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Solvent Extraction Separation of Beryllium(II) from Aluminum(III) by Cyanex 921 (TOPO)

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ABSTRACT

Cyanex 921, a neutral extractant, has been used for the extraction of beryllium(II) from basic media and employed for the separation of beryllium(II) in the presence of aluminum(III). Cyanex 921 diluted in cyclohexane extracted beryllium(II) in the 8.0–10.0 pH range and aluminum(III) between 4.5–5.5 pH. The selectivity of beryllium(II) over aluminum(III) was high in the 8.0–10.0 pH range. The extracted beryllium(II) was stripped with 0.5 M NaOH without any significant loss of the ligand while loaded aluminum(III) was stripped with 2 M HCl. The extractability of beryllium(II) and aluminum(III) was also studied separately as a function of pH, temperature, equilibration time, and stripping ability with NaOH, KOH, HCl, HNO_3, H_2SO_4, and $HClO_4$. Based on these results, a sequential method was developed for the separation of beryllium(II) from aluminum(III).

Key Words. Solvent extraction; Separation, Beryllium(II); Aluminum(III); Cyanex 921; Recovery

INTRODUCTION

Use of beryllium in nuclear reactors as one of the most effective neutron moderators and reflectors is well known. It is also widely used in x-ray tubes

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since it transmits x-rays 17 times better than aluminum and Lindamenn glass. Aluminum in the sulfate form is used for water treatment, in the paper industry, as a mordant in dyeing, and as a catalyst support. Beryllium is one of the most toxic elements among the environmental metal pollutants with a threshold limiting value (TLV) 2.0 $\mu g/m^3$. Therefore, it is necessary to determine beryllium at microgram concentrations.

During the last decade, alkyl esters of organophosphorous acids as liquid–liquid extraction reagents have been used for both chemical and engineering purposes. Neutral extractants such as Cyanex 921, Cyanex 923, Cyanex 925, TBP, TBPO, and TPPO are used for several purposes including the recovery of uranium, thorium, and plutonium as well as in many other chemical separation techniques and hydrometallurgical processes (1–4).

Beryllium(II) was extracted quantitatively with 0.5 M dibutyl phosphoric acid in toluene (5) and with a 0.1 M HCl–TBP system in LiCl medium (6). Extraction of beryllium(II) with other chelating reagents has also been reported (7–9). Quantitative extraction of beryllium(II) into chloroform is also possible from an aqueous solution containing 0.05 M cupferron at about pH 3 (10). Aluminum(III) was extracted with TBP from hydrochloric acid solution containing thiocyanate ion as $Al(SCN)_3 \cdot 3TBP$ (11). Acetylacetone is often used for the extraction of aluminum(III). The extraction is about 90% with pure acetylacetone or a 0.1 M solution in benzene above pH 5 (12–14). Aluminum(III) is also selectively and quantitatively extracted from an acetate-buffered solution containing 0.1 M cupferron at pH 2.5 to 4.5 into MIBK with 5 minutes of shaking (15). Separation of gallium(III) from basic sodium aluminate solution by 10% alkanoyl oxines in $CHCl_3$ was also carried out at pH 13 (16).

There has been much less work done on the extraction and separation of aluminum(III) and beryllium(II) with neutral extractants; most of the work carried out was with acidic extractant like di(2-ethylhexyl) phosphoric acid, i.e., HDEHP. Beryllium(II) was extracted quantitatively with HDEHP in toluene (17) while aluminum(III) was quantitatively extracted with 0.1 M HDEHP solution in kerosene around pH 3.6 by rapid stirring for 3 hours (18). The species extracted was reported to be probably solvated by three acid molecules in the organic phase (19). The separation of aluminum(III) and beryllium(II) was carried out quantitative by HDEHP in toluene by taking advantage of some difference in their stripping agents (20).

In the present study the separation of aluminum(III) and beryllium(II) from their mixture is found to be possible by taking advantage of the pH, the reagent concentration, and the stripping agent. The method was extended for the separation of aluminum(III) and beryllium(II) in different ratios.

EXPERIMENTAL

Apparatus and Reagents

The extractant tri-*n*-octyl phosphine oxide (Cyanex 921), also known as TOPO, was supplied by American Cyanamid Company and used without further purification. Known amount of $BeCO_3$ and $Al_2(SO_4)_3 \cdot 18H_2O$ were dissolved separately in a minimum quantity of concentrated H_2SO_4 and diluted to 1 L with doubled distilled water and standardized by a gravimetric method (21). All the other chemicals used were of analytical grade. An Elico model LI-120 pH meter with a combined electrode was used for pH measurement studies and a GBC UV-Visible 911A spectrophotometer with 10 mm corex quartz cuvettes was used for absorbance measurements.

Procedure

Both beryllium(II) and aluminum(III) aliquots containing 1.5 μg/mL were taken separately and equilibrated with Cyanex 921 dissolved in cyclohexane for the required shaking time, i.e., 5–6 minutes, after adjusting their aqueous solutions to pH 8.0 and 5.0, respectively. The aqueous to organic phase ratio was maintained at 1:1 for both metals. The organic phase containing the metal-extracted species was then stripped with such different stripping agents as HCl, HNO_3, H_2SO_4, and $HClO_4$ acids and such bases as NaOH and KOH. It was found that NaOH (0.5–1.0 M) was very effective for the quantitative recovery of beryllium(II) and that of HCl (2.0–2.5 M) was effective for the recovery of aluminum(III). The amount of metals extracted was determined by methods given in the literature, i.e., beryllium(II) by the quinalizarin method and aluminum(III) by the aluminon method (22). All the experiments were carried out at room temperature except for those on the effect of temperature on distribution equilibria.

RESULTS AND DISCUSSION

Effect of pH and Reagent Concentration on the Extraction of Beryllium(II) and Aluminum(III)

The effect of pH on the percentage extraction of beryllium(II) and aluminum(III) with 5×10^{-3} M and 1×10^{-1} M Cyanex 921 in cyclohexane, respectively, was determined. The extraction of beryllium(II) was quantitative in the 8.0–10.0 pH range and that of aluminum(III) in the 4.5–5.5 pH range (Fig. 1). Hence, all the extraction was carried out at pH 8.0 [for beryllium(II)] and pH 5.0 [for aluminum(III)].

Extraction of beryllium(II) and aluminum(III) was carried out by varying the reagent concentration (1×10^{-1} M to 5×10^{-3} M) while keeping other parameters like pH, period of equilibration, diluent, and temperature constant.

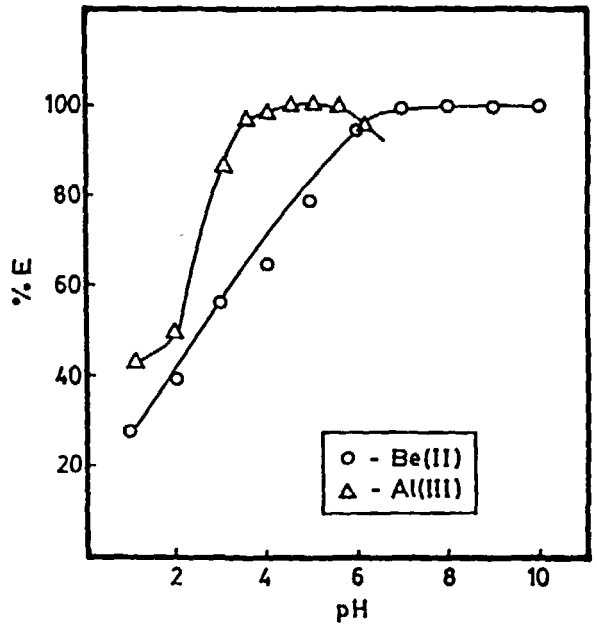


FIG. 1 Effect of pH on the percentage extraction of Al(III) and Be(II).

Extraction increased with an increase in reagent concentration. The extraction of beryllium(II) was quantitative with 5×10^{-3} M Cyanex 921; that of aluminum(III) with 1×10^{-1} M Cyanex 921 in cyclohexane.

Effect of Diluents

The extraction of beryllium(II) and aluminum(III) was performed with 5×10^{-3} M and 1×10^{-1} M Cyanex 921 in different diluents. The extraction was found to be quantitative with cyclohexane, toluene, and xylene, but it was not quantitative with chloroform, carbon tetrachloride, methyl isobutyl ketone, and hexane (Table 1). Cyclohexane was the best diluent for extraction because it provided better phase separation.

Effect of Various Stripping Agents

The metals beryllium(II) and aluminum(III) were stripped from their loaded organic phases with different strength mineral acids like HCl, HNO_3, H_2SO_4, and $HClO_4$ and bases such as NaOH and KOH. The stripping of beryllium(II) was quantitative with 0.5 M NaOH while that of aluminum(III) was quantita-

TABLE 1
Effect of Various Diluents on the Distribution Ratio of Be(II) and Al(III)[a]

Diluents	Be(II) (D)	Al(III) (D)
Cyclohexane	999	999
Toluene	999	6.352
Xylene	11.333	999
Hexane	999	—
Dichloromethane	2.546	0.669
$CHCl_3$	1.739	0.428
CCl_4	4.980	0.669
MIBK	3.201	—

[a] Amount of Be(II)/Al(III) added = 15 μg/10 mL. Reagent concentration = 5×10^{-3} M (for Be) and 1×10^{-1} M (for Al). pH 8.0 (for Be) and 5.0 (for Al).

tive with 2.0 M HCl. Therefore, NaOH and HCl were preferred as respective stripping agents for beryllium(II) and aluminum(III) since spectrophotometric determination could be done without the need for dry ashing. No effective separation was observed with H_2SO_4 and $HClO_4$ (Table 2).

TABLE 2
Effect of Stripping Agents on the Percentage Recovery of Beryllium(II) and Aluminum(III)[a]

	0.5 M	1.0 M	1.5 M	2.0 M
% Recovery of Be(II):				
HCl	88.3	94.3	99.9	99.9
HNO_3	46.7	53.2	58.1	99.9
H_2SO_4	15.8	10.0	3.0	0.0
$HClO_4$	0.0	0.0	0.0	5.0
NaOH	99.9	99.9	[b]	[b]
KOH	45.8	58.3	50.0	30.1
% Recovery of Al(III):				
HCl	90.1	98.3	99.0	99.9
HNO_3	98.0	99.9	99.9	99.9
H_2SO_4	30.5	23.8	15.5	5.0
$HClO_4$	0.0	0.0	6.8	10.0
NaOH	06.5	05.3	02.1	00.0
KOH	00.0	03.1	02.0	01.0

[a] Amount of Be(II) and Al(III) added is 15 μg/10 mL each. Reagent concentration = 5×10^{-3} M (for Be) and 1×10^{-1} M (for Al) in cyclohexane. pH 8.0 (for Be) and 5.0 (for Al).
[b] Emulsion.

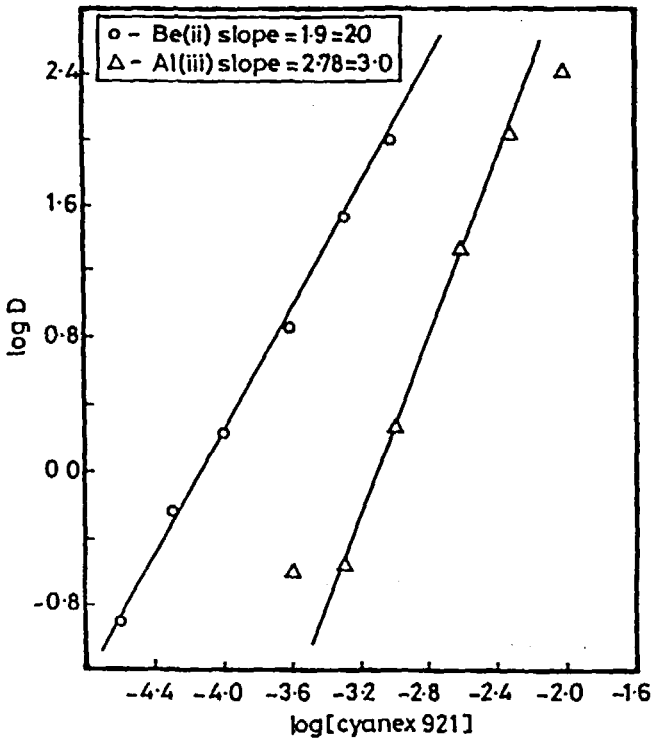


FIG. 2 Dependency of the distribution coefficients of Al(III) and Be(II) on the reagent concentration.

Nature of the Extracted Species

It was necessary to evaluate the distribution coefficient (D) while varying the extractant concentration to ascertain the nature of the extracted species. The composition of the extracted species was first ascertained from a graph of log D_{Me} vs log[Cyanex 921] at fixed pH values of 8.0 and 5.0 for beryllium(II) and aluminum(III), respectively. The slopes obtained were 1.9 and 2.87 (Fig. 2). Hence the probable compositions of the extractable species of beryllium(II) and aluminum(III) are 1:2 and 1:3, respectively. Their probable species formed are [BeO·2(Cyanex 921)] and [$AlCl_3$·3(Cyanex 921)].

Influence of Temperature

Extractions of beryllium(II) and aluminum(III) with 5×10^{-3} M and 1×10^{-1} M Cyanex 921 in cyclohexane at a fixed pH 8.0 and 5.0, respectively,

TABLE 3
Effect of Temperature on the Distribution Ratio of Beryllium(II) and Aluminum(III)[a]

Temperature (K)	$D_{(Be)}$	$D_{(Al)}$
303	499.0	0.335
313	199.0	0.794
323	9.75	2.580
333	3.17	7.080
343	1.17	16.54

[a] Amount of Be(II) and Al(III) added is 15 μg/10 mL each. Cyanex 921 concentration = 0.1 M in cyclohexane.

were carried out at different temperatures (up to 70.0°C). For beryllium(II) the distribution ratio decreased with an increase in temperature while for aluminum(III) the distribution ratio increased with an increase in temperature (Table 3). The Van't Hoff equation is

$$\log D_{\text{Be or Al}} = -\frac{\Delta H^\circ}{2.303\,RT} + C$$

where $D_{\text{Be or Al}}$ represents the beryllium(II) or aluminum(III) distribution ratio, ΔH° is the enthalpy change for the extraction reaction, and C is a constant. The slopes obtained from plots of log D vs $1000/T$ were 6.36 and -4.24, respectively, for beryllium(II) and aluminum(III) (Fig. 3). The ΔH° values obtained for Be (-127.06 kJ·mol^{-1}) and Al (81.14 kJ·mol^{-1}) show that the reactions are exothermic and endothermic, respectively, which offers a good method for the separation of beryllium(II) and aluminum(III). The effect of diluent–extractant interaction is relatively weak owing to a great tendency for self-association by the extractant. Therefore, if slight evaporation of the cyclohexane will not have any effect on the percentage extraction of beryllium(II) and aluminum(III) (23).

Effect of Various Diverse Ions

The effect of various diverse ions (listed in Table 4) on the extraction of beryllium(II) and aluminum(III) was studied at pH 8.0 and pH 5.0 with 5×10^{-3} M Cyanex 921 and 1×10^{-1} M Cyanex 921 in cyclohexane, respectively. The tolerance limit was set at not more than a ±2% error in the recovery of beryllium(II) and aluminum(III) (Table 4). The extraction separation of beryllium(II) and aluminum(III) can be done quantitatively in the presence of such impurities. If any coextraction occurs in the organic phase,

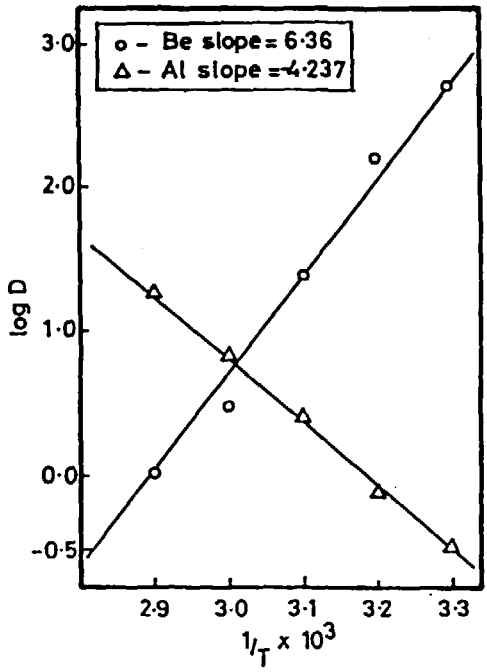


FIG. 3 Effect of temperature on the extraction of Al(III) and Be(II) with 0.1 M Cyanex 921 in cyclohexane.

TABLE 4
Effect of Various Diverse Ions on the Extraction of Beryllium(II) and Aluminum(III)

Tolerance limit (μg)				
<150	<75	<30	<15	<5
(a) Beryllium(II) [15 μg]				
Bi^{2+}, Pb^{2+}, Br^-, NO_3^-, EDTA, di-Na-tartrate	Na^+, Cr^{3+}, tri-Na-citrate	Co^{2+}	Mn^{2+}, Hg^{2+}, Sr^{2+}, Ba^{2+}, Ca^{2+}, As^{2+}, K^+, Tl^+, In^{3+}, SCN^-, SO_4^{2-}, SO_3^-, PO_4^{2-}	Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cs^+
(b) Aluminum(III) [15 μg]				
Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, NO_3^-, S^{2-}, SCN^-, tri-Na-citrate, PO_4^{3-}	Ca^{2+}, Sr^{2+}, Cr^{6+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Tl^+	Ba^{2+}, V^{5+}, Cu^{2+}, SO_4^{2-}	Zn^{2+}, Pb^{2+}, Bi^{2+}, NO_2^-, Cl^-, Br^-, SO_3^{2-}	Cd^{2+}, Hg^{2+}

it does not affect the percentage extraction of beryllium(II) or aluminum(III) respectively.

Separation of Beryllium(II) from Aluminum(III)

In order to separate aqueous solutions containing both beryllium(II) and aluminum(III), the aqueous pH was first adjusted to 8.0 with dilute NaOH and the final volume was made up to 10 mL by adding double distilled water. It was then equilibrated with 5×10^{-3} M Cyanex 921 dissolved in cyclohexane by shaking it in a separating funnel for 5–6 minutes at room temperature. After allowing the two phases to separate, the aqueous phase containing unextracted aluminum(III) was put aside and the organic phase was stripped with 0.5 M NaOH in order to recover beryllium(II) followed by stripping with 2.0 M HCl to recover aluminum(III). The amount of beryllium(II) in the stripped phase was determined spectrophotometrically by the quinalizarin method (22) while aluminum in the unextracted aqueous phase and in the stripped phase were determined together by the aluminon method (22) (flow chart as Table 5).

If the separation factor (β) is defined as

$$\beta = D_{Be}/D_{Al}$$

then the preferential extraction of beryllium over aluminum is as shown in Fig. 4 with β as a function of temperature. There is reasonable selectivity in the extraction system at room temperature which favors the separation of Be(II) from Al(III) solution. The value of β obtained at 70°C is 1489.5 with a constant reagent concentration, i.e., 0.1 M Cyanex 921 dissolved in cyclohexane.

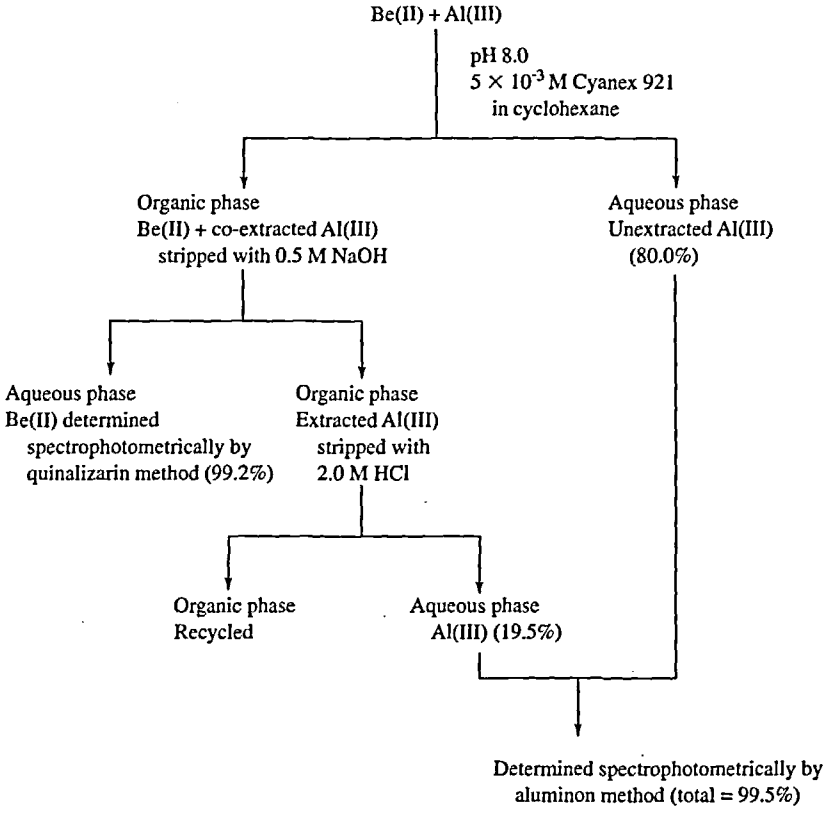
A mixture containing a tenfold excess of Al(III) added to Be(II) or a twofold excess of Be(II) added to Al(III) can be separated effectively (Table 6). Any further addition of beryllium and aluminum to their mixture beyond the above ratio results in a decrease in the value of the extraction of aluminum and beryllium. The effective separation of Be(II) and Al(III) was observed to be 99.2 and 99.5%, respectively, in a short time period by the above method.

CONCLUSION

The results obtained show that extraction of beryllium(II) and aluminum(III) is possible with Cyanex 921 dissolved in cyclohexane at pH 8.0 and 5.0, respectively. The separation factor and $\Delta H°$ values for exothermic and endothermic reactions are also calculated. $\Delta H°$ values for beryllium(II) and aluminum(III) are -127.06 and $81.14\ kJ \cdot mol^{-1}$, respectively, while the separation factor, $\beta = D_{Be}/D_{Al}$, is 1489.5 at 70°C with 0.1 M Cyanex 921 in

TABLE 5

Flow Chart for Separation of Be(II) and Al(III) using Cyanex 921 in Cyclohexane at Room Temperature



cyclohexane. From the values of ΔH° it is clear that the extraction of beryllium(II) with Cyanex 921 dissolved in cyclohexane is an exothermic reaction and the extraction of aluminum(III) with Cyanex 921 dissolved in cyclohexane is an endothermic reaction.

The concentration of the reagent required for the extraction of Be(II) and Al(III) is less compared with dibutyl phosphoric acid (0.5 M), TBP (0.1 M),

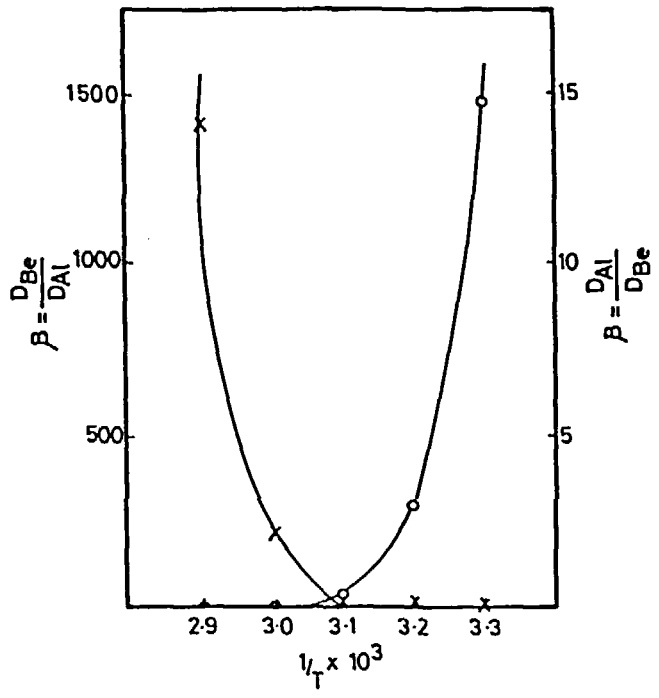


FIG. 4 Separation factor (β) of Be(II) over Al(III) and of Al(III) over Be(II) as a function of temperature.

TABLE 6
Separation of Beryllium(II) and Aluminum(III) in Various Proportions Using Cyanex 921 in Cyclohexane

	Added (μg)		Found (μg)		% Recovery	
Mixture	Be(II)	Al(III)	Be(II)	Al(III)	Be(II)	Al(III)
1	15	15	14.9	15.0	99.3	98.6
2	30	15	29.5	14.8	98.3	98.6
3	45	15	45.1	14.4	100.2	96.0
4	15	30	14.9	29.5	99.3	98.3
5	15	45	14.8	44.5	98.6	98.8
6	15	75	14.5	75.1	96.6	100.1
7	15	90	14.8	89.5	98.6	99.4
8	15	105	14.6	104.8	97.3	99.8
9	15	120	14.8	111.6	98.6	99.6
10	15	150	14.8	149.4	98.6	99.6

HDEHP (0.1 M), etc. The above method can be employed for the separation of beryllium(II) and aluminum(III) by exploiting such conditions as reagent concentration, pH, or stripping agents, whereas the separation of beryllium(II) and aluminum(III) with HDEHP can only be done by taking advantage of some difference in their stripping agents. The method developed can also be used for the separation of beryllium(II) and aluminum(III) from beryl ore, from which the yields are 99.5% Be and 99.0% Al.

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