Preconcentration and Atomic Absorption Spectrometric Determination of Cadmium, Cobalt, Copper, Iron, Lead, Manganese, Nickel and Zinc in Water Samples Using 6-Methyl -2-pyridinecarboxaldehyde-4-phenyl-3-thiosemicarbazone

M.Y. KHUHAWAR, P. DAS AND V.K. DEWANI

Institute of Chemistry, UniversityOf Sindh
Jamshoro, Sindh, Pakistan

Summary: The reagent 6-methyl-2-pyridinecarboxaldehyde-4-phenyl-3-thiosemicarbazone (MPAPT) has been examined for the pre-concentration of metal ions and determinations using air acetylene flame atomic absorption spectrometer. The method is based on the complexation and extraction of cadmium(II), cobalt(II), cobalt(III), copper(II), lead(II), nickel(II), iron(II), iron(III), manganese(II) and zinc(II) in chloroform. The metal ions are back extracted in nitric acid (1:1) or after evaporation of solvent the residue is digested in nitric acid. After necessary adjustment of volume the metal ions were determined in aqueous solution. Pre-concentration is obtained 10- 25 times. Metal ions recovery was 95.4-100.8% with coefficient of variation 0.2-7.5%. The method was used for the determination of metals in canal and sewerage waters, within 2-6433 µg/L with C.V 0.2-5.2%.

Introduction

The interest in the determination of cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc in natural water (River, canal and sea) and sewerage water continues, because of the possibility of increase in the pollution of these metals as a function of time. The concentrations of the metal ions in fresh and sea water are generally below the detection limits of flame atomic absorption spectrometry. A number of pre-concentration techniques such as liquid-liquid extraction [1] ion exchange [2,3], co-precipitation [4]. evaporation [5] freeze drying [6] and floaton [7] have been suggested before their determinations. Liquid liquid extraction methods are generally considered as superior, because of simplicity and low blank levels. For simultaneous multielemental analysis a number of complexing reagents have been investigated including diethyl dithiocarbamate (DDC), ammonium pyrolidine dithiocarbamate (APDC) [8-11], hexamethylene dithiocarbamate [12,13], pentamethylene dithiocarbamate [14], 8-hydroxyquinoline [1,13,15] and dithizone [15]. A reagent [10,15] or a mixture of two reagents [8,16] have been used to complex as many of the required metals as possible before liquid liquid extraction. Preconcentration of 10-100 is commonly reported. Bruland et al., [8] have used dithiocarbamates (DDC and APDC) for the extraction of copper, cadmium, zinc and nickel in chloroform, followed by back extraction of metal ions in nitric acid. McLeod et al.,

[9] have used same dithiocarbamates and a similar procedure for the determination of cadmium, copper, iron molybdenum, nickel, vanadium and zinc using inductively coupled plasma atomic emission spectrometry. Vernon and Wani [3] have carried out comparative study of pre-concentration and determination of copper, cadmium lead and zinc in surface water. Their procedure includes extraction of ADPC complexes in chloroform, followed by evaporation of solvent, acid digestion in nitric acid and determination by atomic absorption spectrometry.

The reagent 6-methyl-2-pyridinecarboxaldehyde-4-phenyl-3-thiosemicarbazone (MPAPT) has been reported for spectrophotometric determi-nation of cobalt and iron [17]. In the present work MPAPT has been examined for the simultaneous extraction and determination of metal ions using flame absorption spectrometry, following a similar proce-dures as reported by Bruland et al., [8] and Vernon and Wani [3].

Results and Discussion

The reagent MPAPT reacts with copper(II), nickel(II), cadmium(II), cobalt(II), cobalt(III), iron (II), iron(III), lead(II), manganese(II) and zinc(II) to form coloured complexes in aqueous methanolic solution. The effect of pH on the extraction of metal
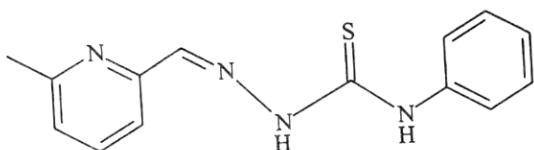
Fig. 1: Structure diagram of reagent.

ions in chloroform, followed by back extraction into nitric acid (1:1) was examined. It was observed that copper(II), nickel(II), cadmium(II), cobalt(II), cobalt (III) and lead(II) were extracted at pH 3-8, with maximum within 5-7. Thus a pH 6 was selected for their optimal extraction. Zinc(II) and manganese(II) could be extracted at pH 4-11, with maximum within 8-10. An optimal extraction occured at pH 9. Iron after complexation in slightly acidic solution could be extracted at either pH 6 or 9, but extract of iron(II) complex at pH 9, showed better solution stability [15]. Attmept was made to extract all the metals at the pH 6, but the recovery of zinc and manganese(II) was in the range of 50-60%. Thus after the extraction of metal ions at pH 6, the pH of the solution was raised to 9 and one more extraction was repeated for the quantitative transfer of metal ions from aqueous to organic phase.

The transfer of metal chelates from aqueous to chloroform was fairly rapid, but transfer of cobalt chelate required the shaking time of 5 min. Different concentrations of ntiric acid for back extraction of metal ions from chloroform to acid solution was examined and nitric acid (1:1 v/v) proved effective for quantitative determinations. The final volume of the aqueous phase could be adjusted to any desired value, but in the present work the final volume was adjusted to 10-25 ml to enable to determine all the metals using air acetylene flame atomization.

The instrument was calibrated with five metal ion solution in 0.1N nitric acid and the % recovery of the pre-concentration procedure was evaluated. At

least four solutions containing different amoutns of metal ions were examined. The average % recovery (coefficient of variation %) was cadmium 98.4 (3.2) cobalt 95.1 (7.5), copper 97.9 (2.28), lead 95.4 (4.36), nickel 95.8 (1.74), iron 100.8 (2.861), manganese 100 (0.5), zinc 100 (0.5).

The % recovery of metals using evaporation of solvent followed by acid digestion procedure was also checked and results obtained were cadmium 100 (0.1), cobalt 99(2.23), copper 97.22 (2.61), iron 99.44, (0.99), lead 99.44 (0.48), nickel 99.44 (5.12), manganese 100 (0.2) and zinc 100 (0.2). The results obtained indicate a quantitative recovery of all the eight elements, but analytical procedure B indicated a better results. With an improvement in % recovery and C.V.% Cobalt complex which is stable in higher acidity indicated C.V. of 7.5% using analytical procedure A, but it reduced to 2.2% using B.

Finally, some of the water samples collected from Fuleli canal and municipal sewerage added to Fuleli canal were analysed for metal contents. The results are summarized in table 1. A of high water discharge in river Indus and Fuleli canal (267.12 M^3/s) in month of August carried a large amount of particulate material Thus high amount of iron, (4.7-6.4 mg/L), zinc (100-109 ug/L) and lead (150-200 ug/L) were observed due to extraction of these metals in acid (sulphuric acid 1 ml/liter added) from particulate material. However consistent results were obtained with C.V within 0-6.4%.

Experimental

The reagent MPAPT was prepared as reported [17] by warming together equimolar solution (.01M) of 6-methyl-2-pyridinecarboxaldehyde and phenyl-thiosemicarbazide in ethanol.

A. Preconcentration Analytical Procedure

To separating funnel (500 ml) was transferred sample (250-350 ml) containing cadmium, zinc (0-50

Table-I: Quantitative Metal Analysis Data of Fuleli Canal and Sewrage Water Amount µg/L (C.V)

S.No.	Cd	Co	Cu	Fe	Pb	Mn	Ni	Zn
1.	8.0	30.0	40.0	6433.0	150.0	38.0	2.0	140.0
	(2.6)	(1.6)	(0.2)	(0.2)	(5.2)	(4.4)	(0.9)	(1.3)
2.	8.0	30.00	41.0	1364.0	150.0	229.0	4.0	119.0
	(1.0)	(1.2)	(1.4)	(0.5)	(4.1)	(1.3)	(0.9)	(0.3)
3.	8.0	30.0	39.0	5383.0	180.0	58.0	3.0	100.0
	(4.9)	(1.0)	0.4	(1.9)	(3.0)	(0.9)	(4.2)	(0.1)
4.	8.0	32.0	52.0	1670.0	190.0	125.0	50.0	174.0
	(5.5)	(4.0)	(0.7)	(0.8)	(5.1)	(2.4)	(3.5)	(0.4)
5.	8.0	30.0	40.0	4716.0	200.0	56.0	14.0	109.0
	(2.1)	(3.0)	(0.6)	(0.2)	(0.6)	(1.5)	(2.0)	(0.2)

µg), copper(II), manganese(II) (0-125 µg), cobalt, lead, iron and nickel (0-250 µg). It was added MPAPT (8 ml, 0.5% W/V in methanol), sodium acetate buffer pH 6 (4 ml) and pH was adjusted to 6. The well mixed solution was added chloroform 10-12 ml and mixture was shaken for 5 min. The layers were allowed to separate and organic layer was transferred to separating funnel (100 ml). The aqueous layer was added 2 ml of reagent solution, 4 ml of ammonium chloride ammonia buffer pH 9.5 and pH was adjusted to 9. The well mixed solution was added chloroform (8-10 ml) and extraction was repeated. The combined extraction was added nitric acid (1:1) (10-12 ml) and the mixture was shaken well for 5 min. The acid layer was transferred to a beaker and was heated gently to reduce the volume to 2-3 ml. The residue was added water and final volume was adjusted to 10 or 25 ml.

B.   Solvent Extraction Followed by Acid Digestion

The metal ions cadmium, cobalt, copper, lead, nickel, iron, manganese and zinc were extracted in chloroform, following the procedure A and organic layer was transferred to a beaker. Chloroform was evaporated on water bath and the residue was added nitric acid (65%) 4-5 ml. The mixture was heated on hot plate and solution 1-2 ml was dissolved in water. The final volume was adjusted to 10 or 25 ml.

Varian Spectr AA-20 atomic absorption spectrometer with air-acetylene nebulizer was used. The operating conditions were adjusted as recommended by the manufacture. The analysis was carried out in triplicate with integration and delay time 3 sec.

Water samples for metal analyses were collected from Fuleli canal and municipal sewerage ending in Fuleli canal. Fuleli canal takes off from left Bank of river Indus and passes through Hyderabad city with population of about 2.0 million. Most of the municipal sewerage and industrial effluents are thrown in Fuleli canal. Exact description about Fuleli canal and sampling scheme is reported elsewhere [16]. Following samples were collected. (1) From Fuleli canal near Akhand Village before entry of sewage water (2) Cantonment waste pumping station water, before entry in Fuleli canal (3) from Fuleli canal half k.m down the entry of cantonment water (4) from Kali Mori open gutter line (5) half k.m. down the entry point of open gutter in Fuleli canal. Samples from the surface of water within 3-10 cm were collected. Unfiltered samples (1 L) was added

sulphuric acid (1 ml, 98%) and was stored at room temperature. The samples were analysed following procedure A or B.

Conclusions

Preconcentration of cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc has been achieved by the factor of 10-25, by solvent extraction with 6-methyl-2-pyridinecarboxaldehyde-4-phenyl-3-thiiosemicarbazone as complexing reagent. The % recovery of metal ions were obtained in the range 95.2-100.08% with C.V 0.2-7.5%. The metal ions found in samples were in the range of 2-6433 ug/L with C.V 02.-5.2%.

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