

## DETERMINATION OF TRACE METALS IN SEA WATER BY ICP-MS AFTER MATRIX SEPARATION

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### Abstract

The analysis of ultra trace elements in sea water samples is one of the most difficult analytical tasks in the field of environmental monitoring, as extremely low detection limits for elements buried in a highly saline matrix is required. The use of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for direct sea water analysis is currently limited by spectral and non-spectral interferences caused by the sea water matrix. Sample dilution is always a way out at the expense of inadequate sensitivity after such dilution especially for open ocean sea water. In order to approach this complex analytical task by ICP-MS there are two common strategies studied so far: first the use of pre-concentration technique and matrix removal and second the use of double focussing ICP-MS instruments. The use of Ammonium tetramethylene dithiocarbamate (APDC)/Methyl isobutyl ketone (MIBK) solvent extraction for matrix removal and direct estimation of trace elements in sea waters by ICP-MS are discussed in this paper.

### Introduction

In recent years the determination of trace elements in seawater has received an increasing attention in the field of environmental monitoring and since most of the heavy metals occur at extremely low concentrations, very sensitive techniques are required. With the ever-increasing use of ICP-QMS as a routine analytical tool, the demand for the technique to handle a wider variety of sample matrices has increased. Although the technique of ICP-QMS is very powerful by virtue of its selectivity and sensitivity, the use of ICP-QMS for direct seawater analysis is currently limited by spectral and non spectral interferences caused by the sea-water matrix.<sup>1</sup> Suppression of analyte signal in ICP-QMS in the presence of high concentration matrix salts is due to several factors: (a) the ionization of the element from the salt and possibly their total contribution to the electron densities in the plasma, (b) changing aerosol transport efficiency at high salt concentrations and (c) MS sampling conditions.<sup>2</sup> In particular, the effect of oxide/hydroxide adduct ions of alkali and alkaline earth elements, common constituents in sea water can effectively mask the determination of most transition elements as seen

in Table 1.<sup>3</sup> Sample dilution is always a way out at the expense of inadequate sensitivity after such dilution, specially for open ocean sea-water. In order to approach this complex analytical task by ICP-QMS, there are two common strategies studied so far: first, the use of pre-concentration techniques and matrix removal (using chelating ion exchange resins, co-precipitation and liquid-liquid extraction) before ICP-QMS detection and second, the use of double focusing ICP-MS instruments (for direct trace metal determination after a simple dilution of the sample).<sup>4,5</sup> By operating at 3000 resolving power ( $m/\Delta m$ ) most of the spectral interference coming from molecular ion due to sea water matrix elements (eg., Ca, Na, Cl etc.,) can be satisfactorily resolved.<sup>6</sup> Also the sensitivity attainable at low resolving power ( $m/\Delta m=300$ ) with the ICP-MS is at least 10-100 times better than with ICP-QMS, due to comparatively low instrumental background and higher transmission than in the ICP-QMS instrument.<sup>7</sup> Currently a lot of work is being done to reduce or eliminate matrix interference in ICP-MS by collision/reaction cell technology.<sup>8</sup> The dynamic reaction cell (DRC) provides an excellent technology for eliminating the interference that are derived from the plasma gas as well as the sample matrices. Unlike other approaches DRC technology completely eliminates interference and produces ultra trace detection in the difficult samples like seawater.

The pre-concentration technique applied for the sea water analysis should achieve the following requirements for the interference free estimation:<sup>3</sup> a) Selective removal of most interfering ions from solution, b) elimination of cone blockage problems, c) retention of long term calibration integrity, d) reduction of polyatomic interferences, e) capability to pre-concentrate for further enhancement of detection limits, f) offline sample processing for maximum productivity.<sup>3,9</sup>

Pre-concentration techniques such as solvent extraction, ion exchange and carrier precipitation have been extensively studied with reference to sea water analysis.<sup>10, 11</sup> Pre-concentration is usually accomplished by solvent extraction using pyrrolidine N-carbodithioate (APDC),<sup>12</sup> chloroform and combined ammonium tetramethylenedithiocarbamate (APDC), diethylammonium diethyldithiocarbamate (DDDC)<sup>13</sup> or APDC/MIBK<sup>14</sup> techniques or by ion exchange with a resin such as chelex-100<sup>15</sup> or adsorption on immobilized 8-hydroxyquinoline (I-8-HOQ).<sup>16</sup> In the present work seawater samples were pre-concentrated following the ammonium pyrrolidine

dithio carbamate (APDC)/methyl isobutyl ketone (MIBK) solvent extraction technique prior to analysis by ICP-QMS.

**Table 1.** Major interferences of alkali and alkaline earth adduct ions on transition metal isotopes in a typical seawater matrix.

Isotope	Cl	Ca	Na	K	Ar
V <sup>51</sup>	<sup>35</sup> ClO				
Cr <sup>52</sup>	<sup>35</sup> ClOH				ArC
Cr <sup>53</sup>	<sup>37</sup> ClO				
Mn <sup>55</sup>			<sup>23</sup> NaO <sub>2</sub>	<sup>39</sup> KO	ArNH
Fe <sup>56</sup>		<sup>40</sup> CaO		<sup>39</sup> KOH	ArO
Fe <sup>57</sup>	<sup>40</sup> CaOH				ArOH
Ni <sup>58</sup>	<sup>42</sup> CaO				
Co <sup>59</sup>		<sup>42</sup> CaOH, <sup>43</sup> CaO			
Ni <sup>60</sup>		<sup>44</sup> CaO, <sup>43</sup> CaOH			
Cu <sup>63</sup>			ArNa		
Zn <sup>64</sup>		<sup>48</sup> CaO			
Cu <sup>65</sup>		<sup>48</sup> CaOH			
Zn <sup>67</sup>	ClO <sub>2</sub>				

## Experimental

### Instrumentation and Calibration

An Ultra Mass 700 ICP-MS (Varian, Australia) was used for the determination of trace metals in seawater and the instrument parameters (RF power 1.4 kW, Nebulizer gas flow 0.81 L/min, Plasma flow 18 L/min, Spray chamber temperature -10°C) were set according to the manufacturers instructions.<sup>17</sup> Standardization of the instrument was based on a two-point calibration procedure, using a multi element standard (J. T. Backer, Inc Phillipsburg NJ) as the high standard, and double distilled water (zero metal concentration) as the low standard. Standardization of the instrument was repeated after every three sets of seawater extracts to minimize the effect of instrument drift. Distilled water and a check standard were also included in the analysis sequence. The accuracy of the method was confirmed by analysis of certified reference material CASS-3 (near sea shore water). For interlaboratory testing a Perkin-Elmer (Elan DRC II) ICP-QMS and Varian (Spectra AA 800) GF-AAS present in the Geochemistry laboratory of National Geophysical Research Institute (NGRI) was used.

### Reagents and Standards

Multielement stock standard solutions were prepared from 1000 ppm stock solution (J. T. Backer, Inc Phillipsburg NJ) after appropriate dilution. All chemicals used were of analytical grade. Glass double distilled water was used for the preparation of all solutions. Nitric acid used in the present study was of AR grade (Merck, Mumbai).

A 1% aqueous solution of APDC (Eastman Chemicals): the solution which was prepared daily was purified by shaking with an equal volume of MIBK, separating the phases and filtering the lower aqueous phase. Since APDC is only slightly soluble in MIBK whereas metal complexes are highly soluble, the reagent is easily purified in this manner. Reagent grade MIBK was used throughout without further purification. Ammonium acetate (Sigma, Mumbai) buffer (5N) was prepared and metallic impurities were removed by adding a few milliliters of APDC solution and extracting with MIBK.

**Sea Water Source:** Sea water samples were provided by Institute of Petroleum Safety and Environmental Management (IPSEM), Oil and Natural Gas Corporation (ONGC), Goa, India as part of their study to monitor the extent of pollution due to various industrial activities. They supplied 200 samples per each season (pre-monsoon and post-monsoon) for the last three years. The values presented in Table 5 is a representative samples of seawater provided by IPSEM.

**Pre-concentration Procedure:** The dissolved metals were simultaneously extracted from filtered water samples by chelation with APDC followed by MIBK extraction according to method described in literature.<sup>18-21</sup> All experiments were carried out in a pH range of 2-6. Extractions were done in a separatory funnel shaken for 2 min. by hand with 50 mL of aqueous volume, 1ml of APDC solution and 10ml of MIBK. When the highest possible accuracy was required the organic phase was placed in a 10 mL volumetric flask and diluted to volume with water saturated MIBK. This eliminated the error caused by variation in the volume of organic phase lost because of solubility.

All sample preparations were carried out in a clean laboratory equipped with laminar flow benches and fume cupboards. All laboratory wares were cleaned in 1:1

HNO<sub>3</sub> and rinsed in DIW. Once in use, they were rinsed with DIW between determinations.

## Results and discussion

### Pre-concentration procedure

The efficiency of separation of matrix elements and pre-concentration by the APDC/MIBK extraction was studied by taking three NIST drinking water standards 1643a, 1643b, 1643c and adding different concentrations of salt matrix. The results are presented in Table 2 which shows very good extraction efficiency, except for the sample NIST 1643d where the recoveries are higher which may be due to the high salt concentration (4%). From the results it is clear that we can adopt APDC/MIBK extraction for our seawater (where the salinity is around 3-3.5%) samples for removing salt matrix and pre-concentration.

### Seawater standard analysis

Having effected the removal of interferences from seawater analysis a test on analytical performance of the method is carried out. In Table 3 results of ICP-QMS analysis of near sea shore seawater reference material CASS-3 by both standard addition and direct analysis are compared with the certified values. For critical assessment of accuracy there is no substitute for seawater standard reference material certified for elemental composition but unfortunately we do not have such standards in our lab. The accuracy of the procedure was therefore tested by preparing three synthetic standards. The concentration of metals were kept similar to CASS-1, CASS-2, NASS-4 standards with a salt matrix of 3%. These three standards were analysed directly after solvent extraction as mentioned above. From these figures it can be seen that direct analysis may not be possible due to the interferences from alkali and alkaline earth metals which are present in high concentrations in sea water matrix (Table 1), even after pre-concentration. To overcome these polyatomic spectral interferences an online elemental correction equation (C.E.) is applied and these values are presented in Table 3. The values obtained are in good agreement with the certified/accepted values which indicates

that sea water samples can be analysed directly using ICP-QMS after matrix separation and application of C.E.

**Table 2.** Study on the efficiency of APDC/MIBK extraction/pre-concentration method.

Elements	Certified value	Analysed by ICP-QMS	Addition of NaCl matrix	After APDC/MIBK Extraction and Preconcentration
NIST 1643b				
Mn	27.5	26.8±1.2		27.9±1.2
Co	25.3	24.3±2.1		26.1±2.0
Ni	47.7	48.4±3.0		46.2±1.7
Cu	21.2	22.0±2.1	3%	22.2±1.7
Zn	67.1	66.1±1.9		68.7±2.3
Cd	19.9	18.8±2.0		18.7±1.1
Pb	24.3	25.7±2.2		26.1±2.7
Cr	18.8	19.0±2.0		19.1±1.0
NIST 1643c				
Mn	35.1	36.2±2.1		34.2±1.3
Co	23.5	22.7±1.8		24.2±1.6
Ni	61.0	62.1±3.1		58.6±2.1
Cu	22.3	22.1±2.1	3.5%	23.2±1.9
Zn	74.0	74.2±1.8		77.1±1.1
Cd	12.2	12.8±1.2		14.1±1.0
Pb	35.3	36.6±1.4		36.1±1.1
Cr	19.0	19.0±1.7		17.9±2.1
NIST 1643d				
Mn	37.6	38.0±2.1		35.1±1.2
Co	25.0	25.7±2.0		20.2±2.2
Ni	58.0	58.2±1.8		63.1±1.7
Cu	20.5	21.2±1.5	4.0%	26.6±2.1
Zn	72.5	73.0±2.1		80.1±3.1
Cd	6.5	6.6±2.0		9.9±1.2
Pb	18.1	18.8±1.7		22.3±2.1
Cr	18.5	19.1±1.8		23.1±1.6

All values are in ppb. The values reported are a mean of five readings ± SD.

**Table 3.** Direct analysis and recoveries of seawater standards using ICP-MS and online correction equation.

Metals		Mn	Co	Ni	Cu	Zn	Cd	Pb	Cr
CASS-3	Certified/ Accepted	2.51 ± 0.36	0.04 ± 0.009	0.38 ± 0.06	0.51 ± 0.06	1.24 ± 0.25	0.03 ± 0.005	0.01 ± 0.004	–
	Standard Addition (\$)	1.98 ± 0.06	0.06 ± 0.005	0.31 ± 0.03	0.50 ± 0.04	1.20 ± 0.16	0.02 ± 0.008	0.01 ± 0.002	–
CASS-1*	Certified/ Accepted	2.11 ± 1.01	0.06 ± 0.007	0.31 ± 0.02	0.29 ± 0.01	1.02 ± 0.11	0.03 ± 0.007	0.37 ± 0.09	0.22 ± 0.06
	Direct Analysis	3.56 ± 1.56	0.12 ± 0.05	0.91 ± 0.32	0.56 ± 0.15	0.53 ± 0.09	0.21 ± 0.06	0.48 ± 0.19	1.09 ± 0.25
	Standard Addition (\$)	1.78 ± 0.06	0.04 ± 0.003	0.29 ± 0.006	0.31 ± 0.007	1.01 ± 0.006	0.02 ± 0.002	0.39 ± 0.01	0.23 ± 0.09
CASS-2*	Certified/ Accepted	2.02 ± 0.52	–	0.31 ± 0.14	0.26 ± 0.12	1.88 ± 0.31	0.11 ± 0.02	0.04 ± 0.007	0.22 ± 0.09
	Direct Analysis	1.56 ± 0.26	–	0.12 ± 0.04	0.45 ± 0.25	0.85 ± 0.25	0.25 ± 0.09	0.09 ± 0.06	0.36 ± 0.14
	Standard Addition (\$)	2.14 ± 0.12	–	0.30 ± 0.12	0.28 ± 0.12	1.92 ± 0.28	0.20 ± 0.11	0.06 ± 0.009	0.27 ± 0.11
NASS-4*	Certified/ Accepted	0.41 ± 0.12	0.02 ± 0.001	0.26 ± 0.008	0.28 ± 0.09	0.19 ± 0.01	0.02 ± 0.003	0.16 ± 0.007	–
	Direct Analysis	0.58 ± 0.25	0.32 ± 0.007	0.15 ± 0.06	0.32 ± 0.22	0.31 ± 0.006	0.15 ± 0.05	0.32 ± 0.05	–
	Standard Addition (\$)	0.40 ± 0.02	0.01 ± 0.002	0.29 ± 0.004	0.25 ± 0.1	0.21 ± 0.07	0.03 ± 0.005	0.18 ± 0.006	–

All values are in ppb. (\$): After applying correction equation. \*synthetic standards prepared in our laboratory corresponding to the composition of the standards. The values reported are a mean of five readings ± SD.

### Precision Studies

Precision of the method was tested by replicate analysis of near sea shore sea water SRM CASS-3 and sea water samples 12 times after applying C.E. From the values in Table 4 it can be concluded that the method has a very good precision except for Mn, which may be due to polyatomic interference from  $^{23}\text{NaO}_2$ ,  $^{39}\text{KO}^{16}$ , ArNH (Table 1).

**Table 4.** Precision studies.

Element	CASS-1	%RSD	Seawater real samples	%RSD
Mn	2.1	8.7	1.2	10.1
Co	0.06	1.8	1.6	2.7
Ni	0.3	3.1	20.2	5.4
Cu	0.3	3.9	92.4	3.3
Zn	1.0	3.7	453.5	5.8
Cd	0.03	1.6	58.6	2.0
Pb	0.4	2.3	206.9	2.8
Cr	0.2	1.2	141.2	1.1

### Analysis of sea water samples

The analytical results for sea water sample was given in Table 5. The sample was analysed directly (after solvent extraction by APDC/MIBK and online C.E) and by standard method. Interlaboratory tests were performed by using two different techniques (ICP-QMS, GF-AAS) in our sister laboratory (NGRI) for quality assurance and quality control checks. The values presented in Table 5 were in good agreement indicating the analysis is accurate.

**Table 5.** Direct analysis of sea water samples and interlaboratory testing  $\pm$  S.D.

Element	Direct analysis by ICP-MS	Concentration Found After Standard Addition		
		ICP-MS (IICT)*	ICP-MS (NGRI)	GF-AAS (NGRI)
Mn	1.2 $\pm$ 0.3	1.5 $\pm$ 0.1	1.4 $\pm$ 0.2	1.4 $\pm$ 0.07
Co	1.6 $\pm$ 0.2	1.9 $\pm$ 0.2	1.9 $\pm$ 0.2	1.9 $\pm$ 0.08
Ni	20.2 $\pm$ 1.9	25.0 $\pm$ 0.5	25.2 $\pm$ 0.4	25.5 $\pm$ 0.1
Cu	92.4 $\pm$ 6.1	113.6 $\pm$ 1.1	114.1 $\pm$ 1.0	112.8 $\pm$ 0.7
Zn	452.5 $\pm$ 20.1	580.1 $\pm$ 1.3	577.6 $\pm$ 4.1	579.2 $\pm$ 2.7
Cd	58.6 $\pm$ 4.8	69.1 $\pm$ 0.9	68.7 $\pm$ 1.0	68.4 $\pm$ 0.7
Pb	206.9 $\pm$ 11.2	280.7 $\pm$ 2.7	282.1 $\pm$ 2.7	281.7 $\pm$ 1.8
Cr	141.2 $\pm$ 7.1	242.6 $\pm$ 3.1	241.8 $\pm$ 2.1	242.7 $\pm$ 1.1

\*With C.E. The values reported are a mean of five readings  $\pm$  SD.

### Conclusions

Over the last two decades there has been an increasing need for trace and ultra trace determination of heavy metals in seawater in order to monitor possible pollution of natural environments and also oceanographic studies. The serious matrix effects arising from seawater salts often cause the determinations more difficult. The philosophy of

removing the sample matrix prior to analysis by ICP-QMS has many advantages. Interferences are removed, stability is improved and calibration is more straightforward.<sup>6</sup> In this paper use of APDC/MIBK pre-concentration technique is used in order to analyse seawater samples directly. The results presented demonstrate the effectiveness of ICP-QMS for the analysis of most difficult environmental samples, seawater overcoming the previous limitation-total dissolved solids. In this manner the previous limitation on total dissolved solids with ICP-QMS is eliminated and the flexibility of the ICP-MS technique can now be fully utilized for this difficult matrix.

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### **Povzetek**

Določevanje elementov v sledovih v vzorcih morske vode je ena izmed težjih nalog na področju okoljskega monitoringa zaradi visoke koncentracije NaCl v matrici. Ta otežuje uporabo masne spektrometrije z induktivno sklopljeno plazmo (ICP-MS) za neposredno analizo morske vode zaradi spektralnih in nespektralnih motenj. Redčenje vzorca je ena od možnosti, da motnje zaobidemo, a pri tem izgubimo potrebno občutljivost metode. Drugi dve strategiji, ki sta še v uporabi, sta uporaba predkoncentracije in ločitev matrice ter uporaba ICP-MS instrumenta z dvojnim fokusiranjem. Uporaba ekstrakcije z amonijevim tetrametilenditiokarbamatom (APDC)/metilizobutylketonom (MIBK) za ločitev matrice in neposredna določitev sledov elementov v morski vodi je tema tega prispevka.