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Sorption study of beryllium (II) in glycine medium using poly [dibenzo-18 crown-6] and column chromatography

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Abstract
A simple chromatographic separation method has been developed for quantitative sorption of Beryllium(II) from an aqueous solution of 1×10^{-3}M Glycine using poly [dibenzo-18-crown-6] as stationary phase. The sorption of Beryllium (II) was quantitative 1×10^{-3}M to 1×10^{-8}M Glycine. The elution of Beryllium (II) was quantitative with 0.1–8.0 M HCl, 3.0-8.0M HBr and 7.0-8.0 M H2SO4. The capacity of poly [dibenzo-18-crown-6] for Beryllium (II) was found to be 0.65 ± 0.01 mmol/g of crown polymer. The effects of concentrations of Glycine, Beryllium (II), foreign ions and eluents have been studied. Beryllium (II) was separated from a number of cations in multicomponent mixtures. The applicability of the proposed method was ascertained for the determination of Beryllium (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%).

Keywords: sorption, separation, Beryllium (II), Glycine, poly [dibenzo-18- crown-6], Chromatography

1. Introduction

Beryllium is industrially valuable metal due to its unique physico-chemical properties. Beryllium is rare in the earth's crust and its presence is of importance. Beryllium is particularly valuable in specific areas of nuclear technology. Beryllium is widely used in metal-alloys, salts and X-ray tubes. Due to the ability of beryllium to reflect neutrons and its efficiency in the production of neutrons, when exposed to alpha emitter has led to its use in nuclear reactors and nuclear weapons. However use of beryllium carries with it some serious health hazards, including cancer and chronic beryllium disease (CBD) [1-4].

CBD has no known cure usually and result in death. Beryllium has been linked to a number of other health effects resulting from inference of enzyme function, DNA synthesis, protein phosphorylation and cell division. An estimated 10-20 million pounds per year of beryllium are emitted during coal and refuse incineration, which can contaminate air, drinking water, soil and agricultural products [5]. Due to the high toxicity of beryllium, there is a need to separate a beryllium from other. Beryllium is one of the toxic elements, which causes some health hazards. Hence, it is necessary to analyze microgram levels concentrations of beryllium in industry and environment sample.

In the growing field of separation science numerous methods have been describe for the separation and determination of beryllium viz. Solvent extraction [6-8] ion exchange [9-11] and solid phase extraction [12-14] 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 [15] 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 [16].

No attempts were made for the separation of beryllium from associated element using amino acid media and column chromatography. This chapter describes in detail the sorption study and separation of beryllium(II) using glycine required medium on poly [dibenzo-18-crown-6].The concentration of glycine required for quantitative sorption of beryllium (II) is very low, clean cut separation with good separation yield was achieved. The beryllium was successfully determined in beryl ore 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 beryllium(II) was prepared by dissolving 9.828 g of beryllium sulphate tetrahydrate(AR grade, BDH, Poole, England) in 100mL distilled deionised water and standardized gravimetrically [17].

A solution containing 10µg/mL of beryllium (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

10µg of beryllium (II) was mixed with glycine the concentration range of 1×10^{-1}M to 1×10^{-11} 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 beryllium (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 beryllium(II) was determined spectrophotometrically by Eriochrome cyanine R at 525nm [18] using a calibration graph.

3 Results and Discussion

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

Sorption studies of beryllium (II) were carried out from glycine medium. The concentration of glycine was varied from 1×10^{-1}M to 1×10^{-11} M. After sorption, the elution of beryllium (II) was carried out with 4.0 M hydrochloric acid. It was found that there was quantitative (100%) sorption of beryllium (II) from 1×10^{-3} M to 1×10^{-8} M glycine. The results are shown in (Table 1). The subsequent sorption studies of beryllium (II) were carried out with 1×10^{-5} M glycine.

Table 1: Sorption of beryllium (II) as a function of glycine concentration

Concentration of Glycine (M)	Percentage of sorption (%)
$1X\ 10^{-1}$	80.85
$1X\ 10^{-2}$	81.03
$1X\ 10^{-3}$	100
$1X\ 10^{-4}$	100
$1X\ 10^{-5}$	100
$1X\ 10^{-6}$	100
$1X\ 10^{-7}$	100
$1X\ 10^{-8}$	100
$1X\ 10^{-9}$	84.57
$1X\ 10^{-10}$	81.48
$1X\ 10^{-11}$	77.32

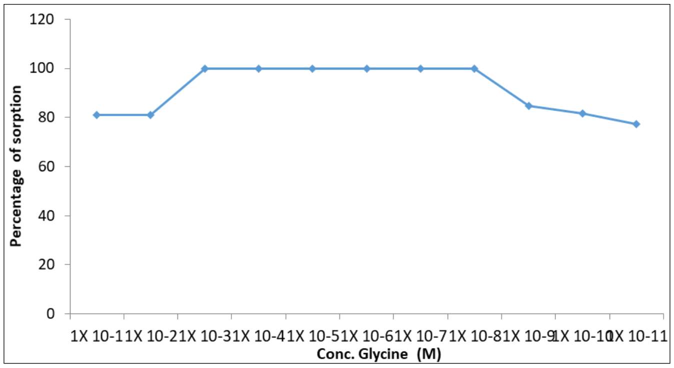

Fig 1: Sorption of beryllium (II) as a function of glycine concentration

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

10 µg/mL of beryllium (II) was sorbed on the poly [dibenzo-18-crown-6] column at 1×10^{-5} M glycine concentration. After sorption, elution of beryllium (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 profile of beryllium (II) with various eluting agents is shown in (Table 2). Showed that beryllium (II) was quantitatively eluted with 0.1 M to 8.0 M hydrochloric acid, 7.0 -8.0 M sulphuric acid and 3.0 -8.0M hydrobromic acid where as perchloric acid and acetic acid were found to be inefficient eluents for beryllium (II). Further elution studies of beryllium (II) in this work was carried out with 4.0 M hydrochloric acid.

Table 2: Elution study of beryllium (II) with various eluting agent

Conc. Acid	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	75.98	78.19	80.08	89.18	91.76	94.50	95.74	98.02	100	100
$HClO_4$	66.93	69.53	71.65	78.66	82.20	84.20	85.40	87.78	91.66	92.67
HBr	90.07	92.37	96.15	98.16	100	100	100	100	100	100
CH_3COOH	45.39	54.67	61.17	65.19	68.89	71.37	74.56	77.03	88.23	92.39

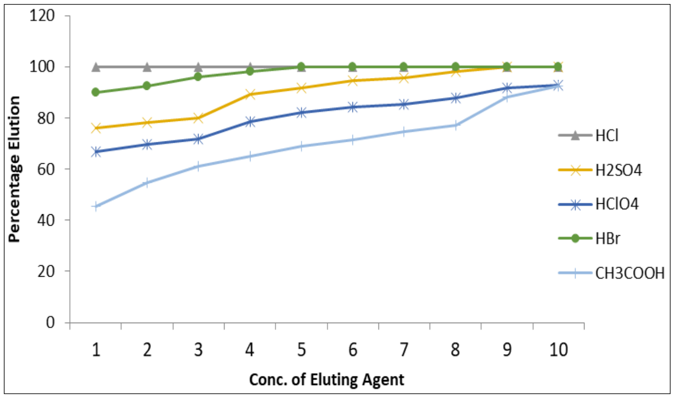

Fig 2: Elution study of beryllium (II) with various eluting agents

3.3 Effect of varying concentration of beryllium (II)

In order to find out the capacity of poly[dibenzo-18-crown-6] for the beryllium(II), the concentration of beryllium(II) was varied from 20-90 µg/10 mL in glycine and 4.0 M hydrochloric acid as eluent. The results (Table 3) showed that the sorption of beryllium(II) was quantitative (100%) up to 60 µg. With increase in concentration of beryllium(II) there was decrease in the percentage sorption of beryllium(II) and is shown in the (Figure 3) From this study it was found that the capacity of poly[dibenzo-18-crown-6] for beryllium(II) was found to be 0.65 ± 0.01 mmol/g of crown polymer.

Table 3: Effect of varying concentration of beryllium (II)

Concentration of Be(II) µg	Percentage of Sorption (%)
10	100
20	100
30	100
40	100
50	100
60	100
70	97.78
80	95.34
90	86.11

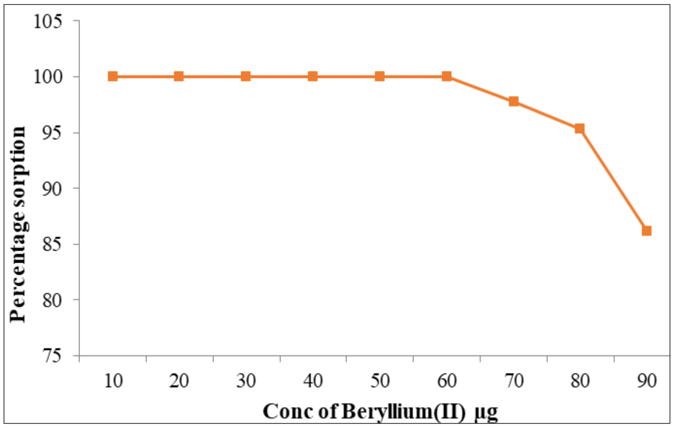

Fig 3: Effect of varying concentration of beryllium (II)

3.4 Separation of beryllium (II) from binary mixtures

An aliquot of solution containing 10 µg of beryllium (II) was mixed with foreign ions and glycine was added so that its concentration was 1×10^{-5}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 beryllium (II). The solution was passed through a poly [dibenzo-18-crown-6] column, preconditioned with 1×10^{-5} M glycine at a flow rate of 0.5 mL/min. Subsequently the column was washed with 15 mL of 1×10^{-5} M glycine to remove unsorbed metal ions. Various foreign ions were not sorbed and hence passed through the column. The effluent was collected and analyzed for foreign ion content. The tolerance limit of various foreign ions is shown in Table 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) highest tolerance limit. Amongst the inner transition elements, As compared lanthanum (III), cerium (III), gadolinium (II) low tolerance limit. The anion of inorganic and organic acids showed high tolerance limit

Table 4

Ion	Added as	Tolerance limit(mg)	Ion	Added as	Tolerance limit(mg)
Li^+	LiCl	1	Th^{4+}	$Th(NO_3)_4.6H_2O$	0.05
Na^+	NaCl	7	Sb^{3+}	$SbCl_3$	0.05
K^+	KCl	6	Sn^{2+}	SnCl2 2 H2O	1
Cs^+	CsCl	1	Ce^{3+}	$CeCl_3\,6H_2O$	0.5
Cr^{3+}	$Cr(NO_3)_3,9H_2O$	0.05	Gd3+	Gd(NO3)3, 6H2O	0.01
Mg^{2+}	$MgCl_2.6H_2O$	0.01	W^{6+}	$Na_2WO_4,4H_2O$	5
Ca^{2+}	$CaCl_2$	20	Zr^{4+}	$Zr(NO_3)_4,\ 4H_2O$	0.5
Sr^{2+}	$Sr(NO_3)_2$	18	La^{3+}	$La(NO_3)_3$	1
Ba^{2+}	$Ba(NO_3)_2$	0.01	NH_4^+	NH_4OH	3
Co^{2+}	$CoCl_2.6H_2O$	0.05	Citrate	Citric acid	8
Ni^{2+}	$NiCl_2.6H_2O$	0.01	CH_3COO^-	CH_3COOH	3
Mn^{2+}	$MnCl_2.4H_2O$	0.05	SO_4^{2-}	H_2SO_4	0.01
Zn^{2+}	$ZnCl_2$	0.1	Tartarate	Tartaric acid	4
Cd^{2+}	$(CH_3COO)_2\,CdH_2O$	0.05	EDTA	EDTA	0.05
Pb^{2+}	$Pb(NO_3)_2$	7	Ascorbate	Ascorbic acid	5
Fe^{3+}	$FeCl_3.6H_2O$	0.1	ClO_4^-	$HClO_4$	0.1
Al^{3+}	$AlCl_3.16H_2O$	<0.01	SCN^-	NaSCN	23
Cu^{2+}	CuCl2	0.05	Cl^-	HCl	0.1
Tl^{3+}	$Tl(NO_3)_3.3H_2O$	0.05	PO_4^{3-}	H_3PO_4	18
Mo^{6+}	$(NH_4)_6Mo_7O_{24}.4H_2O$	0.01	Bo_3^{3-}	H_3BO_3	0.5

3.5 Separation of beryllium (II) from multicomponent mixtures

Separation of beryllium (II) was carried out from number of associated elements in multicomponent mixture. The mixture containing Lithium(I), Copper(II), Lead(II), Cadmium(II), Nickel(II), Zinc (II) was passed through the poly[dibenzo-18-crown-6] column at 1×10^{-5} M glycine concentration, lithium(II) was not sorbed and hence passed through the column. The Copper (II), Lead (II), Cadmium (II), Nickel (II), Zinc (II) were sorbed. The sorbed Copper (II), was first eluted with 25 mL of 0.5 M LiOH. After that beryllium (II) were eluted with 4.0 M hydrochloric acid and effluents are analyzed spectrophotometrically. Using this method, separation of Lead (II), Cadmium (II), Nickel (II), Zinc(II) mixtures was achieved. The results are shown in (Table: 5).

Table 5: Separation of beryllium (II) from other elements (multicomponent mixture).

No.	Mixture	Taken µg	Recovery* %	Eluent
1	Li(I)	50	99.00	NSPC**
	Be(II)	10	99.5	4.0 M HCl
	Cu(II)	40	99.50	0.5 M LiOH
2	Li(I)	50	99.20	NSPC**
	Pb(II)	40	99.5	0.2M A.C
	Be(II)	10	98.5	4.0 M HCl
3	Li(I)	50	99.50	NSPC**
	CdII)	40	99.0	0.5M LiOH
	Be(II)	10	99.5	4.0 M HCl
4	Li(I)	50	99.50	NSPC**
	NiII)	40	98.5	0.2M LiOH
	Be(II)	10	99.5	4.0 M HCl
5	Li(I)	50	99.50	NSPC**
	Zn(II)	40	97.00	0.2M LiOH
	Be(II)	10	99.5	4.0 M HCl

*Average of triplicate analysis

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

3.6 Determination of beryllium (II) in beryl ore sample

A finely powdered 0.5 g of beryl ore sample was fused with a mixture of sodium hydroxide and sodium peroxide. The cooled mass was loosened with water. The precipitated hydroxides of beryllium, magnesium and iron were digested on water bath and later filtered. The precipitated mass was dissolved in dilute hydrochloric acid and diluted to 250 mL [19]. An aliquot of sample solution was taken and subjected to proposed method. The separated beryllium (II) content was analyzed by spectrophotometer using Eriochrome cyanine-R indicator. The amount of beryllium (II) found by triplicate determination is 13.35 % as against the reported value of 13.4%.

4. Conclusion

The important feature of this method is that using column chromatographic method and poly [dibenzo-18-crown-6] the separation of beryllium (II) from associated element in glycine medium has been achieved. The capacity of poly [dibenzo-18-crown-6] for beryllium (II) was found to be 0.65 ± 0.01 mmol/g of crown polymer. Beryllium (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%).

5. References

1. De K., Khopkar SM, Chalmers RA, 1970, 46.
2. Choppin G, Liljenzin J, Rydberg J. Jouranal Radiochemistry and Nuclear Chemistry 3rd Edition. Butterworth-Heinmann USA, 2002.
3. Toxicological Profile for Beryllium U. S. Department of Health and Human services Agency for toxic substances and Disease Registry, Atlanta, Georgia, 2002.
4. Meyer KC, Chest. 1994; 106:942.
5. Taylor TP, Ding M, Ehler DS, Koreman TM, Kaszuba JP, Sauer NN. Journal of. Enviromental science Engineering Toxic Hazard Subst. Contrl. 2003; A38:439.
6. Skine T, Hasegawa Y. Solvent extraction chemistry fundamental and applications Marcel Dekker, New York, 1977.
7. Khuhawar MY, Lanjwani SN. 1995; 43(12):1925.
8. Kamble PN, Mohite BS. Research Journal Chemistry and Environment. 2015; 19(7):19-22.
9. Walton HF, Rocklin RD. Ion exchange in analytical chemistry CRC press Boca Raton FL, 1990.
10. Korkish J, Ahluwalia SS. Talanta. 1964; 11:1623.
11. Ryabchikov DI, Bukhtiarov VE, Jouranl Anal. Chem. 1954; 9:196.
12. Suvardhan K, Suresh Kumar K, Rekha D, Jayraj B, Krishnamurti NG, Chiranjeevi P. Talata. 2006; 68(3):735.
13. Nukatsuka I., Ohba T, Ishida H, Satoh H, Ohzeki K, Ishida R. Analyst. 1992; 117:1513.
14. Hsu M, Chen M, Yang S, Kuo M. Anal Sci. 2004; 20:1967.
15. Pederson CJ. J Am.Chem.Soc. 1967; 89:7017.
16. Kolthoff JM. Anal. Chem. 1979; 51(5):21R.
17. Vogel AI. A textbook of quantitative inorganic analysis including elementary Instrumental analysis, The English language book society and Longman, 3rd edition, 1975, 558.
18. Marczenko Z. Spectrophotometric Determination of Elements Ellis Horword Limited, Chichester, 1976, 145.
19. [Sabale SR, Mohite BS. Journal of Chemistry and Chemical. Engineering. 2009; 3(6):37-43.