

# Extraction - Chromatographic Separation of Beryllium With Bis(2-ethylhexyl)phosphoric Acid

Miss Yi Yu Vin and Shripad M. Khopkar

Department of Chemistry, Indian Institute of Technology, Powai, Bombay-400 076, India

Beryllium was extracted from 0.01 M hydrochloric acid on a silica gel column impregnated with bis(2-ethylhexyl)phosphoric acid. The beryllium was stripped with 1 M hydrochloric acid and was determined spectrophotometrically at 525 nm as its complex with Eriochrome Cyanine R. Beryllium was separated from the alkali and alkaline earth metals, manganese, iron(III), cobalt, nickel, copper, zinc, aluminium, thallium(III), gallium, molybdenum and germanium in binary mixtures and from copper, zinc, iron(III), aluminium, lead, barium and calcium in multi-component mixtures. The method was extended to the determination of beryllium in beryl.

**Keywords:** *Beryllium determination; bis(2-ethylhexyl) phosphoric acid; extraction - chromatography*

Bis(2-ethylhexyl)phosphoric acid (HDEHP) is slightly soluble in water but extremely soluble in organic solvents, in which it exists as a dimer. On account of its low solubility in water and stability towards hydrolysis it has proved to be an effective extractant for the reversed-phase extraction - chromatographic separation of lanthanides<sup>1</sup> and gold.<sup>2</sup> In batch extraction beryllium has been quantitatively extracted with 0.5 M HDEHP from 0.5 M nitric acid,<sup>3</sup> but in column work these conditions of extraction had to be modified. Beryllium has been shown to exhibit the maximum extractability of the alkaline earth metals in HDEHP.<sup>4</sup> The alkali and alkaline earth metals have been separated on paper with HDEHP as the mobile phase,<sup>5,6</sup> and aluminium has been separated on paper from hydrochloric acid media.<sup>7</sup> Beryllium has been separated from many elements with liquid anion exchangers,<sup>8</sup> and from zinc, aluminium and magnesium in thiocyanate media with tributyl phosphate as the extractant.<sup>9,10</sup> Attempts have also been made to separate beryllium from zirconium, thorium and uranium(VI) with Aliquat 336 S.<sup>11</sup>

However, systematic investigations into the extraction - chromatographic separation of beryllium with HDEHP as the stationary phase on a silica gel column have not been reported so far and such studies are reported in this paper.

## Experimental

### Apparatus

An ECIL Model 866C spectrophotometer with matched Corex glass cuvettes (optical path length 1 cm), an ELICO Model LI-120 pH meter with a combined glass electrode and a Pyrex chromatographic column (20 × 0.8 cm i.d.) with a glass-wool plug at the bottom were used.

### Reagents

Bis(2-ethylhexyl) phosphoric acid (Schuchardt, Munich, FRG) was used without purification.

A beryllium stock solution was prepared by dissolving 2.270 g of beryllium nitrate tetrahydrate (AnalaR grade, BDH Chemicals) in 5 ml of concentrated hydrochloric acid. The solution was evaporated to dryness, extracted with distilled water and made up to 100 ml, before being standardised gravimetrically.<sup>12</sup> The solution contained 0.99 mg ml<sup>-1</sup> of beryllium. A solution containing 10 µg ml<sup>-1</sup> of beryllium was prepared by appropriate dilution.

Silica gel (100–200 mesh) was rendered hydrophobic and coated with HDEHP by the following procedure. Silica gel

was first dried at 120 °C for 2 h. A stream of dry nitrogen was then passed through a small durant tube containing 25 ml of dimethyldichlorosilane. The dimethyldichlorosilane vapours were passed through a U-tube containing silica gel for 2–3 h to replace the free hydroxyl group near the surface of the silyl groups. Anhydrous methanol was used for washing the treated silica gel in order to form methoxy derivatives. The treated gel was then dried at 100 °C. On average 2–3 ml of dimethyldichlorosilane were adequate to render 10 g of silica gel hydrophobic.

A homogeneous solution of 5 ml of HDEHP in benzene was prepared and was transferred into a flask containing 20 g of hydrophobic silica gel. Benzene was slowly removed from the suspension using a rotary vacuum evaporator until dry silica gel was obtained. A low vacuum was applied to remove air from the micropores and to accelerate the evaporation of benzene. About 4 g of coated silica gel were slurred with distilled water and poured into the column. An 8-cm column bed was employed.

### General Procedure

To an aliquot of solution containing 10 µg ml<sup>-1</sup> of beryllium, 1 ml of 0.01 M hydrochloric acid was added and the mixture was passed through the column at a flow-rate of 1 ml min<sup>-1</sup>. The retained beryllium was stripped with various mineral acids. Ten 2-ml fractions were collected and beryllium was determined spectrophotometrically at 525 nm in each fraction as its complex with Eriochrome Cyanine R.<sup>13</sup>

## Results and Discussion

In batch experiments<sup>3</sup> beryllium was quantitatively extracted with 0.5 M HDEHP in toluene from 0.25 M nitric acid. These conditions were modified in the extraction - chromatographic method reported here.

Systematic studies on the extraction of beryllium on the silica gel column coated with HDEHP indicated that beryllium was quantitatively extracted and retained on the column from 0.01–0.25 M hydrochloric or nitric acid. Similar extraction was not possible from sulphuric acid. Therefore, all extractions were carried out from 0.01–0.25 M hydrochloric acid. This also facilitated the spectrophotometric determination of beryllium from chloride media.

After extraction beryllium was stripped from the column with various mineral acids such as 1–3 M hydrochloric, 2–3 M nitric and 1–2 M sulphuric acid. With lower concentrations of nitric and sulphuric acids the stripping was not quantitative. The results obtained are given in Table 1.

**Table 1.** Results of the stripping of beryllium

Eluent	Concentration of eluent/M	Peak elution volume/ml	Volume required for total recovery/ml	Recovery, %
HCl . . . .	1.0	4	16	101.8
	1.5	4	16	95.0
	2.0	4	16	100.0
	3.0	4	16	101.0
HNO <sub>3</sub> . . . .	1.0	4	16	59.9
	1.5	4	16	47.0
	2.0	4	16	101.3
	3.0	4	16	103.7
H <sub>2</sub> SO <sub>4</sub> . . . .	0.5	2	16	75.8
	1.0	2	16	100.0
	2.0	4	16	100.0

**Table 2.** Separation of beryllium from binary mixtures. Amount of Be = 10 µg

Foreign ion	Amount taken/mg	Beryllium found/µg	Recovery of Be, %	Stripping agents for other ions	Volume of stripping agent/ml
Li . . . .	2.5	9.9	99.0	H <sub>2</sub> O	20
Na . . . .	5.0	10.05	100.5	0.01 M HCl	15
K . . . .	2.5	9.25	92.5	0.01 M HCl	15
Rb . . . .	2.5	10.1	101.0	0.01 M HCl	15
Mg . . . .	4.8	10.0	100.0	0.01 M HCl	15
Ca . . . .	2.5	9.8	98.0	0.1 M HCl	18
Sr . . . .	5.0	9.9	99.0	H <sub>2</sub> O	20
Ba . . . .	5.0	9.8	98.0	0.01 M HCl	15
Mn <sup>II</sup> . . . .	5.0	10.0	100.0	0.1 M HCl	15
Fe <sup>III</sup> . . . .	0.5	9.75	97.5	4 M HCl	20
Co <sup>II</sup> . . . .	5.1	10.0	100.0	H <sub>2</sub> O	20
Ni . . . .	4.8	10.1	101.0	H <sub>2</sub> O	20
Cu . . . .	5.0	10.2	102.0	0.01 M HCl	10
Zn . . . .	1.0	9.76	97.6	0.1 M HCl	15
Al . . . .	1.0	10.02	100.2	0.01 M HCl	20
Ga . . . .	2.5	9.4	94.0	H <sub>2</sub> O	20
Tl <sup>III</sup> . . . .	2.5	9.9	99.0	H <sub>2</sub> O	20
Ge . . . .	2.5	9.95	99.5	H <sub>2</sub> O	15
Pb . . . .	5.0	9.82	98.2	0.1 M HCl	15
Mo . . . .	1.0	9.64	96.4	0.01 M HCl	15

### Separation of Beryllium from Binary Mixtures

When beryllium was extracted on to the column from 0.01 M hydrochloric acid, lithium, sodium, potassium, rubidium, magnesium, strontium, barium, cobalt, nickel, copper, aluminium, gallium, thallium, germanium and molybdenum were not retained and passed through. Hence after washing the column with water, beryllium was stripped with 1 M hydrochloric acid and was separated from these elements. Although manganese, calcium, iron(III), zinc and lead were retained along with beryllium, they were stripped from the column before beryllium with dilute hydrochloric or nitric acid; beryllium was then stripped with 1 M hydrochloric acid. Finally, beryllium and iron(III) were separated by first stripping beryllium with 1 M hydrochloric acid followed by stripping iron(III) with 4 M hydrochloric acid. The results of these separations of beryllium from binary mixtures are given in Table 2.

### Separation of Beryllium from Tertiary Mixtures

When a mixture of copper, zinc, beryllium and iron(III) was passed into the column in 0.01 M hydrochloric acid, copper was not retained and passed through the column. The extracted zinc was stripped with 0.1 M hydrochloric acid then beryllium with 1 M hydrochloric acid and finally iron(III) with 4 M hydrochloric acid.

When a mixture of aluminium or magnesium, lead and beryllium was passed into the column in 0.01 M hydrochloric acid, aluminium or magnesium were not retained and passed

through the column. The retained lead was stripped with 0.1 M hydrochloric acid and beryllium with 1 M hydrochloric acid.

When a mixture of aluminium, beryllium and iron(III) was passed into the column in 0.01 M hydrochloric acid, aluminium was not retained and passed through. The retained beryllium was stripped with 1 M hydrochloric acid followed by stripping of iron(III) with 4 M hydrochloric acid.

When a mixture of barium, calcium and beryllium was passed into the column in 0.01 M hydrochloric acid, barium was not retained, whereas calcium was stripped with 0.1 M hydrochloric acid and beryllium with 1 M hydrochloric acid.

In all these separations the volume of the eluent employed was 20 ml and after stripping the elements were determined spectrophotometrically in the aqueous phase using the chromogenic ligands listed in Table 3. An attempt to separate beryllium sequentially from alkaline earth metals was not successful.

### Analysis of Beryl

A 0.5-g amount of finely powdered beryl ore was fused with a mixture of sodium hydroxide and sodium peroxide. The cooled melt was dissolved with water. The precipitated hydroxides of beryllium, magnesium and iron were digested on a steam-bath and then filtered. The precipitated mass was dissolved in dilute hydrochloric acid and diluted to 250 ml with distilled water.

An aliquot of sample containing beryllium, magnesium and iron was passed through the column with 0.01 M hydrochloric

**Table 3.** Separation of beryllium from tertiary mixtures

Sample No.	Metal ion	Stripping agent	Amount taken/ $\mu\text{g}$	Recovery, %	Reagents used for spectrophotometric determination	$\lambda_{\text{max}}$ / nm
1	Cu	0.01 M HCl	100	101.5	Cupral	436
	Zn	0.1 M HCl	100	99.0	Zircon	620
	Be	1 M HCl	10	93.5	Eriochrome Cyanine R	525
	Fe	4 M HCl	50	97.0	1,10-Phenanthroline	515
2	Al/Mg	0.01 M HCl	100	101.5	Alizarin Red S/Xylenol Orange	530
	Pb	0.1 M HCl	100	98.0	Pyrogallol Red	520
	Be	1 M HCl	10	102.0	Eriochrome Cyanine R	525
3	Al	0.01 M HCl	100	96.0	Alizarin Red S	490
	Be	1 M HCl	10	98.5	Eriochrome Cyanine R	525
	Fe	4 M HCl	50	99.0	1,10-Phenanthroline	515
4	Ba	0.01 M HCl	100	99.8	Sulphonazo III	640
	Ca	0.1 M HCl	100	99.5	Flame emission spectrometry	526
	Be	1 M HCl	10	100.5	Eriochrome Cyanine R	525
5	Mn	0.1 M HCl	100	98.0	Formaldehyde	455
	Be	1 M HCl	10	96.5	Eriochrome Cyanine R	525
	Fe	4 M HCl	100	99.5	1,10-Phenanthroline	515

acid at a flow-rate of  $1 \text{ ml min}^{-1}$ . Magnesium was not retained and passed through the column. The extracted beryllium was stripped with 20 ml of 1 M hydrochloric acid followed by stripping of iron with 4 M hydrochloric acid. Beryllium was determined spectrophotometrically as described previously.

The results of triplicate analyses of beryl solution indicated that the amount of beryllium present was 4%, the same as determined by atomic absorption spectrometry.

### Conclusion

The proposed method for the separation of beryllium is rapid, simple and selective. The separation of beryllium from most of the alkali and alkaline earth metals is important as they belong to the same group of S-block elements and are generally associated in nature. The separation of beryllium from zinc, copper, aluminium and lead is also important as they are associated in various alloys. The method is reproducible and requires just 3 h for separation and determination.

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