Determination of trace metals in seawater by ICP-MS after preconcentration and matrix separation by dithiocarbamate complexes

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A rapid single extraction procedure using dithiocarbamate complexing agent in methyl-isobutyl ketone (MIBK) organic phase and acid exchange back-extraction is described for the simultaneous quantitative preconcentration of Fe, Mn, V, Cr, Ni, Co, Cu, Zn, As, Mo, Cd, Pb and U in seawater followed by its determination by inductively coupled plasma mass spectrometry (ICP-MS). This method gives quantitative recoveries for all above metals at pH 4.1-6.4. A matrix matching seawater certified reference material (CRM), NASS-5, was used for calibration so as to minimize the matrix and other associated effects. Blanks and detection limits were in ng/l range. The method gives a recovery of 94-100% for 100 ml sample, facilitating the rapid and interference-free analysis of seawater samples. Excellent agreement was obtained with the certified values of another seawater CRM, CASS-4, when it was analyzed as an unknown. The major advantage of this procedure is that rapid analysis can be performed for a wide range of metals from relatively small samples.

[**Key words**: Trace metals, seawater; extraction, preconcentration, dithiocarbamate, ICP-MS, matrix separation]
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Introduction

Trace metals in seawater are widely studied to understand their geochemical and biological cycles in marine environment and for environmental monitoring. They provide valuable information on distinctive characteristics of hydrothermal activity along mid-oceanic ridge systems and are used as conservative/non-conservative tracer signals for locating hydrothermal vent sites. With the development of more sensitive analytical techniques, marine chemists are capable of detection and estimation of trace metals in seawater even at µg/l to ng/l level. However the presence of high salt matrix have always posed problems creating analytical complexities[1].

Several methods are adopted to preconcentrate the trace metals and to separate the salt matrix from seawater prior to trace metal determination. Techniques such as solvent extraction[2-8], ion exchange[9-11] and carrier precipitation[12,13] have been extensively used to achieve selective removal of most interfering ions and to preconcentrate for further lowering of detection limits. The method based on metal complexation with ammonium pyrolidine dithiocarbamate (APDC) and extraction into methyl isobutyl ketone (MIBK)[14-16] is widely adopted with some modification even today by several researchers. Sometimes di-ethylammonium diethyldithiocarbamate (DDDC) was added in combination with APDC to improve complex stability and broaden the effective working pH range[6,17]. Chelating ion-exchangers having iminodiacetic acid (IDA) functional groups such as Chelex-100, Muromac A-1, Chelite-C and Toyopearl F-Chelate, silica immobilized 8-hydroxyquinoline (I-8-HOQ), C18 bonded silica gel, polymer sorbents, and activated alumina etc., were also used for sample pretreatment[14]. Although on-line preconcentration procedures are preferred in view of the green chemistry concept and automation, many laboratories estimate trace metals by following off-line methods due to technical constraints.

Initially the dithiocarbamate preconcentration method was adopted to determine few trace metals (viz., Ag, Cd, Cr, Co, Cu, Fe, Ni, Pb, Zn) in seawater by atomic absorption spectrometry[4,16]. There have been several problems with respect to calibration by using synthetic multi-element solutions as the matrices of standards and samples never match in this kind of analysis and create matrix interferences. Hence, an attempt is made to use matrix matching reference sample for calibrations for the first time, thereby minimizing matrix and associated interferences. With the growing use of ICP-MS as a rapid multi-element instrumental detection system, a wide range of trace metals (viz., Fe, Mn, V, Cr, Ni, Co, Cu, Zn, As, Mo, Cd, Pb and U) were determined

in seawater by ICP-MS following APDC/MIBK solvent extraction technique for preconcentration and matrix removal. The effect of pH of seawater over extraction efficiency was studied at pH varying from 2.0 to 8.9, to estimate the optimum pH for complete recovery of trace metals.

Materials and Methods

Chemicals

Acids and ammonia (25%) were of Suprapure™ quality (Sigma Aldrich, Germany). Complexing agents were of analytical grade. Technical grade methyl-isobutyl ketone (MIBK) (Merck, Germany) was used. Distilled water (Millipore™ water system) was used to make up all solutions. Dithiocarbamate complexing solution and 1% APDC was prepared prior to use in 100 ml volumetric flasks with pH 2.5 (HNO_3) double distilled water. This solution was purified by extraction with MIBK. Stock ammonia (3 M)/acetic acid (2 M) buffer was prepared and used as such.

Seawater

Seawater (~ 1300 m depth) was collected from Northern Central Indian Ridge (7°06′53.45″S; 67°55′49.2″E) during the Cruise SK-201 of *ORV Sagar Kanya* (March 2004). All the Niskin sampling bottles were rinsed thoroughly with 0.2N ultra pure nitric acid and then washed with Mill-Q water before attaching them to the CTD-rosette. Niskin bottles have both ends which are held by springs. The sample is collected by opening both ends of the bottles at desired depth by release/ocking mechanism. Seawater was collected from the Niskin bottle in an acid-washed (10% HNO_3) 20 L polyethylene container and acidified with 0.02 M HNO_3. A near-shore seawater certified reference material (CASS-4) was obtained from the National Research Council of Canada to validate the method.

Preconcentration procedure

The extraction procedure was performed in a clean environment. To limit exposure and potential contamination, caps were removed from separating funnels/centrifuge tubes only for the introduction or removal of sample/reagents. All labwares were acid washed.

Acidified seawater (100 ml) was placed in a separating funnel and pH was adjusted to the required pH with acetic acid/ammonia buffer. About 1 ml of 1% APDC and 5 ml of MIBK were added. MIBK is preferred because of its efficiency to extract wide range of dithio carbamate-metal chelates[4,18,19]. The

samples were shaken for 5 minutes and allowed to stand for 20-30 minutes for phase separation. The lower seawater phase was drained and the organic phase was transferred in a separating funnel. About 5 ml of 4N HNO_3 was added and shaken for 10 minutes acid-back extraction. After phase separation, the lower aqueous phase was transferred in a test tube for further analysis by ICP-MS. Blanks were determined by extraction of 100 ml of acidified double distilled water.

Optimization of extraction procedure

To optimise the extraction procedure, replicates of seawater certified reference material, CASS-4 procured from National Research Council, Canada, were extracted at varying pH (from 2.0 to 8.9) following the above procedure. Extraction efficiencies were calculated on the basis of trace metal recoveries.

Instrumental parameters

A Perkin Elmer SCIEX® (Toronto, Ontorio, Canada) (Model 6100 ELAN DRC II) ICP-Mass Spectrometer was used throughput. The sample introduction system consisted of a standard Meinhard® nebulizer with a cyclonic spray-chamber. All quantitative measurements were performed using instrument software (ELAN® version 4.0). Several well-known isobaric interferences were programmed, and the corrections were automatically applied. Instrumental and data acquisition parameters are listed in Table 1 and their details were published earlier[20].

Calibration

Both NASS-5 and CASS-4, seawater certified reference materials, procured from National Research Council (NRC), Canada, were subjected to same way

Table 1 — Instrument settings of ICP-MS

RF Power	1100 W
Argon gas-flow	
Nebulizer	0.86 L/min
Auxillary	1.2 L/min
Plasma	15 L/min
Lens Voltage	5
Sample uptake rate	0.80 ml/min
Measuring mode	Peak hopping
Point per peak	1
Number of sweeps	50
Dwell time (microseconds)	50
Integration time (ms)	2500
Replicates	3
Internal standard	^{103}Rh[a]

[a]At an overall concentration of 20ng/ml

of solution preparation as for the other samples, by adopting the recommended procedure. These reference materials are well characterized and possesses certified values for most of the trace metals (viz., Fe, Mn, V, Cr, Ni, Co, Cu, Zn, As, Mo, Cd, Pb and U), thus assuring reasonable accuracy. Calibration was performed using NASS-5, to minimize matrix and other associated interference effects, while CASS-4 was used to check the precision and accuracy of the analysis. The RSD was found to be better than 6% in majority of the cases.

Results and Discussion

Method optimization

Optimization of this method using CASS-4 at different pH (varying from 2.0 to 8.9) was carried out for all trace metals by ICP-MS. Advantage of ICP-MS is that sample volume that should be sprayed is ~ 2-3 ml for single analysis of several element determination. In order to attain quantitative recoveries of Fe, Mn, V, Cr, Ni, Co, Cu, Zn, As, Mo, Cd, Pb and U with the solvent extraction technique it was essential to improve the extraction efficiency of the system to get optimum % recovery of trace metals. The optimum conditions for this system, including reagent type, quantity, extraction pH and shaking times were investigated. Initially the solvent volume was reduced from 15 ml to 10 ml and agitated for 10 minutes. Attempts to reduce the extraction time showed that a 5-min extraction was sufficient for all metals except Fe, which required a 10-min extraction.

The effect of pH extraction efficiency

The pH dependence of APDC extraction into MIBK was examined, and as extraction is solvent dependent[21], we examined the extraction efficiency over the pH range from 2.0 to 8.9 (Table 2). The recovery of Fe, Mn, V, Cr, Ni, Co, Cu, Zn, As, Mo, Cd, Pb and U quantitatively increased between pH varying from 4.1 to 6.4. The recoveries of trace metals were found to vary at different pH. Vanadium was extracted efficiently at pH 2.8, 4.1 and 8.0. Manganese was recovered at pH 4.1 and 6.4, and could not be extracted at higher pH. Iron was recovered efficiently at pH 4.1 and extraction diminished with increasing pH due to formation of Fe hydroxy complexes[4,22,23]. Excellent recoveries of V, Cr, Co, Cu, Cd, Pb and U were obtained at pH 4.1 (Table 2). It is suggested that using this method, a pH of 4.1 is sufficient to estimate majority of trace metals in seawater. This will also eliminate laborious task involved in sample preparation, particularly when dual preconcentration step is involved.

Optimization of acid back extraction

To optimize the strength of acid to be used for back-extracting the metals and to know whether increasing normality of acid will subsequently lead to better recoveries, 4N and 6N HNO_3 were used in seawater reference samples. To extract all the investigated trace metals efficiently 4N HNO_3 is sufficient.

Seawater analysis by adopting the recommended procedure

Seawater collected from the Northern Central Indian Ridges were analyzed for trace elements by varying the pH from 2.0 to 8.9. The results (Table 3) showed similar trend that was observed as in the case of recovery of seawater certified reference material (CASS-4), except for Cu, Zn and Cd. The optimized pH for Cu, Zn and Cd was 4.1 in CASS-4 (Table 3)

Table 2 — Recovery of trace metals (in %) in seawater certified reference material CASS-4 at different pH (varying from 2.0 to 8.9)

Elements	pH						
	2.0	2.8	4.1	6.4	7.3	8.0	8.9
V	76 ± 4.6	100 ± 6.0	101 ± 6.1	65 ± 3.9	89 ± 5.4	98 ± 5.9	76 ± 4.6
Cr	74 ± 4.5	63 ± 3.8	101 ± 6.0	57 ± 3.4	66 ± 4.0	55 ± 3.3	61 ± 3.7
Mn	66 ± 4.0	69 ± 4.2	77 ± 5.9	99 ± 5.9	86 ± 5.2	72 ± 4.3	57 ± 3.4
Fe	50 ± 3.0	86 ± 5.2	107 ± 6.4	96 ± 5.8	77 ± 4.6	71 ± 4.3	58 ± 3.5
Ni	60 ± 3.6	60 ± 3.6	100 ± 6.0	57 ± 3.4	76 ± 4.6	73 ± 4.4	50 ± 3.0
Co	58 ± 3.5	85 ± 5.1	96 ± 5.8	37 ± 2.2	34 ± 2.0	68 ± 4.1	44 ± 2.6
Cu	24 ± 1.4	37 ± 2.2	100 ± 6.0	98 ± 5.9	22 ± 1.3	27 ± 1.6	33 ± 2.0
Zn	55 ± 3.3	81 ± 4.9	102 ± 6.1	55 ± 3.3	91 ± 5.5	92 ± 5.5	94 ± 5.6
As	35 ± 2.1	99 ± 6.0	106 ± 6.4	73 ± 4.4	60 ± 3.6	97 ± 5.8	48 ± 2.9
Mo	99 ± 6.0	98 ± 5.9	78 ± 4.7	100 ± 6.0	97 ± 5.8	102 ± 6.1	93 ± 5.6
Cd	100 ± 6.0	77 ± 4.6	92 ± 5.5	42 ± 2.5	24 ± 1.4	69 ± 4.1	10 ± 0.6
Pb	60 ± 3.7	111 ± 6.8	100 ± 6.1	100 ± 6.1	51 ± 3.1	69 ± 4.2	60 ± 3.7
U	79 ± 4.8	97 ± 5.8	94 ± 5.6	91 ± 5.4	58 ± 3.5	47 ± 2.8	57 ± 3.4

Table 3 — Recovery of trace metals (in %) in seawater collected from Northern Central Indian Ridges at different pH
(varying from 2.0 to 8.9)

Elements	pH						
	2.0	2.8	4.1	6.4	7.3	8.0	8.9
V	36 ±2.1	58 ± 3.5	100 ± 5.0	32 ± 1.9	40 ± 2.4	43 ± 2.6	36 ± 2.1
Cr	77 ± 4.6	55 ± 3.3	100 ± 6.0	61 ± 3.7	70 ± 4.2	60 ± 3.6	66 ± 3.9
Mn	65 ± 3.9	64 ± 3.8	73 ± 4.4	100 ± 6.0	35 ± 2.1	76 ± 4.5	48 ± 2.9
Fe	43 ± 2.6	70 ± 4.2	100 ± 5.2	80 ± 4.8	64 ± 3.9	60 ± 3.6	49 ± 2.9
Ni	16 ± 1.0	60 ± 3.6	100 ± 6.0	57 ± 3.4	76 ± 4.6	73 ± 4.4	50 ± 3.0
Co	78 ± 4.7	61 ± 3.7	100 ± 5.5	52 ± 3.1	48 ± 2.9	91 ± 5.5	61 ± 3.7
Cu	69 ± 4.2	86 ± 5.2	74 ± 4.4	100 ± 5.0	64 ± 3.9	76 ± 4.5	94 ± 5.6
Zn	91 ± 5.5	81 ± 4.8	55 ± 3.3	100 ± 5.5	92 ± 5.5	94 ± 5.6	93 ± 5.6
As	9 ± 0.5	21 ± 1.2	100 ± 6.0	17 ± 1.0	14 ± 0.9	35 ± 2.1	12 ± 1.7
Mo	51 ± 3.1	44 ± 2.7	36 ± 2.2	100 ± 5.0	45 ± 2.7	58 ± 3.5	100 ± 6.0
Cd	43 ± 2.6	37 ± 2.2	17 ± 1.0	100 ± 5.1	26 ± 1.5	70 ± 4.2	12 ± 1.5
Pb	77 ± 4.6	92 ± 5.5	85 ± 5.1	100 ± 6.0	69 ± 4.2	85 ± 5.1	77 ± 4.6
U	82 ± 4.9	100 ± 5.6	63 ± 3.8	94 ± 6.0	60 ± 3.6	49 ± 3.0	60 ± 3.6

Table 4 — Detection limits and blank values of the proposed method

Element	Mass No.	Detection limit (ng/l)	Blank (μg/l)
V	51	0.061	0.027
Cr	52	0.007	0.003
Mn	55	0.045	0.048
Fe	57	0.023	0.016
Ni	58	0.014	0.005
Co	59	0.300	0.001
Cu	63	0.039	0.005
Zn	64	0.007	0.006
As	75	0.315	0.012
Mo	98	9.360	0.189
Cd	114	0.508	BDL
Pb	208	0.001	BDL
U	238	1.675	0.043

BDL-below detection limit

and 6.4 in seawater sample (Table 4). This anomaly may be due to the differences in the concentrations of concomitant elements, total dissolved solids and physico-chemical properties of different elements in seawater, which affect the signals in ICP-MS analysis. In addition, analytical error arising out of adsorption/precipitation behaviour of trace metals will also add to the variations.

For the trace metals V, Cr, Fe, Ni, Co, As, most favorable pH was 4.1, whereas extraction of Mn, Cu, Zn, Mo, Cd and Pb, were 100% at pH 6.4 (Table 3). This compares well with the dual extraction procedures[4,19,21] and with the single 20-min chloroform extraction method[24]. The analytical data obtained for CASS-4 with the recommended procedure is in excellent agreement with the certified values. The detection limits and blank values (Table 4) were found to be sufficient for routine analysis following the solvent extraction procedure. The use of small reagent volume and dilute reagent concentrations reduce the blank levels and allow very low detection limits to be obtained.

Conclusion

The proposed procedure is applicable to the determination of trace metals (viz., Fe, Mn, V, Cr, Ni, Co, Cu, Zn, As, Mo, Cd, Pb and U) in seawater by ICP-MS at pH 4.1 and 6.4. The procedure has been successfully applied at our laboratory on seawater samples collected from Northern Central Indian Ridges. Matrix matching reference samples (NASS-5 and CASS-4) were used to calibrate the system and verify the method for the first time, by which matrix and associated interferences were minimized. The major advantage of this procedure is that large preconcentration factor sufficient to detect by ICP-MS can be rapidly achieved for a wide range of metals from relatively small sample volume at pH 4.1 and 6.4.

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