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DETERMINATION OF TRACE ELEMENT BY ATOMIC ABSORPTION SPECTROSCOPY (AAS) AFTER PRECONCENTRATION ON A SUPPORT IMPREGNATED WITH CONIINE DITHIOCARBAMATE

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Abstract

A procedure is developed for the determination of Cd, Cu, Mo, Pb, Te and Ni in water by Atomic Absorption Spectroscopy (AAS) after preconcentration on a coniine dithiocarbamate supported by polyurethane. The sorbed elements are subsequently eluted with 5 mol L⁻¹ HNO₃ and the acid eluates are analysed by AAS. A 20 mL syringe served as a chromatographic preconcentration column. The sorption recoveries of elements were higher in the order of 99%. The method is also applied successfully for the determination of Cu, Cd, Mo, Pb, Te and Ni in natural and spiked water samples.

Introduction

Environmental pollution monitoring requires determination of toxic heavy elements in trace levels. The Atomic Absorption Spectrometry (AAS) technique, which offers fast multielemental analysis, suffers from a poor sensitivity in the determination of heavy elements in environmental samples like natural water and other real samples. This draw back can be overcome by a combination of a suitable preconcentration technique with subsequent AAS determination. Preconcentration methods that can be used for water samples are solvent extraction, coprecipitation, resin chelation and various chromatographic technique¹⁻⁸. These preconcentration methods provides low detection limits and also help to avoid matrix interferences in the analysis of real samples. Extraction of the dithiocarbamate complexes of metals in the isobutyl methyl ketone (1 BMK) and subsequent determination has been widely applied in the determination of metals in natural water. However, this simple solvent extraction concentration procedure cannot be combined with AAS⁹⁻¹⁰. In view of this, several workers tried a column solid phase extraction method for the determination of metals by AAS.

Column solid-phase extraction has some advantages over liquid-liquid extraction. The possibility of combination with ICP-AES as well as with AAS allows preconcentration from a larger sample volume, establishing higher concentration factors, simple storage and transportation of the pretreated samples¹¹. Here authors report a method for preconcentration of trace elements, viz., Cd, Cu, Mo, Pb, Te and Ni on a polyurethane foam support impregnated with coniine dithiocarbamate. The sorbed elements were sequentially eluted with 5 mol L⁻¹ HNO₃. The acid eluates were further analysed by AAS.

Experimental

Material and Methods

All reagents and chemicals used were of Analytical reagent grade. Deionized doubly distilled water was used throughout the experiments. A multielement standard solution (0.1 mg mL⁻¹) was prepared by appropriate dilution of AAS standards (Merck Germany) of Cd, Cu, Mo, Pb, Te and Ni. Working standards of (0.1, 0.2, 0.5, 0.8 and 1.0 µg mL⁻¹) were prepared by appropriate dilution of multielement standard with deionized distilled water.

Nitric acid was used without additional purification. Sodium salt of coniine dithiocarbamate was prepared by slowly adding 80g of carbondisulphide to a solution of coniine (85g) in 25 mL of water at 5^oC with constant stirring, followed by 40 g of sodium hydroxide dissolved in 20 mL of water as shown in Fig.1. The product was warmed to room temperature, washed repeatedly two or three times with purified acetone. The reaction product was purified by recrystallization in acetone. The compound thus produced has a melting point of 303-308^oC at 740 mm pressure.

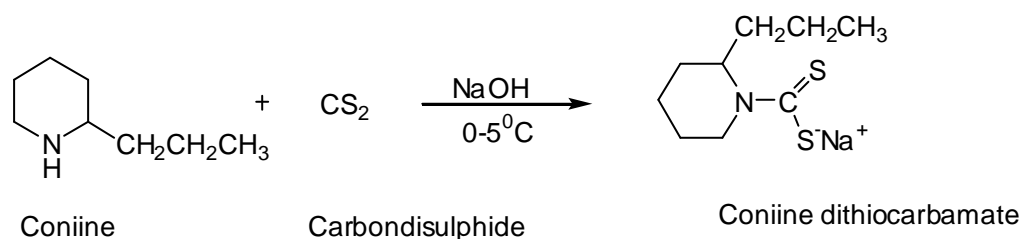


Fig.1 : Synthesis of coniine dithiocarbamate reagent.

Acetate buffer was prepared by dissolving 8.2 g sodium acetate in 800 mL water. It was adjusted by pH 6.0 with high purity glacial acetic acid. It was stored in a clean polyethylene bottle.

20 plus varian atomic absorption spectrometer with a hollow cathode lamp, using an N₂O - acetylene flame for determination of traces of heavy metals. The AAS

determination of all other cations was performed under the recommended conditions for each metal. The pH was determined with a model 632 Metrohm pH meter with a combined glass-calomel electrode.

Column Preparation

Medical Syringes (20 mL) were used as columns. The support was prepared from soft polyurethane foam in the following manner. 1 cm thick segments with diameter of 2.5 cm were cut. The segments were soaked in 5 mol L⁻¹ nitric acid for 15 h, washed in deionized doubly distilled water and dried prior to use. The syringes were then filled with the air-dried segments. The column consists 7-8 separate segments. Then 3.0 g of solid coniine dithiocarbamate was introduced between the segments. This amount of the complex forming agent was necessary to retain the 100 µg of each element in 200 mL sample. Prior to passing the next 200 mL sample, an additional 3.0 g of solid coniine dithiocarbamate was introduced in to the column by replacing the polyurethane foam segments with a new set of segments.

Procedure

The 20 mL of standard solution containing elements Cd, Cu, Mo, Pb, Te and Ni was taken and the pH was adjusted to 6 ± 0.2 with ammonia solution (1:1) or HCl (1+1) and 2 mL of acetate buffer. The solution of the elements was sucked in the column and allowed to contact for 30 min, then the liquid phase was allowed to drain by removing the piston. Elution was performed by adding 10 mL of 5 mol L⁻¹ HNO₃ to the column by removing the piston. This solution was then allowed to pass through the column. The acid eluent was collected in the polyethylene bottle. Then 2 ml of double distilled water was added and the eluent was collected. Both the eluents were combined and nebulized in to N₂O - acetylene flame of AAS.

Preconcentration of Trace Elements in Natural Water Samples

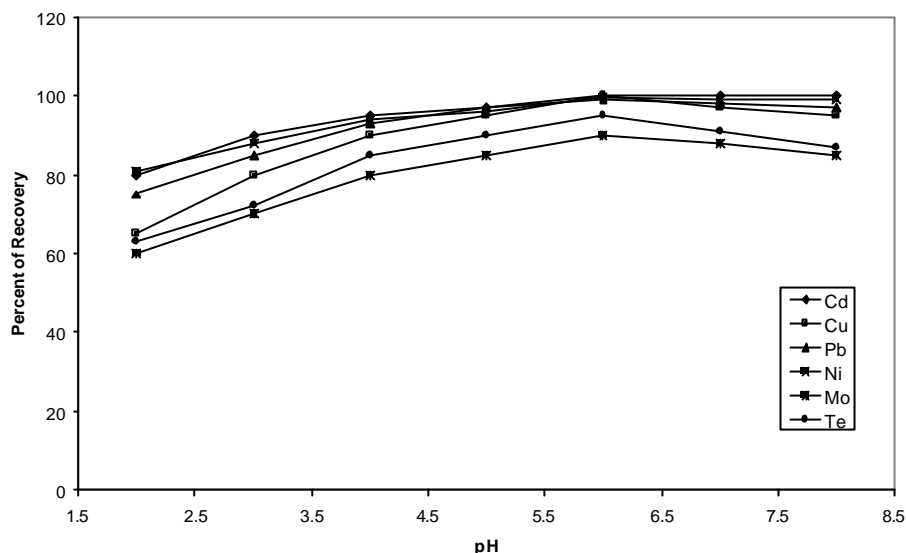
Water sample (200 mL) filtered through a 0.45 µ m membrane filter was taken and pH was adjusted to 6 ± 0.2 with HCl (1+1) or dilute ammonia solution (1:1) and 2 mL of acetate buffer, and passed through the chromatographic columns at a flow rate of 2 mL min⁻¹. The column was then washed with 5 mL of doubly deionized distilled water. The sorbed metal ions were eluted with 10 mL of 5 mol L⁻¹ HNO₃, after which 2 mL of doubly distilled water was added through the sorbent and determined as described above.

Results and Discussion

Influence of pH

The effect of pH on the preconcentration of metals on polyurethane foam loaded with coniine dithiocarbamate was studied by determination of 20 µg of individual elements in the pH range of 2.0-8.0 and by introducing 1.0 g of coniine dithiocarbamate between the polyurethane foam segments. The elution was performed with 5 mol L⁻¹ HNO₃. The data corresponding to each element is shown in Fig.2. At pH 6.0 maximum recovery was obtained for all the elements. So the pH 6.0 ± 0.2 has been selected for the determination of metals in water.

Fig. 2 : Effect of pH on the Complexation of Metal with Coniinedithio Carbamate



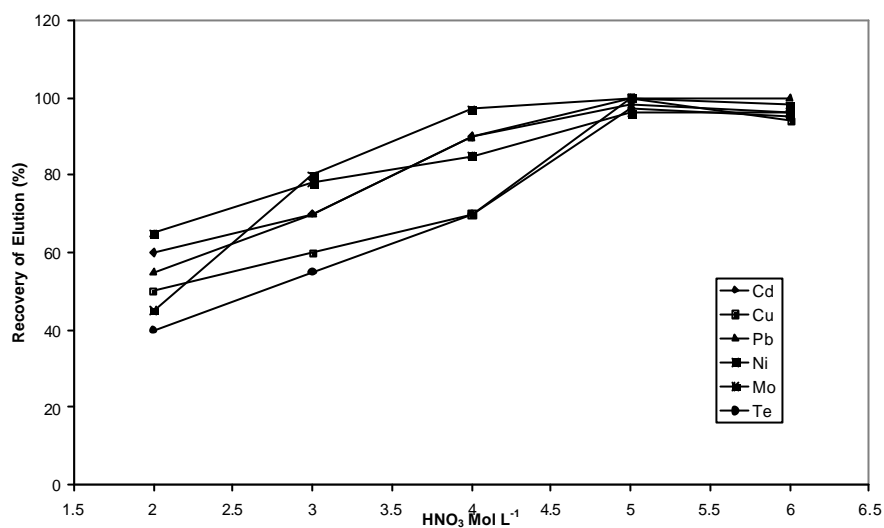
Chromatographic Support

The optimum amount of the chelate forming reagent ensuring quantitative sorption of the studied elements was established. It was observed that the optimum amount of coniine dithiocarbamate depend on the volume of sample passing through the column. Experiments were carried out with solid coniine dithiocarbamate (1.0-10g) spread between the polyurethane foam segments. It was established that 3.0 g of solid coniine dithiocarbamate was enough to provide quantitative retention of 100 μg of each element in a 200 mL water samples at pH 6.0 and subsequent elution was carried out with 5 mol L⁻¹ HNO₃.

Efficiency of Elution

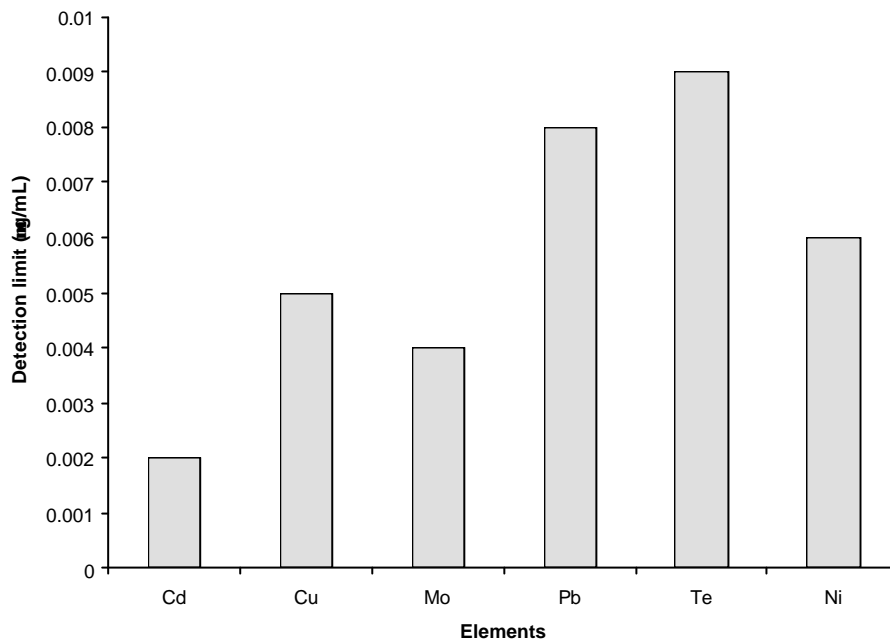
The choice of the eluent was a difficult problem because of the limitation of the AAS to tolerate organic solvents. In addition, the eluent should not destroy the polyurethane foam. Hence for the simultaneous determination of the preconcentrated elements by AAS, the elution was performed with 2.5-6.0 mol L⁻¹ HNO₃. The elution is dependent on the concentration of HNO₃ as shown in Fig.3. Quantitative multielement elution was achieved for 5 mol L⁻¹ HNO₃. Hence 5 mL of 5 mol L⁻¹ HNO₃ was chosen as the optimum eluent for the multielement determination. The recoveries were about 99%.

Fig. 3: Effect of HNO₃ Concentration on Elution of Metals



The precision of the procedure was investigated by determining the elements in spiked water samples. The detection limits of each element was expressed as the amount of analyte in $\mu\text{g} / \text{mL}$ giving a signal to noise ratio of 3. The detection limit and per cent of recovery for each element in spiked water samples are given in Fig.4 and Table 1 respectively. The results show sufficiently high recoveries (99%) for the Cd, Cu, Mo, Pb, Te and Ni with a RSD of 2.75 to 3.32% and determination of trace elements in natural water samples around Tirupati town are shown in Table 2.

Fig.4 : Detection limit for determination Trace Elements by AAS after preconcentration on polyurethane foam loaded with coniine dithiocarbamate.



Conclusion

The synthesised coniine dithiocarbamate loaded on polyurethane foam is selective method for determination of trace elements in low concentrations. The results presented in this paper have confirmed the applicability of the separation and preconcentration of metals.

This method is simple and there is no necessity for elaborate cleanup procedure, but the adsorbed metals are simply eluted with 5 mol L⁻¹ HNO₃ and were analysed by AAS.

Table -1 : Recovery of Trace Elements from Spiked Water samples. After preconcentration on Polyurethane foam loaded with coniine dithiocarbamate

Elements	Concentration of each Element Added (15 ng/L)			Concentration of each Element Added (30 ng/L)			Concentration of each Element Added (60 ng/L)		
	Found (µg/L)	Recovery ^a (%)	RSD ^a (%)	Found (µg/L)	Recovery ^a (%)	RSD ^a (%)	Found (µg/L)	Recovery ^a (%)	RSD ^a (%)
Cd	14.68	97.80	3.31	29.38	97.93	3.32	58.50	97.5	3.29
Cu	14.70	98.0	3.19	29.45	98.16	3.20	59.0	98.0	3.19
Mo	14.62	97.40	2.92	29.30	97.60	2.75	58.70	97.8	2.93
Pb	14.80	98.60	3.19	29.65	98.83	3.21	59.35	98.91	3.20
Te	14.73	98.20	3.05	29.50	98.30	3.08	59.25	98.60	3.10
Ni	14.85	99.0	2.84	29.75	99.16	2.89	59.70	99.50	2.95

^a % Recovery and % RSD for four determination

Table -2 : Determination of Trace Elements in Natural Water samples around Tirupati Town

Samples Collected	Cd		Cu		Mo		Pb		Te		Ni	
	Added (ng/m L)	Found (ng/m L)	Added (ng/m L)	Found (ng/m L)	Added (ng/m L)	Found (ng/m L)	Added (ng/m L)	Found (ng/m L)	Added (ng/m L)	Found (ng/m L)	Added (ng/m L)	Found (ng/m L)
Kalyanidam reservoir	-	19.5"0 .2	-	17.3"0 .4	-	16.2"0 .2	-	18.6"0 .3	-	15.5"0 .4	-	19.8"0 .3
Swarnamukhi river belt	-	20.1"0 .6	-	18.5"0 .5	-	10.5"0 .3	-	20.0"0 .5	-	16.6"0 .2	-	21.2"0 .4
Amararaja Batteries industry	-	24.4"0 .2	-	22.5"0 .4	-	18.2"0 .2	-	25.0"0 .6	-	17.3"0 .3	-	24.6"0 .5
Srikalahastri area	-	19.7"0 .1	-	18.8"0 .2	-	17.5"0 .2	-	19.2"0 .3	-	16.8"0 .2	-	20.6"0 .1

Municipal waste water	- 21.6°0 .2	- 21.8°0 .3	- 17.0°0 .2	- 23.0°0 .2	- 16.1°0 .4	- 24.1°0 .2
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