Preconcentration and Determination of Copper, Cadmium, Nickel and Zinc in Drinking Water by Atomic Absorption and 6-Methyl-2-Pyridinecarboxyaldehyde-4-Phenylsemicarbazone as Complexing Reagent

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Summary: A method has been developed for the extraction and preconcentration of copper, nickel, cadmium and zinc from water samples with 6-methyl-2-pyridinecarboxyaldehyde-4-phenylsemicarbazone (MPPSC) into chloroform at pH9. Chloroform was evaporated and the residue was digested in nitric acid. After adjustment of volume, metal ions were determined using air-acetylene flame atomic absorption spectrometer. The recovery of metal ions were 95-100% with coefficient of variation (C.V) within 3.2%. Preconcentration obtained was 12-30 times. The method was applied for the determination of the metal ions in drinking water of Hyderabad city and Jamshoro.

Introduction

Determination of trace metals in drinking water is important for monitoring environmental pollution. Their concentration are generally below the detection limits of air-acetylene flame atomic absorption spectrometry (FAA). A number of preconcentration methods have been suggested including chelation, followed by solvent extraction [1-7], chelation on ion exchange resins [6,8,9] coprecipitation and flotation [10-12], evaporation [13] and freeze drying [14]. Methods involving chelation followed by solvent extraction are interesting, because of separation of the desired constituents, which results in low background signal due to less matrix effect. A number of complexing reagents have been used for preconcentration of trace metals, including different dithiocarbamates, [1,3,5,6] dithiozones [4] and oxine [2,4]. One or two reagents are added to complex as many as possible to desired analytes. After extraction metal ions could directly be determined in organic phase [1-3] or after striping off with nitric acid into aqueous phase [3-7]. Preconcentration of 10-100 is commonly obtained. The methods have been applied for the determination of metal concentration in natural waters and sea waters.

Vernon and Wani [15] have investigated different preconcentration methods for the determination of cadmium, copper, lead and zinc in river waters, including chelation with ammonium pyrolidine dithiocarbamate and extraction in chloroform. After evaporation of solvent the residue was digested with nitric acid.

The metal ions in aqueous phase were determined by atomic absorption (AA). A similar method has been used in the present work using MPPSC as complexing reagent for the preconcentration of copper, cadmium, nickel and zinc.

Results and Discussion

The reagent MPPSC reacts with copper, nickel, cobalt, cadmium, palladium and zinc to form coloured complexes. Maximum colour development occurs in neutral to slightly basic media. The metal chelates are easily extractable in chloroform. Thus the reagent was examined for preconcentration and simultaneous extraction of copper, nickel, cadmium and zinc. The metal chelates after decomposition in nitric acid enabled to determine them in aqueous phase using atomic absorption. AA was calibrated with five standards and extraction efficiency was evaluated by adding metals to 300 ml distilled water. The analytical procedure was followed. The instrument was recalibrated after five samples. It was observed that percentage recovery was within 95-100% with coefficient of variation (C.V) upto 3.2% (Table-1).

The final volume of aqueous phase could be adjusted to any desired value, but in the present work using air acetylene flame AA, final volume was adjusted to 10-25 ml. It was possible to preconcentrate the sample 12-30 times. The method was applied for the determination of metal ions in drinking water collected from Hyderabad and Jamshoro. Cadmium was found below the

detection limit, but copper and nickel were observed 8-16 µg/L and zinc within 25-133 µg/L (Table-2).

Table-1: Percentage recovery of metal ions by preconcentration, number of replicate determination three, integration time for each determination 3 seconds.

S.No.	Metal Ion	Metal Ion added µg/ml	Metal ion Found µg/ml (C.V)	% Recovery	Mean % Recovery
1.	Cd	0.4	0.4 (1.1)	100	
		0.8	0.8 (1.5)	100	98.4
		1.2	1.2(1.5)	100	
		1.6	1.5 (0.2)	93.8	
2.	Cu	1.0	1.0 (2.0)	100	
		2.0	2.0 (0.6)	100	99.4
		3.0	3.0 (0.1)	100	
		4.0	3.9(0.4)	97.5	
3.	Ni	2.0	2.0 (2.1)	100	
		4.0	3.9 (0.2)	97.5	99.1
		6.0	6.0(2.0)	100	
		8.0	7.9 (1.9)	98.8	
4.	Zn	0.4	0.4 (2.8)	100	
		0.8	0.8 (0.7)	100	100
		1.2	1.2 (0.3)	100	
		1.6	1.6 (0.5)	100	

Table-2: Quantitative metal analysis of drinking water samples collected on Feb. 18, 1995. Amount µg/L (coefficient of variation %)

Sample No.	Cd	Cu	Ni	Zn
1.	0.0 (0.0)	16 (3.6)	8 (2.9)	58 (2.6)
2.	0.0 (0.0)	16 (2.4)	8 (1.5)	25 (1.6)
3.	0.0 (0.0)	8 (1.7)	8 (3.8)	33 (1.6)
4.	0.0 (0.0)	8 (3.5)	8 (1.9)	41 (0.7)
5.	0.0 (0.0)	16 (2.1)	16 (1.9)	133 (1.1)

Sample 1-4 collected from Hyderabad (1) Gulistan-i-Sajjad (2) Hirabad near market (3) Railway Station (4) Latifabad (American Hospital) and sample (5) Institute of Chemistry, University of Sindh, Jamshoro.

Experimental

The reagent 6-methyl-2-pyridinecarboxal-dehyde-4-phenylsemicarbazone (MPPSC) was prepared by simple condensation of 6-methyl-2-pyri-dinecarboxaldehyde and 4-phenylsemicarbazide in ethanol as reported [16] (Fig. 1).
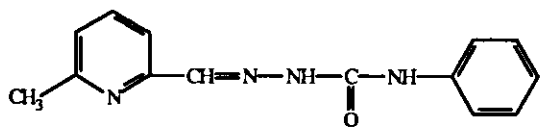

Fig. 1: Structural diagram of 6-methyl-2-pyri-dine-carboxaldehyde-4-phenylsemicarbazone.

Analytical procedure

To a separating funnel (500 ml) was transferred water (300 ml) containing cadmium and zinc (0-50 µg), copper (0-125 µg) and nickel (0-250 mg). It was added reagent MPPSC solution (5 ml, 0.5% w/v in methanol), sodium bicarbonate buffer pH9 (4 ml) and pH was adjusted to 9. Chloroform (10-15 ml) was added and contents were mixed well for 5 min. The layers were allowed to separate and organic layer was transferred to beaker. The extraction was repeated with chloro-form (5-7 ml). The chloroform was evaporated and the residue was added nitric acid (65%) (10 ml). The mixture was heated to 1-2 ml and the clear solution was dissolved in water. The final volume was adjusted to 10-25 ml. The metal contents were determined on Varian Spectr AA-20 atomic absorption spectrometer with air acetylene flame atomizer at the conditions recommended by the manufacturer.

Drinking water samples, four from Hyderabad (1) Gulistan-e-Sajjad, (2) Hirabad near Market (3) Railway Station Plateform, (4) American Hospital Latifabad and sample (5) from Institute of Chemistry, University of Sindh, Jamshoro were collected. The samples were collected in clean $2_{1/2}$ L glass bottle, after flowing the water for 2-5 min. The samples were analysed for the metal contents next day using the above analytical procedure.

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