Extraction of Traces of Chromium, Copper and Lead from Water Using Fluorinated β-Diketone Immobilized on Styrene-Divinylbenzene as Chelating Resin

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Summary: An analytical method using indigenously synthesized fluorinated β-diketone immobilized on styrene-divinylbenzene chelating resin for preconcentration of some trace heavy metals was developed. Sample solutions were passed through a polyethylene column packed with 250 mg of the resin, buffered with ammonium acetate buffer solution. Different variables such as flow rate, pH and concentration of buffer used and eluent concentration were optimized. The optimum conditions established were applied to the determination of chromium, copper and lead in seawater by ICP-OES. Percentage recoveries of the analytes were above 90 % and RSDs were < 5 %.

Introduction

The aim of developments in analytical instrumentation is usually to improve the facilities for the determination of trace and ultra trace level concentrations of different analytes. Despite many advances in this field it is still often necessary to use separation and preconcentration methods prior to the quantitative determination in most of the matrices [1]. Generally, separation and preconcentration of trace elements from matrix are achieved by several methods based on various physical, physicochemical and chemical principles such as solvent extraction, ion-exchange, volatilization and vaporization, precipitation and co-precipitation and electro-deposition etc. However, J. Smiths *et al.*, [2] and R. Boniforti *et al.*, [3] applied different methods for the preconcentration of trace metals and concluded that the use of immobilized metal complexing groups is the simplest method leading to a good recovery ratio. This method provides more flexible working conditions together with good stability, selectivity, high concentrating ability and simple operation. Similarly, several reviews have published on the synthesis of chelating resins and their analytical applications [4-6]. The selectivity of most organic reagents for metals resides predominantly in their ability to form chelates with certain cations. Therefore, the organic polymers could be synthesized that contain chelate-forming groups as exchanging function, and the point of maximal efficiency for a given separation can be established by the variation of pH.

During the last several years, the new functional resins having chelating properties were being prepared by the simple immobilization of complexing organic reagents, by ion-exchange or adsorption onto conventional anion-exchange resins or non-ionic adsorbents. Several organic reagents like bicine [7], dithizone [8], dithiosemicarbazone [9], salicylal-dehyde [10], formylsalicylic acid [11] iminodiacetate [1], *o*-vanillinthiosemicarbazone [12-13], 2-hydroxy, α-hydroxybenzyl phosphonic acid [14], 6-(4-vinyl-benzyloxy)-1,4,8,11-tetrathiacyclo-tetradecane [15], 3-hydroxy,2-methyl-1, 4-naphtho-quinone [16], 8-hydroxyquinoline [17-19], 2-aminoacetylthiophenol [20], and *o*-[3,6-disulfo-2-hydroxy-1-naphthyl-azo]-benzene arsenic acid (thorin) [21] etc. could be immobilized on various solid supports for such purposes. These modified resins can react with a variety of metal ions for complex formation and can preconcentrate their traces by preparing a selective resin.

Similarly, β-diketones have been described in literature for preconcentration of transition and rare earth metals using solvent extraction [22, 23], critical fluid [24] and immobilization on silica etc. [25].

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In this study, we have used a locally synthesized [26] fluorinated β-diketone chelating group immobilized on styrene-divinylbenzene (SDVB) (Fig. 1) for the simultaneous preconcentration of chromium (Cr), copper (Cu) and lead (Pb) prior to their determination by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Analytical applications are demonstrated by analyzing seawater samples collected from coastal area around Karachi (Pakistan) for Cr (III), Cu (II) and Pb (II) simultaneously using ICP-OES.

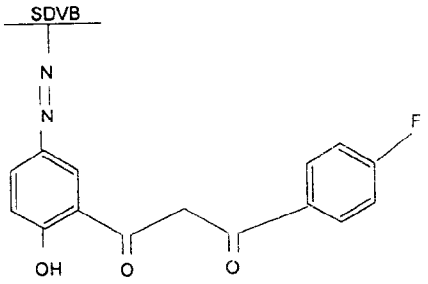

Fig. 1: Styrene-divinylbenzene fluorinated β-diketone resin.

Results and Discussion

In order to determine trace elements accurately and precisely in sample solutions, less contamination, efficient removal of matrix salts, large concentration factor and good recoveries of analyte elements were taken into consideration in the chelating resin preconcentration. To achieve maximum possible recoveries using locally synthesized resin we optimized pH for sorption, flow rate of sample and standard loading, eluent concentration, and removal of matrix effect. This optimization was achieved by univariate method [27].

i) The Optimum Sorption pH

The recoveries of analyte elements were examined in the pH range of 2-10, according to the preconcentration procedure described in the experimental section. A 25 ml-solution containing 0.2 μg/ ml of the three metals separately was passed through the preconditioned column at the flow rate of 6 ml/ min. The solutions were buffered to the chosen pH in the range of 2-10 pH with the acetate buffer before passing through the column. The column pH was maintained to the range of 2-10 before bringing into contact with the solution each time.

The sorbed metal ions were eluted with 2M HCl in 5 ml cylinder and measured by ICP-OES. The optimum pH giving the maximum metal sorption was thus obtained for the resin. The data obtained for the uptake of the three metal ions by the resin is given in Fig. 2. The uptake of Cr (III), Cu (II) and Pb (II) increased almost smoothly up to pH 9. At pH 10 a sharp drop out was observed, which might be due to with some heavy metal ions with higher pH values forming stable hydroxy complexes or hydroxides that affect the quantitative adsorption of the elements on the resin. The value 9 was thus chosen as optimum pH for further work because of the highest values of adsorption at this pH.

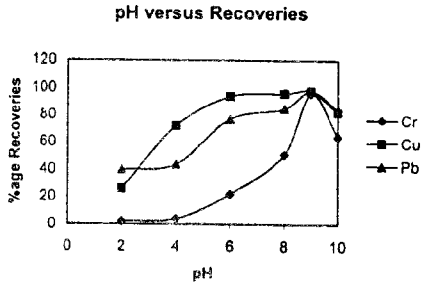

Fig. 2: Effect of pH on the sorption of Cr (III), Cu (II) and Pb (II). 0.2 ppm of each in 25ml of solution eluted in 5ml of 2M HCl.

ii) The Effect of Flow Rate

The rate of sample loading is a highly important parameter regarding analysis time. Different experiments were carried out at various flow rates, ranging between 2-6 ml/ min. It was observed that percent recoveries of Cr (III) and Cu (II) gradually increased with flow rate to reach a maximum at 6 ml/ min while Pb (II) was almost the same at 4-6 ml/ min. Therefore, 6 ml/ min was selected as optimized flow rates both for loading and desorption of metal ions (Fig. 3).

iii) The Effect of Matrix

For evaluating the matrix effect on the sorption of metals, 0.1 μg/ ml of metal ions were spiked in 125 ml of synthetic standard solution [28] and recoveries were calculated after analyzing with ICP-OES (Table-1).

It has been observed that there is no effect of major alkali and alkaline earth metal ions on the

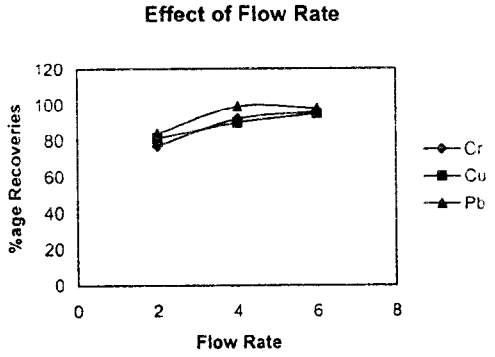

Fig. 3: Variation of percentage sorption of Cr(III), Cu(II) and Pb(II) with flow rate. 0.2 ppm each in 25ml of solution at optimized pH.

Table-1: Matrix effect on percentage recoveries of metal ions

Concentration of Synthetic Standard Solution	Metal Ions Determined	Recovery (%)
Mg = 1300 ppm,	Cr	96
Ca = 420 ppm,	Cu	96
Na = 11,000 ppm	Pb	98

recovery of analyte ions. This could be because of buffering the solution with ammonium acetate, which has been used for the washing of the resin to remove the alkaline earth elements adsorbed on the resin [29].

iv) The Effect of Eluent Concentration

In order to have maximum recoveries, HCl was chosen as eluting acid. Different molarities in the range of 1-4 were optimized. Poor recoveries were obtained with 1 M HCl. At the increased molarities i.e. 2 and 4M HCl, almost same recoveries were obtained (Table-2). Therefore, 2 M HCl was selected as eluting acid.

Application to Analyze Water Samples

To check the applicability of the present method for preconcentrating and determining Cr (III), Cu (II) and Pb (II), the resin was subjected to water samples analysis. Water samples were collected from sites of Kimari, Clifton and Sonmiani. For the determination of Cr (III), Cu (II) and Pb (II) by the optimized method, 125 ml of water samples were passed through the column first without spiking the analytes to collect 5 ml of 2 M HCl (Table-3) and

Table-2: Percentage recoveries of metal ions at different concentrations of HCl

Metal Ions	Percentage Recoveries		
	1 molar	2 molar	4 molar
Cr	36.1	96	93
Cu	42.3	98	95
Pb	50.4	98	97

Table-3: Determination of Cr (III), Cu (II) and Pb (II) in seawater samples

Samples	Metal Ions					
	Cr (III)		Cu (II)		Pb(II)	
	Amount (ppb)	R.S.D (%)	Amount (ppb)	R.S.D (%)	Amount (ppb)	R.S.D (%)
Kimari	10	< 5	60	< 5	100	< 5
Clifton	7	< 5	40	< 5	60	< 5
Sonmiani	7	< 5	35	< 5	50	< 5

then by spiking 0.1 μg/ ml analyte ions in the same volume of water samples and percent recoveries were calculated (Table-4). It has been observed that the percentage recoveries of the spiked seawater samples is lower than synthetic standard solution possibly due to the very complex and heavy matrix of seawater constituting dissolved materials including organics etc.

Table-4: Percentage recoveries of metal ions in real seawater samples using optimized method.

Metal Ions	Concs. in (ppm)	Conc. of spiked Sample (ppm)	Recoveries of spiked sample (%)
Cr	0.01	1.95	77.6
Cu	0.06	1.94	75.2
Pb	0.10	2.47	94.8

Experimental

Apparatus and Reagents

An ARL model, 3580 ICP-OES was used for the determination of metal ions in sample solutions. The operating conditions for the instrument are given below: -

Model	3580 ICP-OES (ARL)
Spectrometer	1 m Simultaneous
	1 m Sequential
Grating	1035 grooves/ mm
Torch	Fassel type
Nebulizer	Meinhard type
Gas Flow	
Outer	12 L/ min

Intermediate	0.8 L/ min
Aerosol	1L / min
Incident power	1.5 kw
Observation height	15mm above coil
Integration time	10-15 sec
Resolution	0.06 nm

The pH measurements were performed on digital pH meter of model WTW pH 530.

For the loading of metal ions from the sample solution on the column, DESAGA PLG Peristaltic pump (Model No. 851107) was used. The preconcentration system consisted of a polyethylene column (5.5cm x 4mm I.D) packed with 0.25 g of resin with glass wool at both ends of the column. All chemicals used in this work were of analytical grade from E. Merck. Double distilled de-ionized water was used for dilutions etc. The fluorinated β-diketone resin (Fig. 1) was provided by the Department of Chemistry, Quaid-i-Azam University, Islamabad. Its synthesis method was reported previously [26]. Specpure solutions of Cr (III), Cu (II) and Pb (II), obtained from E-Merck were used as standard. The pH adjustments were made with ammonia solution or hydrochloric acid according to the requirement. For buffering of the column, ammonium acetate buffer solution was used. The water samples were iso-kinetically collected in clean polyethylene bottles from Karachi coastal area, Pakistan.

Sample Preparation

The seawater samples were collected from different locations of coastal area around Karachi, Pakistan with the help of Pakistan Coast Guards. The samples were filtered with a 0.45 μm pore size membrane filter and stored at 4 °C. Polyethylene bottles were used for collection and preservation of samples. The bottles were washed according to EPA recommended method (D3370-76).

Column Preparation

0.25 g of air-dried resin was immersed in de-ionized distilled water and allowed to swell overnight. A 4mm diameter polyethylene column was then packed with this swollen resin. Glass wool was placed at both ends of the column. This mini column was then connected to a peristaltic pump with Tygon tubings and conditioned by washing thoroughly with 2M HCl followed by de-ionized water.

Determination of Resin Capacity

Batch equilibration technique was used to determine the total sorption capacity of the resin. 0.2g resin beads were stirred with 25 ml of 80 μg/ ml Cu solution at optimum pH was left for 24 hours to ensure complete equilibrium. Then, the loading capacity for the metal ions on the resin was calculated by the equation [27].

$$Nf = \frac{(X - Y)}{Z}$$

Where X is the initial amount of metal ion, Y is the amount of metal ion adsorbed and Z is the amount of chelating resin. The loaded metal ion was eluted with 2 M HCl and was determined by ICP-OES. It was found out to be 0.03 m moles/ g.

Optimized Pre-Concentration Procedure

The resin prepared in the column was conditioned by passing 20 ml of 2 M HCl followed by de-ionized water and then with the ammonium acetate buffer solution at optimized pH. After conditioning of the resin, 125 ml seawater (buffered at pH 9) was passed at a flow rate of 6ml/ min through the column. The retained metal ions were eluted with 5 ml of 2 M HCl and analyzed by ICP-OES.

Conclusions

Fluorinated β-diketone immobilized on SDVB can be used as a chelating reagent for the preconcentration of heavy metals in water samples. The proposed method is simple, and low cost because of homemade resin, which can not only be exploited for the preconcentration or separation of heavy metals in seawater but also in different matrices.

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