Direct Seawater Analysis by High-Resolution ICP-MS Provides Insights into Toxic Metal Accumulation in Marine Sediments

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ABSTRACT: In this study, new insights into the contamination of marine ecosystems are provided by the simultaneous analysis of concurrently collected bottom seawater and upper sediment layer samples with inductively coupled plasma mass spectrometry (ICP-MS). Precise and interference-free quantification of the trace levels of selected heavy metals in seawater diluted 100 times was directly obtained by high-resolution ICP-MS, with the recovery (from 94 to 109% against the certified reference material CASS-6), repeatability (3–5%), intermediate precision (averaging 6.5%), and limits of detection (0.002–0.3 $\mu\text{g L}^{-1}$) being systematically assessed. The same metal contaminants accumulated in the surface sediments were determined - after sample digestion prior to measurements - by quadrupole ICP-MS using a previously optimized and validated protocol. Both sets of metal concentration data expressed as a function of distance from the coast show a decline, followed by a flattening where the transfer of insoluble material and the associated metal fluxes carried by the river watercourse tend to end an action. This occurrence was confirmed by quantifying the natural seawater constituents, such as potassium and lithium, whose concentrations remained constant after the distance of 250 km from the estuary due to a reduced dilution by freshwater.

INTRODUCTION

When analytical approaches for the accurate quantification of trace metals in seawater are considered, inductively coupled plasma mass spectrometry (ICP-MS) advances to the forefront. The examination of recent publications reveals that the ICP-MS technique, operating in high-resolution mode, received highest response from the field. Particularly, there are frequent successful attempts of using sector-field (SF) ICP-MS to determine a variety of metals occurring in seawater at low and even sub-ng L^{-1} levels (see refs. 1–5 to mention a few). However, sample preparation is typically mandatory and involves analyte pre-concentration and matrix separation to transfer the enriched metals into a solution, thus ensuring ICP-MS measurements free from interferences from the salt matrix. Evidently, such treatment, commonly based on using the chelating resins variable in complexation chemistry,^{6–8} makes the analytical protocol more complicated and prone to

uncertainties. Examples of the simultaneous determination of trace metals in seawater by SF-ICP-MS without intricate sample treatment are very few^{9,10} and other direct applications are single-element approaches.^{11,12}

As a matter of fact, dilution may serve as an alternative to cope with the high salinity matrix, at least when determining more abundant metals,^{9,10,12} given the extremely high sensitivity of SF-ICP-MS. This approach has been explored in our study aimed at validating an analytical procedure for the simultaneous measurement of various metals in seawater, which can be suitable for large-scale monitoring of metal contaminants (where high sample throughput is a prerequisite). The satisfactory analytical performance of the method was proved through the analysis of certified reference material (CRM), CASS-6, and systematic metal determinations in bottom seawater, collected from 50 to 450

km from the continental shelf, with the limits of quantification at the low- to sub- $\mu\text{g L}^{-1}$ levels.

Our particular interest in such an analysis is because in the case of shallow seas, such as the Kara Sea (part of the Arctic Ocean) and part in our investigation, the water column may be contaminated by toxic metals carried by river current, the effect of which remains in force over a long distance from the estuary. Another important source of contamination may be the inflow of aerosol material, including particles of mineral dust, volcanic ash, organic combustion products from forest fires, industry and transport products.^{13,14} However, in the case of the Kara Sea, river runoffs are thought to make the main contribution. In the event of an assumed geochemical scenario, metal accumulation in the sediments would present one of the largest threats to the environment. Therefore, we consider the harmonized surveying of surface sediments and overlaying seawater in terms of the level of selected heavy metals, performed here by the verified ICP-MS method, as a valid strategy to assess the ecological state of this marine environment.

EXPERIMENTAL

Reagents and materials. Stock solutions (10 mg L^{-1}) used to prepare the mixed standard solutions and the internal standard (High-Purity Standards, Charleston, SC, USA) were diluted appropriately with 3% HNO_3 , prepared from ultrapure nitric acid (65%, Merck, Germany) and ultrapure water. Seawater CRM (CASS-6, A33-11-02-CASS) was purchased from the National Research Council of Canada (Ottawa, ON, Canada). All plastic, quartz and glassware were soaked in $4 \text{ mol L}^{-1} \text{HNO}_3$ for at least 24 h and rinsed repeatedly with ultrapure water before use.

Instrumentation. The seawater analyses were performed on an Element-2 SF-ICP-MS instrument (Thermo Fisher Scientific, Waltham, MA, USA) with high resolution capacity. The instrument was used in three nominal resolution settings: low ($R = 300$), medium ($R = 4000$) and high ($R = 10000$). The metal isotopes were analyzed in appropriate resolutions (see Table 1 for more detail) to eliminate polyatomic interferences. The internal standard ^{115}In ($1 \mu\text{g L}^{-1}$) was analyzed in both resolutions to account for any drift variation within and between the resolution settings over time. Prior to measurements, the instrumental conditions (including torch position, sample gas flow rate, and lens settings) were optimized to achieve high, reproducible signal intensities and a low oxide level (UO^+) in a $1 \mu\text{g L}^{-1}$ tune solution ($<4\%$). The ICP-MS operating parameters are listed in Table 1. In the case of sediment analyses, the instrumental and measurements conditions were as previously described.¹⁵

Sampling. Both the seawater and sediment samples were collected in August-September 2019 on the continental shelf of the Kara Sea during a research oceanographic cruise aboard the R.V.

Fig. 1 Sampling area.

Table 1. SF-ICP-MS Measurement Parameters

Parameter	Setting
Plasma gas flow, L/min	14
Auxiliary gas flow, L/min	0.9
Nebulizer Ar flow, L/min	0.9
Sample gas flow, mL/min	0.8
RF power, W	1250
Dwell time, ms	10, 20 or 50 for low, middle or high resolution mode, respectively
Spectral resolution mode	low (^{209}Bi , ^{111}Cd , ^7Li , ^{95}Mo , ^{208}Pb , ^{85}Rb , ^{121}Sb , ^{118}Sn , ^{88}Sr , ^{232}Th , ^{205}Tl , ^{238}U); medium (^{55}Mn , ^{51}V); high (^{75}As , ^{39}K)

Academician Mstislav Keldysh. The sediment material was the upper layer (maximum 10 cm in depth), while the seawater was the part of the water column in direct contact with the surface layer collected in duplicate (each sample 1 L) into Teflon-lined lever-action Niskin bottles (General Oceanics, Miami, FL, USA) at the same sampling site. The geographical location of the sampling sites is detailed in Fig. 1.

Sample preparation

Seawater. All seawater samples were filtered through acid pre-cleaned cellulose nitrate membrane filters (Whatman, $0.45 \mu\text{m}$) under vacuum and acidified (with HNO_3 to 3%) on board, stored at 4°C and later analyzed at the laboratory facilities, following dilution with 3% HNO_3 .

Sediment. Upon collection, the samples were air-dried and homogenized using an agate mortar, oven dried at 50°C for 6 days prior to digestion (for more details, see ref. 16) and then transferred to the laboratory for digestion using the previously optimized and validated procedure.^{15,17,18}

RESULTS AND DISCUSSION

Sample dilution factors. When SF-ICP-MS is applied for seawater analysis, dilution is required not only to avoid substantial salt built-up in the sample introduction system but also to reduce

Table 2. SF-ICP-MS Detection Limits for Seawater Analysis ($\mu\text{g L}^{-1}$)

Metal	NASS-5 ¹⁰	NASS-5 ¹²	NASS-5 ²¹	NASS-5 ²²	CASS-3 ¹⁹	CASS-4 ²⁰	CASS-6 (this study)
As	-	-	0.001	0.05	-	-	0.24
Bi	-	-	-	-	-	-	0.13
Cd	-	-	-	-	0.013	-	0.007
Mn	0.005	-	-	-	0.27	0.12	0.13
Mo	0.011	-	-	-	-	-	0.29
Pb	-	-	-	-	0.05	-	0.003
Sb	-	-	-	-	-	-	0.08
Sn	-	-	-	-	-	-	0.06
Th	-	-	-	-	-	-	0.004
Tl	-	0.10	-	-	-	-	0.09
V	0.002	-	-	-	0.01	0.12	0.08
U	0.0004	-	-	-	-	-	0.002

Table 3. Trueness and Precision for SF-ICP-MS Analysis of CASS-6 ($\mu\text{g L}^{-1} \pm \sigma$; n = 3)

Metal	Certified value	Confidence interval	September 8th		September 16th		October 10th	
			Measured value	Recovery (%)	Measured value	Recovery (%)	Measured value	Recovery (%)
As ^a	1.04	0.94-1.14	1.08±0.11	104	1.09±0.07	105	0.97±0.08	93
Cd	0.022	0.020-0.024	0.024±0.007	109	0.020±0.004	91	0.024±0.005	109
Mn	2.22	2.10-2.34	2.1±0.1	95	2.03±0.05	91	2.31±0.05	104
Mo	9.15	8.63-9.67	8.8±0.4	96	9.67±0.03	106	8.62±0.04	99
Pb	0.011	0.007-0.015	0.012±0.004	109	0.012±0.004	105	0.012±0.003	109
V ^a	0.50	0.38-0.62	0.47±0.01	94	0.48±0.02	96	0.48±0.03	96
U	2.92	2.5-3.3	2.8±0.1	96	2.84±0.05	97	2.86±0.04	98

^a Reference values.

the matrix effect on instrumental sensitivity, which shows itself in the functioning of ion optics. Therefore, prior to injection, the seawater samples need to be diluted. From previous studies, typical dilution factors used for the direct analysis of seawater do not exceed 10.⁹⁻¹² We found that a 100-fold dilution is superior for system performance pertaining the accuracy of the obtained results and eliminates signal suppression due to the high sea-matrix salinity (for common metal constituents, i.e., K, Ca, and Mg, a higher dilution factor of 1000 was found more practical). This ensures sufficiently low limits of detection (LODs) to quantify a variety of toxic metals found at typical seawater concentrations not influenced by high anthropogenic input, which in many cases compared well with the sensitivity thresholds obtained by other investigators (where available for direct analysis, see Table 2). It should be mentioned that the fairly lower LODs reported by Field *et al.*¹⁰ were due to using a complicated nebulization setup, a shielded torch, and hot plasma high-resolution ICP-MS.

Method validation. Since the only sample treatment used was dilution, and the dilution factors were multi-fold, it was deemed obligatory to run blank analyses for evaluating contamination or spectral interference effects (with complex matrices, not all interferences could be separated, even when using the SF technique⁴). The precision of the method was determined by analyzing the CASS-6 CRM on three different days (the data summarized in Table 3). It can be seen that trueness, calculated from the deviations of the certified values as a percentage recovery,

Table 4. Limits of quantification ($\mu\text{g L}^{-1}$)

Metal	LOQ	Metal	LOQ
As	0.00051	Sn	0.22
Bi	0.35	Th	0.018
Mn	0.42	Tl	0.31
Mo	0.86	V	0.14
Pb	0.009	U	0.0066
Sb	0.16		

varies from 94 to 109% and the results are within-day repeatable in the range from 3 to 5% (with an exception for the least abundant Cd and Pb). The data of between-day measurements also accord fairly well since the calculated intermediate precision falls within the range of 3.8–9.1%. The limits of quantification of the assay, defined as 10 σ /slope of the calibration curve at a standard 100-fold dilution, are presented in Table 4.

It is noteworthy to mention that the data for other metals that are less critical pollutants, including rare-earth elements, are not presented here and will be discussed elsewhere. Therefore, only some of the metals (as listed in Table 2) are included for systematic measurements as below. Of these, uranium and thorium are rather scarce but show a marked toxicity because of their radioactive properties.

Application to marine samples. There are various sources of material that deposit on the seafloor to form marine sediments, and most of these may cause sediment contamination from toxic

Fig. 2 Metal concentrations in seawater (open circles; $\mu\text{g L}^{-1}$) and surface sediment (black circles; $\mu\text{g g}^{-1}$) at different distance from the coast. For manganese, the concentrations are given in mg L^{-1} and mg g^{-1} , respectively.

metals. Our earlier research^{15,23} suggests that it is insoluble material, primarily rock and soil particles, transported from land areas to the sea by rivers (mostly by the Ob River in this case), that has the greatest ecological impact. For the reason of proving this hypothesis, the simultaneous analysis of bottom seawater and upper sediment layer samples, collected as described in the Sampling subsection, was undertaken in this study.

The typical dependence of the heavy metal concentration of As, Mn, Pb, Th, and U is based on the distance from the coast and is shown in Fig. 2. For both types of sample material, they have a similar character with first a steady decrease and then a gradual flattening of the metal content based on the increase in the distance. The most plausible explanation of such concentration profiles is

due to the mass transfer being marked from the estuary to about 250 km from the coastline and turning out to be negligible beyond this distance. As a result, the contribution of the contaminated material exported by the Ob River influx fades and far from the estuary, the toxic metal concentrations become fairly constant, corresponding to natural seawater levels.

To prove the latter occurrence, the seawater constituents of non-contaminant nature were quantified in the same seawater samples using SF-ICP-MS. Here it is necessary to mention that for offshore aquatic areas, seawater has a rather conservative composition which is directly connected with the components included in Table 5. From the comparison of the concentrations of minor conservative metals at different distances from the shore and their global open

Table 5. Minor Conservative Seawater Metals Quantified at Different Distance from the Coast and Their Typical Offshore Concentrations (mg L⁻¹)

Metal	Distance (km)					Concentration in ocean water ^a
	50	80	130	250	450	
K	82±3	139±6	320±12	385±10	390±13	391
Li	0.03±0.001	0.04±0.001	0.10±0.003	0.14±0.005	0.15±0.005	0.14
Rb	0.04±0.002	0.06±0.002	0.11±0.003	0.17±0.002	0.17±0.003	0.17
Sr	1.5±0.1	2.4±0.1	5.6±0.3	7.8±0.2	7.9±0.2	7.9

^a Ref. 22.

ocean levels (in ref. 22), given in the table, it is evident that while initially affected by the influx of the river into the sea, the concentration of K, Sr, Li, and Rb turns out to be invariable after 250 km from the estuary due to a faded dilution effect by freshwater. It is worth noting that for some target analytes, *e.g.*, arsenic and cadmium, the concentrations measured after this distance are also typical for offshore areas that are far from natural or anthropogenic influences.²⁴ This fact can be considered an additional demonstration of the validity of the proposed method.

CONCLUSIONS

While seawater analysis belongs to the most often-used active applications areas of ICP-MS,²⁵⁻²⁷ the direct determination of trace metals remains a key sticking point. In the present study, we present a simple strategy for the direct analysis of offshore seawater, employing higher sample dilutions than accustomed in the reports of previous research. The results from the simultaneous determination of As, Cd, Mn, Mo, Pb, U and V in the CRM and the longitudinal profiling of the Arctic Ocean water are in good agreement with certified and global open ocean values, respectively. The performance characteristics, obtained due to high sensitivity and resolution as well as the robustness of the SF-ICP-MS method, suggest its utility for a broader range of analytes. Furthermore, unlike previous methods relying on the concentration and separation of trace metals from the seawater matrix, our approach allows the sample throughput to be greatly increased. Another important aspect of the method is that in combination with marine sediment analysis, it lends itself to gaining geochemically important results, such as assessing the extent of sediment contamination by toxic metals or the effect of river influx on marine ecosystems.

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Notes

The authors declare no competing financial interest.

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