Sorption Study of Nickel(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 Ni(II) from an aqueous solution of 1×10^{-3} M Glycine using poly [dibenzo-18-crown-6] as stationary phase. The sorption of Ni(II) was quantitative 1×10^{-2}M to 1×10^{-6} M Glycine. The elution of Ni(II) was quantitative with 0.1–8.0 M HCl, 7.0-8.0M $HClO_4$, 5.0-8.0 M HBr M 0.1-8.0 M H_2SO_4 and 2.0-8.0M CH_3COOH The capacity of poly [dibenzo-18-crown-6] for Ni(II) was found to be 3.15 $\pm$ 0.01 mmol g^{-1} of crown polymer. The effects of concentrations of Glycine, Ni(II), foreign ions and eluents have been studied. Ni(II) was separated from a number of cations in multi component mixtures. The applicability of the proposed method was ascertained for the determination of Ni(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$\pm$2%).

Graphical Abstract
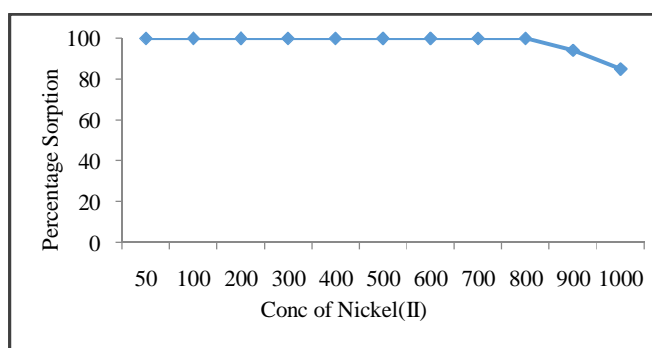
Effect of varying concentration of Ni(II)

Keywords: Sorption, Separation, Ni(II), Glycine, poly [dibenzo-18- crown-6], Chromatography.
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INTRODUCTION

Nickel in nature is mainly available in the form of ores like Gernirite, Magnesium nickel silicate of variable composition. The important oxidation state of nickel is Ni(II). In olden days nickel is used as a coinage metal. Now days nickel becomes an important element, not only for industry, but also for biological systems. In rapidly expanding analytical fields, such as environmental, biological and material monitoring for trace metals. Nickel is used in ceramic industry and also used in batteries which are in convincing to the environment, dietary deficiency of nickel leading to various pathological manifestations. Nickel is relatively non toxic element. The high concentration of the nickel does show serious health hazards. The high incident of respiratory track moplacia and dermatitis has been observed when exposed by nickel refineries. In views of this separation and determination of nickel from associated elements is indispensable. Therefore, it is very important to develop sensitive, rapid and economical method for quantitative determination of it's trace amount in various samples of environmental importance. Several analytical techniques have been monitored for the determination of trace level Ni(II), it includes atomic absorption spectrometry[1-4] Inductive coupled plasma emission spectrometry[5-7] and X-Fluorence Spectrometry[8, 9] were reviewed. A few reagents are available for the spectrophotometric [10-18] determination of nickel (II).

Literature survey indicated that several spectrophotometric methods [19-36] were reported for the determination of Ni(II) by using various chromogenic reagents.

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

MATERIALS AND METHODS

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 Ni(II) was prepared by dissolving 0.2808 g of nickel sulphate hepta hydrate (AR, Merck) in 100 mL of distilled deionized water and standardized gravimetrically using dimethyl glyoxime from complexometrically [37]. A solution containing 50 µg mL^{-1} of Ni(II) was prepared by appropriate dilution of standard stock solution. Glycine solution (1×10^{-1} M) was prepared by dissolving 1.875 g of glycine in distilled deionized 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.

50 µg of Nil(II) was mixed with glycine in 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^{-1}. The column was then washed with the same concentration of glycine. The sorbed Nil(II) was then eluted with different eluting agents (described later) at the flow rate of 0.5 mL min^{-1}. 5.0 mL fraction were collected and Ni(II) in the aqueous phase was determined spectrophotometrically with dimethyl glyoxime at 445 nm. The concentration of Nil(II) was calculated from a calibration graph.

RESULTS AND DISCUSSION

Sorption of Ni(II) on poly[dibenzo-18-crown-6] as a function of glycine concentration: Sorption studies of Ni(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 Ni(II) was carried out with 4.0 M hydrochloric acid. It was found that there was quantitative (100%) sorption of Ni(II) from 1×10^{-2} M to 1×10^{-6} M glycine. The results are shown in (Table 1) and (Figure 1). The subsequent sorption studies of Ni(II) were carried out with 1×10^{-3} M glycine.
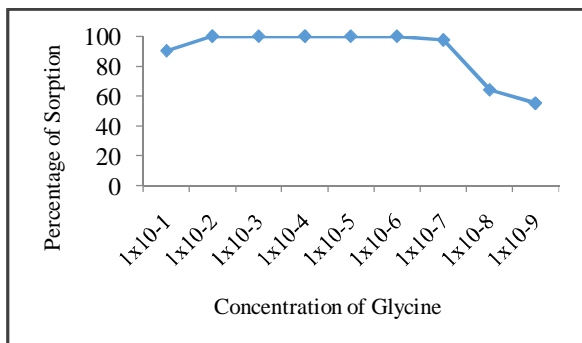

Glycine concentration (M)	Sorption of Ni(II) (%)
1×10^{-1}	90.24
1×10^{-2}	100
1×10^{-3}	100
1×10^{-4}	100
1×10^{-5}	100
1×10^{-6}	100
1×10^{-7}	97.40
1×10^{-8}	64.20
1×10^{-9}	55.33

Figure 1. Sorption of Nil(II) as a function of glycine concentration Ni=50 μgmL^{-1}; Eluent= 4.0 M HCl.

Table 1. Sorption of Nickel(II) as a function of glycine concentration Ni=50 μg mL^{-1}; Eluent= 4.0 M HCl

Elution study of Ni(II) with various eluting agents: 50 μg mL^{-1} of Nickel(II) was sorbed on the poly[dibenzo-18-crown-6] column at 1×10^{-3} M glycine concentration. After sorption, elution of Ni(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 Ni(II) with various eluting agents is shown in (Figure 2). The results (Table 2) showed that Ni(II) was quantitatively eluted with 0.1 M to 8.0 M hydrochloric acid, 0.1 M to8.0 M sulphuric acid and 5.0 M to8.0 M hydrobromic acid, 7.0 M to 8.0 M Perchloric acid and 2.0 M to 8.0 M acetic acid. Further elution studies of Ni(II) in this work was carried out with 1.0 M hydrochloric acid.

Table 2. Elution of Nickel(II) with different eluting agents

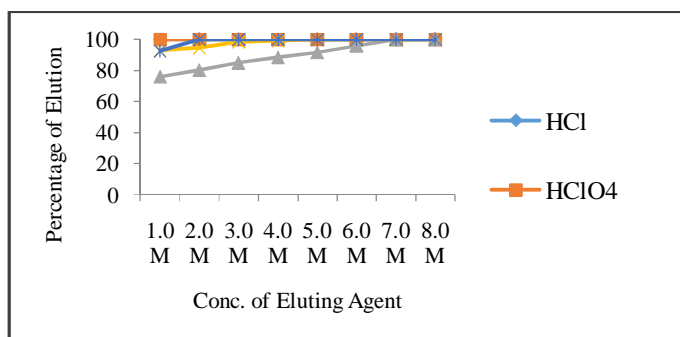| Conc. Acid(M)	0.1M	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M	5.0 M	6.0 M	7.0 M	8.0 M
	Percentage elution of Nickel(II)									
HCl	100	100	100	100	100	100	100	100	100	100
$HClO_4$	100	100	100	100	100	100	100	100	100	100
H_2SO_4	65.15	70.96	75.82	80.12	84.76	88.23	91.56	95.82	100	100
HBr	88.24	90.66	92.81	94.64	98.25	99.20	100	100	100	100
CH_3COOH	85.20	88.49	92.58	100	100	100	100	100	100	100

Figure 2. Elution profile of Ni(II) with various eluting agents

Effect of varying concentration of Ni(II): In order to find out the capacity of poly[dibenzo-18-crown-6] for the Ni(II), the concentration of Ni(II) was varied from 50-1000 µg 10mL^{-1} in glycine and 1.0 M hydrochloric acid as eluent. The results (Table 3) showed that the sorption of Ni(II) was quantitative (100%) up to 800 µg. With increase in concentration of Ni(II) there was decrease in the percentage sorption of Ni(II) and is shown in the (Figure 3) From this study it was found that the capacity of poly[dibenzo-18-crown-6] for Ni(II) was found to be 1.24 ± 0.01 mmol g^{-1} of crown polymer.

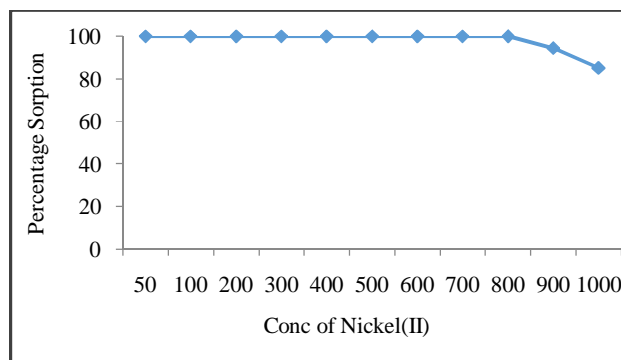| Concentration of Ni(II) (µg)	Percentage sorption
50	100
100	100
200	100
300	100
400	100
500	94.29
600	85.12
700	82.45
800	78.20

Table 3. Effect of varying concentration of Ni(II)

Figure 3. Effect of varying concentration of Ni(II)

Separation of Ni(II) from binary mixtures: An aliquot of solution containing 50 µg of Nickel(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 $\pm2\%$ deviation in the recovery of Ni(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^{-1}. Subsequently the column was washed with 15 mL of 5×10^{-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 analyzed for foreign ion content. The tolerance limit of various foreign ions is shown in table 4. The most of the alkali metals show high tolerance limit. In case of alkali metal lithium(I) cesium(I) and alkaline earth

Table 4. Separation of Ni(II) from binary mixtures Ni(II)- 50 µg,
sorption- 1×10^{-3} M L-glycinee eluent- 4.0 M HCl

Ion	Added as	Tol. Limit (mg)	Ion	Added as	Tol. Limit
Li$^+$	LiCl	24	Tl^{3+}	Tl(NO$_3$)$_3$.3H$_2$O	6
Na$^+$	NaCl	12	La^{3+}	La(NO$_3$)$_3$.6H$_2$O	4
K$^+$	KCl	8	Ce^{3+}	CeCl$_3$.6H$_2$O	1
Rb$^+$	RbCl	5	V^{4+}	VOSO$_4$.4H$_2$O	2
Cs$^+$	CsCl	30	Th^{4+}	Th(NO$_3$)$_4$	0.1
NH$_4^+$	NH$_4$Cl	16	Cr^{6+}	K$_2$Cr$_2$O$_7$	2.5
Be^{2+}	BeSO$_4$.4H$_2$O	5	Mo^{6+}	(NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O	0.3
Mg^{2+}	MgCl$_2$.6H$_2$O	18	W^{6+}	Na$_2$WO$_4$O.4H$_2$O	7
Ca^{2+}	CaCl$_2$	16	Cl$^-$	HCl	7
Sr^{2+}	Sr(NO$_3$)$_2$	3	Br-	HBr	11
Ba^{2+}	Ba(NO$_3$)$_2$	1	SCN$^-$	NaSCN	13
Co^{2+}	CoCl$_2$.6H$_2$O	0.6	ClO$_4^-$	HClO$_4$	7.4
Mn^{2+}	MnCl$_2$.4H$_2$O	0.5	CH$_3$COO$^-$	CH$_3$COOH	14
Zn^{2+}	ZnCl$_2$	5.8	SO$_4^{2-}$	H$_2$SO$_4$	9
U^{6+}	UO$_2$(NO$_3$)$_2$.6H$_2$O	10	BO$_3^{3-}$	H$_3$BO$_3$	4
Pb^{2+}	Pb(NO$_3$)$_2$	4.5	Tartrate	Tartaric acid	9
Cr^{3+}	Cr(NO$_3$)$_3$.9H$_2$O	0.1	EDTA	EDTA	2.5
Fe^{3+}	FeCl$_3$.6H$_2$O	1.7	Ascorbate	Ascorbic acid	8
Al^{3+}	Al(NO$_3$)$_3$.9H$_2$O	0.05			

metals calcium(II) and magnesium(II) tolerates strongly. Most of the p-block and d-block elements were sorbed and shows low tolerance limit. Amongst the inner transition elements chromium(VI) and aluminum(III) show low tolerance limit. The anion of inorganic and organic acids showed high tolerance limit (Table 4).

Separation of Ni(II) from Multicomponent mixtures: Separation of Ni(II) was carried out from number of associated elements in multi component mixture. The mixture containing lithium(I), zinc(II), lead(II), cadmium (II), thorium(IV), uranium(VI), magnesium (II), calcium (II) and strontium (II) was passed through the poly[dibenzo-18-crown-6] column at 1×10^{-3} M glycine concentration, lithium(I), magnesium (II), calcium (II) and strontium (II) was not sorbed and hence passed through the column. The zinc(II), lead(II), cadmium (II), thorium(IV), uranium(VI) were sorbed. The sorbed zinc(II) was first eluted with 25 mL of 0.5 M LiOH. After that Ni(II) were eluted with 4M hydrochloric acid and effluents are analyzed spectrophotometrically. Using this method separation of lead(II), cadmium (II), thorium(IV) and uranium(VI) mixtures was achieved. The results were shown in table 5.

Table 5. Separation of Ni(II) from multi component mixture

No.	Mixture	Taken μg	Found* μg	Recovery %	Sorption Condition	Eluent
1	Li(I)	50	49.5	90.0	1×10^{-3} M Glycine	NSPC**
	Zn(II)	40	39.9	99.80		0.5 M LiOH.
	Ni(II)	50	49.5	99.00		4.0 M HCl
2	Li(I)	50	50	100	1×10^{-3} M Glycine	NSPC**
	Pb(II)	40	39.8	99.50		0.2MA.C.
	Ni(II)	50	49.9	99.80		4.0 M HCl
3	Mg(II)	50	49.5	90.0	1×10^{-3} M Glycine	NSPC**
	Th(IV)	40	39.7	99.25		0.2M A.C.
	Ni(II)	50	49.8	99.60		4.0 M HCl
4	Li(I)	50	50	100	1×10^{-3} M Glycine	NSPC**
	Cd(II)	40	39.6	99.20		0.2MLiOH.
	Ni(II)	50	50	100		4.0 M HCl
5	Ca(II)	50	49.7	99.40	1×10^{-3} M Glycine	NSPC**
	Th(IV)	40	39.8	99.50		0.2M A.C.
	Ni(II)	50	49.8	99.60		4.0 M HCl
6	Sr(II)	50	49.6	99.20	1×10^{-3} M Glycine	NSPC**
	U(VI)	40	39.7	99.25		0.2M A.C.
	Ni(II)	50	49.8	99.60		4.0 M HCl
7	Mg(II)	50	49.7	99.40	1×10^{-3} M Glycine	NSPC**
	U(VI)	40	39.5	98.75		0.2M A.C.
	Ni(II)	50	49.9	99.80		4.0 M HCl

* Average of triplicate analysis
** NSPC = No Sorption Passing through the Column

APPLICATION

Determination of Ni(II) in Aluminium based alloy: About 0.4 g alloy samples was treated with 15 mL of 1:1 HCl, to this 3 mL of HNO_3 was added and the contents boiled until dissolution was complete. Then, 10 mL of water and 40 mL of 4N ammonium hydroxide solution were added and filtered through a Whatman filter paper (No.41). The filtrate was collected into 25 mL volumetric flask and made up to the marks with distilled water.

Sample	Present%	Found %
BAS-20	1.93	1.91
BAS-85	0.91	0.90
Cu-Ni alloy	31.20	31.15

Determination of Ni(II) in Vegetable Oils: 100g of hydrogenated groundnut oil (edible) was dried in a hot air oven at 100°C and subsequently dissolved in 20ml mixture of 1:2:5 H_2SO_4:H_3PO_4:HNO_3. The contents were heated until sulphurous fumes were evolved and the volume was reduced to about 5 mL. A little quantity of distilled water was added and filtered through an acid washed Whatman 41 filter paper into a 100 mL volumetric flask and made up to the mark with distilled water.

Sample	Present µg mL^{-1}	Found µg mL^{-1}
Hydrogenated Groundnut Oil	0.56	0.55

CONCLUSION

The important feature of this method is that using column chromatographic method and poly[dibenzo-18-crown-6] the separation of Ni(II) from associated element in Glycine medium has been achieved. The capacity of poly[dibenzo-18-crown-6] for Nickel(II) was found to be 1.24 ± 0.01 mmol g^{-1} of crown polymer. Ni(II) was separated from number of cations in binary as well as multi component mixtures. The method was extended to the determination of nickel in real sample. The aim of present investigation is to demonstrate a simple, selective and cheap method and has good reproducibility (approximately $\pm 2\%$).

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