Determination of Trace Metals in Karachi Coastal Waters Using Atomic Absorption Spectrometry

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Summary: Trace metal (Co, Cu, Fe, Pb and Zn) concentrations were determined in Karachi coastal waters (Bath Island, Keamari and Korangi) using atomic absorption spectrometric technique. These metals have been quantitatively separated from sea water matrices as metal-APDC complex using MIBK as an extractant. The extract was directly aspirated into atomic absorption spectrometer and a reproducible signal was obtained. The results showed prominent variations in metal concentration with distance and also from one sampling area to another. Seasonal variations were also monitored.

Introduction

Of the different kinds of pollution that plague us, water pollution has been with us for the longest time [1-4].

Determination of trace metals in sea water has been constantly developing into a field of increasing attention for most of the analytical, environmental and industrial chemists.

The literature of marine water analyses reflects the considerable difficulty in establishing an accurate and precise method of analysis for trace metals. A sea water matrix defies a simplified approach [5-7].

Riley [8] has summarized available data and it would appear that X-ray flourescence spectrometry neutron activation analysis, isotope dilution, mass spectrometry, spectrophotometry, anodic stripping voltametry and atomic absorption (AAS) may offer the best hope for reliable analyses of trace constituents in sea water [8]. Out of these AAS is most widely used method [6, 11-15].

Adequate pre-concentration techniques are, however, required prior to AAS measurements to get enhanced sensitivity [7,9,16-20].

In this study, extraction with MIBK - APDC is evaluated for the pre-concentration followed by absorption spectrometric measurement [6,21]. Che-lates of ammonium-1-pyrrolidinecarbodithioate (APDC) [22] with metal ions were chosen for this study. APDC was described by Malissa and co-workers [10,23] as a chelating agent for over thirty metals in acidic solutions and has found wide use in atomic absorption measurements for the solvent extraction of metals into methylisobutylketone (MIBK), prior to the analyses [24]. The reliability and reproducibility of the results was checked by analysing standard metal solutions.

Present work holds two fold purpose. It not only deals with the determination of trace metal concentration in Karachi coastal waters but also experiments were designed to establish most appropriate analytical parameters through which maximum efficiency could be obtained.

Results and Discussion

Effect of cyclohexane on the solubility of MIBK in sea water

The comparative solubility of MIBK taken alone and in combined form with cyclohexane is shown in Table 1.

Cyclohexane was meant to reduce the extent of solubility of MIBK in sea water. It is evident from the data (Table 1) that when MIBK was taken in a 4:1 (v/v) ratio with cyclohexane, a 20%

Table 1: Effect of cyclohexane on the solubility of MIBK in sea water at 30°C

Vol. of MIBK c.c c.c	Vol. of cyclo-hexane c.c	Vol. of sea water retained	Vol. of extract-ant c.c.	Vol. of extract-dissol-ved	Percent solubi-lity c.c
35.0	0.00	1500	8.0	27.0	1.8
26.3	8.80	1500	11.0	24.0	1.6

Table 5: Instrumental and Analytical Parameters

Metals	Cd	Co	Cu	Pb	Fe	Zn
Wave length (nm)	228.0	240.7	324.8	283.3	248.3	213.9
Lamp current (mA)	8.0	30.0	10.0	15.0	30.0	10.0
Slith width (nm)	0.7	0.2	0.7	0.7	0.2	0.7
Acetylene flow rate (ml/min)	10-14	10-14	10-14	10-14	10-14	10-14
Air flow rate (ml/min)	40-45	40-45	40-45	40-45	40-45	40-45
Air pressure (psi)	60-80	60-80	60-80	60-80	60-80	60-80
Acetylene pressure (psi)	12.0	12.0	12.0	12.0	12.0	12.0
Coefficient of variation for replicate analyses (%)	3	16	3	9	6	1

reduction in the solubility of MIBK in sea water was achieved. This provides more of the MIBK available for extraction which, in turn, results in increased signals.

Effect of aqueous to organic phase ratio on extraction efficiency

Several samples were analysed using different aqueous to organic phase ratios to formulate an optimum ratio of maximum extraction.

It is obvious from Fig. 1 that maximum peak height for each element was obtained at an aqueous to organic phase ratio of approximately 1:21 i.e. when 35 ml of extraction was used per 750 ml of sea water.

Effect of pH on extraction efficiency

Fig. 2 shows the effect of pH on the signals of each metal by extraction with MIBK-APDC system.

The necessity of complexation introduces a pH dependence into extraction [25]. Alongwith the
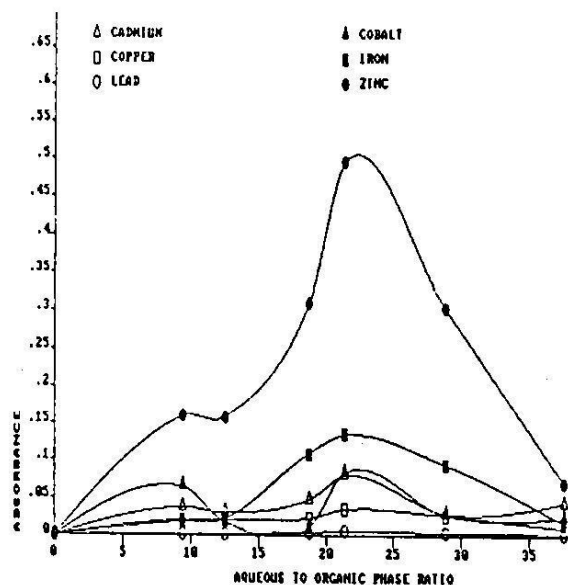

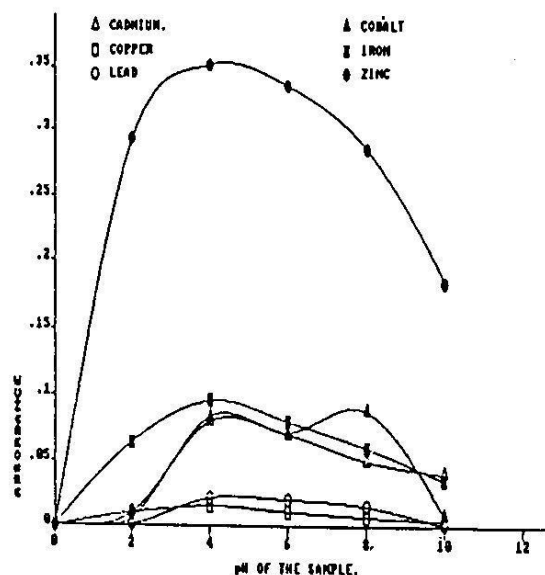Fig. 1: Effect of Vaq/Vorg ratio on extraction

Fig. 2: Effect of pH on extraction efficiency

equilibria which exists between metal and complexing agent, the stability of the complex, extraction, or separation of other ions and other factors will also enter into a selection of the appropriate pH. The effect of pH on the extraction was investigated by simultaneous extraction of metals from a series of aqueous (sea water) solutions maintained at various pH values, while other variables in standard

procedure were kept constant. The maximum extraction was obtained when the acidity lay at about pH 4. Brook's [26] range is 4-5 which also seems to be in this case.

Stability of metal-APDC complex with time

The stability of complexes was measured at different intervals of time ranging from 0-220 hours. From Fig. 3 it is quite obvious that the absorption signals for all the metal-APDC complexes in MIBK are showing a continuous decrease. This can be attributed to the instability of metal-APDC complex. To avoid any appreciable loss in stability, samples were analysed within three hours of extraction.

Variation in trace metal concentration of sea water with distance

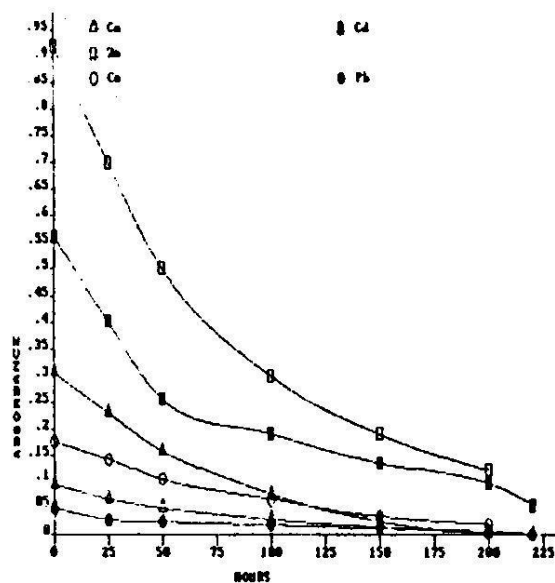The results in Table 2 suggest that the values of Cd, Co, Cu, Fe, Pb, and Zn show a steady

Fig. 3: Stability of APDC complex with time

Table 2: Variation in metal concentration with distance

Sampling Site	Sampling Month	Location	Concentration (PPb) in sea water					
			Cd	Co	Cu	Fe	Pb	Zn
Bath Island	September	R.P.[*].	4.04 + 0.02	7.7 + 0.03	7.3 + 0.01	11.4 + 0.01	4.0 + 0.01	6.2 + 0.02
		Half Km away from R.P.	2.8 + 0.005	7.1 + 0.01	6.0 + 0.02	8.0 + 0.02	3.7 + 0.005	4.0 + 0.01
		One Km away from R.P.	0.9 + 0.001	3.2 + 0.01	1.0	5.4 + 0.03	2.1 + 0.01	0.6 + 0.02
Keamari	July	R.P.[*]	4.4 + 0.01	10.2 + 0.04	7.0 + 0.02	11.7 + 0.03	6.1 + 0.002	8.2 + 0.02
		Half Km away from R.P.	3.4	6.4 + 0.01	5.7 + 0.02	7.8 + 0.001	5.0 + 0.01	4.1
		One Km away from R.P.	3.4 + 0.01	4.6 + 0.02	4.0	7.2 + 0.001	4.1	3.1 + 0.01
		One and half Km away from R.P.	1.0	0.33	1.4 + 0.01	3.0	0.9	1.4 + 0.02
Korangi	May	R.P.[*]	4.1 + 0.02	5.2 + 0.02	11.7 + 0.01	12.8 + 0.01	8.9 + 0.02	4.1
		one Km away from R.P.	2.8 + 0.02	3.0 + 0.01	10. + 0.03	006. + 0.02	13.5 + 0.001	2.2
		One and half Km away from R.P.	2.1 + 0.01	2.3 + 0.01	2.9 + 0.02	4.0 + 0.01	1.4 + 0.01	1.0 + 0.01

[*]Reference point.

Table 3: Variation in Metal concentration with seasons

Sampling point	Month sampling	of Concentration (ppb) in sea water					
		Cd	Co	Cu	Fe	Pb	Zn
Bath Island	May	5.6 ± 0.01	2.4 ± 0.02	12.7 ± 0.005	8.3 ± 0.01	9.5	5.8 ± 0.01
	September	4.04 ± 0.02	7.7 ± 0.03	7.3 ± 0.01	11.4 ± 0.01	4.0 ± 0.01	6.2 ± 0.02
Korangi	May	2.8 ± 0.02	3.0 ± 0.01	10.0 ± 0.01	8.1 ± 0.03	3.5 ± 0.02	2.2 ± 0.001
	August	8.5 ± 0.01	8.0 ± 0.005	5.3 ± 0.02	8.3 ± 0.02	6.6	4.8 ± 0.01

decrease as the sampling point moves progressively away from reference point.

The reduction (Table 3) in concentration of Zn followed by Cu and Fe may be attributed to their atomic weights i.e. lightest travel large distances while the heaviest settles down in its passage. On the other hand Cd, Co and Pb show no such specific behaviour and seem to be independent of their atomic weights.

Variation with seasons

Metals show seasonal variation also. According to the overall situation evident from Table 3, an increasing pattern for Co, Fe and Zn towards the end of the year is observed while Cu, Cd, and Pb show a prominent reduction for all the samples collected from different sampling areas.

All these variations in concentration suggest that the presence of present levels of trace metals in our marine environment is something not natural. If it would have been so then there must be no prominent change in the determined trace metal concentration. These variations indicate that these levels of trace metals are a result of introduction of these metals in marine environment by man. A very rough estimate of the relative contribution of all potential pollutants from various human activities entering the sea is as follows [27]:

Source	All Pollutants (% Contribution)
1. Off shore production	1
2. Maritime transportation	12
3. Dumping	10
4. Runoff and land based discharges	44
5. Atmosphere	33

These figures clearly demonstrate that marine pollution is derived mainly from land based sources and can have long residence time in water which is relatively enclosed by either geographic or hydrographic structure. Table 4 provides a comparison of our experimental results with those reported by workers from some foreign coasts. From this comparison it is evident that the levels of metal concentration as found in our coasts are quite considerable. The relative contribution of these from each source are different in different sea areas. For instance, the industries which are situated in Korangi and Landhi area belong to Leather, Food, Beverages, Tanneries, Refineries and the Battery. The untreated effluents from these industries join the Malir River via different channels and these ultimately slip into the Arabian sea. On the other hand Keamari is subjected to ship harbouring, recreational activities and activities like construction.

Experimental

Apparatus

A Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer equipped with a standard burner in which air acetylene flame was used. Standard hollow cathode lamps were used for all elements. The operating conditions for AAS are summarized in Table 5.

Reagents

Solutions were prepared in de-ionised distilled water. Hydrochloric acid was redistilled before use. Methylisobutylketone (E.Merk) and cyclohexane (E. Merck) was used as an organic ex-

Table 4: A comparison of our results with those obtained from some foreign coasts

| Collecting Place | Cd | Co | Concentration (PPb) | | | |
			Cu	Fe	Pb	Zn
Newzeland coast(27)	-	-	4.8	-	-	30.0
South California coast (6)	-	-	3.0 to 1.3	11.0 to 0.6	-	10.0 to 4.0
Medit, Red & Arabian sea (28)	-	-	-	-	-	1.0
Tokyo Bay (9)	0.06	0.0	1.0	9.4	0.2	4.3
Land sea of Japan (9)	0.04	0.5	1.08	67.0	5.0	67.0
North Pacific ocean(9)	0.02	0.02	0.0	0.2	0.2	0.20
Wajima (16)	0.038	0.30	1.1	-	1.8	-
Sosogi (16)	0.33	0.10	1.4	-	1.7	-
Noroshi (16)	0.031	0.20	1.4	-	0.6	-
Kolji (16)	0.031	-	1.1	-	0.7	-
Anamizu (16)	0.088	0.20	1.0	-	0.7	-
Manzen (16)	0.029	-	1.0	-	0.7	-
Bath Island	5.61 to 0.89	7.66 to 3.19	12.7 to 0.88	11.4 to 5.4	9.46 to 2.05	6.21 to 0.64
Korangi	4.07 to 2.02	5.23 to 2.34	11.7 to 2.92	12.8 to 4.84	8.87 to 1.43	4.08 to 0.89
Keamari	4.43 to 0.90	10.20 to 0.33	6.87 to 3.96	11.73 to 7.21	6.05 to 0.86	8.19 to 3.08

Table 5: Instrumental and Analytical Parameters

Metals	Cd	Co	Cu	Pb	Fe	Zn
Wave length (nm)	228.0	240.7	324.8	283.3	248.3	213.9
Lamp current (mA)	8.0	30.0	10.0	15.0	30.0	10.0
Slith width (nm)	0.7	0.2	0.7	0.7	0.2	0.7
Acetylene flow rate (ml/min)	10-14	10-14	10-14	10-14	10-14	10-14
Air flow rate (ml/min)	40-45	40-45	40-45	40-45	40-45	40-45
Air pressure (psi)	60-80	60-80	60-80	60-80	60-80	60-80
Acetylene pressure (psi)	12.0	12.0	12.0	12.0	12.0	12.0
Coefficient of variation for replicate analyses (%)	3	16	3	9	6	1

tractant in 4:1 (v/v) ratio. A 1% aqueous solution of APDC (Fluka Chemie) was used as a complexing agent. 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 very soluble, the reagent is very easily purified in this matter [6].

A standard aqueous solution (pH 4) containing 1000 ppm each of Cd, Co, Cu, Fe, Pb and Zn

was made and stored. All other reagents used were of analytical reagent grade.

Sea water samples

Several surface sea water samples were collected from Keamari, Korangi and from Bath Island. The samples were filtered through a 0.45 nm filter paper immediately after sampling, acidified to pH 4 with HCl and stored in polyethylene bottles [5]. All polyethlene and polypropylene bottles were rinsed well with pure water after soaking in 30% HNO$_3$ for over three days.

Analytical procedure

A 750 ml aliquot of the filtered acidified sea water was placed into a liter polypropylene bottle and 7 ml of 1% APDC were added followed by 35 ml of extractant (1:4 cyclohexane - MIBK). The sample solution was allowed to equilibrate for 30 minutes on an electrical shaker. The phases were separated by means of a separatory funnel. To the organic phase a further 750 ml of the sample was added and was then subjected to an equilibration for another 30 minutes on the electrical shaker. The phases were separated and organic phase was stored and analysed using atomic absorption spectrometer within three hours of extraction.

In order to prepare a working curve, a further 20 ml of MIBK were added to each sample of extracted sea water and phases were separated after 5 minutes equilibration. This was to get rid of trace elements which might possibly be present. All the samples purified in this manner were recombined so as to get a homogenous aqueous phase. To each 750 ml of the extracted sea water, incremental volumes of stock standards were added to get a concentration 200, 500, 800, 1000, 1400 and 1800 microgram per litre of the element of interest (as required).

The volume of MIBK remaining after the first equilibration (11 ml) was calculated. This volume of MIBK and 7 ml of APDC solution were then added to the contents of each flask containing standard solutions. Equilibration and phase separations were carried out as before.

The blank solution was prepared under the same procedure as was used for standard solutions

except that in this case metals were not introduced from outside.

The organic phase of the standards and the sample was aspirated into a fuel lean air acetylene flame under the optimum working conditions shown in Table 2. Calibration curve was plotted and concentrations in organic phase were determined. The concentration of the desired element in water was calculated using the following equation:-

$$C = Y \times Z/X$$

where,

C = Metal's concentration in sea water
Y = Concentration of metal in organic phase
Z = Volume of extractant retained
X = Volume of sea water used for extraction.

All experiments were carried out at ambient temperature.

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