

Trace element analysis of solutions with high salt content



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Introduction and aim

Metals and metalloids can have harmful impacts on the environment and human health, especially when they are mobilized by human activities. In order to monitor and assess the potential risks associated with these potentially toxic elements (PTEs), it is important to analyze surface waters and solutions obtained by in-vitro digestion for their presence at trace and ultra-trace levels.

However, the high salt content in seawater and estuarial regions can pose challenges for the reliable determination of PTEs using inductively coupled plasma mass spectrometry (ICP-MS). This is because the high salt content can interfere with the ionization and detection processes in ICP-MS, leading to inaccurate measurements.

To overcome this challenge, various techniques have been developed to improve the accuracy and precision of PTE measurements in high-salt water samples. These include sample pre-concentration, matrix removal, and the use of alternative analytical techniques such as electrothermal atomic absorption spectrometry (ETAAS) or inductively coupled plasma optical emission spectrometry (ICP-OES).

Overall, accurate and reliable determination of PTEs in surface water and in-vitro digestion solutions is crucial for assessing the potential risks associated with metal and metalloid contamination in the environment and human food chain.

Material and methods

All sea water samples were filtered through 0.20 µm PTFE (polytetrafluoroethylene) syringe filters and stabilized by addition of 1 % (m/m) sub-boiled nitric acid. Analysis was carried out using two different ICP-MS instruments with different experimental settings. Lower dilution factors resulted in significant ionization suppression of the plasma by the high salt concentration. Higher dilution factors may lead to concentrations of the elements of interest below their limits of quantification (LOQ).

Prior to quadrupole (Q-) ICP-MS measurements, all water samples were diluted 1:100 and Rh as internal standard (10 µg/L) was added.

Prior to high resolution (HR-) ICP-MS measurements, 100 µL were diluted with 5.90 mL internal standard solution in a way that all aspirated test samples contained 20 µg/L Sc and 10 µg/L In and Ti.



Figure 1. Q-ICP-MS instrument (Agilent 7500cx)



Figure 2. HR-ICP-MS instrument (Thermo Finnigan Element 2)

HR-ICP-MS Calibration

Matrix-matched (fresh water) calibration standards that contained 20 µg/L Sc and 10 µg/L In and Ti as internal standard were applied. Four standard solutions were used for calibration of Ca, Na, Cl, Mg, S, K, C, Si, P and B. Five calibration solutions were used for Fe, Al, Ba, Sr, Mn, Zn, Rb, As, Cr, Cu, Li, Mo, Ni, Pb, Sb, Se, Sn, U, V, Ce, Ag, Be, Bi, Cd, Co, Cs, Ga, Hg, La, Nd, Pr, Gd, Te. These solutions also contained the major elements Ca, Na, Cl, Mg, S, K, C, Si at the second highest level of the standards above. To evaluate the influence of sodium chloride on the method's sensitivity, the second highest level standard was spiked with NaCl at the level of the aspirated test samples: 200 mg/L Na and 300 mg/L Cl.

Quantification of 29 elements was accomplished using five- or six-point external calibration based on multi-elemental standard solutions prepared from ICP multi-element standard solution VI (Merck, Germany). The calibration ranges were adjusted to the expected concentration of the respective analyte. To compensate for non-spectral interferences, rhodium was added as an internal standard to all standard solutions, blanks, reference materials, and test samples, with a final mass concentration of 10 µg/L. Certified Multielement Standard Solution 5 for ICP (Fluka) was used as reference material to determine the trueness of the applied method at 1:100 and 1:10,000 dilution levels. The concentrations in the solutions were determined using inductively coupled mass spectrometry (ICP-MS Agilent 7500cx). A MicroMist nebulizer was used, the sample flow being 0.3 mL/min. Output power was 1500 W, Argon flows were 15 L/min plasma, 0.9 L/min auxiliary and 0.2 L/min nebulizer, connected to a Scott double pass spray chamber. The collision cell was on for K, V, Cr, Fe, Cu, As, and Se with a He-flow of 5 mL/min. The following nuclides were measured: ⁷Li, ⁹Be, ²³Na, ²⁴Mg, ²⁷Al, ³⁹K, ⁴³Ca, ⁵¹V, ⁵³Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷⁵As, ⁸²Se, ⁸⁵Rb, ⁸⁸Sr, ⁹⁵Mo, ¹⁰³Rh, ¹⁰⁷Ag, ¹¹¹Cd, ¹²⁵Te, ¹³⁷Ba, ²⁰⁵Tl, ²⁰⁴⁺²⁰⁶⁺²⁰⁷⁺²⁰⁸Pb, ²⁰⁹Bi, and ²³⁸U. All measurements were performed in triplicate.

HR-ICP-MS measurements

Determination of elements was carried out on a double-focusing sector field ICP-MS instrument, Finnigan ELEMENT2 from Thermo Electron Corporation. It was equipped with a cyclonic spray chamber and a conical nebuliser, both made from borosilicate glass by Glass Expansion, connected to a 700 µL/min self-aspiration capillary (0.5 µm inner diameter). Argon cool gas flow was 16 L/min, auxiliary (plasma) gas and sample (nebuliser) gas flows were optimised daily before each measurement series to obtain maximum signal intensity, the former typically at 0.70 L/min, the latter 1.00 L/min. RF power was 1185-1195 W. The nuclides ¹⁰⁹Ag, ¹¹¹Cd, ¹¹⁵In, ¹²¹Sb, ²⁰¹Hg, ²⁰⁵Tl, ²⁰⁸Pb, ²⁰⁹Bi and ²³⁸U were measured in low-resolution mode, $R_s = 300$, 10 % valley definition. ⁷Li, ⁹Be, ¹¹B, ¹²C, ²³Na, ²⁴Mg, ²⁷Al, ²⁸Si, ³¹P, ³²S, ³⁵Cl, ³⁹K, ⁴⁴Ca, ⁴⁵Sc, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁶⁹Ga, ⁸⁸Sr, ⁹⁷Mo, ¹¹⁵In, ¹¹⁸Sn, ¹²⁵Te, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr and ¹⁴³Nd were determined in medium-resolution mode, $R_s = 4000$, whereas ³⁹K, ⁴⁵Sc, ⁷⁵As, ⁷⁷Se, ⁸⁵Rb, ¹¹⁵In, ¹¹⁸Sn and ¹⁵⁷Gd were measured in high-resolution mode $R_s = 10000$.

Results and Discussion

Comparing low and high resolution ICP-MS for the given task and considering the total number of quantifiable elements, the latter is the preferred one for the given task.

Table 1: LOQ alongside mean values and RSD of the 42 elements analysed in sea water samples

Above LOQ	Mean val	This st.	Comparison values	Unit			
(all 101 samples)	RSD (n=101)	(1)	(2)	(3,4)			
Cl	0.15	10%	20	18	µg/L		
Na	0.002	9%	11	11	µg/L		
Mg	0.0003	9%	1.2	1.3	µg/L		
S	0.0002	4%	0.95	0.93	µg/L		
Ca	0.0015	10%	0.46	0.41	µg/L		
K	0.0004	10%	0.38	0.38	µg/L		
Sr	0.003	10%	7.6	8.5	µg/L		
B	0.07	9%	4.3	4.5	µg/L		
Si	0.05	106%	0.37	1	µg/L		
Li	0.0007	10%	0.17	0.18	µg/L		
Rb	0.0012	10%	0.12	0.12	µg/L		
Mo	3	14%	20	10	µg/L		
Ba	1.5	47%	7.5	50	µg/L		
U	0.016	11%	3.3	3.3	µg/L		
As	0.3	28%	1.8	2.3	1.6	2.1	µg/L
V	0.09	11%	1.8	1.5	1.9	µg/L	
Ce	0.5	33%	0.9	1	µg/L		
Sb	0.10	14%	0.27	0.5	µg/L		

At	LOQ	> LOQ	Mean	Comparison values	Unit		
		n (n=101)	(1)	(2)	(3,4)		
P	10	31	15	70	µg/L		
Fe	8	21	14	3	0.1	µg/L	
Al	2	90	8.9	5	µg/L		
Cu	0.8	49	1.1	3	0.25	0.79	µg/L
Ni	0.8	22	0.6	2	0.6	1.1	µg/L
Cr	0.2	99	0.6	0.6	0.2	0.79	µg/L
Pb	0.2	37	0.22	0.03	0.003	µg/L	
La	17	25	31	3.4	µg/L		
Nd	32	21	18	2.8	µg/L		
Ce	5	61	10	1.2	µg/L		
Pr	5	8	1	µg/L			
Zn	93	5	5	0.6	0.47	µg/L	
Mn	4	0	2	0.01	2.3	µg/L	
Se	3	0	0.45	0.009	µg/L		
Hg	0.7	2	0.05	0.002	0.020	µg/L	
Ag	0.6	3	0.1	0.002	µg/L		
Bi	0.2	4	0.02	0.000003	µg/L		
Sm	0.13	11	0.01	0.0006	µg/L		
Co	0.13	2	0.08	0.002	µg/L		
Be	60	4	0.6	0.2	µg/L		
Gd	60	1	0.7	µg/L			
Cd	57	2	50	100	27	µg/L	
Ga	37	0	30	µg/L			
Ti (IS)			1	10	µg/L		

There was no evidence that Ni interface parts caused significantly elevated results.

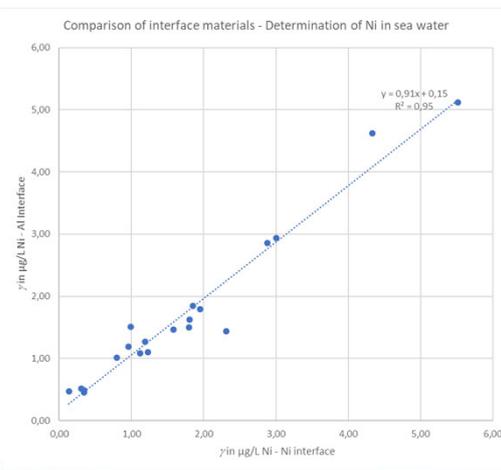


Figure 3: Comparison of Ni concentration results determined using different interfaces

Figure 4. Sample Easter egg

References
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The addition of 200 mg/L Na and 300 mg/L Cl⁻ lead to a signal depression of down to approximately 80% depending on the element. As the internal standards partially compensated for this, the recoveries of all elements were in the range of 85% to 115% and their average deviation from 100% was about 6%. Thus, the contribution to the measurement uncertainty was reasonable. However, the appropriate adaptation of the calibration solutions can be fully recommended, when the dilution factor of the test samples is fixed.