Analytical application of poly[dibenzo-18-crown-6] for chromatographic separation and Determination of Zinc(II) in glycine medium

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Abstract-A simple chromatographic separation method has been developed for quantitative sorption of Zn(II) from an aqueous solution of 1×10-3 M Glycine using poly [dibenzo-18-crown-6] as stationary phase. The sorption of Zn(II) was quantitative 1×10-2M to 1×10-6 M Glycine. The elution of Ni(II) was quantitative with 0.1–8.0 M HCl, 0.1-8.0 M HBr M and 0.1-8.0 M H2SO4 The capacity of poly [dibenzo-18-crown-6] for Zn(II) was found to be 0.65 ± 0.01 mmol g-1 of crown polymer. The effects of concentrations of Glycine, Zn(II) foreign ions and eluents have been studied. Zn(II) was separated from a number of cations in multi component mixtures. The applicability of the proposed method was ascertained for the determination of Zn(II) in real samples. The reliability of method was checked by comparison of the results with those obtained using flame photometer. The method is very simple, rapid and selective with good reproducibility (approximately±2%).

Keyword- Uranium, Glycine, Sorption, Zinc, Chromatography

1 Introduction

The presence of heavy metals such as zinc, cadmium, chromium, lead, etc. in industrial waste is an issue of increasing importance because of their hazardous properties to human beings, such as toxicity, persistence, bioaccumulation and carcinogenicity[1-6]. Zinc is an essential element for all animals including human beings. It plays an important physiological role in human blood distributed 75-85% in erythrocytes (mostly as carbonic anhydrase), 12 to 22% in plasma and 3% in leukocytes. One third of zinc in plasma is loosely bound to serum albumins, the reminder being more firmly attached to α-globulins, with minor fractions complexed in histidine and cysteine [7-10]. So it is important to develop simple methods for separation and recycling of such metals from environmental point of view.

There are various methods available for separation of zinc such as precipitation, solid phase extraction, membrane based separation, chromatography, etc.

In the growing field of separation science numerous methods have been describe for the separation and determination of zinc viz. Solvent extraction [11-13]ion exchange [14-16] and solid phase extraction [17-19] are among them but conventional extraction chromatography –liquid chromatography is comparatively fast, efficient and popular method.

Macrocyclic compound are uncharged and contain a cavity in which a cation can be encapsulated. The complexes thus formed are of great analytical interest. It was in 1967 when Pedersen [20] published his first paper on crown ether under the title "Cylic Polyethers and their Complexes with Metal Salts." Since then these ligand have been used by physical, organic, inorganic, biochemists and also analytical chemists [21].

No attempts were made for the separation of Zinc from associated element using amino acid media and column chromatography. This chapter describes in detail the sorption study and separation of Zinc(II) using glycine medium on poly[dibenzo-18-crown-6].The concentration of glycine required for quantitative sorption of Zinc(II) is very low, clean cut separation with good separation yield was achieved. The Zinc was successfully determined in various real samples by using this method.

2 Experimental

2.1 Apparatus and reagents

A Ziess (German) Spectrophotometer, a digital pH meter (Model LI-120, ELICO, India) with glass and calomel electrodes and a digital Flame photometer (PI, Model No. 041, India) were used. A stock solution of Zinc(II) was prepared by dissolving 5.210 g of zinc Chloride (AR grade, BDH, Poole, England) in 500 mL distilled deionised water and standardized gravimetrically[22]. A solution containing 40µg/mL of Zinc (II) was prepared by appropriate dilution of the standard stock solution. Glycine solution (1×10^{-1} M) was prepared by dissolving 1.875 g of glycine in distilled deionised water and diluted to 250 mL.

Poly[dibenzo-18-crown-6] (E Merck Darmstadt, Germany) was used after screening to 100-200 mesh. A total of 0.5 g of polymer was slurred with distilled

deionised water and poured into a Pyrex glass chromatographic column (20×0.8 cm i.d.). The column was used after preconditioning with glycine solution.

2.2 General procedure

40µg of Zinc (II) was mixed with glycine the concentration range of 1×10^{-1} M to 1×10^{-9} M in a total volume of 10 mL. The solution was then passed through poly [dibenzo-18-crown-6] column, preconditioning with same concentration of glycine as that of the sample solution at flow rate of 0.5 mL/min. The column was then washed with the same concentration of glycine. The sorbed Zinc(II) was then eluted with different eluting agents (described later) at the flow rate of 0.5 mL/min. 5.0 mL fraction were collected and Zinc(II) was determined spectrophotometrically by PAR at 520nm [23]using a calibration graph.

3 Results and Discussion

3.1 Sorption of Zinc (II) on poly[dibenzo-18-crown-6] as a function of glycine concentration.

Sorption studies of Zinc(II) were carried out from glycine medium. The concentration of glycine was varied from 1×10^{-1}M to 1×10^{-9} M. After sorption, the elution of Zinc(II) was carried out with 4.0 M hydrochloric acid. It was found that there was quantitative (100%) sorption of Zinc(II) from 1×10^{-3} M to 1×10^{-8} M glycine . The results are shown in **(Table 3.1).** The subsequent sorption studies of Zinc(II) were carried out with 1×10^{-3} M glycine.

Table 3.1: Sorption of Zinc(II) as a function of glycine concentration

Concentration of Glycine (M)	Percentage of sorption
1×10^{-1}	75.12
1×10^{-2}	88.45
1×10^{-3}	100
1×10^{-4}	100
1×10^{-5}	100
1×10^{-6}	100
1×10^{-7}	100
1×10^{-8}	100
1×10^{-9}	95.20

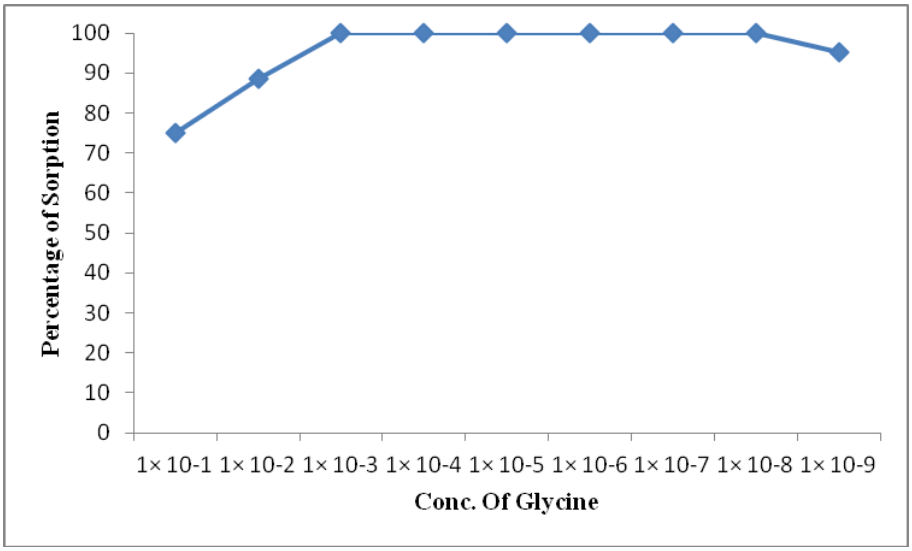

Figure 2.3.1: Sorption of Zinc(II) as a function of glycine concentration.

3.2 Elution study of Zinc(II) with various eluting agents

40 µg/mL of Zinc(II) was sorbed on the poly[dibenzo-18-crown-6] column at 1×10^{-3} M glycine concentration. After sorption, elution of Zinc(II) was carried out using hydrochloric acid, hydrobromic acid, sulphuric acid, perchloric acid and acetic acid. The concentration of eluting agents varied from 0.1 M to 8.0 M. The elution data of Zinc(II) with various eluting agents is shown in **(Table 3.2).** Showed that Zinc(II) was quantitatively eluted with 0.1 M to 8.0 M hydrochloric acid, sulphuric acid and hydrobromic acid ,6.0 -8.0M perchloric acid,2.0-8.0M acetic acid. Further elution studies of Zinc(II) in this work was carried out with 4.0 M hydrochloric acid.

Table 3.2: Elution study of Zinc(II) with various eluting agent.

Conc. Acid (M)	**0.1**	**0.5**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	**8.0**
	Percentage of Elution									
HCl	100	100	100	100	100	100	100	100	100	100
H_2SO_4	100	100	100	100	100	100	100	100	100	100
$HClO_4$	55.60	62.25	74.65	81.26	86.56	90.25	94.40	100	100	100
HBr	100	100	100	100	100	100	100	100	100	100

CH_3COOH	75.20	80.56	86.47	100	100	100	100	100	100	100

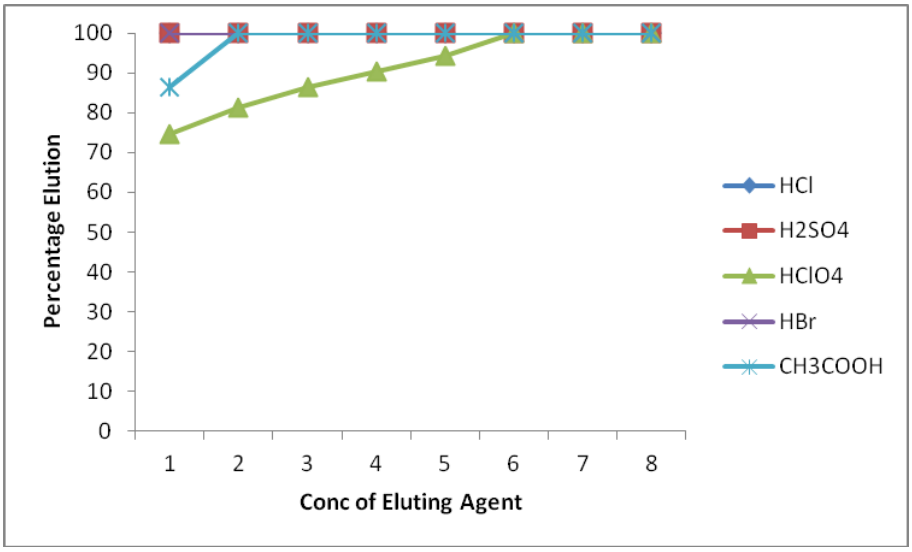

Figure 3.2: Elution study of Zinc(II) with various eluting agents**.**

3.3 Effect of varying concentration of Zinc(II)

In order to find out the capacity of poly[dibenzo-18-crown-6] for the Zinc(II), the concentration of Zinc(II) was varied from 40-960 µg/10 mL in glycine and 1.0 M hydrochloric acid as eluent. The results **(Table 3.3)** showed that the sorption of Zinc(II) was quantitative (100%) up to 800 µg. With increase in concentration of Zinc(II) there was decrease in the percentage sorption of Zinc(II) and is shown in the **(Figure 3.3)** From this study it was found that the capacity of poly[dibenzo-18-crown-6] for Zinc(II) was found to be 0.85 ± 0.01 mmol/g of crown polymer.

Table 3.3: Effect of varying concentration of Zinc(II)

Concentration of Zn(II)	Percentage of Sorption
40	100
80	100
120	100
160	100
200	100
240	100
280	100
320	100
360	100
400	100
440	100
480	100
520	100
560	100
600	100
640	100
680	100
720	100
760	100
800	100
840	95.20
880	88.60
920	82.40
960	75.35

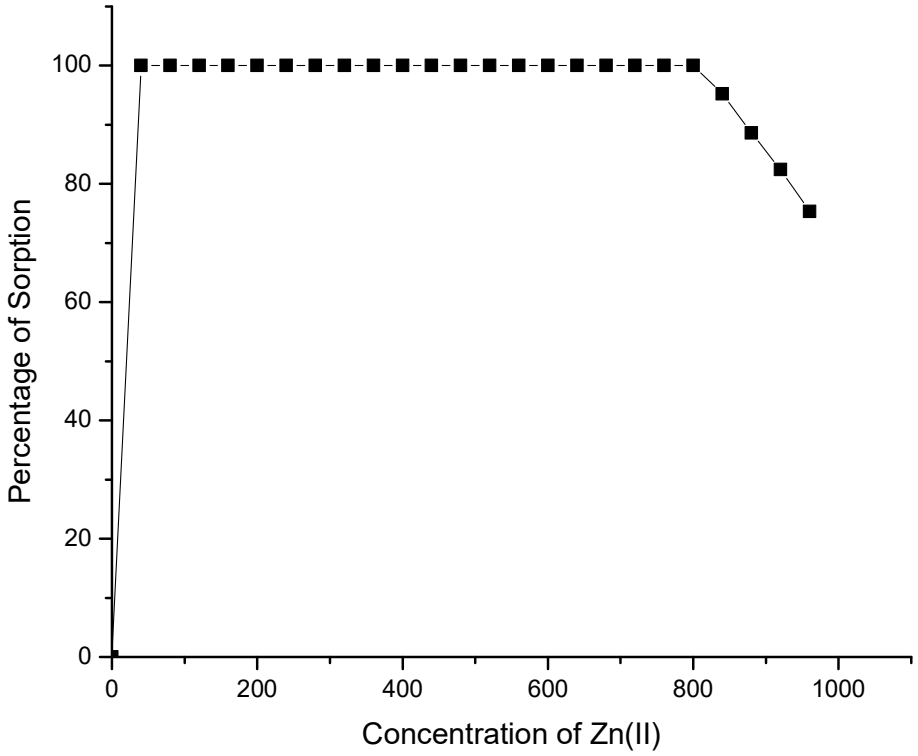

Figure 3.3: Effect of varying concentration of Zinc(II)

3.4 Separation of Zinc(II) from binary mixtures

An aliquot of solution containing 40 µg of Zinc(II) was mixed with foreign ions and glycine was added so that its concentration was 1×10^{-3}M in total volume of 10 mL. The tolerance limit was set as the amount of foreign ions required to cause ±2% deviation in the recovery of Zinc(II). The solution was passed through a poly[dibenzo-18-crown-6] column, preconditioned with 1×10^{-3} M glycine at a flow rate of 0.5 mL/min. Subsequently the column was washed with 15 mL of 1×10^{-3} M glycine to remove unsorbed metal ions. Various foreign ions were not sorbed and hence passed through the column. The effluent was collected and analysed for foreign ion content. The tolerance limit of various foreign ions is shown in **Table 3.4.** The most of the alkali metals and alkaline earth metals show high tolerance limit except barium(II) and magnesium(II). In case of alkaline metal sodium(I) potassium(I) and alkaline earth metals calcium(II),strontium(II) tolerates strongly. Most of the p-block and d-block elements were sorbed and shows low tolerance limit but tungsten(VI) and

lead(II) shows highest tolerance limit. Amongst the inner transition elements, As compared lanthanum(III), cerium(III), gadolinium (II) shows low tolerance limit. The anion of inorganic and organic acids showed high tolerance limit

Table: 3.4: Separation of Zinc(II) from binary mixture

Ion	Added as	Tolerance limit (mg)	Ion	Added as	Tolerance limit (mg)
Li^{+}	LiCl	22	Th^{4+}	$Th(NO_3)_4.6H_2O$	0.045
Na^{+}	NaCl	18	Sb^{3+}	$SbCl_3$	0.05
K^{+}	KCl	27	Sn^{2+}	$SnCl_2$ 2 H2O	0.5
Cs^{+}	CsCl	2	Ce^{3+}	$CeCl_3$ $6H_2O$	0.5
Cr^{3+}	$Cr(NO_3)_3$,$9H_2O$	0.5	Gd3+	$Gd(NO_3)_3$, 6H2O	0.01
Mg^{2+}	$MgCl_2.6H_2O$	0.5	W^{6+}	Na_2WO_4 ,$4H_2O$	8
Ca^{2+}	$CaCl_2$	22	Zr^{4+}	$Zr(NO_3)_4$, $4H_2O$	0.5
Sr^{2+}	$Sr(NO_3)_2$	14	La^{3+}	$La(NO_3)_3$	1
Ba^{2+}	$Ba(NO_3)_2$	0.5	NH_4^{+}	NH_4OH	4
Co^{2+}	$CoCl_2.6H_2O$	0.1	Citrate	Citric acid	9
Ni^{2+}	$NiCl_2.6H_2O$	0.1	CH_3COO^{-}	CH_3COOH	2
Mn^{2+}	$MnCl_2.4H_2O$	0.1	SO_4^{2-}	H_2SO_4	0.5
Cd^{2+}	$(CH_3COO)_2$ CdH_2O	0.1	EDTA	EDTA	0.1
Pb^{2+}	$Pb(NO_3)_2$	6	Ascorbate	Ascorbic acid	1
Fe^{3+}	$FeCl_3.6H_2O$	0.5	ClO_4^{-}	$HClO_4$	0.1
Al^{3+}	$AlCl_3.16H_2O$	0.05	SCN^{-}	NaSCN	20
Cu^{2+}	CuCl2	0.1	Cl^{-}	HCl	0.05
Tl^{3+}	$Tl(NO_3)_3.3H_2O$	0.1	PO_4^{3-}	H_3PO_4	12
Mo^{6+}	$(NH_4)_6Mo_7O_{24}.4H_2O$	0.5	Bo_3^{3-}	H_3BO_3	0.1

3.5 Separation of Zinc(II) from multicomponent mixtures

Separation of Zinc(II) was carried out from number of associated elements in multicomponent mixture. The mixture containing Lithium(I), Zinc(II), Beryllium(II),Lead(II), Cadmium(II), Copper(II) was passed through the poly[dibenzo-18-crown-6] column at 1×10^{-3} M glycine concentration, lithium(I) was not sorbed and hence passed through the column. The Copper(II), Lead(II), Cadmium(II) were sorbed . The sorbed Copper(II), was first eluted with 25 mL of 1.0M HCl. After that Zinc(II) were eluted with 4.0 M hydrochloric acid and effluents are analyzed spectrophotometrically. Using this method, separation of Lead(II), Cadmium(II), Copper(II), Zinc(II) mixtures was achieved. The results are shown in (Table: 3.5).

Table 3.5: Separation of beryllium (II) from other elements (multicomponent mixture).

No.	Mixture	Taken µg	Found µg	Recovery* %	Eluent
1	Li(I)	50	49.5	99.00	NSPC**
	Zn(II)	40	39.9	99.80	0.5MLiOH
	Be(II)	10	9.95	99.50	4.0M HCL
2	Li(I)	50	50	100	NSPC**
	Pb(II)	40	39.8	99.50	0.2M A.C
	Zn(II)	40	39.9	98.80	4.0 M HCl
3	Li(I)	50	50	100	NSPC**
	Cd(II)	40	39.6	99.20	4.0M HCL
	Zn(II)	40	40	100	0.2M LiOH
4	Li(I)	50	50	100	NSPC**
	Cu(II)	40	39.6	99.20	1.0MHCL
	Zn(II)	40	39.9	99.8	0.5M CH_3COOH

*Average of triplicate analysis

**NSPC- No Sorption Passing through the Column, A.C.-Ammonium carbonate.

3.6 Determination of Zinc(II) in real Samples-

1. Analysis of zinc(II) from alloys-

The proposed method was applied for the determination of zinc(II) in different alloys. Known weight of alloy was heated up to 700 ^{0}C for 2 hours to remove organic matter. The solution was treated with concentrated aqua-regia and heated to moist dryness. The solution was filtered through Whatmann filter paper No.1 and diluted to 100 mL with distilled deionised water. The sample solutions of plant samples were analyzed as per the proposed method and zinc(II) content was determined. The results obtained with proposed method shows good agreement with those obtained by AAS

Determination of zinc from Alloys

Alloy	Zn %		
	Certified Value AAS	Found	S.D %
Brass	30.0	29.50	0.11
Zinc Aluminium Alloy	15.5	15.20	0.08

2. Determination of zinc in biological samples

Human blood (2-5 mL) or urine (20-50 mL) was collected in polyethane bottles from the affected persons. Immediately after collection, they were stored in a salt-ice mixture and later, at the laboratory, were kept at -20oC. The samples were taken into a 100 mL micro-Kjeldahl flask. A glass bead and 10 mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating. When the initial brisk reaction was over, the solution was removed and cooled following a method recommended by Stahr. 2 mL volume of concentrated sulfuric acid was added carefully, followed by the addition of 2 mL of concentrated HF and heating was continued to dense white fumes, repeating nitric acid addition if necessary. Heating was continued for at least ½ hr and then cooled. The content of the flask was filtered then neutralized with dilute NH4OH solution in the presence of 1-2 mL of a 0.01 % (w/v) tartrate or EDTA solution. The resultant solution was then transferred quantitatively into a 10-mL calibrated flask and made up to the mark with deionized water. A suitable aliquot (1-2-mL) of the final solution was pipetted into a 10-mL calibrated flask and the zinc content was determined as described under the Procedure

using tartrate or EDTA as masking agent. The results of biological analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS.

Determination of Zinc in biological samples

Sample	Zn %		
	Certified Value	Found	R.S.D %
Blood	1.15	1.21	1.0
Urine	0.32	0.34	1.5

3 Determination of zinc in soil samples

An air dried homogenized soil sample (100 g) was weighed accurately and placed in a 100-mL micro-Kjeldahl flask. The sample was digested. The content of the flask was filtered through a Whatman No. 40 filter paper into a 25 mL calibrated flask and neutralized with dilute NH4OH solution in the presence of 1-2 mL of a 0.01% (w/v) tartrate or EDTA solution. Then the solution of the flask was made up to the mark with deionized water.

Determination of Zinc in soil samples

Sample	Zn (mg $Kg^{-1)}$	
	Certified Value	Found
Industrial Soil	70	68.70
Agricultural Soil	15	14.30

4. Determination of Zinc in Milk Sample

Determination of zinc in milk samples Each 10g amount of milk powder or liquid milk sample (100 mL) containing different composition metals was accurately taken and evaporated nearly to dryness with a mixture of 3 mL concentrated H_2SO_4 and 10 mL of concentrated HNO_3 to sulfur trioxide fumes in a fume cupboard. After cooling the residue was heated with 10 mL of deionized water in order to dissolves the salts.

Determination of Zinc in Milk Sample

Sample	Zn (mg $Kg^{-1)}$	
	Certified Value	Found

Cow Milk	0.95	0.94
Goat Milk	0.73	0.72

5. Determination of Zinc aquatic plants

Analysis of zinc(II) from aquatic plants The proposed method was employed for the analysis of zinc(II) in aquatic plants. The aquatic plant sample was washed to remove periphyton, dust and sediment particles. The plant sample was dried for 8 to 10 days and heated in oven at 1100C. The dried sample was grounded using mortar till finely dry powder was formed. The dried sample was weighed accurately and dissolved in nitric acid and perchloric acid mixture (3:1). The resulting mixture was evaporated to dryness and extracted with distilled deionised water. The solution was heated to boiling and filtered using Whatmann filter paper No. 1. An aliquot sample solution was analyzed as per the general procedure and zinc content was determined.

Determination of Zinc aquatic plants

Aquatic Plants	**Zn µg/10g**		
	Certified Value	**Found**	**S.D %**
Eicchornia Crassipes	652	648	0.14
Hydrilla	814	812	0.08
Salvinia	1122	1118	0.07

4 Conclusion

The important feature of this method is that using column chromatographic method and poly[dibenzo-18-crown-6] the separation of Zinc(II) from associated element in glycine medium has been achieved. The capacity of poly[dibenzo-18-crown-6] for Zinc(II) was found to be 0.65 ± 0.01 mmol/g of crown polymer. Zinc(II) was separated from number of cations in binary as well as multicomponent mixtures. The method was extended to the determination of beryllium in real sample. The aim of present investigation is to demonstrate a simple, selective and cheap method and has good reproducibility (approximately ± 2%).

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