APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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The Analysis of Brines With the Avio 200 ICP-OES

Introduction

Brines are available in several forms, the most common being sodium chloride (NaCl)-based. These brines are used primarily in the production of chlorine gas (Cl_2) via electrolysis and the polymeric membrane cell process.[1] In this process, brines (usually 20-30% NaCl) are passed through an ion-exchange membrane, where the brine is de-chlorinated via electrolysis to produce chlorine gas. This is the most widely used means of producing Cl_2 because the membrane cell process consumes the least amount of energy compared to other Cl_2 production processes.

In order to maximize the process' efficiency, the membrane must remain clean, as contamination will poison it. Since replacing the membrane is expensive, it should only be changed when needed, and this can be defined by monitoring the elemental concentrations in the brine, particularly elements which can poison the membrane. Critical elements include aluminum (Al), barium (Ba), calcium (Ca), iron (Fe), magnesium (Mg), nickel (Ni), silicon (Si), and strontium (Sr). These elements should all be present at less than 0.1 mg/L in the brine, meaning that low concentrations have to be measured accurately.

Brine analysis presents a challenge due to the extremely high levels of total dissolved solids (20-30%) and the low analyte levels. Because of its ability to handle high levels of dissolved solids, ICP-OES is the preferred analytical technique for brine analysis.

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This work will focus on the determination of critical elements in brines using PerkinElmer's Avio® 200 ICP-OES. The requirements of being able to measure low concentrations in a matrix with a very high level of dissolved solids makes the Avio 200 hybrid-scanning ICP-OES the perfect instrument for this analysis. The key to Avio 200's ability to handle high levels of dissolved solids is PlasmaShear™ technology, generating a thin stream of air which cuts off the top of the plasma, eliminating deposition on the interface window, resulting in exceptional stability in difficult matrices with no maintenance required. The unique optical design of the Avio 200 results in exceptional sensitivity for an ICP-OES instrument, allowing accurate analysis of low analyte concentrations, and paired with Dynamic Wavelength Stabilization, which virtually eliminates wavelength drift by correcting for any residual spectral shifts, the Avio 200 delivers robust performance with challenging matrices. Plus, the fast startup of the Avio 200 system means you can be analyzing samples in 10 minutes from a cold start, giving you the flexibility to analyze samples only when you have a need. The combination of the fast startup, robustness and sensitivity makes the Avio 200 ICP-OES the ideal instrument for the determination of important elements in brines.

Experimental

Samples and Sample Preparation

High-purity NaCl was purchased from several vendors. Although these NaCls had purities better than 99.99%, they still had significant levels of the critical elements, as shown in Table 1, which reports the certificate values of the analytes.

Table 1. Certificate Concentrations of the Analytes in High-Purity NaCl.

Element	99.999% NaCl (µg/g)	99.995% NaCl (µg/g)
Al	---	<0. 1
Ba	---	< 0.1
Ca	1.6	2.0
Fe	---	< 0.1
Mg	0.3	< 0.1
Ni	0.3	< 0.1
Si	---	---
Sr	---	< 0.1

--- = not specified on certificate

Brines containing 10% and 15% NaCl were prepared in 1% HNO_3 to simulate concentrated brines (20-30% NaCl) diluted 2x prior to analysis.

Calibration standards were also prepared in 10% and 15% NaCl to matrix-match the samples, which is recommended due to the matrix effects caused by such high levels of NaCl in the plasma. Yttrium (Y) was added to all samples and standards as an internal standard.

Instrumental Parameters

All analyses were performed on an Avio 200 ICP-OES (PerkinElmer, Shelton, Connecticut USA) using the conditions and parameters shown in Table 2; the elements and wavelengths used are shown in Table 3. Due to the high salt content of the samples, a SeaSpray™ nebulizer along with an argon humidifier were used to prevent NaCl deposition on the tip of the nebulizer and injector. All analyses were performed in axial view to maximize sensitivity, allowing the measurement of low concentrations.

Table 2. Avio 200 ICP-OES Instrumental Parameters and Conditions.

Parameter	Value
Sample Uptake Rate	1 mL/min
Nebulizer	SeaSpray™
Spray Chamber	Baffled Glass Cyclonic
Injector	Sapphire, 2 mm id
Torch Type	1-slot
Torch Position	-3
RF Power	1500 W
Integration Time	0.5-2 sec
View Mode	Axial

Table 3. Elements and Wavelengths.

Element	Wavelength (nm)
Al	396.153
Ba	455.403
Ca	393.366
Fe	259.939
Mg	280.271
Ni	221.648
Si	251.611
Sr	407.771
Y (int std)	371.029

Results and Discussion

In the absence of reference materials, accuracy was demonstrated by constructing low-level calibration curves in the 2x diluted brines, as shown in Figures 1 and 2 for 10% NaCl and 15% NaCl. Calibration curves were created from 2, 4, 6, 8, and 10 µg/L standards for Al, Be, Fe, Mg, and Sr, and at 5, 10, and 20 µg/L for Ca, Ni, Si. The ability to accurately and consistently measure low concentrations is limited by the contamination of the NaCl, as shown in Table 1. With regressions > 0.998, the accuracy of these low-level measurements is demonstrated.

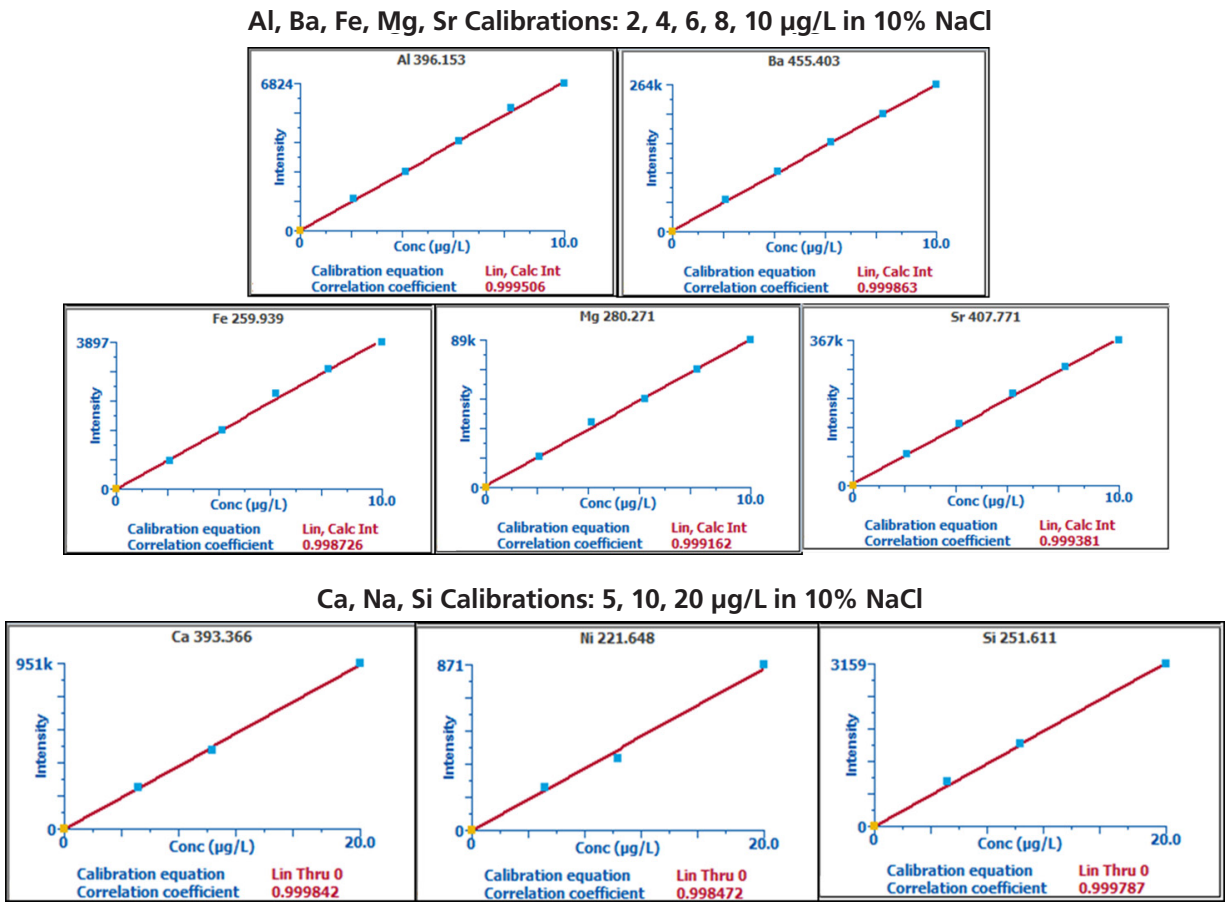

Figure 1. Calibration curves in 10% NaCl.

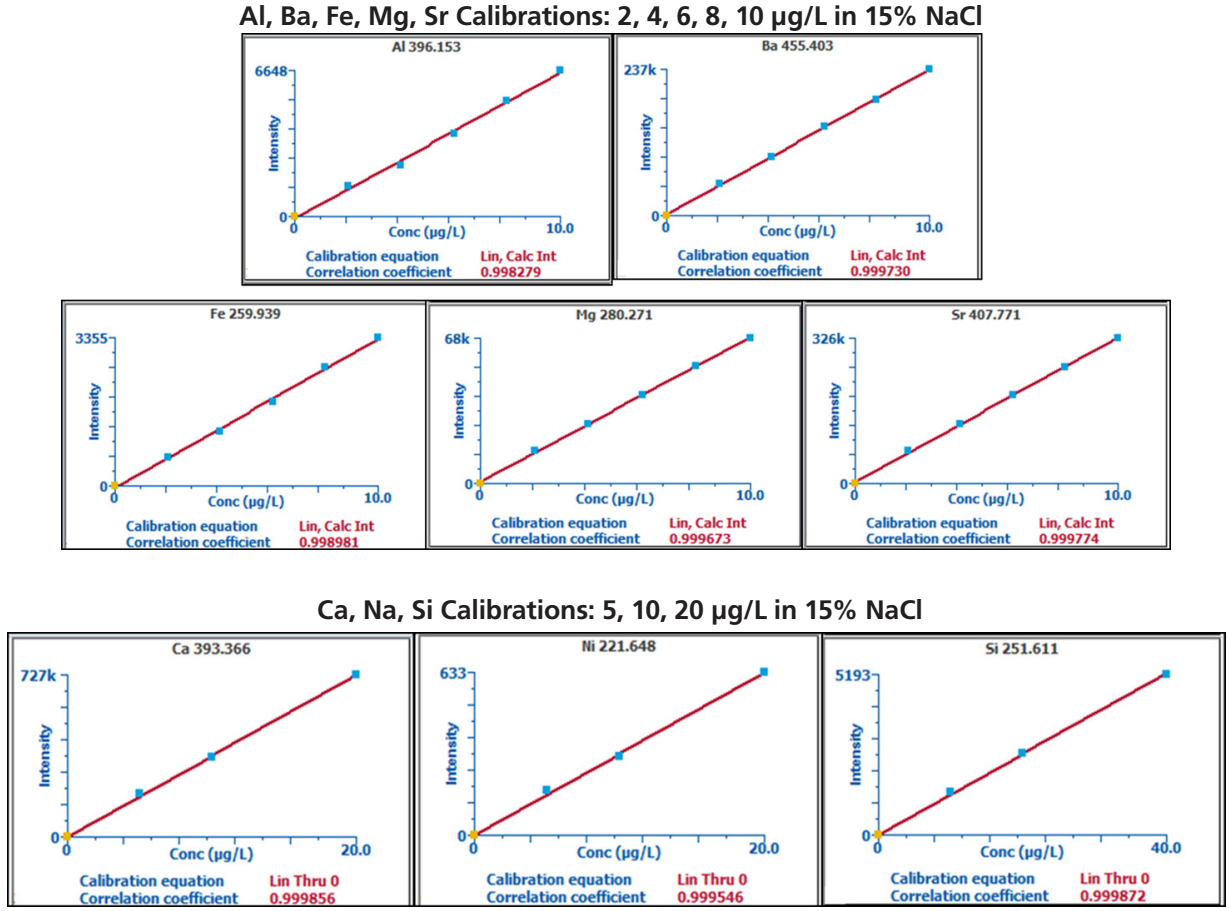

Figure 2. Calibration curves in 15% NaCl..

Detection limits were determined by analyzing blank 10% NaCl and 15% NaCl solutions seven consecutive times (i.e. as seven samples) against calibration curves. The standard deviation of these seven measurements was multiplied by three to give the detection limits, as shown in Table 4. For most of the elements, the detection limits were slightly higher in the 15% NaCl than 10% NaCl, which results from the presence of impurities in the NaCl: higher impurity levels result in higher signals in the blank, which yield higher standard deviations. The detection limits for all elements are less than 2 µg/L, demonstrating the ability to perform low-level analyses in 2x diluted brines.

Table 4. Detection Limits in 10% NaCl and 15% NaCl.

Element	10% NaCl (µg/L)	15% NaCl (µg/L)	DL Ratio: 15%/10% NaCl	Influenced by Impurities?
Al	0.69	0.56	0.81	No
Ba	0.02	0.04	1.7	Yes
Ca	0.31	0.49	1.6	Yes
Fe	0.32	0.53	1.6	Yes
Mg	0.12	0.19	1.6	Yes
Ni	1.51	1.19	0.79	No
Si	1.62	1.82	1.1	Yes
Sr	0.02	0.02	0.91	No

Taken together, the calibrations and the detection limit studies show that equivalent results are obtained in both 10% and 15% NaCl, demonstrating that the NaCl concentration does not affect the ability to measure low levels of these analytes.

Accuracy was next determined by calibrating with 5, 10, and 20 µg/L standards in 10% and 15% NaCl and reading back 15 µg/L as a check standard. Table 5 shows that all recoveries are within 10%, further demonstrating that the NaCl concentration does not affect the ability to accurately measure low concentrations.

Table 5. 15 µg/L Recoveries in 10% and 15% NaCl.

Element	10% NaCl (µg/L)	15% NaCl (µg/L)
Al	103%	103%
Ba	100%	101%
Ca	108%	105%
Fe	99%	103%
Mg	100%	102%
Ni	103%	105%
Si	100%	100%
Sr	99%	107%

With the accuracy established, the stability of the overall method was evaluated by measuring a 50 µg/L analyte spike in both 10% and 15% NaCl over a four-hour time period. Figures 3 and 4 show the stability plots, where the signals are normalized to the first sample. With deviations of 10% or less for all analytes over four hours, the robustness and stability of the methodology are demonstrated.

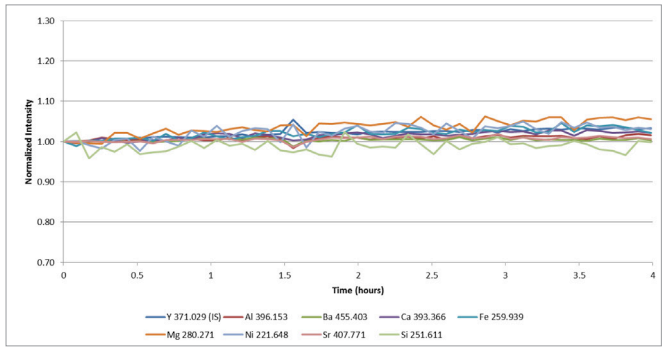

Figure 3. Four-hour stability of 50 µg/L analyte spike in 10% NaCl. All signals normalized to the first reading.

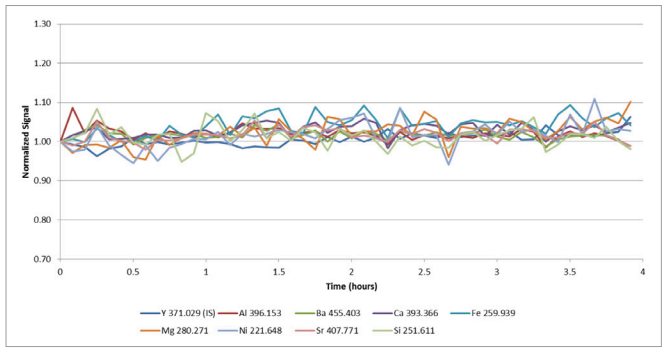

Figure 4. Four-hour stability of 50 µg/L analyte spike in 15% NaCl. All signals normalized to the first reading.

Conclusion

This work has demonstrated the capability of the Avio 200 ICP-OES to accurately measure the critical elements in brines diluted 2x. Accuracy at low concentrations was shown with both low-level calibrations in the brine and low-level spike recoveries. Stability was established through a four-hour analysis of 2x diluted brines. With similar results being obtained in both 10% and 15% NaCl, it has been established that the NaCl concentration has little or no effect on the analysis, meaning that this methodology can be applied to both 25% and 30% NaCl brines simply diluted 2x.

Reference

1. "The Membrane Cell Process", http://www.eurochlor.org/the-chlorine-universe/how-is-chlorine-produced/the-membrane-cell-process.aspx Euro Chlor, 2017.

Consumables Used

Component	Part Number
Drain Tubing: Red/Red (1.14 mm id) PVC	09908585
Sample Uptake Tubing: Black/Black (0.76 mm id), Flared	N0777043
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)
Instrument Calibration Standard 2	N9301721 (125 mL)
Pure Grade Silicon Standard (1000 mg/L)	N9303799 (125 mL) N9300150 (500 mL)
Pure Grade Yttrium Standard (1000 mg/L)	N9303810 (125 mL) N9300167 (500 mL)

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