Challenge
Determination of trace element concentrations in the saline matrix of sea water.

Solution
A simple and effective method for routine seawater analysis using ICP-MS without the need for sample preconcentration or matrix removal.

Determination of Trace Elements in Seawater using ICP-MS

Introduction

The analysis of trace elements in seawater is one of the most challenging analytical tasks in the field of environmental monitoring – the trace element concentrations are usually quite low, often in the low ng/L range, and the seawater matrix causes interferences from its high dissolved salt content (3.5% m/v).

For ICP-MS, the seawater matrix is challenging physically and chemically. Continuous nebulization leads to salt deposition on the sampler and skimmer cones, resulting in a loss in sensitivity and poor long-term stability. The chemical composition of the sea water matrix causes polyatomic ion interferences and non-spectroscopic interferences, particularly for the determination of the first-row transition elements.

To overcome these analytical challenges, a sample dilution by a factor of 10 or 20 is the first choice to obtain good signal stability for each sample run but also for a series of samples. A range of different methods such as solvent extraction [1,2], coprecipitation [3–6], and chelating resin adsorption [7,8] have been developed for matrix removal and preconcentration of trace metals in seawater. Among those, the chelating resin adsorption technique is the most promising approach, as it does not require harmful organic solvents and has a low risk of contamination.

This application note describes a method for the reliable determination of multiple elements in seawaters on a PlasmaQuant MS, ICP-MS.

This method was validated by analyzing seawater certified reference materials (CRMs; CASS-6 and NASS-7) issued by the National Research Council of Canada (NRCC) and a real Portuguese seawater sample. All samples were diluted by a factor of 10.

Materials and Methods

Instrumentation

A PlasmaQuant MS, ICP-MS in combination with ASPQ 3300 autosampler and ESI injection valve was used for the analysis of 15 elements in seawater samples. The PlasmaQuantMS is equipped with the patented integrated Collision Reaction Cell (iCRC) for the removal of polyatomic species formed in the plasma and an improved precision and accuracy for the analysis of delicate matrices.

The analysis was carried out in a routine analytical laboratory, and not under ‘clean room’ conditions. Instrument operating conditions are summarized in table 1, including the iCRC settings using helium and hydrogen gases to remove problematic spectroscopic interferences on first row transition metals. The total sampling time, including the sample uptake and rinse delays, was approximately three minutes per sample.

Table 1: Instrument settings – PlasmaQuant MS

Parameter	Specification
Plasma Gas Flow	10.5 L/min
Auxiliary Gas Flow	1.50 L/min
Nebulizer Gas Flow	1.08 L/min
iCRC Gas Setting	No Gas for ^{238}U He – 120 mL/min for ^{52}Cr, ^{60}Ni, ^{65}Cu, ^{98}Mo and $^{206+207+208}$Pb; He – 150 mL/min for ^{51}V and ^{59}Co, H$_2$ – 140 mL/min for ^{11}B, ^{55}Mn, ^{56}Fe, ^{66}Zn, ^{75}As, ^{78}Se and ^{114}Cd
Plasma RF Power	1.55 kW
Dwell Time	30 ms
Scans per Replicate	10 (peak hopping, 1 pt/peak)
No. of replicates	4
Pump Rate	12 rpm – black/black PVC pump tubing
Sample uptake time	4 s – OneFAST Sample Introduction system used
Sampling depth	6.0 mm
Nebulizer type	MicroMist (quartz concentric)
Ion Optics	Auto-optimized
Spray chamber type	Glass, double pass - Scott type
Spray chamber temperature	3°C
Internal Standards	Sc, Y, Rh and Ir, 5 µg/L, interpolate correction

Materials and Methods

Samples and reagents

The following high purity reagents were used for preparing all solutions:

- Deionized water (>18.2 MΩ.cm, Millipore MiliQ)
- Nitric acid supra-quality 69% (ROTIPURAN® Supra)

Calibration standards

A six-point external calibration was used for quantification. Standard concentrations were chosen in relation to the expected concentration in the samples. Calibration solutions were prepared from high-purity, single (Boron and Uranium standards, CertiPUR® 1000 mg/L) and multi-element solutions (CertiPUR® XVI) in 1% HNO3 covering the concentration range from 0.05 to 5 µg/L for V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Pb and U and from 1 to 500 µg/L for B.

Sample preparation

Seawater samples, diluted 1:10, were placed on the auto sampler. The diluents containing internal standards were added online (between OneFast valve and nebulizer) using a T-piece to achieve a final ratio of seawater and diluent of 1:20. Online dilution is recommended to minimize unnecessary contamination. The NASS-7 and CASS-6 seawater reference material standards for trace metals were selected to evaluate accuracy. In addition spike recoveries of 1 and 10 ppb were performed for most of the elements tested. Only Boron was spiked with 25 ppb due to its major concentration.

A Portugese seawater sample was filtered, acidified, diluted 1/10 and subsequently spiked with 1ppb for a range of elements to evaluate the long-term stability. The sample dilution reduces the matrix concentration, however the polyatomic interferences remain and can cause inaccurate results. Table 2 lists potential polyatomic interferences based on matrix elements and Argon gas.

Table 2: Polyatomic interferences due to seawater matrix and Argon

Isotope	Natural Abundance (%)	Matrix-based polyatomic interferences	Ar-based polyatomic interferences
$^{11}\mathrm{B}$	80.1		
$^{51}\mathrm{V}$	99.75	$^{35}\mathrm{Cl}^{16}\mathrm{O}^{+}$, $^{37}\mathrm{Cl}^{14}\mathrm{N}^{+}$, $^{34}\mathrm{S}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$	
$^{52}\mathrm{Cr}$	83.79	$^{40}\mathrm{Ar}^{12}\mathrm{C}^{+}$, $^{35}\mathrm{Cl}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$, $^{40}\mathrm{Ca}^{12}\mathrm{C}^{+}$	$^{36}\mathrm{Ar}^{16}\mathrm{O}^{+}$, $^{38}\mathrm{Ar}^{14}\mathrm{N}^{+}$
$^{55}\mathrm{Mn}$	100	$^{39}\mathrm{K}^{16}\mathrm{O}^{+}$, $^{41}\mathrm{K}^{14}\mathrm{N}^{+}$, $^{43}\mathrm{Ca}^{12}\mathrm{C}^{+}$, $^{40}\mathrm{Ca}^{15}\mathrm{N}^{+}$,	$^{40}\mathrm{Ar}^{15}\mathrm{N}^{+}$
$^{56}\mathrm{Fe}$	91.75	$^{40}\mathrm{Ca}^{16}\mathrm{O}^{+}$, $^{39}\mathrm{K}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$, $^{44}\mathrm{Ca}^{12}\mathrm{C}^{+}$, $^{42}\mathrm{Ca}^{14}\mathrm{N}^{+}$	$^{40}\mathrm{Ar}^{16}\mathrm{O}^{+}$
$^{59}\mathrm{Co}$	100	$^{42}\mathrm{Ca}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$, $^{43}\mathrm{Ca}^{16}\mathrm{O}^{+}$, $^{36}\mathrm{Ar}^{23}\mathrm{Na}^{+}$	$^{40}\mathrm{Ar}^{18}\mathrm{O}^{1}\mathrm{H}^{+}$
$^{60}\mathrm{Ni}$	26.22	$^{44}\mathrm{Ca}^{16}\mathrm{O}^{+}$, $^{24}\mathrm{Mg}^{36}\mathrm{Ar}^{+}$, $^{48}\mathrm{Ca}^{12}\mathrm{C}^{+}$, $^{42}\mathrm{Ca}^{17}\mathrm{O}^{1}\mathrm{H}^{+}$	
$^{65}\mathrm{Cu}$	30.83	$^{25}\mathrm{Mg}^{40}\mathrm{Ar}^{+}$, $^{48}\mathrm{Ca}^{16}\mathrm{O}^{1}\mathrm{H}^{+}$, $^{33}\mathrm{S}^{16}\mathrm{O}_2{}^{+}$, $^{32}\mathrm{S}^{16}\mathrm{O}_2{}^{1}\mathrm{H}^{+}$	
$^{66}\mathrm{Zn}$	27.90	$^{26}\mathrm{Mg}^{40}\mathrm{Ar}^{+}$, $^{34}\mathrm{S}^{16}\mathrm{O}_2{}^{+}$, $^{33}\mathrm{S}^{16}\mathrm{O}_2{}^{1}\mathrm{H}^{+}$, $^{32}\mathrm{S}^{16}\mathrm{O}_2{}^{1}\mathrm{H}^{2+}$	
$^{75}\mathrm{As}$	100	$^{40}\mathrm{Ar}^{35}\mathrm{Cl}^{+}$, $^{39}\mathrm{K}^{36}\mathrm{Ar}^{+}$	
$^{78}\mathrm{Se}$	23.77		$^{78}\mathrm{Kr}$, $^{38}\mathrm{Ar}^{40}\mathrm{Ar}^{+}$
$^{114}\mathrm{Cd}$	28.73	$^{98}\mathrm{Mo}^{16}\mathrm{O}^{+}$	

Results and Discussion

Tables 3 and 4 show the average concentrations, standard deviation (SD) and spike recoveries determined for elements in CASS-6 and NASS-7 seawater reference materials.

Table 3: Concentration results (in µg/L) of CASS-6, precision and accuracy (n=3; n.d. not determined)

Isotope	Measured	SD	Certified	Uncertainty	1 ppb spike REC (%)	10 ppb spike REC (%)	25 ppb spike REC (%)
^{11}B	4102	50	4090	100	-	-	105
^{51}V	n.d.	-	0.50	0.12	99	106	-
^{52}Cr	0.05	-	0.100	0.016	101	116	-
^{55}Mn	2.19	0.06	2.22	0.12	98	97	-
^{56}Fe	1.7	0.3	1.56	0.12	103	110	-
^{59}Co	0.07	0.007	0.067	0.005	99	97	-
^{60}Ni	0.74	0.002	0.418	0.040	102	88	-
^{65}Cu	0.57	0.02	0.530	0.032	95	-	-
^{66}Zn	1.27	0.02	1.27	0.18	104	91	-
^{75}As	1.32	-	1.04	0.10	101	86	-
^{78}Se	n.d.	-	-	-	100	101	-
^{98}Mo	9.15	0.07	9.15	0.52	99	101	-
^{114}Cd	0.02	0.002	0.022	0.002	103	99	-
$^{206+207+208}$Pb	0.010	0.001	0.011	0.004	99	105	-
^{238}U	2.6	0.12	2.92	0.42	102	104	-

Table 4: Concentration results (in µg/L) of NASS-7, precision and accuracy (n=3, except for Cr, Fe, Co and Cu; n.d. not determined)

Isotope	Measured	SD	Certified	Uncertainty	1 ppb spike REC (%)	10 ppb spike REC (%)	25 ppb spike REC (%)
^{11}B	3755	169	3750	120	-	-	96
^{51}V	n.d.	-	1.3	0.08	111	106	-
^{52}Cr	0.17	-	0.107	0.016	103	104	-
^{55}Mn	0.73	0.06	0.75	0.06	100	94	-
^{56}Fe	0.50	-	0.35	0.03	105	96	-
^{59}Co	0.02	-	0.015	0.001	102	91	-
^{60}Ni	0.67	0.096	0.248	0.018	98	84	-
^{65}Cu	n.d.	-	0.199	0.014	99	93	-
^{66}Zn	0.41	0.05	0.42	0.08	112	87	-
^{75}As	2.97	0.00	1.26	0.06	95	98	-
^{78}Se	1.4	0.36	-	-	96	99	-
^{98}Mo	9.14	0.06	9.29	0.40	100	112	-
^{114}Cd	0.02	0.003	0.016	0.002	101	103	-
$^{206+207+208}$Pb	0.016	0.001	0.003	0.001	100	96	-
^{238}U	2.98	0.053	2.870	0.160	103	102	-

The recoveries for the 1 ppb spike prove an accurate and reliable performance in seawater matrices (1:10 fold dilution) for ppt level determinations. Recoveries for a 10 ppb spike were performed due to the higher analyte concentration (Mn, Fe, Zn, As, Mo and U). B as a certified reference element with concentration levels in ppm range was spiked with 25 ppb. Figure 2 shows that all recoveries are within the interval [83-112%]. iCRC optimization allowed a simple removal of polyatomic interferences occuring in seawater analysis including chloride interferences, such as $^{35}Cl^{16}O$ and $^{40}Ar^{35}Cl$ on ^{51}V and ^{75}As, or calcium interferences such as $^{44}Ca^{16}O$ on ^{60}Ni.

The iCRC technology allows matrices with high total dissolved solids, such as seawater, to be aspirated and analyzed for a long period of time without any significant drift or loss of sensitivity which are often observed in this kind of matrix (figure 3). This robustness extends maintenance intervals on the cones and provides better performance of Control Checks without compromizing LOD over time..

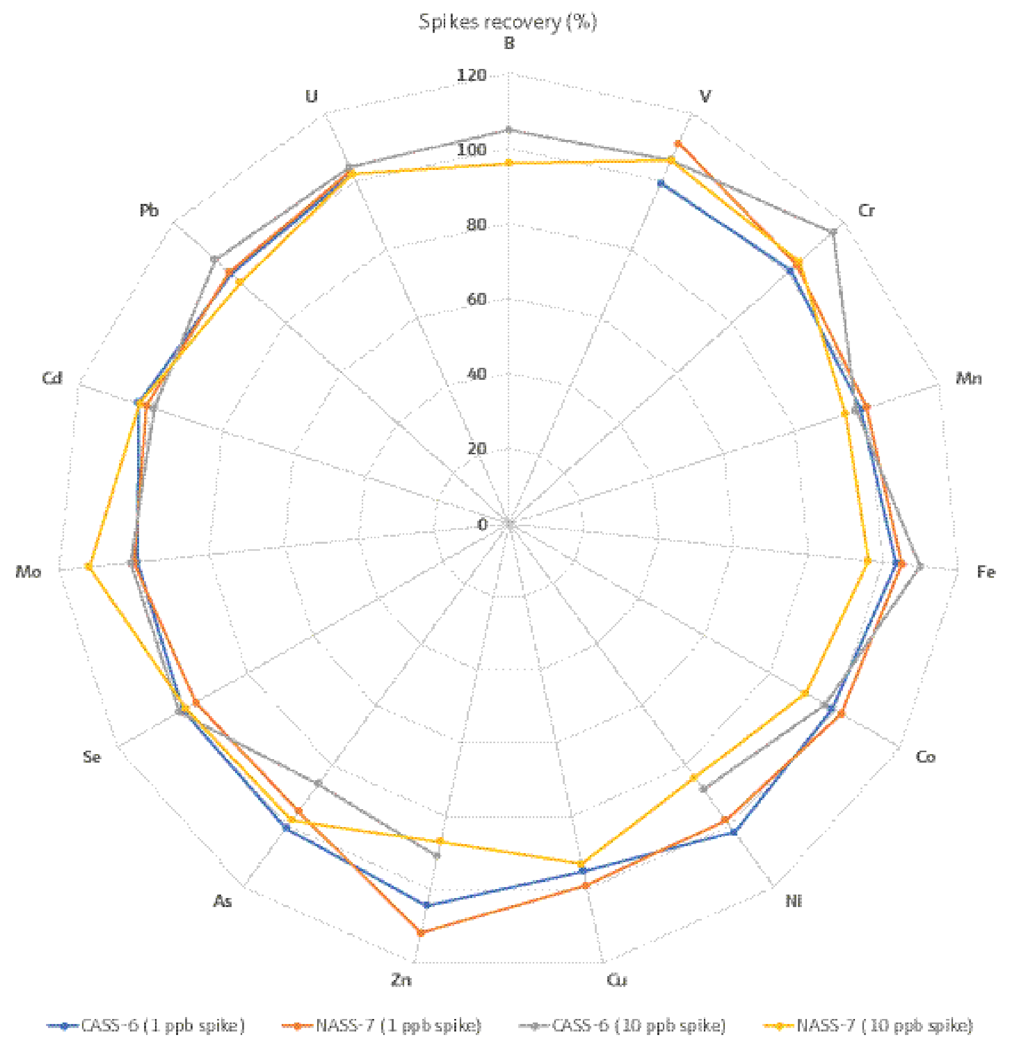

Fig. 2: Spike (1, 10 and 25 ppb) recoveries (%) obtained for CASS-6 and NASS-7 (1:10 folds diluted).

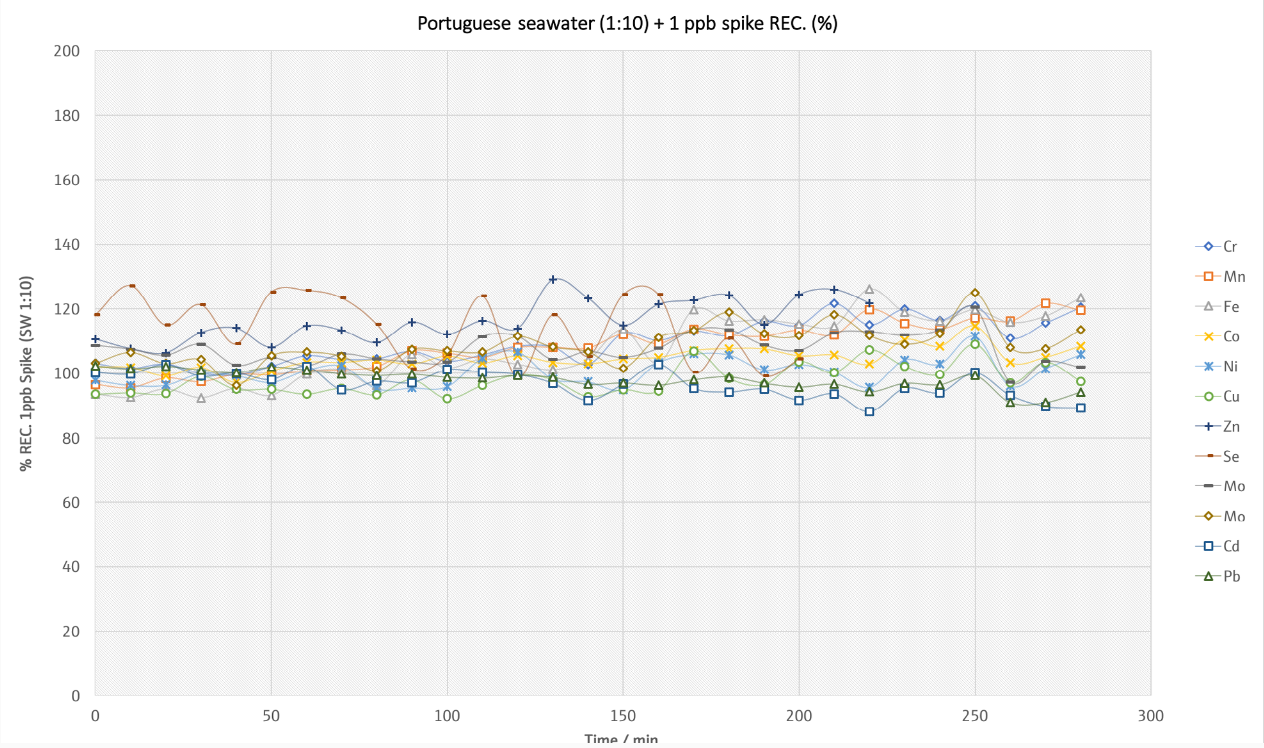

Fig. 3: Stability test (five hours) of 1 ppb spike in 1:10 diluted Portuguese seawater.

Summary

This application note presents a simple and effective method for routine seawater analysis without the need of matrix removal or preconcentration steps. The robust method for seawater minimizes the risk of contamination due to extensive sample preparation and avoids the use of harmful chemicals.
With its robustness for tough matrices such as seawater and meeting the target values, the PlasmaQuant MS proved to be well suited for the determination of trace metals in seawater samples. In addition, the PlasmaQuant MS's unique patented technologies significantly lower running costs and provide greater ease-of-use without compromising performance. This includes Eco Plasma, the only plasma system running on <10 L/min of argon gas without compromising plasma robustness or analyte sensitivity, and the iCRC, a powerful yet simple-to-use interference management system to remove spectroscopic interferences on important elements, as V, Cr, Fe, Cu, Ni, Zn, As, Se, or Cd.

Figure 2: PlasmaQuant MS

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