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Matrix Matching for ICP-MS

Analysis of High Salinity Samples by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

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Introduction

In many analytical methods, the sensitivity to a certain substance is influenced by the remaining compounds of the measurement sample. Ideally, a signal is caused only by the analyte of interest, which is referred to as (extremely) high selectivity and often provided by advanced methods. Anyhow, compounds of the sample matrix may lead to signal depression or sometimes signal enhancement. Matrix matching is advantageous, when the composition of the samples in a measurement sequence is well understood and similar. It does not increase instrument measuring time significantly. However, the preparation of matrix-matched calibration standards may be complex, time-consuming and requires additional checks.

The proportions of dissolved major ions are quite constant in all oceans, as hypothesized already 200 years ago by Marcet. Thus, for sea water analysis, matrix matching is highly reasonable and its adaptation to samples with different salinity is easily possible.

Materials and methods

A double-focusing sector field ICP-MS instrument, Finnigan ELEMENT2 from Thermo, equipped with a CETAC ASX-520 autosampler, a 700 μL/min self-aspiration capillary connected to conical nebuliser and a 20 mL cyclonic spray chamber, both made from borosilicate glass, and Ni interface parts were used. Argon cool gas flow was 16 L/min, auxiliary (plasma) gas 0.70 L/min and sample (nebuliser) gas 1.00 L/min. RF power was 1200 W. Multielement calibration standards were prepared from 18.2 MΩcm water, ultrapure HNO_3 (69%) and 39 single element spectroscopy standard solutions (each 1 g L^{-1} in 2% HNO_3, 10% hydrochloric acid or pure water). An artificial seawater matrix was made by dissolution of the salts $CaCl_2.4H_2O$, KCl, $MgCl_2.6H_2O$, $NaCl$ and Na_2SO_4, all in trace analysis quality. Aspirated solutions contained 20 μg L^{-1} Sc, and 10 μg L^{-1} In as internal standards.

Results

The experiment aimed to evaluate the influence of the most abundant matrix elements (Cl, Na, Mg, S, Ca, K cover 99.87% *m/m*) in sea water, at 100- to 10-fold dilution, on the sensitivity of all other determined elements (see Tables 1 and 2). Higher matrix concentration led to signal depression that varied considerably: Whereas the signals of some elements (Li, Al, Si, Sc, V) were hardly influenced by the matrix, others came down to approximately 50% (e.g. Cd). Signal depression caused by sea water matrix addition can be described by flattening curves. Greater changes were observed, when increasing this matrix from 0% to 1% than from 1% to 5%. Signal depression appeared to follow a linear trend over the logarithmic dilution factor. Besides, a polyatomic interference at [97]Mo was discovered that likely has not been described before.

For basic validation, a 25-fold dilution with 0.5% HNO_3 was chosen. Thus, measuring samples contained slightly above 1 g/L dissolved solids, which was well tolerated by the interface parts, even over several hours of measuring time. Signal depression was reasonable and not more than one third, depending on the element. By application of five different certified reference materials, results were verified for most of the evaluated elements.
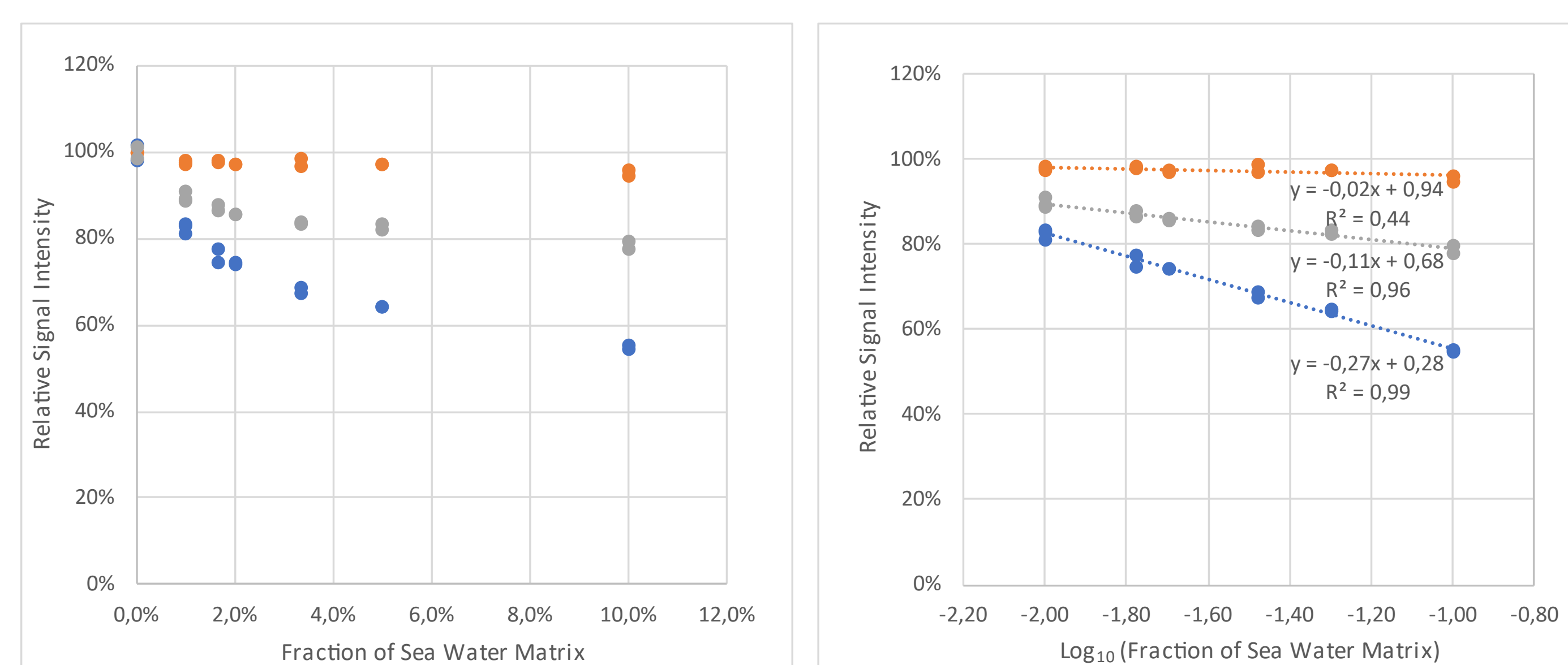

Fig. 1: Illustration of signal depression caused by diluted sea water matrix. The signal of Al (orange dots) was hardly influenced, whereas the Cd signal (blue dots) was lowered by more than 40 % in the case of 1:10 dilution. Mn (grey dots) was in between. Right: signal depression caused by diluted sea water matrix showed a linear trend in the range of 1:10 to 1:100 dilution on a logarithmic scale.

Table 1: Ranking of elements by signal depression caused by a tenfold increase of seawater matrix concentration, calculated from linear regression.

To 10 % (-0.10)	Li, Si, Mo, Sc, Al, Cr, V, La, Sr, Rb, Te, Cs, Ga
11 % to 20 % (-0.11 .. -0.20)	Mn, Pr, Ce, Ba, Nd, Gd, Fe, In, Co, P, Be, Sn, U, Ni, Tl, Bi
21 % to 34 % (-0.21 .. -0.34)	B, Ag, Hg, Cu, Sb, Zn, As, Pb, Cd, Se

Table 2: Limits of quantification in comparison to concentration levels in common sea water from literature (1) and own samples. From the 43 elements that were investigated, 24 could be quantitated (green), three were at the limit of quantitation (yellow) and 16 below (orange).

Element	loq (μg/L) NM129-168 for 25-fold dilution	loq (μg/L) matrix	Ocean water (μg/L) literature (1)	Ocean water (μg/L) own samples (median, n=10)	Element	loq (μg/L) NM129-168 for 25-fold dilution	loq (μg/L) matrix	Ocean water (μg/L) literature (1)	Ocean water (μg/L) own samples (median, n=10)
Cl	7E+03		1,8E+07	1,8E+07					
Na	3E+02		1,1E+07	1,0E+07	V	0,03	0,07	1,5	1,7
Mg	76		1,3E+06	1,2E+06	Sb	0,2	1,3	1	1,4
S	1,8E+02		9E+05	9,0E+05	Cr	0,19	0,3	0,6	0,34
Ca	1E+03		4E+05	4,4E+05	Cs	0,10	0,07	0,5	0,23
K	1,5E+02		4E+05	3,8E+05	Se	0,6	1,7	0,45	<1,7
Sr	4	16	9E+03	7,1E+03	Ag	0,2	0,17	0,10	<0,2
B	32	12	5E+03	4,3E+03	Co	0,05	0,03	0,08	<0,03
Si	96	18	1,0E+03	2,0E+02	Cd	0,03	0,013	0,05	<0,01
Li	0,5	0,3	1,8E+02	1,7E+02	Hg	0,4	0,05	0,05	<0,05
Rb	0,4	1,1	1,2E+02	1,2E+02	Ga	0,03	0,20	0,03	<0,03
P	12	20	70	<20	Pb	0,4	0,7	0,03	<0,7
Ba	0,8	0,8	50	6,5	Bi	0,3	0,04	0,02	<0,04
Mo	1,1	0,3	10	11	Sn	0,8	0,9	0,01	<0,9
Al	5	10	5	5,1	La	0,02	0,06	0,0034	<0,06
Zn	21	85	5	<85	Nd	0,02	0,21	0,0028	<0,2
U	0,04	0,003	3,3	3,0	Ce	0,018	0,06	0,0012	<0,06
Cu	0,9	0,7	3	1,9	Tl	0,5	0,10	0,0010	<0,1
Fe	4	10	3	5,1	Gd	0,03	0,19	0,0007	<0,2
As	0,16	0,23	2,3	1,7	Be	0,04	0,07	0,0006	<0,07
Mn	0,7	0,19	2	0,50	Pr	0,006	0,022	-	<0,02
Ni	0,8	0,6	2	1,0	Te	0,00	0,16	-	?

Literature: Lomax-Vogt, M. C., Liu Fang, Olesik, J. W., 2021, *Spectrochimica Acta Part B: Atomic Spectroscopy*

Falk, H., Geerling, · R., Hattendorf, ·B., Krengel-Rothensee, K., Schmidt,· K. P., 1997, *Fresenius J Anal Chem*

Marcet, A. J. G., 1819, *Philosophical Transactions of the Royal Society of London*

Summary

- 43 elements evaluated: 24 above, 3 at and 16 below loq
- Elevated concentrations in samples that exceed these limits can be correctly identified
- Calibration with matrix-matched standard solutions for seawater and even freshwater analysis significantly improves recoveries in ICP-MS