

Analysis of Four Elements (Ca, Mg, Si, Sr) in Brine Using the Agilent 5100 ICP-OES

Application note

Speciality chemicals

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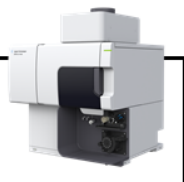
Introduction

The chloralkali process is an industrial process for the electrolysis of NaCl used to produce chlorine and sodium hydroxide (caustic soda), which are commodity chemicals required by industry.

The most common chloralkali process involves the electrolysis of aqueous sodium chloride (a brine) in a membrane cell. The sodium chloride solution being used must have a high degree of purity and if it contains any other metal ions, these will also pass through the membrane and so contaminate the sodium hydroxide solution.

Thus, prior to the chlorakali process, sodium chloride needs to be treated by an ion exchange system. The ion exchange system is used to further reduce the calcium, magnesium and strontium concentrations in the brine stream to the levels required to operate and sustain good overall performance of a chloralkali membrane cell electrolyser. The ion exchange system consists of three columns with associated

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pipng, valves and instruments. The calcium content of brine passing through the ion exchange system is lowered from 3 to 5 ppm to less than 20 ppb. During normal operation, brine flows through two columns which operate in series (one primary column and one secondary column). Alkaline brine enters the top of the column and flows downward through the resin bed. As the brine contacts the resin, the calcium, magnesium and strontium ions in solution are “exchanged” for sodium ions in the resin. The resin bed becomes “exhausted” where there is too few sodium ions left to exchange with the calcium, magnesium and strontium ions, resulting in the “break-through” of calcium ions in concentrations exceeding 20 ppb in the exiting brine. Lab analysis of the brine downstream of the primary column every 8 hours is used to determine when break-through has occurred indicating the need to regenerate the primary column. Calcium, magnesium, strontium should be monitored for break-through.

In this study, the Agilent 5100 ICP-OES was used for the analysis of 4 impurities elements (Ca, Mg, Si, Sr) in sodium chloride brine sampled at different steps of purification process in order to evaluate purification efficiency:

1. At the input to the first purification tower (sample type A)
2. At the input to the last purification tower (sample type B)
3. The output of the last purification tower (sample type C).

Samples were collected on three different days, resulting in three samples of each sample type e.g. A1, A2 and A3, where A1 was collected on Day 1 at the input to the first purification tower, through to C3, which was collected on Day 3 from the output of the last purification tower.

The 5100 VDV ICP-OES is highly suited to the analysis of brines. It uses a vertically orientated torch and a solid state radiofrequency (SSRF) system operating at 27 MHz to provide a robust plasma capable of handling high dissolved solids solution and delivering long term analytical stability with less cleaning and less replacement torches.

In this study, the accuracy and robustness of the Agilent 5100 ICP-OES were evaluated for the determination of Ca, Mg, Sr and Si in brine.

Experimental

Instrumentation

All measurements were performed using an Agilent 5100 ICP-OES. The sample introduction system consisted of a Seaspray glass concentric nebulizer, double-pass cyclonic spray chamber and a 1.8 mm i.d. injector torch.

All measurements were performed in axial plasma viewing mode. An Agilent SPS 3 Sample Preparation System was used for automatic sample delivery. The instrument operating conditions are summarized in Table 1 and the wavelengths selected for the analysis are given in Table 2.

Table 1. Agilent 5100 VDV ICP-OES method and instrument operating parameters

Parameter	Setting
RF Power (kW)	1.35
Aux Flow (L/min)	1.1
Plasma Flow (L/min)	13.5
Nebulizer Flow (L/min)	0.7
Pump speed (rpm)	10
Sample pump tubes	White/White
Drain pump tubes	Blue/Blue
Background correction	Fitted
Read time (s)	10
Replicates	3
Sample uptake delay (s)	30 (fast pumping: On)
Stabilization time (s)	15
Rinse time (s)	40 (fast pumping: On)
Autosampler Rinse Solution	2% HCl

Table 2. Wavelengths selected for the analysis

Element	Wavelengths
Ca	396.847 nm
Mg	279.553 nm
Sr	407.771 nm
Si	288.158 nm

Standard and sample preparation

All brine (30% NaCl) samples were diluted 2x with pure water.

As no pure enough sodium chloride is available to prepare matrix matched standards, the method of standard additions (MSA) was used for the analysis to give the best accuracy in determining sample concentrations.

Typical concentrations of the 4 elements in the three types of samples prior to dilution are shown in Table 3.

Standard additions were prepared by spiking 1:2 diluted brines with different volumes of a stock solution. Spiked concentrations are shown in Table 4.

Table 3. Typical concentration in µg/L of analyte in the brine samples prior to dilution

	Ca	Mg	Sr	Si
Type A	1000	10	1000	4000
Type B	10	1	20	4000
Type C	<8	<1	<10	4000

Table 4. Concentration, in µg/L, spiked into brine samples for standard addition

Sample A				
Ca	Mg	Sr	Si	
500	20	500	1000	
1000	40	1000	2000	
2000	80	2000	4000	
Sample B				
Ca	Mg	Sr	Si	
20	10	100	1000	
40	20	200	2000	
80	40	400	4000	
Sample C				
Ca	Mg	Sr	Si	
5	5	10	1000	
10	10	20	2000	
20	20	40	4000	

Results and discussion

All following tests were carried out on the collected samples.

Calibration

Figures 1a, 1b, 1c and 1d show that the method has the linearity and sensitivity required for the determination of Ca, Mg, Si and Sr at very low concentrations in diluted 1:2 brine C1 (approximately 150 g/L of NaCl).

Excellent correlation coefficients were obtained for all measured elements.

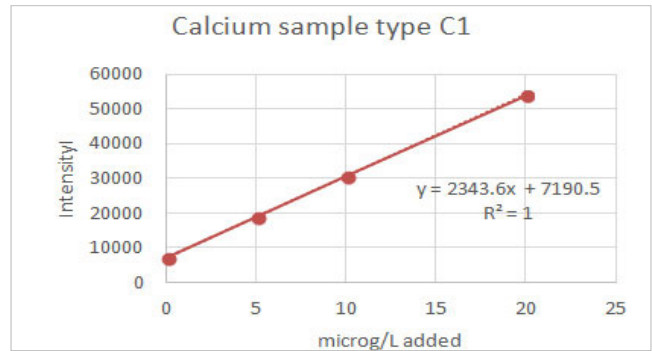


Figure 3a. Standard addition curve for Ca in Sample C1

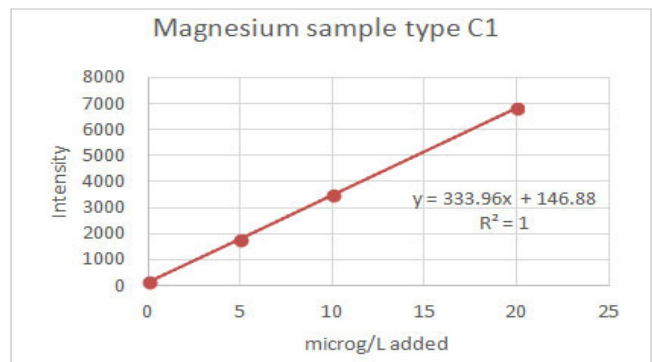


Figure 3b. Standard addition curve for Mg in Sample C1

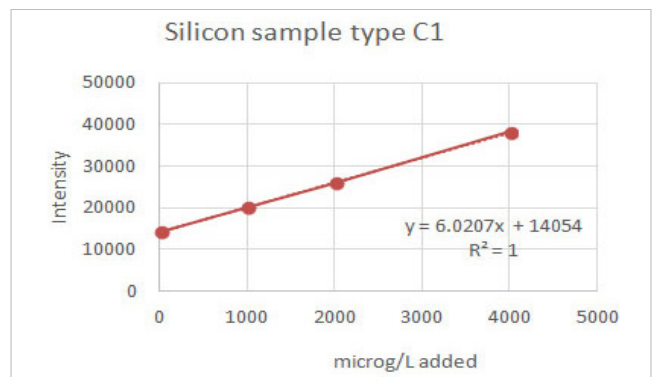


Figure 3c. Standard addition curve for Si in Sample C1

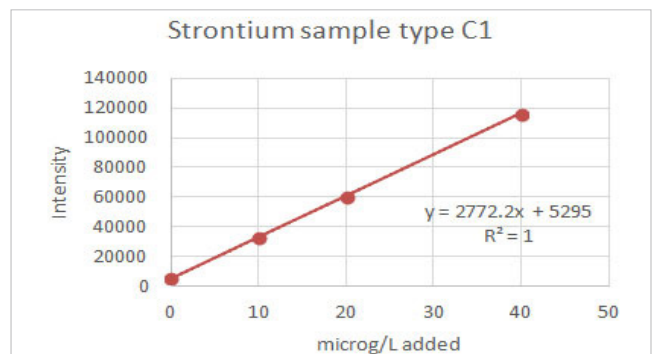


Figure 3d. Standard addition curve for Sr in Sample C1

Purification efficiency

As the samples (A, B, C) were taken at different steps of the ion exchange purification process, they could be used to determine the purification efficiency for Ca, Mg and Sr. Table 5 shows the efficiency achieved on the first day of sampling (samples A1, B1 & C1).

Table 5. Measured concentration of Samples A1, B1 and C1

Elements	Input to the first purification tower (sample A1) µg/L	Input to the third purification tower (sample B1) µg/L	Output to the third purification tower (sample C1) µg/L
Ca	1100	6.2	6.14
Mg	4.76	0.92	0.88
Sr	821.5	17.9	3.82
Si	4938	4759	4669

Repeatability

In order to check repeatability and stability of the 5100 ICP-OES, sample C2 (diluted as described in Sample Preparation) was spiked with 10 µg/L of Ca and Mg, and 5 µg/L of Sr and then measured approximately 50 times, over a one and a half hour period

Excellent repeatability was obtained for all elements analyzed over this period, with less than 6% RSD as shown in table 6.

Table 6. Repeatability results of spiked elements in diluted sample C2

	Ca	Mg	Sr	Si
Spiked sample C2 (µg/L)	13.53	10.78	9.95	3171
Standard Deviation	0.69	0.13	0.039	19.07
%RSD	5.10	1.21	0.39	0.60

Table 7. Measured values and spike recoveries for 4 elements in diluted sample C3

Sample type C					
Elements	Spiked Conc. µg/L in diluted sample C3	Measured Conc of Diluted Sample C3 µg/L	Measured Conc of Spiked diluted Sample C3 µg/L (average of 5 measurements)	Calculated Conc of undiluted Sample C3 µg/L	Spike % Recovery
Ca	10	3.74	13.84	7.47	101.0
Mg	10	1.72	11.80	3.43	100.9
Sr	20	1.35	21.51	2.70	100.8
Si	2000	3359	5380	6718	101.1

Spike recoveries

In order to check the accuracy of the method, sample C3 (diluted as described in Sample Preparation) was spiked with 10 µg/L of Ca and Mg, 20 µg/L of Sr and 2000 µg/L of Si. Table 7 shows the measured concentrations and recovery results of the four elements in the diluted brine sample C3. The recovery results for Ca, Mg, Sr, Si in diluted brine sample C3 using this method were within ±2% of the spike concentration values. These excellent recoveries demonstrate the ability of the 5100 ICP-OES to accurately determine Ca, Mg, Si and Sr at the levels required in brines.

Instrument efficiency

During the sample analysis, the time taken to analyze each sample and the volume of argon consumed were determined. The sample measurement time was 115 seconds per sample. The argon consumption was 36 L per sample.

Conclusions

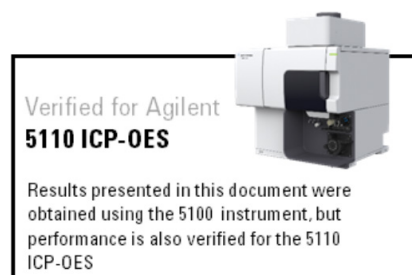
Agilent's 5100 ICP-OES was able to perform the routine analysis of brine samples with excellent sensitivity, accuracy and robustness. Only a 2 fold dilution of the samples was required without the need for an argon humidifier.

The method, which uses a vertical torch, operating in axial-viewing mode, is highly productive and cost-effective.

The method of standard additions gave excellent results, overcame the issues of finding pure NaCl for matrix matching, and eliminated the need for an internal standard.

References

Benefits of a vertically oriented torch— fast, accurate results, even for your toughest samples, Agilent publication, (2016), 5991-4854EN.



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Published May 15, 2017

Publication number: 5991-7914EN