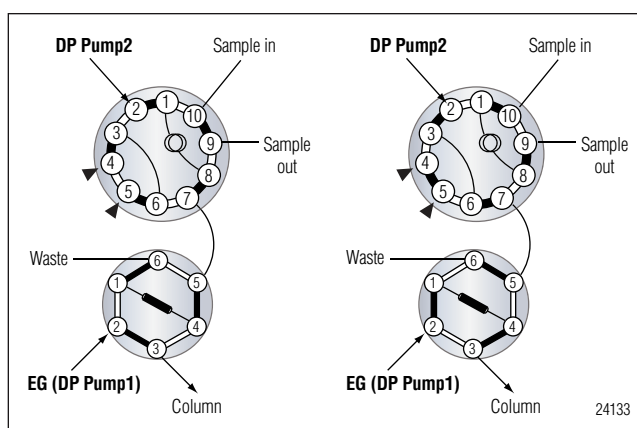


Figure 1. Left: Sample was pushed onto the MetPac. Right: Mn on MetPac eluted to column.

Table 1. Preconcentration Steps for Mn on the MetPac CC-1 Column

DP Pump2 %A: 2M ammonium acetate pH 5.4 %B: 100 mM acetic acid %C: DI water							
Pump and Valve program:							
Time (min)	%A	%B	%C	Flow (mL/min)	AM_HP (10-Port Valve) Position	Injection Valve (6-Port Valve) Position	Comment
-35.10	100	0	0	2.0	A (10-1)	inject	Inject the sample to fill the 1 mL loop.
-35.00	100	0	0	2.0	B (1-2)	load	Sample pushed onto the MetPac.
-20.10	100	0	0	2.0	B (1-2)	load	
-20.00	0	100	0	2.0	A (10-1)	load	MetPac washed with acetic acid.
-10.10	0	100	0	2.0	A (10-1)	load	
-10.00	0	0	100	2.0	A (10-1)	load	MetPac flushed with DI water.
0.00	0	0	100	2.0	A (10-1)	inject	Mn trapped on MetPac eluted onto the analytical column.

the solution. Calibrate a pH meter to pH 7. Pour about 10 mL of this buffer into a small container (scintillation vial, 10-mL disposable beaker) and measure the pH. If the pH is below 5.3, add about 5 mL of ammonium hydroxide to the buffer solution. If above pH 5.5, add 5 g of acetic acid. Adjust the pH of the ammonium acetate to 5.4 ± 0.1 using acetic acid if the pH is greater than 5.5, or ammonium hydroxide if the pH is less than 5.3. Once the pH is 5.4 ± 0.1 , bring to a volume of 1.0 L with 18-M deionized water.

100 mM acetic acid

Prepare 1 M acetic acid as the stock solution. Place 200 mL of deionized water into a clean 1-L polyethylene bottle. Add 60.0 g (57.1 mL) of trace metal grade acetic acid and dilute to 1 L. Label 1.0 M acetic acid.

To prepare 100 mM acetic acid, place 900 mL of deionized water into a clean bottle. Add 100 mL of stock 1 M acetic acid and mix thoroughly.

Stock Standard Solution

Prepare 1000 mg/L standards for each of the cations in DI water. Standards should be prepared from the highest purity compounds available. Table 2 provides the amounts needed to prepare 100 mL of each standard. Concentrated standards are stable for at least one month when stored at 4 °C.

Table 2. Masses of Compounds Used to Prepare 100 mL of 1000 mg/L Cation Standards

Cation	Compound	Amount (g)
Lithium	Lithium hydroxide	0.345
Sodium	Sodium chloride	0.254
Ammonium	Ammonium acetate	0.428
Potassium	Potassium chloride	0.191
Magnesium	Magnesium sulfate	0.495
Calcium	Calcium chloride	0.277
Manganese	Manganese sulfate monohydrate	0.307

Samples

Analyze liquid samples without dilution. Dissolve approximately 5 g of each solid sample in 100 mL of deionized water prior to analysis.

RESULTS AND DISCUSSION

Sample Preparation and Separation

To determine $\mu\text{g/L}$ concentrations of manganese in sodium chloride brines, manganese must be concentrated while sodium is eliminated. Dionex AN 120 shows how this can be accomplished for magnesium and calcium using a MetPac column to bind them while binding very little sodium, after adjusting the sample pH to 11.5. Unfortunately, these conditions cannot be used to achieve the required sensitivity and recovery for manganese. Therefore, it is necessary to alter the sample preparation conditions on the MetPac column to capture manganese by chelation while excluding most of the sodium. Apply the sample with 2M ammonium acetate, pH 5.4, rinse the majority of the sodium from the MetPac with an acetic acid rinse, remove the acetic acid with a water rinse, and elute the bound manganese to the IonPac C12A column set for separation from sodium, magnesium and calcium. This method requires two valves and a second pump for sample preparation, and is easily setup with an ICS-3000 equipped with a dual pump and an automation manager.

Figure 2 shows a chromatogram of the water blank and chromatograms of four manganese standards of 10, 20, 50, and 100 $\mu\text{g/L}$, determined using the chelation IC method. These standards were used for method calibration and yielded a correlation coefficient for a linear fit of 0.9985. The chromatogram of the blank indicates there is no manganese in the water nor in any of the reagents used for sample preparation. There are significant concentrations of magnesium and calcium in the blank due to the presence of these cations in either the ammonium acetate and/or the acetic acid. This method cannot be used to determine low $\mu\text{g/L}$ concentrations of magnesium and calcium in brine. If those analytes must be determined, use the method in AN 120. Figure 2 shows that manganese is well resolved from magnesium, calcium, and the remaining sodium.

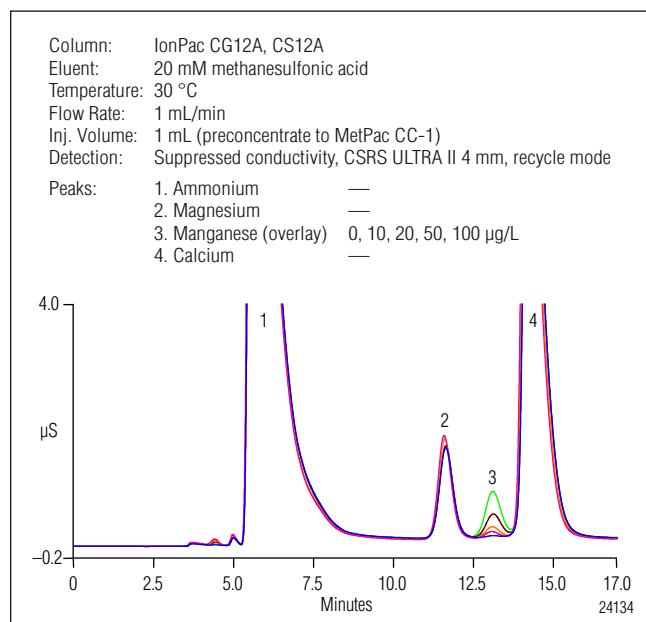


Figure 2. Determination of manganese at µg/L concentrations (0, 10, 20, 50, 100 µg/L) using chelation IC.

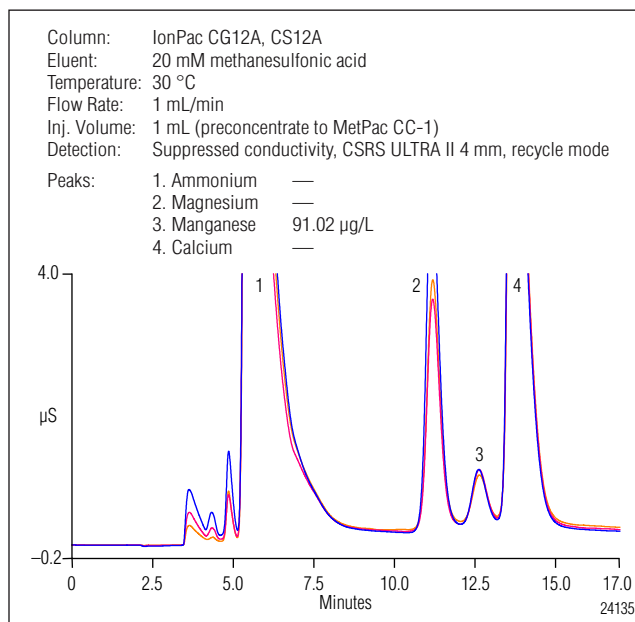


Figure 3. Overlay of three injections of liquid sample #1. Average amount of manganese (peak 3): 91.02 µg/L.

Sample Analysis

Manganese was determined in eight liquid and two solid sodium chloride samples provided by a company specializing in the production of these products (see Acknowledgements). Figures 3 and 4 show chromatograms for three injections each of two liquid samples, #1 and #2. These samples had two of the highest concentrations of manganese of the ten samples tested. The chromatograms in Figures 2, 3, and 4 had retention time RSDs of 0.14 and 0.10. The peak area RSDs were 8.97 and 7.51. Tables 3 and 4 show the results for all 10 samples. The results for samples 5, 7, 9 and 10 represent single analyses. All other results represent the mean of three analyses. Manganese concentrations in the liquid samples ranged from <1 to 90 µg/L.

To judge method recovery, manganese was spiked into four of the liquid samples, and the manganese measured in spiked and unspiked samples (Table 5). These samples were analyzed separately from those reported in Table 3. Table 5 shows acceptable recovery, demonstrating that manganese is not lost during sample preparation.

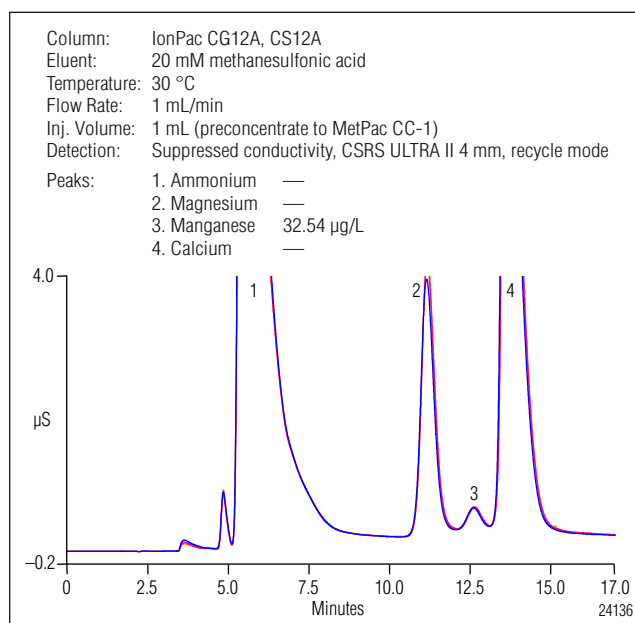


Figure 4. Overlay of Three Injections of Liquid Sample #2. Average amount of manganese (peak 3): 32.54 µg/L.

Table 3. Analysis of Liquid Samples

Sample Number	Ret.Time (min)	Area (µS*min)	Height (µS)	Amount (µg/L)
1	12.630	0.405	0.773	91.02
2	12.626	0.158	0.317	32.54
3	12.529	0.161	0.400	43.05
4	12.572	0.049	0.132	14.98
5	12.783	0.046	0.108	6.29
6	12.083	0.008	0.028	0.33
7	12.820	0.115	0.227	22.60
8	12.667	0.091	0.251	23.65

Table 4. Analysis of Solid Samples

Sample Name	Ret.Time (min)	Area (µS*min)	Height (µS)	Amount (dissolved sample) (µg/L)	Amount in Solid (µg/g)
#9 5.092g /100 mL	13.06	0.118	0.2069	23.16	0.455
#10 5.192g /100mL	13.08	0.103	0.177	19.65	0.378

Table 5. The Recovery of Manganese from Liquid Samples

Sample Name	Average* Amount (µg/L)			
	Sample	Spike	Spike + Sample	% Recovery
#3	43.05	20	66.88	119
#4	14.98	20	33.73	93.8
#6	0.33	20	17.11	83.9
#8	23.65	20	38.23	72.9

* Each sample, including spiked samples, was injected three times.

SUMMARY

This application determines trace concentrations of manganese in sodium chloride brines, with automated sample preparation. Manganese and alkaline earth cations are selectively preconcentrated on-line, and most of the sodium is removed. The manganese and other cations are eluted from the concentrator column to the cation-exchange column, where they are separated and detected by suppressed conductivity. This method exhibited good linearity in the concentration range of interest, and good recovery.

REFERENCES

1. *Determination of Calcium and Magnesium in Brine*; Application Note 120, LPN #0990; Dionex Corporation, Sunnyvale, CA, 1998.

ACKNOWLEDGEMENTS

Dionex would like to thank Keith Hand of Riotinto Corporation for providing the brine samples.

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LPN 1891 09/16
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