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Determination of Traces of Pb, Cu and Cd in Seawater around Thane Creek by Anodic Stripping Voltammetry Method

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Abstract Trace metals (Pb, Cu and Cd) in seawater samples were pre-concentrated for the simultaneous quantitative determination using solvent extraction procedure in the presence of ammonium pyrrolidine dithiocarbamate (APDC) as complexing agent and methyl isobutyl ketone (MIBK) as organic phase and acid exchange back – extraction followed by its determination by Differential Pulse Anodic Stripping Voltammetry (DPASV). Concentrations of Pb, Cu and Cd vary from 3.0 to 9.44 ng/mL, 12.7 to 28.6 ng/mL and 0.31 to 1.21 ng/mL respectively in seawater samples collected from different locations across Thane Creek area, Mumbai, India. Pb, Cu, Cd concentration were observed to be higher in the eastern side of the Thane Creek as it is covered by various industries.

Keywords Trace metal · Seawater · Solvent extraction · Electro analytical technique

Trace metals (Pb, Cu and Cd) are introduced to the marine environment by domestic and industrial activities as anthropogenic pollutants. Much of this input ultimately accumulates in the estuarine zone and continental shelf, which are important sinks for suspended matter and associated land-derived contaminants (Leong and Tanner 1997). Sediments not only reflect the current quality of surface waters, but also provide vital information on the transportation and fate of pollutants (Santschi 1984; Finney and Huh 1989). Once pollutants are discharged into the marine environment they distribute into water, sediment and biota. In areas characterized by metal-bearing formations, metals occur at elevated concentrations in water and bottom sediments of the marine zones receiving runoff (Shumilin et al. 2001; Munksgaard and Parry 2002). The study of metals in the marine environment has received considerable attention because of their biological significance as well as the possibility of their transfer to man through the food chain in quantities that can be harmful (GESAMP 2001). Many contaminants such as Pb, Cu and Cd though occur at extremely low concentration in seawater, are accumulated by marine organisms and concentrations in their body tissue can be hundreds of times greater than seawater. As human being consume different marine organisms like biota, can lead potential health problem to human being. Copper and cadmium can be toxic under some conditions (Brand et al. 1986; Tortell and Price 1996). Other trace metals, such as lead, document the impact of anthropogenic trace metal inputs to the ocean for the past two centuries (Boyle et al. 1986; Wu and Boyle 1997a, b). However, for sea-water, the high salt content and low levels of trace metals invariably preclude direct analysis by DPASV. Hence the analysis of seawater by DPASV generally requires a preliminary matrix separation. Several methods are adopted to pre-concentrate the trace metals and to separate the salt matrix from seawater prior to trace metal determination. Techniques such as solvent extraction (Wu and Boyle 1997a, b), ion exchange (Chandrasekhar et al. 2003) and carrier precipitation (Nicolai et al. 1999) have been extensively used to achieve selective removal of most interfering ions and to pre-concentrate for further lowering of detection limits. The method based on metal complexation with ammonium pyrolidine dithicarbamate (APDC) and extraction into MIBK (Hirata et al. 2003) is widely adopted with some modification even today by several researchers.

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Sometimes di-ethylammonium diethyldithiocarbamate (DDDC) was added in combination with APDC to improve complex stability and broaden the effective working range (Wu and Boyle 1997a, b). Determination of distribution of Pb, Cu and Cd in seawater is very much important. Among different analytical techniques, electro analytical technique is a versatile analytical tool and proved to be selective, fast, precise and simultaneous quantitative and qualitative determination of trace metals in various matrices. Sensitivity of DPASV for determination of Pb, Cu and Cd is better technique compare to Flame Atomic Absorption Spectrometry (FAAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). DPASV was found to be the choice of instrument for the determination of Pb, Cd and Cu in complex environmental matrix like estuarine sediment (Maity et al. 2016).

In the present study solvent extraction procedure has been optimized in terms of equilibration time and pH. Trace metals (Pb, Cu and Cd) concentrations were determined in seawater samples collected from different locations across Thane Creek area, Mumbai, India using DPASV.

Materials and Methods

Thane Creek (Fig. 1), which is adjacent to Mumbai harbour bay, is a triangular mass of brackish water which widens out and opens to the Arabian Sea in the south. Along the east and west sides of the creek, many industrial units have come up. Thane Creek is the ultimate recipient of all the liquid discharges from these industries. The Thane Creek Industrial area houses a number of major, medium and small scale industrial units largely involved in the manufacture, storage and use of chemicals, petrochemicals, pharmaceuticals and fine chemical products, pesticide formulation, etc. Of the 1800 odd industries registered in the area, nearly 50 could be termed as major and the rest classified as small and

Fig. 1 Sampling location

medium scale. The effluent discharges both treated and untreated are left into the creek. The principal discharge channels into the creek from the city are Ghatkopar and Mulund suburbs situated in the west side of the creek and industrial discharge channels from eastern side of the main land at Airoli, Ghansoli, Koperkhairane, Vashi and Juinagar. The discharges from the eastern side of the city are dominated by the sewerage and industrial effluents. Industrial complexes, including the textile mills of South and Central Mumbai, the petrochemical, fertilizer and thermal plants at Chembur, the pharmaceutical and chemical complexes at Vikhroli, Bhandup and Mulund, the engineering and metallurgical units of Thane–Belapur region surround the creek and discharge their toxic effluents into it. The Mumbai harbor in the west and the new Navy Sea port in the east, handling more than 30 million tons per year, additionally contribute to the pollutants to the creek by way of leakage and spill. Being landlocked with very few freshwater inlets and a large amount of sewerage and industrial effluent discharges, the creek is relatively stagnant.

Seawater samples were collected in polypropylene container previously treated with one molar solution of hydrochloric acid and rinsed with distilled water from 14 different locations (Fig. 1) across Thane Creek area, Mumbai, India.

The pH of seawater was estimated using a pH meter (DPH-500) which was calibrated using standard buffer (pH 4, 7 and 9) before testing.

All the apparatus were cleaned properly by electronic grade nitric acid, and then thoroughly washed using double distilled water before starting the experiment. Seawater samples were filtered and then acidified to prevent wall adsorption of trace metals. Filtered seawater (400 mL) was placed in a separating funnel and pH was adjusted to the required pH with acetic acid ammonia buffer. 4 mL of 1% APDC and 20 mL of MIBK were added into it. MIBK is preferred because of its efficiency to extract wide range dithio carbamate-metal chelates (Danielsson et al.1982; Bone and Hibbert 1979). The samples were shaken for 30 min and allowed to stand for 20 min for phase separation. The lower seawater phase was drained and the organic phase was transferred in a separating funnel. About 20 mL of 4 (N) HNO_3 was added and shaken for 30 min for acid-back extraction. After phase separation, the lower aqueous phase was transferred in 50 mL beaker and evaporated near to dryness and finally volume was prepared in 0.25% HNO_3 medium in 25 mL volumetric flask after filtration and analysed using DPASV. In the field of Pb, Cu and Cd analysis of natural waters and geological samples, DPASV has become accepted as one of the best techniques.

Equilibration time was optimized in the solvent extraction procedure for determination of Pb, Cu and Cd in the seawater samples. Solvent extraction was carried out at different pH (2.0 ± 0.01 to 9.0 ± 0.02) for 20 min to understand the extraction efficiency of Pb, Cu and Cd at different pH.

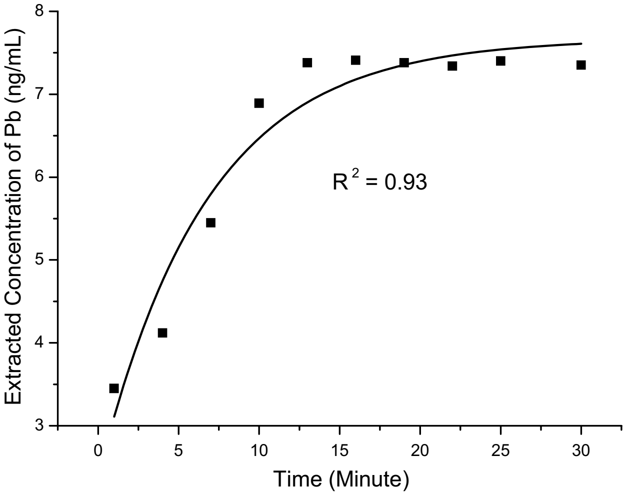

Fig. 2 Equilibration time for lead in the extraction procedure

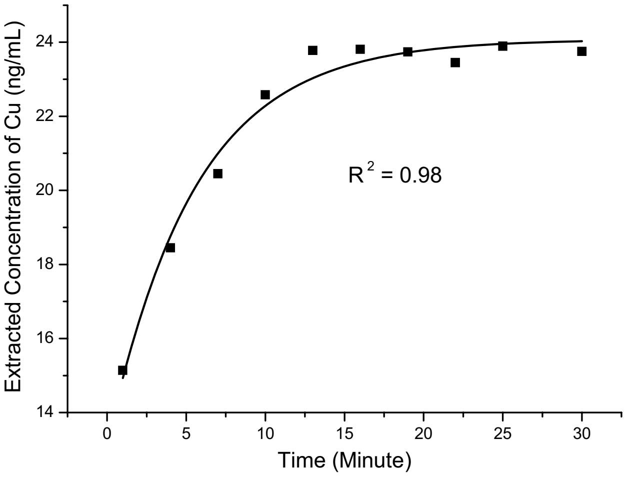

Fig. 3 Equilibration time for copper in the extraction procedure

Pb, Cd and Cu were analyzed simultaneously with a deposition potential of −0.8 V for a pre concentration time of 60 s in DPASV (663 VA Stand Metrohm). Pb, Cd and Cu peaks were observed at −0.4, −0.6 and 0.02 V respectively. In DPASV platinum (Pt) is used as the reference electrode and Ag/AgCl is used as counter electrode.

Results and Discussion

Equilibration time was optimized in the solvent extraction procedure for determination of Pb, Cu and Cd in the seawater samples. In the Figs. 2, 3 and 4 it is clearly observed

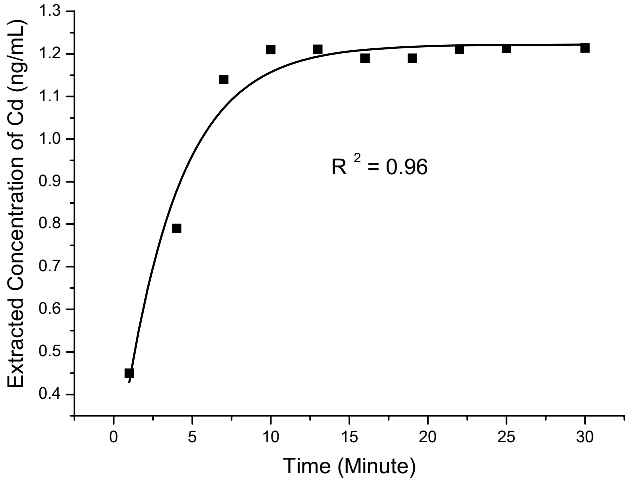

Fig. 4 Equilibration time for cadmium in the extraction procedure

that after certain time interval concentration of the metals are not increasing in the extraction procedure. That means equilibration time has been achieved in the solvent extraction procedure for determination of particular trace metal. Equilibration time for Pb, Cu and Cd observed 13, 13 and 10 min respectively shown in Figs. 2, 3, 4 respectively.

Solvent extraction procedure was carried out at different pH (2 ± 0.01 to 9 ± 0.02) for 20 min to standardize the solvent extraction procedure for the determination of Pb, Cu and Cd using DPASV. After solvent extraction procedure at different pH it is clearly observed that percentage recovery of Pb, Cu and Cd are extremely different at different pH and represented in Table 1. For percentage recovery determination spike study was carried out (known concentration of Pb (50 ng/mL), Cu (150 ng/mL) and Cd (10 ng/mL) were added in the seawater before solvent extraction). Simultaneously another solvent extraction procedure was carried out at different pH (2 ± 0.01 to 9 ± 0.02) without spiking in the seawater to know the blank. From the experimental results it is observed that in the pH 6 ± 0.02, Pb, Cu, and Cd recovery are 97 ± 4%, 100 ± 5%, and 98 ± 4% respectively in the solvent extraction procedure.

After standardization of solvent extraction procedure at different pH, for the determination of Pb, Cu and Cd solvent extraction procedure was carried out at the particular pH for the respective metals (Pb, Cu and Cd solvent extraction at pH 6 ± 0.02). pH of the seawater samples vary from 7.42 to 8.25. After solvent extraction and finally acid digested solution preparation Pb, Cu and Cd were determined by DPASV. Simultaneous analysis of Pb, Cu and Cd using DPASV in seawater samples is represented in Fig. 5. Concentration of Pb, Cu and Cd varies from 3.0 to 9.44 ng/mL, 12.7 to 28.6 ng/mL and 0.31 to 1.21 ng/mL respectively in seawater samples (Fig. 6) collected from different locations across Thane Creek area, Mumbai, India. From the experimental results it is clearly observed that concentration of Pb, Cu and Cd are higher in locations 1, 2, 3 and 4 compare to other locations. Industries are situated in the eastern bank of the Thane creek and that may be the reason of getting higher concentrations of Pb, Cu and Cd in these locations. Nakatsuka et al. (2007) have reported concentrations of Ni (3.0 ng/mL), Cu (3.5 ng/mL), Zn (9.5 ng/mL), Cd (0.17 ng/L) and Pb (3.0 ng/L) in the open waters of the Indian Ocean. Robin et al. (2012) have reported concentrations of Cu (0.62–3.46 ng/mL), Cd (0.12–0.17 ng/mL) and Pb (1.78–1.99 ng/mL) in the seawater samples of Arabian sea along the south west coast of India.

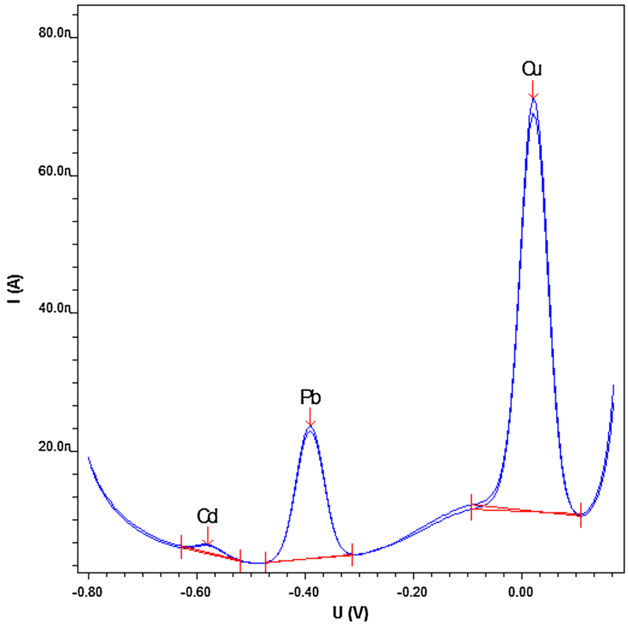

Fig. 5 Simultaneous analysis of Pb, Cu and Cd in DPASV

Table 1 Recovery of trace metals (%) in seawater in the solvent extraction procedure at different pH

Element	pH							
	2.0 ± 0.02	3.0 ± 0.02	4.0 ± 0.03	5.0 ± 0.01	6.0 ± 0.02	7.0 ± 0.03	8.0 ± 0.02	9.0 ± 0.02
Pb	73 ± 3	87 ± 3	80 ± 4	85 ± 3	97 ± 4	65 ± 2	83 ± 3	70 ± 2
Cu	66 ± 3	85 ± 5	73 ± 4	78 ± 5	100 ± 5	63 ± 3	73 ± 4	93 ± 4
Cd	45 ± 3	39 ± 2	20 ± 1	63 ± 2	98 ± 4	33 ± 2	73 ± 3	19 ± 2

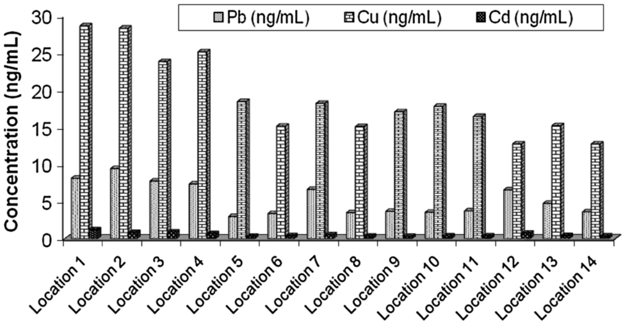

Fig. 6 Distribution of Pb, Cu and Cd in seawater samples collected from different locations across Thane Creek area, Mumbai, India

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