Challenge

Analysis of trace element impurities and major components in saline matrices such as brines or sea water with high precision, accuracy, and long-term stability.

Solution

HR ICP-OES with high-resolution optical system and superior sensitivity and matrix tolerance to achieve sub-ppb detection limits for trace element analysis in saline matrices.

Direct Analysis of Saline Matrices by HR ICP-OES

Introduction

Brines play an important role in many industrial processes, e.g., in the production of magnesium and chlorine by electrolysis, as agent for water-injection in oil-wells, or as starting material for the fabrication of high-purity salts and preservatives. In some regions, naturally occurring brines and sea water are also considered to be an attractive candidate for drinking water production. Yet the direct elemental analysis of saline matrices using ICP techniques in routine laboratories is challenging in respect to (a) achieving good signal stability with low signal to noise levels, (b) ionization interferences of alkali and alkaline earth metals that often lead to intensity deviations in the range from ± 5 to 10%, and (c) maintenance issues, memory effects, and short lifetime of glassware and clogging.

Since saline matrices are used for various purposes, a large number of elements with limits of detection as low as possible are of interest. Due to its high sensitivity, ICP-MS is typically the method of choice to achieve limits of detection in the ppt range. However, ICP-MS typically tolerates matrix concentrations not higher than 0.3%, which requires high dilution of the samples. Thus, matrix-specific limits of detection are compromised depending on the applied dilution factor. In general, ICP-OES instrumentation is more matrix tolerant compared to ICP-MS. The comparatively low sensitivity of conventional ICP-OES, however, hampers achieving sufficiently low limits of detection.

The HR ICP-OES PlasmaQuant 9100 Elite exhibits excellent matrix and plasma robustness, being able to tolerate salt concentrations of up to 300 g/L.

Additionally, the high-resolution optical system achieves high sensitivity and ensures free line selection. The PlasmaQuant 9100 Elite allows for running undiluted saline samples of almost any salt concentration with the highest sensitivity amongst ICP-OES instrumentation. Matrix specific limits of detection (ppt to ppb range) can be achieved.

Within this study, the performance of the PlasmaQuant 9100 Elite was studied on an exemplary saline matrix of 35 g/L NaCl for concentrations, limits of detection, and long-term stability of B, Ba, Be Br, Ca, Co, Cr, Fe, I, K, Li, Mg, Mn, Mo, Na, P, S, Si, Sr, V, and Zn.

Materials and Methods

Samples and Reagents

Two samples with a nominal NaCl content of 35 g/L were submitted as-received to a standard calibration routine using a 100 mg/L aqueous multi-element standard and 1000 mg/L single-element standards from SIGMA ALDRICH in 2% $HNO_{3.}$

Calibration

Table 1: Concentration of calibration standards

Standard	Unit	Cal.0	Cal.1	Cal.2
B, Sr	mg/L	0	0.1	1
Ba, Be, Co, Cr, Fe, Li, Mn, Mo, V, Zn	µg/L	0	20	50
Br, Ca, I, K, S,	mg/L	0	10	100
Mg	mg/L	0	10	200
Si	mg/L	0	10	500
Na	mg/L	0	100	1000
P	mg/L	0	50	500

Instrument Settings/Method Parameters

For the analysis, a PlasmaQuant 9100 Elite equipped with Salt-Kit and ASPQ 3300 autosampler was used. The detailed system configuration is given in Table 2.

Table 2: Plasma configuration and set-up of the sample introduction system

Parameter	Unit
Power	1400 W
Plasma gas flow	15 L/min
Auxillary gas flow	1.0 L/min
Nebulizer gas flow	0.5 L/min
Nebulizer	concentric nebulizer for high salt content, borosilicate, 2.0 mL/min
Spray chamber	cyclonic spray chamber with dip tube[1], 50 mL, borosilicate
Injector	quartz, inner diameter 2 mm
Outer tube/ Inner tube	Syalon[2] / quartz
Pump tubing	PVC
Sample pump rate	1 mL/min
Rinse/ Read delay	45 s
Auto sampler	ASPQ 3300

1 … the double-path geometry improves precision for high matrix-loadings
2 … ceramic outer tube prolongs the life-time of torch in sodium-rich matrices

Evaluation Parameters

Table 3: Overview of method-specific evaluation parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixel	Baseline fit	Polynomial degree	Correction
B	249.773	axial	peak	3	3	ABC[1]	auto	Y[2]
Ba	455.403	axial	peak	3	3	ABC	auto	Y
Be	313.107	axial	peak	3	3	ABC	auto	Y
Br	163.283	axial	peak	3	3	ABC	auto	Y
Ca	239.856	axial plus	peak	3	3	ABC	auto	Y
Co	228.615	axial	peak	3	3	ABC	auto	Y
Cr	267.716	axial	peak	3	3	ABC	auto	Y
Fe	259.940	axial	peak	3	3	ABC	auto	Y
I	178.218	axial	peak	3	3	ABC	auto	Y
K	766.491	radial plus	peak	3	3	ABC	auto	Y
Li	670.791	radial	peak	3	3	ABC	auto	Y
Mg	285.213	radial	peak	3	3	ABC	auto	Y
Mn	257.610	axial	peak	3	3	ABC	auto	Y
Mo	203.844	axial	peak	3	3	ABC	auto	Y
Na	330.237	radial plus	peak	3	3	ABC	auto	Y
P	177.436	axial	peak	3	3	ABC	auto	Y
S	180.672	axial plus	peak	3	3	ABC	auto	Y
Si	251.611	axial	peak	3	3	ABC	auto	Y
Sr	421.552	radial	peak	3	3	ABC	auto	Y
V	292.464	axial	peak	3	3	ABC	auto	Y
Y	371.030	axial[3]	peak	3	3	ABC	auto	-
Zn	206.200	axial	peak	3	3	ABC	auto	Y

1 … automatic baseline correction (ABC)
2 … correction by internal standard; no mathematical correction of spectral interferences by CSI tool required
3 … in addition line was measured in axial Plus, radial and radial Plus plasma view

Results and Discussion

The detection power of ICP-OES for matrix-rich saline samples is highly dependent on plasma stability. For samples like brines and sea water, effective limits of detection will be best when excellent plasma and signal stability are achieved while sample dilution is kept at a minimum.

The here developed method for undiluted saline samples (35 g/L NaCl) uses the most sensitive lines for all investigated trace elements resulting in matrix specific limits of detection of significantly less than 1 ppb, respectively (e.g. 0.14 µg/L for Cr). From the same run, major contents of Na, Ca, Sr, Br, K, Li, Mg and S could be obtained be employing the Dual View Plus plasma observation modes of the PlasmaQuant 9100 Elite. Long-term stability testing was performed by continuous aspiration of a spiked saline solution. RSD values of less than 3% over a period of 8 hours of aspiration without intermediate cleaning of the glassware (Figure 1) proves the applicability of the used methodology for routine analyses.

Table 4: Overview of results of two saline samples

Isotope	Expected range		Sample A	RSD[1] [%]	Sample B	RSD [%]	matrix specific LOD
	Value	Unit					
B	4	mg/L	4.60	0.31	4.55	0.63	0.46
Ba	< 10	µg/L	7.78	0.22	7.89	0.63	0.02
Be	< 1	µg/L	0.21	3.31	0.22	2.19	0.02
Br	60	mg/L	54.9	7.98	56.0	6.96	8.65
Ca	400	mg/L	400	0.22	396	0.21	-[2]
Co	< 1	µg/L	< LOD[3]	–	< LOD[3]	–	0.32
Cr	< 1	µg/L	0.78)[4]	5.67	0.55)[4]	9.16	0.14
Fe	< 1	µg/L	< LOD	–	< LOD	–	1.63
I	< 60	mg/L	< LOD	–	< LOD	–	0.02
K	400	mg/L	388	0.31	393	0.16	-[3]
Li	200	µg/L	192	0.95	209	0.42	1.88
Mg	1,300	mg/L	998	0.01	999	0.01	1.40
Mn	< 2	µg/L	0.28	2.69	0.31	4.24	0.03
Mo	< 12	µg/L	10.5	7.06	10.8	4.22	2.16
Na	10,000	mg/L	10,880	2.93	10,960	1.29	-[2]
P	< 50	µg/l	36.0	4.73	39.8	6.4	8.96
S	900	mg/L	919	0.93	894	0.18	9.46
Si	< 500	µg/L	411	0.78	402	1.47	1.66
Sr	8	mg/L	7.36	0.31	7.25	0.38	0.05
V	< 1	µg/L	0.77)[4]	10.8	0.80)[4]	518	0.45
Zn	< 5	µg/L	1.30	4.77	1.42	4.62	0.24

1 ... RSD values obtained from three replicate measurements
2 ... no values obtained
3 ... value below detection limit
4 ... value in the range or above of matrix-specific detection limit, hence leading to high RSD values

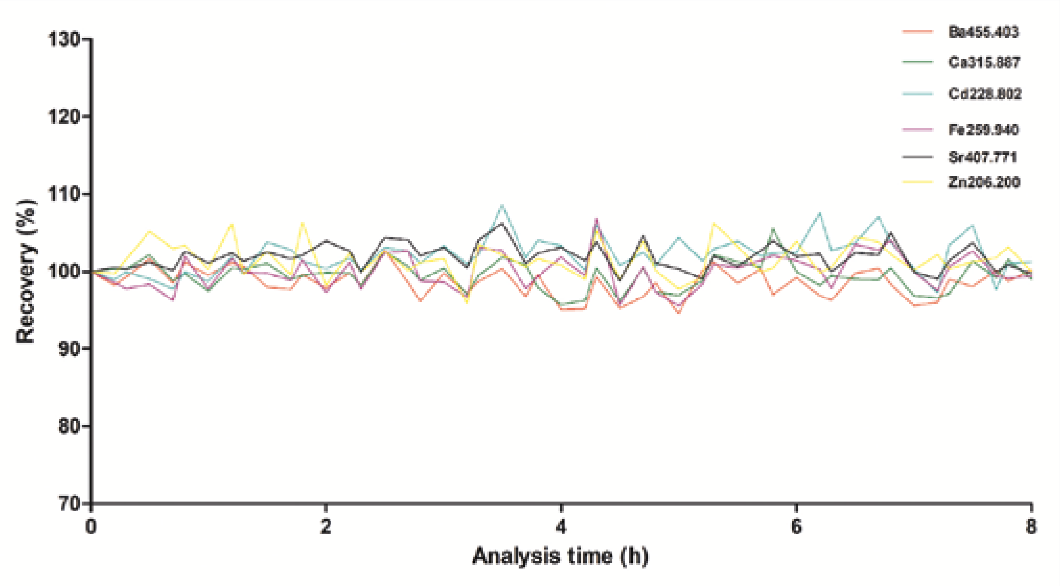

Figure 1: Percentage recoveries of an 8 hour measurement of exemplary elements (100 µg/L) in NaCl matrix (35 g/L)

Conclusion

The analysis of samples such as brines or sea water often demands the quantification of elements in trace or ultratrace levels. At the same time, the salinity of the samples poses a highly demanding challenge, since this salinity has a negative impact on signal stability. For most instrumentation (ICP-OES and ICP-MS), dilution is often the only solution in order to guarantee signal stability, which is crucial if the small analyte signals are to be detected.

In contrast to ICP-MS instrumentation, the PlasmaQuant 9100 Elite HR ICP-OES is able to run undiluted saline samples. Moreover, its industry-leading optical resolution and sensitivity allows for unmatched matrix specific limits of detection among ICP-OES instrumentation. Since sample dilution is not required, limits of detection comparable to ICP-MS can be achieved.

Due to the highly robust plasma, even medium salt concentrations (e.g. 35 g/L) can be measured by using a simple aqueous calibration. Complex sample and standard preparation procedures such as matrix-matching or standard-additions are not required.

In addition to trace elements, major components can be analyzed from the same run by exploiting the wide working range offered as DualView Plus by the PlasmaQuant 9100 Elite. Its high sensitivity, exceptional plasma robustness, and wide working range make the it the ideal tool for the analysis of highly saline samples.

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