

Industrial

Managing the challenges of analyzing brine solutions of variable concentration using inductively coupled plasma mass spectrometry (ICP-MS) equipped with argon gas dilution

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Keywords

Argon gas dilution, brine solution, high matrix, high resolution, ICP-MS, KED, single quadrupole

Goal

To highlight how ICP-MS can be used to determine impurities in highly concentrated brine solution (up to 25% w/w) with high sensitivity, accuracy, and robustness using automated sample dilution with argon gas delivered from the instrument.

Introduction

Brine is a solution of sodium chloride in water, containing up to 25% w/w of dissolved salt. It is a key sample type that needs to be analyzed in a variety of industrial applications and is commonly measured in environmental monitoring studies (for example, when analyzing brackish or sea waters). With the fast transition to electric vehicles (EVs) and sustainable energy storage, another important application requiring the analysis of brine solutions has emerged. Underground brines¹ and lithium-rich minerals and rocks² are key sources for meeting the rapidly growing global demand for lithium. While brine solutions can be potentially rich, relatively easy-to-access sources of lithium, consideration must be given to the potential impact of the exploitation activities themselves on climate change, related environmental risks, and raw material supply.³ Therefore, the lithium and common impurities content should be assessed, and less abundant impurities monitored. One key class of such impurities is the lanthanide elements. Extraction of rare earth elements (REEs) in brine is also a significantly important process for a range of industrial purposes, even though REEs are present at low concentrations in brine water (typically ng·L⁻¹ level).⁴

In general, inductively coupled plasma mass spectrometry (ICP-MS) is the preferred analytical technique for the analysis of metals and related contaminants at low levels. However, the analysis of samples containing higher levels of dissolved solids (typically above 0.5% w/v) is a known challenge in ICP-MS. The complexity of the sample matrix can significantly affect the sensitivity of the instrument, cause intensity fluctuation of the internal standard (suppression and drift), and lead to increased system maintenance with unwanted downtime due to clogging of the interface cone orifices, torch injector, or nebulizer tip. To analyze complex samples such as brine, dilution must be performed, either using liquid dilution or, alternatively, dilution of the sample aerosol with an inert gas such as argon. Dilution with argon gas is a particularly attractive option, as samples can be placed directly on the autosampler without the need of a manual, time-consuming dilution step prior to analysis. This application note describes an optimized analytical method for the analysis of a variety of brine samples using the Thermo Scientific™ iCAP™ RQplus ICP-MS. To overcome the analytical challenges described above, the instrument was operated using argon gas dilution (AGD).

Experimental

Experimental optimization of instrument parameters

An iCAP RQplus ICP-MS fitted with the AGD option, and operated using the highest dilution setting, was used for all analyses. Within Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, three different dilution settings are available and can be intuitively selected by the user when creating a LabBook (Figure 1). In addition to the standard set up for AGD, the additional gas flow added to the sample aerosol before it enters the plasma was humidified. The use of a humidifier (*pergo*, Elemental Scientific (ESI), Omaha, USA) significantly improves the analysis of elements with high ionization potential, such as arsenic and selenium, which could otherwise suffer from reduced recovery in the matrix. The sample introduction system consisted of a Peltier cooled (set at 2.7 °C), baffled cyclonic spray chamber, PFA microflow nebulizer, and quartz torch with a 2.5 mm i.d. removable quartz injector. The instrument was operated using kinetic energy discrimination (KED) to facilitate interference free analysis of all analytes over the full mass range using helium in the QCell collision/reaction cell (CRC). To allow the signal of the only isotope of sodium (sodium is monoisotopic at m/z 23) to be monitored as well, the quadrupole resolution for this analyte was reduced to decrease the number of recorded ions and prevent excessive use of the detector system. To automate the sampling process, an autosampler was used. Table 1 summarizes the instrument configuration and analytical parameters. Measurement modes were optimized using the default autotune procedures available through the Qtegra ISDS Software.

Identifier	Δ	Dwell time (s)	Measurement mode	Resolution
7Li (KED AGD hig		0.1	KED AGD high	Normal
23Na (KED AGD		0.1	KED AGD high	High
27Al (KED AGD h		0.1	KED AGD high	Normal
45Sc (KED AGD		0.1	KED AGD high	Normal
51V (KED AGD hi		0.1	KED AGD high	Normal
52Cr (KED AGD		0.1	KED AGD low	Normal
55Mn (KED AGD		0.1	KED AGD mid	Normal
56Fe (KED AGD		0.1	KED	Normal
59Co (KED AGD		0.1	STD AGD high	Normal
63Cu (KED AGD		0.1	STD AGD low	Normal
66Zn (KED AGD		0.1	STD AGD mid	Normal
71Ga (KED AGD		0.1	STD	Normal
75As (KED AGD		0.1	KED AGD high	Normal
78Se (KED AGD		0.1	KED AGD high	Normal
85Rb (KED AGD		0.1	KED AGD high	Normal
88Sr (KED AGD h		0.1	KED AGD high	Normal
89Y (KED AGD hi		0.1	KED AGD high	Normal
103Rh (KED AGD		0.1	KED AGD high	Normal
107Ag (KED AGD		0.1	KED AGD high	Normal
111Cd (KED AGD		0.1	KED AGD high	Normal

Figure 1. Acquisition parameters on Qtegra ISDS Software

Table 1. Instrument configuration and operating parameters

Parameter	Value
Nebulizer	ESI PFA MicroFlow ST, orange cap, 400 $\mu\text{L}\cdot\text{min}^{-1}$
Peristaltic pump tubing	PVC orange-green tubing, 0.38 mm i.d. (both: sample and internal standard)
Peristaltic pump speed	25 rpm
Spray chamber	Quartz cyclonic, cooled at 2.7 °C
Torch	Quartz torch
Injector	2.5 mm i.d., Quartz
Interface	Nickel sampler and skimmer cone with high matrix insert
Plasma power	1,550 W
AGD setting	High
Nebulizer gas	0.22 $\text{L}\cdot\text{min}^{-1}$
Additional gas flow (Ar) for dilution	0.80 $\text{L}\cdot\text{min}^{-1}$
CRC gas	100% He 4.2 $\text{mL}\cdot\text{min}^{-1}$
KED	3 V
Scan setting	0.1 s dwell time, 5 sweeps, 3 main runs
Analysis time per sample	Total 3 min 46 s: including uptake and wash out

Data acquisition and data processing

Instrument control (auto tuning, calibration, etc.) as well as data acquisition, processing, and reporting were carried out using the Qtegra ISDS Software. This software provides a wide range of features, including a comprehensive feature set for quality control testing, and enables both new and experienced users to leverage the full potential of the instrument. In addition, Qtegra Software includes the Thermo Scientific™ Hawk™ Instrument Health Monitoring system, which allows the user to monitor usage of all components of the sample introduction system, and hence helps to streamline instrument uptime through fully planned maintenance.

Sample preparation

Polypropylene bottles were used for the preparation of all blanks, standards, and samples.

A brine solution containing 25% w/w of NaCl was prepared by dissolving 25 g of pure NaCl (Sigma-Aldrich, 99.0%) in 100 g 2% v/v HNO₃ (Optima™ grade, Fisher Scientific™).

All blanks, calibration standards, matrix spike, and quality control (QC) solutions were prepared using a mixed acid diluent (2% v/v HNO₃ and 0.5% v/v HCl (Optima™ grade, Fisher Scientific™)) and multi-element standards (SPEX™ CertiPrep™, Metuchen, NJ, USA) to result in the concentration ranges listed in Table 2. The details of the measurement modes, acquisition parameters, and internal standards used for each element are shown in Table 3.

To assess the potential for fully quantitative analysis of brine solutions, the internal standards were closely monitored for matrix suppression. To demonstrate the capability of the instrument for accurate and precise analysis despite the challenging sample matrix, spike recovery tests were performed with brine solutions ranging from 0.5% w/w to 4% w/w, prepared from the original 25% w/w brine solution described earlier.

To test the performance of the method for the analysis of such sample types over longer periods and demonstrate analytical robustness for a high throughput orientated laboratory, a brine solution with a concentration of 2.5% w/w was analyzed over a period of 9 hours.

An internal standard solution, containing 1,000 µg·L⁻¹ Sc and 200 µg·L⁻¹ Y, Rh, Te, and Lu in 2% v/v HNO₃, was added on-line to all samples via a T-piece (mixing rate between internal standard and samples 1:1) before entering the nebulizer.

Results and discussion

Sensitivity and linearity

Table 3 summarizes the instrument detection limits (IDLs) obtained, together with the coefficient of determination (R²), for all 34 elements analyzed in this study. The IDLs were calculated as three times the standard deviation of ten replicate measurements of the calibration blank. As no manual dilution was performed prior analysis, these IDLs directly correspond to the method detection limits (MDLs). Note that these method detection limits include the dilution factor applied using AGD.

Table 2. Summary of the concentration details of the CCB (Continuing Calibration Blank), CCV (Continuing Calibration Verification), and spike recovery test QC solutions

QC items	QC solution detail
CCB	2% v/v HNO ₃
CCV (lanthanides)	0.2 µg·L ⁻¹
CCV (others)	10 µg·L ⁻¹
Spike recovery (lanthanides)	0.1 and 0.2 µg·L ⁻¹ spiked in between 0.5% and 4.0% brine samples
Spike recovery (others)	25 µg·L ⁻¹ spiked in between 0.5% and 4.0% brine samples

Table 3. Summary of calibration results, MDLs, and internal standard assignment for all target analytes

	LODs (MDLs) [$\mu\text{g}\cdot\text{L}^{-1}$]	BEC [$\mu\text{g}\cdot\text{L}^{-1}$]	R ²	Concentration range in calibration solutions [$\mu\text{g}\cdot\text{L}^{-1}$]	CCV and spike recovery group	Internal standard
⁷ Li	1.89	2.728	0.9991	5–50	Others	⁴⁵ Sc
²⁷ Al	1.88	0.963	0.9977	5–50	Others	⁴⁵ Sc
⁵¹ V	0.116	0.121	0.9996	1–50	Others	⁸⁹ Y
⁵² Cr	0.079	0.143	0.9992	1–50	Others	⁸⁹ Y
⁵⁵ Mn	0.069	0.348	0.9998	1–50	Others	⁸⁹ Y
⁵⁶ Fe	0.161	0.189	0.9998	1–50	Others	⁸⁹ Y
⁵⁹ Co	0.014	0.249	0.9986	1–50	Others	⁸⁹ Y
⁶³ Cu	0.113	0.396	0.9997	1–50	Others	⁸⁹ Y
⁶⁶ Zn	0.48	0.979	0.9991	1–50	Others	¹²⁵ Te
⁷¹ Ga	0.019	0.005	0.9994	1–50	Others	⁸⁹ Y
⁷⁵ As	0.301	0.297	0.9996	1–50	Others	¹²⁵ Te
⁷⁸ Se	1.11	0.031	0.9997	5–50	Others	¹²⁵ Te
⁸⁵ Rb	0.015	0.005	0.9996	1–50	Others	¹⁰³ Rh
⁸⁸ Sr	0.073	0.057	0.9998	1–50	Others	¹⁰³ Rh
¹⁰⁷ Ag	0.015	0.015	0.9997	1–50	Others	¹⁰³ Rh
¹¹¹ Cd	0.042	0.014	0.9997	1–50	Others	¹²⁵ Te
¹³³ Cs	0.004	0.001	0.9998	1–50	Others	¹⁰³ Rh
¹³⁷ Ba	0.034	0.017	0.9996	1–50	Others	¹⁰³ Rh
¹³⁹ La	0.004	0.001	0.9999	0.1–0.5	Lanthanides	¹⁰³ Rh
¹⁴⁰ Ce	0.005	0.004	0.9989	0.1–0.5	Lanthanides	¹⁰³ Rh
¹⁴¹ Pr	0.003	0.003	>0.9999	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁴⁵ Pm	0.009	0.002	0.9992	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁴⁶ Nd	0.048	0.081	0.9975	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁴⁷ Sm	0.004	<0.001	0.9994	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁵³ Eu	0.001	<0.001	0.9991	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁵⁷ Gd	0.002	<0.001	0.9998	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁵⁹ Tb	0.001	<0.001	0.9999	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁶³ Dy	0.006	0.002	0.9972	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁶⁵ Ho	0.005	0.007	0.9997	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁶⁶ Er	0.007	0.002	0.9994	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁶⁹ Tm	0.001	0.0005	>0.9999	0.1–0.5	Lanthanides	¹⁷⁵ Lu
¹⁷² Yb	0.01	0.007	0.9995	0.1–0.5	Lanthanides	¹⁷⁵ Lu
²⁰⁸ Pb	0.059	0.334	0.9994	1–50	Others	¹⁷⁵ Lu
²³⁸ U	0.011	0.03	0.9997	1–50	Others	¹⁷⁵ Lu

Evaluation of matrix suppression

It is important to validate the performance of this method to reliably allow the analysis of brine solutions over a wide concentration range. In this study, solutions containing between 0.5% and 25% w/w NaCl were analyzed and evaluated for the recovery of the internal standards and spike recovery at a level of $25 \mu\text{g}\cdot\text{L}^{-1}$ for the common impurities.

Figure 2 shows the internal standard recovery observed during the analysis of brine solutions with variable concentrations of between 0.5% and 4.0%. For all internal standards, a stable response with almost no suppression was observed against the initial readback in nitric acid. The only exception was tellurium, showing signal suppression in the range of 40% when analyzing solutions containing more than 3.0% of NaCl. This observation can be explained by the high ionization potential of tellurium (1st IP of 9.00 eV and degree of ionization of 66.74%),⁵ which leads to a reduced signal in the matrix compared to the initial blank.

As the data shows, the use of the highest dilution setting for AGD provided an effective mechanism for reducing the impact of the sample matrix on data quality. Without the use of AGD, or prior manual dilution of the sample, severe suppression and significant drift would occur when such samples are analyzed, rendering the results unusable.

Figure 3 shows the results obtained for the spike recovery test performed on a total of $n=3$ individual samples. Consistent performance was demonstrated, with respect to both accuracy and precision, with typical % recovery falling well within the range of 80% to 120% and the RSD of the three replicate readings below 7%. Again, these results illustrate that the impact of the matrix could be significantly reduced without any manual dilution applied to the samples prior to analysis.

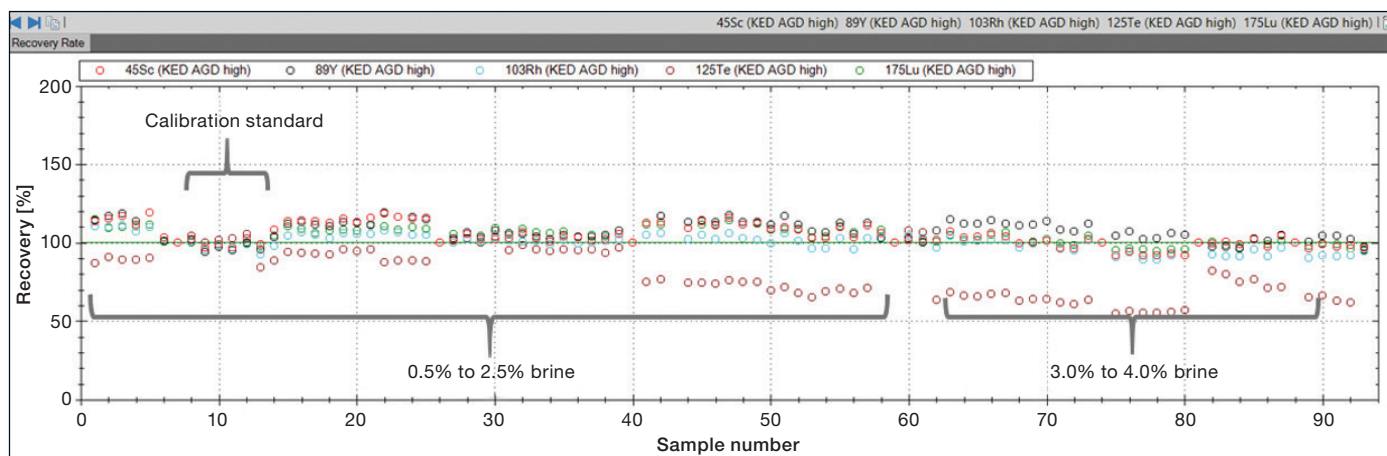


Figure 2. Response of the internal standards when analyzing brine solutions containing 0.5% to 4.0% w/w NaCl

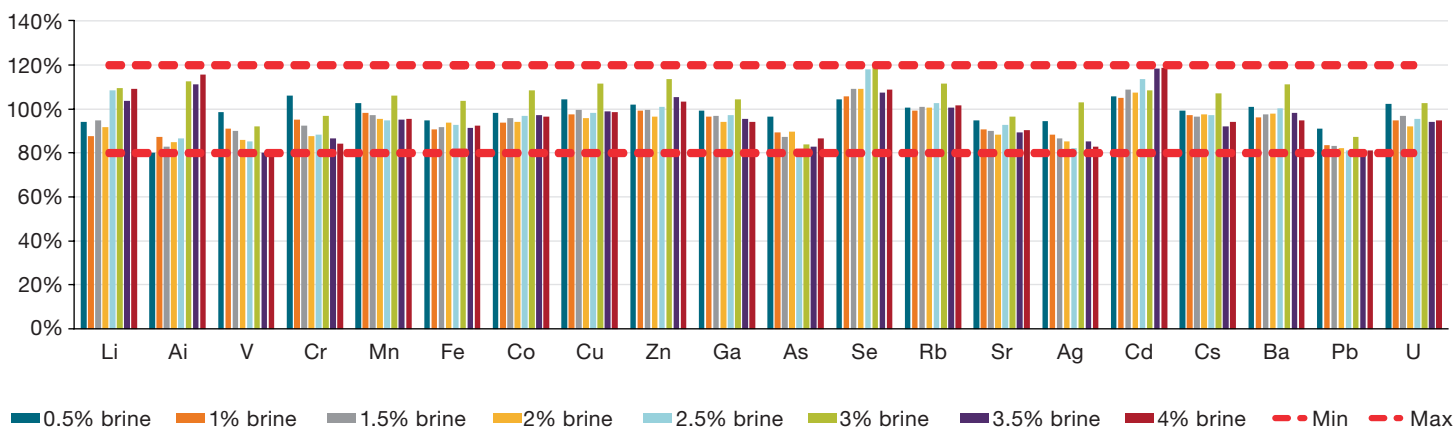


Figure 3. A $25 \mu\text{g}\cdot\text{L}^{-1}$ spike recovery performance with simulated brine water samples containing 0.5% to 4.0% w/w NaCl. Each brine sample differed in concentration from the next by 0.5% w/w.

Finally, the initially prepared concentrated brine solution (with a concentration of 25% w/w) was aspirated directly with no manual dilution performed prior to analysis. It is noteworthy that throughout the analysis the signal for sodium was also monitored, which was only possible due to the ability to increase the resolution of the analyzing quadrupole of the system, for individual elements among a larger suite of elements. This allows to attenuate the expected count rate and extend the analytical range of a method to higher concentration. At the same time, this feature can be used to protect the detector from unnecessarily high signals and extend its lifetime. The internal standard recovery (%) results and ^{23}Na intensity for the first, the middle (9th), and the last sample (17th).

The analysis of the concentrated brine solution was found to be possible using the approach described in this application note. However, signal suppression was unavoidable but found to be acceptable with a recovery ranging between 39% and 46% for the different internal standards (results for tellurium were not

included here due to the aforementioned reasons). The analysis of the concentrated brine solution was carried out over a period of one hour. The sample introduction system was visually inspected afterwards, and as expected, the matrix lead to severe deposition on the surface of both the sample and skimmer cones, ultimately requiring cone cleaning after the analysis. Figure 5 shows an image of the skimmer cone before and after the cleaning process as per the recommended procedure. As can be seen, the matrix deposits could be fully removed, and the analysis then continued. Using the Hawk Instrument Health Monitoring system, appropriate maintenance intervals can be set for all components of the sample introduction system, so that instrument downtime can be efficiently planned. However, although feasible, it is recommended to consider initial sample dilution for such matrices to avoid increased system maintenance. The dilution applied using AGD enables the analysis of brine solutions of lower concentrations over longer periods, as will be demonstrated in the following section.

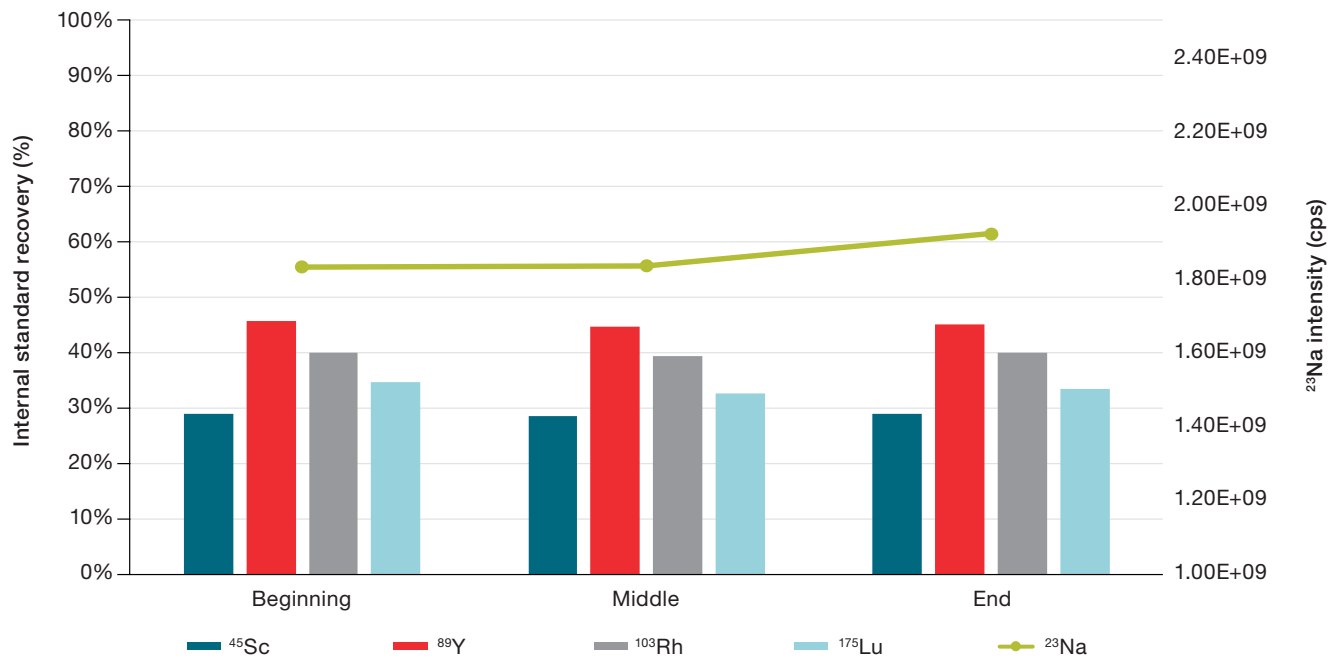


Figure 4. Intensity results by sample for ^{23}Na in 25% w/w simulated brine

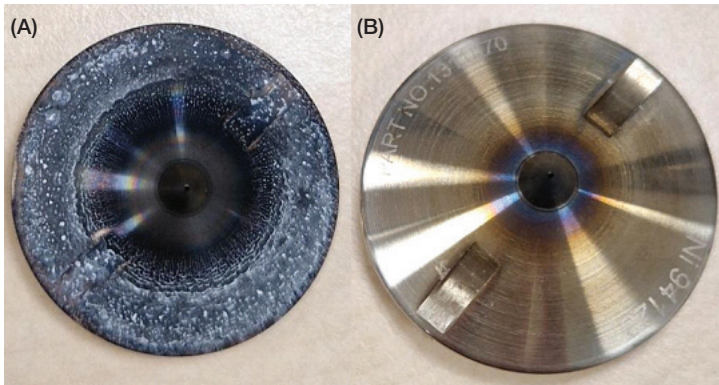


Figure 5. Skimmer cone condition after running all sequences (approximately 200 brine matrix samples over 15 hours) for the brine analysis before (A) and after cleaning (B)

Long-term robustness stability testing

To simulate high throughput analysis, a larger batch of samples containing the 2.5% w/w brine solution previously analyzed was scheduled for analysis. After generating calibration standard curves, the batch contained several blocks containing the brine samples together with the required QC checks. The total number of solutions analyzed was 150 (including 120 unknown samples and 30 calibrants and QC checks), requiring a total analysis time of approximately 9 hours. Figure 6 shows the analysis procedure for this study.

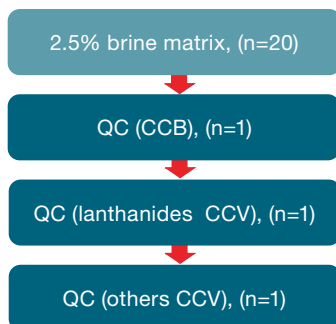


Figure 6. Schematic overview of the batch analyzed for testing the long-term performance of the proposed method. Six blocks, containing 20 unknown samples each, were analyzed.

The relative standard deviation of all CCVs ($n=7$) for all 34 elements showed excellent recovery (within 86% to 119%) with a relative standard deviation of $\pm 3.5\%$ within the batch.

Figure 7 shows a screenshot directly obtained from the Qtegra ISDS Software, highlighting the highly stable response of the QC checks performed over the runtime of the batch.

All internal standards showed reliable and predictable recovery (within approximately 78% to 122%) over the entire runtime of the batch, demonstrating robust analytical performance. While an internal standard recovery of around 78% still allows for accurate correction of matrix effects and potential drift, it is equally important that the initial internal standard response can be retrieved when switching back to lower matrix samples (e.g., for QC checks or less saline samples). The average internal standard recovery found in the subsequent QC checks was found to be approximately 110%, which ultimately demonstrates the ability of the system to effectively analyze a variety of different sample types with vastly different dissolved solids load in a single batch.

In addition, spike recovery was again demonstrated for 34 target elements and was found to be in the commonly accepted range of 80% to 120%. Figure 8 specifically highlights the spike recovery found for the lanthanides as a group of analytes in concentrations typically below $1 \mu\text{g}\cdot\text{L}^{-1}$. To simulate realistic conditions, the spike recovery test was performed at levels of only $0.1 \mu\text{g}\cdot\text{L}^{-1}$ and $0.2 \mu\text{g}\cdot\text{L}^{-1}$, and even at these low concentration levels, excellent results ($n=30$ each) were obtained.

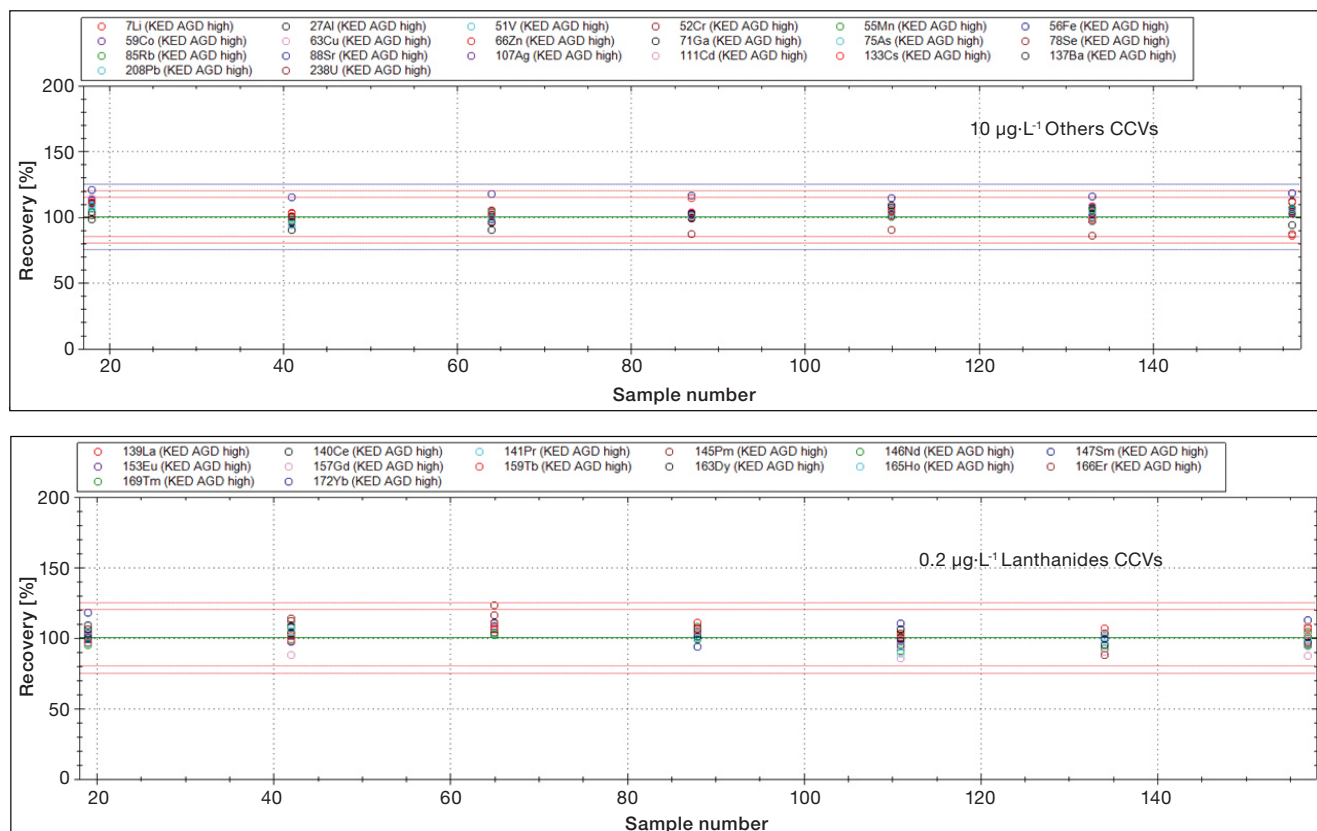


Figure 7. QC calibration verification results with 34 elements

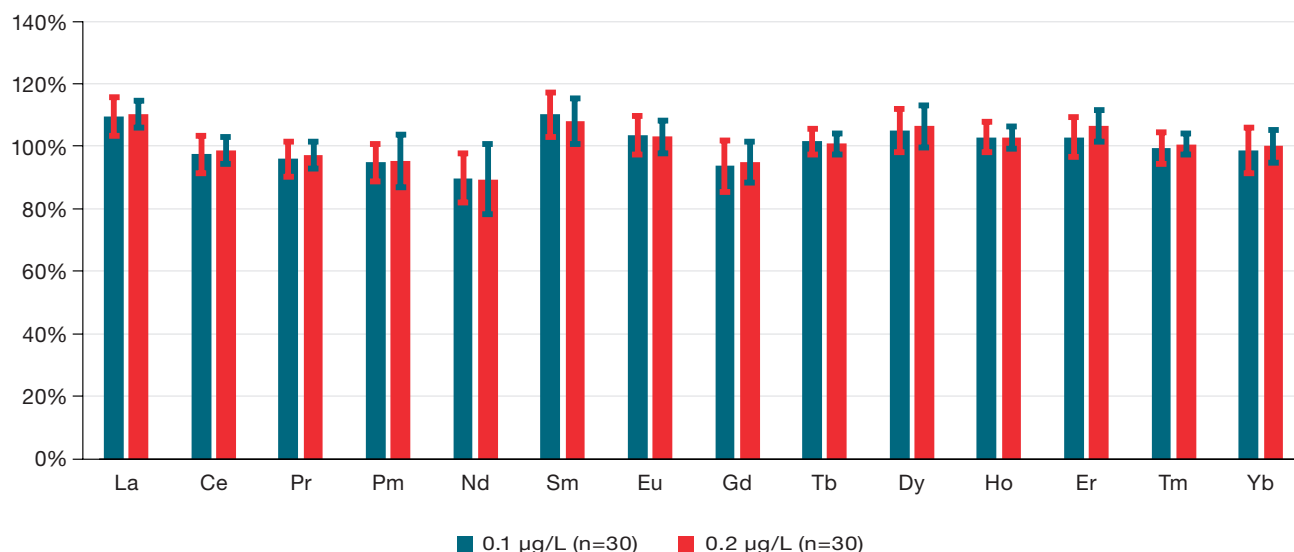


Figure 8. 0.1 µg·L⁻¹ and 0.2 µg·L⁻¹ REEs spike recovery test results (n=30 each) with 2.5% w/w brine samples during the 9-hour analysis

Conclusions

The iCAP RQplus ICP-MS, operated using AGD, enables analysts to perform accurate and reliable elemental analysis in challenging samples such as brine solutions. This was demonstrated for the analysis of 34 elements in a large number of brine samples with varying concentrations. The analytical method was rigorously tested for performance, and the results obtained clearly demonstrated the following analytical advantages for brine solution analysis:

- The AGD maximum dilution mode could be fully optimized through an autotune routine, making instrument set up straightforward for high throughput laboratory operations.
- The highest dilution setting available for AGD allowed the aspiration of up to 25% w/w brine samples and allowed excellent MDLs to be obtained, while eliminating the need for labor-intensive manual sample dilution and accelerating sample throughput.
- Excellent CCV recovery and spike recovery results, as well as stable and consistent internal standards response, were obtained across a batch containing 120 samples of a 2.5% w/w brine solution, demonstrating the reliability of the method.

- The use of He KED mode for all analytes under investigation enabled to achieve high sensitivity and complete interference removal, required for the accurate determination of elements across the entire mass range (from lithium to uranium) with outstanding instrument detection limits and linear response.
- The Hawk Instrument Health Monitoring Assistant facilitated reliable and robust analysis and provided useful and actionable information regarding the instrument performance and consumables status for both daily operation and long-term instrument monitoring.

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