Arabian Journal of Chemistry (2009) **2**, 25–29

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Simultaneous determination of metal ions as complexes of pentamethylene dithiocarbamate in Indus river water, Pakistan

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Received 10 July 2009; accepted 10 July 2009
Available online 6 August 2009

KEYWORDS

Liquid chromatography;
Pentamethylene dithiocarbamate complexes;
Metals;
Fresh water

Abstract River water samples before and after mixing with industrial effluents were collected at an interval of 4 weeks for one year and analyzed for simultaneous determination of Fe^{3+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+} after preconcentration using pentamethylene dithiocarbamate (PMDTC) as derivatizing reagent and subsequent solvent extraction by high performance liquid chromatography (HPLC). The average levels (n = 12) of metal ions were found in the range of 14.2–542 μg/L. The results were then compared with a standard flame atomic absorption spectrophotometric method revealed no significant differences.

1. Introduction

Determination of trace metals in water (Wattoo et al., 2006, 2004; Arain et al., 2001, 2002; Wang and Lee, 1997) is often made possible by the addition of complexing agent and analyzing the sample by spectrophotometry or by liquid chromatography. Most separation methods in use are based on the formation of metal dithiocarbamate especially ammonium pyrrolidine dithiocarbamate and sodium diethyl dithiocarbamate as ligands to stabilize high oxidation states which allow monitoring of the oxidation rather than the reduction of metal dithiocarbamate complex formed in situ in the liquid

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doi:10.1016/j.arabjc.2009.07.007

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chromatographic system (Bond and Wallace, 1981, 1982). Sodium diethyl dithiocarbamate has been used as a derivatizing reagent for gas chromatography as well as liquid chromatography (Arain et al., 2001; Bond and Wallace, 1982; Cardwell et al., 1976) using electrochemical and spectrophotometric detections (Bond and Wallace, 1983).

Mostly chromatographic separations of metal dithiocarbamates were achived using normal phase chromatography with UV–Visible spectrophotometric detection (Liška et al., 1979; Moriyasu and Hashimoto, 1978; Brooks et al., 1967; Jan and Young, 1978; Danielsson et al., 1978; Sturgeon et al., 1980). Babu and Naidu (1991) reported the use of pentamethylene dithiocarbamate for the complexation, solvent extraction and AAS determination of Fe, Ni, Cr and Mn from water. Asolkar et al. (1992) used the same reagent for the determination of Cd^{2+}, Cu^{2+}, Fe^{3+} and Pb^{2+} on thin layer chromatography. Arain et al. (2002) separated the series of six metal ions as chelates of pentamethylene dithiocarbamate by capillary gas chromatography (CGC) and high performance liquid chromatography (HPLC); see Fig. 1.

In the present work, we have investigated the determination of Fe^{3+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} ions from fresh water samples collected from river Indus at Ghulam Muhammad barrage. The metal contents were preconcentrated as complexes of pentamethylene dithiocarbamte, extracted in organic solvent and simultaneously determined by HPLC. The seasonal variations in the metal contents of river Indus water were also evaluated.

2. Experimental

2.1. Instrumentation

A liquid chromatograph (Perkin–Elmer 8700) equipped with LiChrosorb ODS column (150 × 4.6 mm, i.d., 5 μm), UV-detector, Rheodyne 7125 injector and D-2500 chromato-integrator and an atomic absorption spectrometer (Hitachi-18050) were used in present work. Electrochemical measurements were made with Pye Unicame model 292 pH meter. Single channel transfer pipettes using 100 μL (0.1 ml tip) were used to deliver the metal ion solution.

2.2. Reagents and solutions

Stock metal ion solutions containing 1 mg/ml of each metal ion were prepared from their nitrate. Methanol, sulfuric acid, nitric acid, hydrochloric acid, acetic acid, hydrogen peroxide and sodium acetate were all purchased from E. Merck, Germany. All chemicals used were of AR grade purity. Deareated high purity double distilled demineralized water was used for mobile phase and solution preparation.

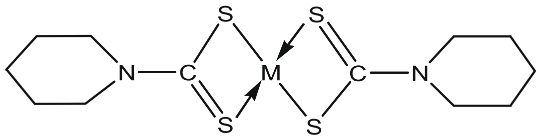

Figure 1 Structural diagram of PMDTC–metal complex.

2.3. Synthesis of pentamethylene dithiocarbamate reagent (PMDTC)

Carbon disulfide (76 g/mol) was slowly added to 80 g freshly vacuum distilled pipridine (80 g/mol) in 25 ml of water at temperature > 5 °C with a constant stirring followed by the addition of 40 g sodium hydroxide dissolved in 20 ml water (Babu and Naidu, 1991). The reagent solution was prepared by dissolving 1 g of the reagent in 100 ml of water.

2.4. Analytical procedure

250 ml of aqueous solution containing chromium, cobalt and manganese (0–20 μg), iron (0–25 μg), nickel and copper (0–30 μg) was transferred to a 500 ml separating funnel. Then the reagent solution of PMDTC (5 ml, 0.1% w/v in water) and acetate buffer (pH 5, 5 ml) were added. pH was adjusted to 5. Chloroform (5 ml) was added and the contents were mixed well for 3 min and aqueous layer was allowed to separate from organic layer, which was transferred to a volumetric flask. The extraction was repeated with chloroform (5 ml). The chloroform layers were combined and volume was made up to 10 ml. 20 μL of this extract was injected into *RP*-HPLC connected with ODS column (150 × 4.6 mm. i.d., 5 μm), with a mobile phase consisting of methanol: 1% 0.1 M acetate (30: 70, v/v), with a flow rate of 1.2 ml/min. and detection was at 260 nm by UV-detector (Arain et al., 2001, 2002).

2.5. Determination of Cr, Mn, Fe, Co, Ni and Cu in river Indus water samples

Indus river water samples ($n = 12$) were collected from Ghulam Muhammad barrage (before mixing of industrial effluents) and near Kotri SITE area (after mixing with industrial waste water), with the interval of one month in 2.5 L glass bottles. Subsurface water samples were collected at the depth of one foot. All samples were preserved as per standard procedure (Wattoo et al., 2006, 2004). The samples were analyzed for the metal contents next day using the above mentioned analytical procedure.

3. Results and discussion

The reagent reacts with iron, chromium, manganese, copper, nickel and cobalt to form color complexes (Arain et al., 2002; Ramana et al., 1991; Kubáň et al., 2005). Maximum color development occurs in neutral to slightly acidic media. The metal chelates are easily extractable in chloroform. The reagent was examined for preconcentration, extraction and simultaneously determination of Fe^{3+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+}. Metal pentamethylene dithiocarbamate chelates (Fig. 1) were separated as reported (Arain et al., 2002) on HPLC column (150 × 4.6 mm. id, 5 μm). HPLC was calibrated with six standards and extraction efficiency was evaluated by adding 250 ml distilled water. The instrument was recalibrated after five samples; it was observed that percentage recovery was 94–100% with a coefficient of variation (C.V) up to 3.9%.

This method was applied for the determination of metal ions in water samples collected from Indus river and were

Table 1 Percentage recovery of metal ions by preconcentration ($n = 5$).

Metal ions	Metal added (µg/ml)	Metal found by HPLC*	Metal found by AAS**	% Recovery
Fe^{3+}	0.25	0.248 ± 0.013	0.249	99.20
	0.50	0.496 ± 0.025	0.496	99.20
	1.00	0.994 ± 0.182	0.999	99.40
	1.50	1.488 ± 0.028	1.492	99.20
	2.00	1.982 ± 0.013	1.995	99.10
	Mean % recovery			99.22
Cr^{3+}	0.25	0.240 ± 0.012	0.244	96.00
	0.50	0.480 ± 0.024	0.495	96.00
	1.00	0.956 ± 0.052	0.980	95.60
	1.50	1.470 ± 0.035	1.473	98.00
	2.00	1.928 ± 0.072	1.990	96.40
	Mean % recovery			96.40
Mn^{2+}	0.25	0.234 ± 0.011	0.242	93.60
	0.50	0.468 ± 0.023	0.489	93.60
	1.00	0.960 ± 0.037	0.983	96.00
	1.50	1.390 ± 0.030	1.486	92.70
	2.00	1.932 ± 0.024	1.964	96.60
	Mean % recovery			94.50
Cu^{2+}	0.25	0.240 ± 0.011	0.246	96.00
	0.50	0.480 ± 0.015	0.493	96.00
	1.00	0.961 ± 0.016	0.983	96.00
	1.50	1.446 ± 0.016	1.486	96.40
	2.00	1.937 ± 0.005	1.970	96.90
	Mean % recovery			96.26
Ni^{2+}	0.25	0.246 ± 0.130	0.249	98.40
	0.50	0.492 ± 0.010	0.498	98.40
	1.00	0.980 ± 0.016	0.992	98.00
	1.50	1.476 ± 0.016	1.486	98.40
	2.00	1.962 ± 0.022	1.983	98.10
	Mean % recovery			98.26
Co^{2+}	0.25	0.234 ± 0.011	0.243	93.60
	0.50	0.468 ± 0.016	0.488	93.60
	1.00	0.928 ± 0.015	0.983	92.80
	1.50	1.376 ± 0.052	1.486	91.70
	2.00	1.858 ± 0.040	1.940	92.90
	Mean % recovery			92.92

Average values, $n = 5$, confidence interval at 95%.
* HPLC = high performance liquid chromatography
** AAS = atomic absorption spectroscopy.

Table 2 Average concentration of metal ions in µg/l ($n = 12$) with confidence interval at 95%.

Metals ions		Fe^{3+}	Cr^{3+}	Mn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}
G.M. Barrage ($n = 12$)	Minimum	15.60	238.00	11.20	22.00	2.14	8.40
	Maximum	82.80	960.00	198.00	106.00	31.20	37.50
	Mean	42.6 ± 17	542.0 ± 188	78.0 ± 21.2	61.0 ± 17	14.2 ± 5.5	23.0 ± 8
Kotri industrial area ($n = 12$)	Minimum	21.20	292	47.40	36.50	4.60	9.20
	Maximum	164.00	1383.00	418.00	285.00	72.00	47.80
	Mean	56.0 ± 21	766.0 ± 212	96.0 ± 29	72.0 ± 22	21.0 ± 7.3	29.0 ± 11.2

Ghulam Muhammad barrage = actual Indus river water, Kotri industrial area = river water after mixing with industrial effluents.

examined quantitatively from April to March ($n = 12$). The percentage recovery (Table 1) of each of the metal ions was examined using analytical procedure and the average recovery ($n = 5$) was observed within 92–99% with coefficient of variation within 1.2–3.9%. The average concentration of Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} observed were 78, 61, 542, 23, 14.2 and 42.6 µg/L, respectively as shown in (Table 2). The concentration of metal ions exhibited the $Fe^{3+} > Cr^{3+} > Mn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+}$, decreasing sequence.

The total metal ions concentration fluctuated between 2.12 and 960 µg/L at Ghulam Muhammad barrage and 4.6–1383 µg/L at Kotri SITE area. The seasonal variation of metal ions (Fig. 2) was uniform and depended upon water flow. High

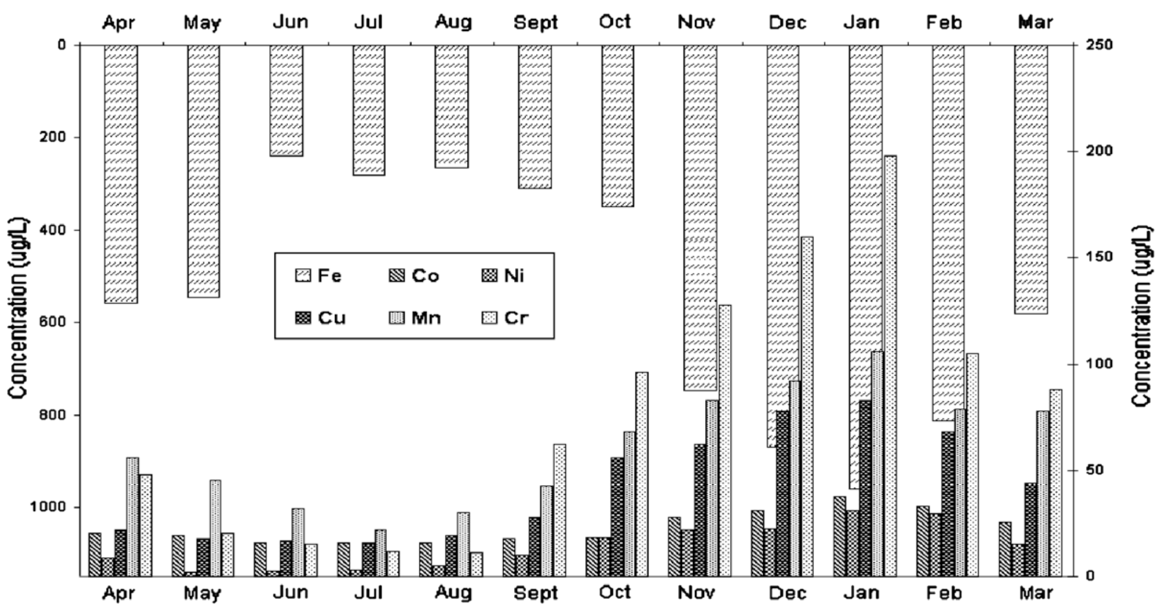

Figure 2 Seasonal variation of metal ions.

flow occurs in summer, when snow melts extensively and dominant monsoon rains augment many fold. Metal contents were diluted in peak flow season June to September and concentration level was high in winter due to the shortage of water especially during December to February (Fig. 2). Fig. 2 also indicates maximum concentration of metal ions in the month of January and minimum in the July, which is due the water discharge in river Indus. The results also indicate highest concentration of iron through out the study.

4. Conclusion

This method have been used for the determination of chromium, manganese, iron, cobalt, nickel and copper ion as pentamethylene dithiocarbamate chelates in Indus river water and effluent water samples (after mixing industrial effluents from SITE area) and good correlation was observed with that of atomic absorption spectrometry. The metal ions contents were observed in a safe limit but concentration of iron and copper contents were slightly on the higher side. This is might be due to the extraction from sediments at acidic pH adjusted for the preservation of water samples.

Acknowledgements

The authors acknowledge continuous support of the research laboratories of National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro, Pakistan. Mr. Saad Iqbal, Senior Scientist, Pakistan Atomic Energy Commission, Islamabad, is acknowledged for his help in necessary computational facilities about this project.

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