RESEARCH ARTICLE

RAPID SOLVENT EXTRACTION OF POTASSIUM (I) WITH DICYCLOHEXANO-18CROWN-6 FROM PICRATE MEDIUM

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ABSTRACT

A novel method has been developed for the solvent extraction of Potassium (I) from 0.001M picric acid with 0.001M Dicyclohexano-18Crown-6in nitrobenzene. Potassium (I) from the organic phase was determined flame emission spectroscopy at 767 nm. Extraction was found to be quantitative in the range of 7-10 Mpicric acid. When the concentration of Dicyclohexano-18Crown-6 was varied from 0.05-20% in nitrobenzene, it showed that optimum concentration was 3%. Amongst diluents like nitrobenzene was found to be an effective diluent. Effect of shaking time, concentration of metal ion. Tolerance limits of various diverse ions were studied. Potassium (I) was separated from associated elements in its ternary mixtures with Sb(III), Bi(III) and Cu(II), Au(III). The proposed method was applied for separation and determination of Potassium (I) in rocks and foodstuffs.

INTRODUCTION

Much attention has been paid to the development of ion selective macrocyclic compounds for the separation of lanthanides either as a group or as elements. The macrocyclic crown ethers achieved considerable importance for separation and determination of a large number of metal ions (Kim *et al*., 1997; Tang and Wai, 1989a,b). Crown ethers showed selective extraction for metal ions, especially alkali and alkaline earth metals, in terms of the correspondence between the extracted metal ion crystal radii and the cavity size of the crown ethers used (Khalifa *et al*., 1988; Danesi *et al*., 1975; Mayers, 1980). Due to their ion size selective nature and ability to transfermetal ions into organicmedia, crown ethers have been frequently used as extractants and phase transfer reagents in solvent extraction and liquid membrane processes (Takeda, 1984; Koshima and Onishi, 1993; Zouhri *et al*., 1995; Potassium is universally present in vegetation and in animal body. Its proportion in total organism and of the mineral varies widely. It is also found in shells, sandstone and seawater. Potassium is an essential constituent of living matter. In the organism sodium and potassium perform vital function of maintaining fixed pH and water balance. In plant material potassium is considerably higher than sodium content. Potassiumis also necessary for transmitting stimulation from

nerves to muscles and for the latter. In the liver, potassium plays a part in the synthesis of glycogen from sugar. Therefore through geochemistry, biochemistry and hydrosphere view point, separation and determination of potassium from the associated element is very important. The method for separation of potassium (I) from alkali metals and other metal ions are very few. potassium (I) can be separated by selective precipitation using perchlorate or tetraphenylborate (173). The limitation of this method is that it is not applicable at trace concentration potassium (I) Some Efforts were made to separate potassium (I) by synergic solvent extraction using β-diketones such as the noyltrofluroacetone and alkyl phosphine oxide (174) but the extraction of potassium (I) was not quantitative. With liquid cation exchanger like bis2- ethylhexyl phosphoric acid (175) extraction of potassium (I) was only 10%. As far as the solvent extraction studies of potassium (I) with various crown ethers are concerned, 18-crown-6 was used for the determination of extraction constant from benzene using picrate as a counter anion (176-178).18-crown-6 was used for the determination ofpotassium (I) spectrophotometric ally with bromocresol green (179), fluorometrically with eosin (180). Dibenzo-18-crown-6 was used for the determination of extraction constant of potassium (I) using picrate (178) and metanil yellow (181) as a counter anions. Benzo-15-crown-5 was used for the determination of potassium (I) spectrophotometrically using hexanitrodiphenyl aminate (182) and for synergic solvent extraction of potassium (I) with tributyl phosphate (183) in benzene as a diluent.

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18- crown-6 was used for the extractive separation analysis of potassium (I) from picrate medium at pH 1.0 to 2.5 using methylene chloride as a diluent (141). From the literature survey it is clear that no attempts were made for the extractive separation analysis of potassium (I) using dicyclohexano-18-crown-6. Therefore it was thought worthwhile to undertake systematic investigations on the solvent extraction separation of potassium (I) with dicyclohexano-18-crown-6 with the major emphasis upon the development of new method for its separation from associated elements at trace concentration.

Experimental

Apparatus

A Zeiss spectrophotometer, a digital pH meter, with glass and Calomel electrodes, a digital Flame photometer and 125 ml separating funnels were used. A stock solution of potassium (I) was prepared by dissolving 1.907 g of potassium (I) chloride (AnalaR) in 1000 ml of distilled deionized water and standardized gravimetrically (184). The solution was found to contain 1.0 mg /ml of potassium. A solution containing 100 µg /ml of potassium (I) was prepared by appropriate dilution of the standard stock solution. Solutions of crown ethers were prepared from 15-crown-5(15C5), Benzo-15-crown-5(B15C5), 18-crown-6(18C6), Benzo-18-crown-6(B18C6), Dibenzo-18-crown-6(DB18C6),   Dicyclohexano-18-crown-6(DC18C6), were used without further purification. All other chemicals were of guaranteed grade and were used without further purification.

Procedure

Solvent Extraction

100 µg of Potassium(I) was mixed with picric acid in the concentration range of 0.00001M to 0.05M in a total volume of 10 mL. The solution was then transferred to a separating funnel and was equilibrated with 10 ml crown ether (0.001M) in nitrobenzene asa diluent for 10 min. on a wrist action flask shaker. Two phases were allowed to settle and separate. From the organic phase potassium (I) was then stripped with 10 ml of stripping agent like picric acid and was determined by flame emission spectroscopy at 767 nm. The concentration of potassium (II) was calculated from the calibration curve.

RESULTS AND DISCUSSION

Extraction of potassium (I) as a function of picric acid Concentration with various crown ethers

In order to ascertain the optimum concentration of picric acid required for the quantitative extraction of potassium (I), the extraction studies were performed with a range of crown ethers of 0.001 M concentration in nitrobenzene. The picric acid concentration as varied from 0.00001 to 0.05M. The results of extraction studies are shown in Table 1. It is clear that amongst various crown ethers only Solutions of crown ethers were prepared from 18-crown-6(18C6), Dicyclohexano-18-crown-6(DC18C6),   and   dicyclohexano-24–crown-8   could quantitatively extract potassium(I) where as other crown ethers

were not efficient extractants for the quantitatively extraction of potassium(I). There was only 87%   extraction   of potassium(I)with 15-crown-5, 85% Benzo-15-crown-5,80% with Benzo-18-crown-6(B18C6), 90% with Dibenzo-18-crown-6(DB18C6) at 0.05 M picric acid. With increase in picric acid concentration, the extraction of potassium (I) was increased and was quantitative between 0.001-0.05 M picric acid. The extraction of potassium (I) was quantitative with Dicyclohexano-18-crown-6(DC18C6), and dicyclohexano-24 – crown -8 from 0.0004 – 0.05M picric acid. Further extraction studies of potassium (I) was carried out with 0.001M DC-18-Crown-6 with nitrobenzene as a diluent.

Table 1. Extraction of potassium (I) as a function of picric acid Concentration with various crown ethers

Potassium (I) -100 µg, Strippant-2M HNO_3 Crown Ether-0.001M in Nitrobenzene

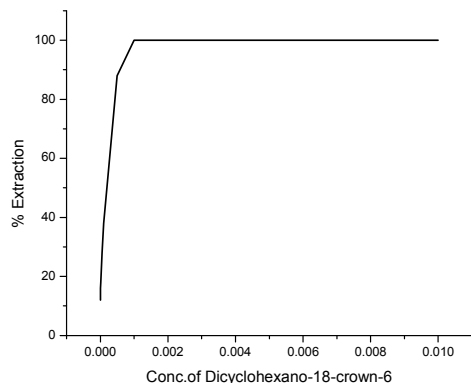| Picric Acid M	Potassium(I) Extraction %						
	15C5	B15C5	18C6	B18C6	DB18C6	DC18C6	DC24C8
0.00001	10	11	15	17	18	23	10
0.00002	14	12	20	18	26	25	13
0.00004	17	20	24	20	30	27	21
0.00006	19	22	32	22	31	30	25
0.00008	23	25	36	35	34	32	33
0.0001	24	26	42	38	38	44	37
0.0002	27	34	70	49	62	78	70
0.0004	36	46	92	65	82	100	100
0.0006	44	56	94	70	84	100	100
0.0008	45	65	98	80	90	100	100
0.001	46	67	100	80	90	100	100
0.002	56	69	100	80	90	100	100
0.004	72	70	100	80	90	100	100
0.006	72	74	100	80	90	100	100
0.008	77	80	100	80	90	100	100
0.01	81	81	100	80	90	100	100
0.02	82	82	100	80	90	100	100
0.03	85	83	100	80	91	100	100
0.04	86	84	100	80	92	100	100
0.05	87	85	100	80	92	100	100

Effect of varying Concentration of Dicyclohexano-18-crown-6

In order to ascertain the optimum concentration of DC-18-Crown-6 required for the quantitative extraction of potassium (I), the extraction studies were performed with a range of picric acid of 0.001 M with varying the concentrationofDC-18-Crown-6 in nitrobenzene. The concentration of DC-18- Crown-6 was varied from 0.0000005-0.1M. The results of extraction studies are shown in Table- 2 and Fig-1 which indicate that the extraction of potassium (I) was increased with increase in DC-18- Crown-6 concentration and was quantitative from 0.001 – 0.1M DC-18- Crown-6. Further extraction studies of potassium (I) was carried out using 10 ml of 0.001M DC-18- Crown-6 in nitrobenzene as a diluent.

Table 2. Effect of varying Concentration of Dicyclohexano-18-crown-6

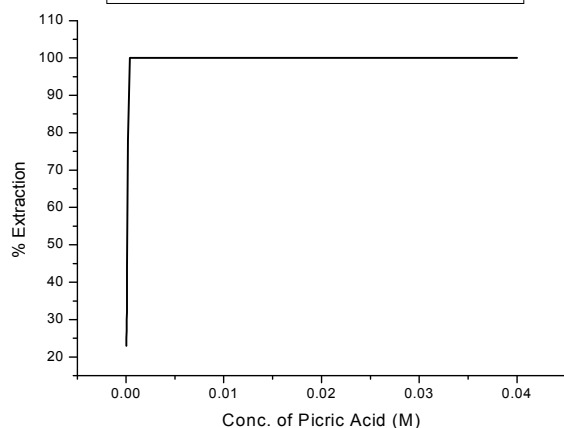| DC-18- Crown-6 Conc.M	Extraction %E	Distribution D
0.0000005	08	0.087
0.000001	12	0.136
0.000005	16	0.190
0.00001	18	0.220
0.00005	28	0.250
0.0001	38	0.538
0.0005	88	7.333
0.001	100	∞
0.005	100	∞
0.01	100	∞

Fig-1 Effect of varying Concentration of Dicyclohexano-18-crown-6

Effect of Picric acid Concentration

The effect of picric acid concentration on the extraction of potassium (I), extractions were performed from 0.001M of 0.001M DC-18- Crown-6 in nitrobenzene by varying the concentration of picric acid in the range of 0.0000005-0.05M. The results of extraction studies are shown in Table- 3 and Fig-2. It was found that the extraction (I) was 23% at 0.00001M picric acid and was quantitative from 0.0006M-0.05M picric acid. Further extraction studies of potassium (I) was carried out with 0.001M picric acid.

Fig-2 Effect of Picric acid Concentration

Effect of Various of Stripping Agents

After extraction of potassium (I) from 0.001 M picric acid with 0.001M DC-18- Crown-6 in nitrobenzene, it was stripped from the organic phase with various stripping agents such as nitric acid , hydrochloric acid, sulphuric acid, perchloric acid acetic acid in the concentration range of 0.1-10 M. The stripping of potassium was quantitative with 2.0-10M nitric, perchloric acid ,hydrochloric acid and 1.0- 8.0Mhydrobromic acid and Acetic acid was found to be an insufficient strippant for potassium (I) in the concentration range of 0.1 -10M. Further stripping studies of potassium (I) were carried out with 2.0M nitric acid. The results of stripping of potassium (I) are shown in Table-4 and Fig-3

Table 3. Effect of Picric acid Concentration

Potassium (I) -100 μg, Strippant-2M HNO3 Crown Ether-0.001M in Nitrobenzene

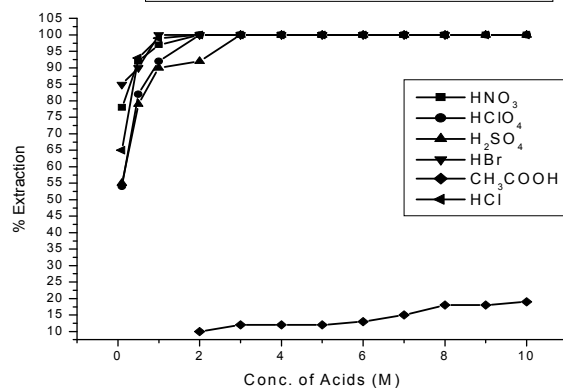| Picric acid Concentration M	% Extraction E	Distribution Ratio D
0.00001	23	0.149
0.00002	25	0.219
0.00004	27	0.25
0.00006	30	0.389
0.00008	32	0.470
0.0001	44	0.613
0.0002	78	3.545.
0.0004	100	∞
0.0006	100	∞
0.0008	100	∞
0.001	100	∞
0.002	100	∞
0.004	100	∞
0.006	100	∞
0.008	100	∞
0.01	100	∞

Fig -3 Effects of Various Stripping Agents

Table 4. Effects of Various of Stripping Agents

Potassium (I) -100 μg, Crown Ether-0.001M in Nitrobenzene,0.001M Picric Acid

Conc	% Stripping					
Molar	HNO_3	$HClO_4$	$H2SO_4$	HBr	CH_3COOH	HCl
0.1	78	54	55	85	03	65
0.5	92	82	79	90	05	93
1	97	92	90	100	08	99
2	100	100	92	100	10	100
3	100	100	100	100	12	100
4	100	100	100	100	12	100
5	100	100	100	100	12	100
6	100	100	100	100	13	100
7	100	100	100	100	15	100
8	100	100	100	100	18	100
9	100	100	100	-	18	100
10	100	100	100	-	19	100

Effect of various Diluents

To study the effect of diluents on the extraction of potassium (I), extractions were performed from 0.001M picric acid using 0.001M DC-18- Crown-6 in various solvents such as benzene, toluene, xylene, carbon tetrachloride, chloroform and nitrobenzene. The phase volume ratio was maintained at unity. It was observed that the extraction of potassium (I) was 32%

with benzene, 30% with toluene,28% with xylene,13% with carbon tetrachloride, 43% with chloroform, and was quantitatively only with nitrobenzene. Therefore studies of potassium (I) were carried out form nitrobenzene as diluent. The results of extraction studies are shown in Table- 5

Table 5. Effect of various Diluents

Potassium (I) -100 µg, DC-18C-6 0.001M, 0.001M Picric Acid, Strippant 2.0M HNO_3

Diluent	Dielectric Constant	Extraction %	Distribution Ratio D
Benzene	2.28	32	0.471
Toluene	2.38	30	0.428
xylene	2.3	28	0.389
Carbon Tetrachloride	2.24	13	0.149
Chloroform	4.8	43	0.754
Tetrachloroethane	8.2	78	3.545
Tetrachloromethane	9.08	73	2.704
Dichloroethane	10.5	80	4.00
Nitrobenzene	34.8	100	∞

Effect of varying Concentration of potassium (I)

Potassium (I) was extracted with 10 ml of 0.001m dicyclohexano-18-crown-6 from 0.001M picric acid using nitrobenzene as a diluent.

Table 6. Effect of varying Concentration of potassium (I)

DC-18C-6 0.001M, 0.001M Picric Acid, Strippant 2.0M HNO_3

Potassium (I) µg	Extraction %	Distribution Ratio D
25	100	∞
50	100	∞
75	100	∞
100	100	∞
125	100	∞
150	100	∞
175	100	∞
200	100	∞
225	98	49.00
250	95	19.00
275	92	11.50
300	89	8.09

Fig-4 Effect of varying Concentration of potassium (I) µg

The Potassium (I) was varied from 25- 300µg per 10 ml. it was found that 10ml of 0.001M DC18C6 solution was adequate to extract potassium(I) quantitatively up to 200µgper 10 ml of sample solution. The results are shown in Table-6 and Fig-4
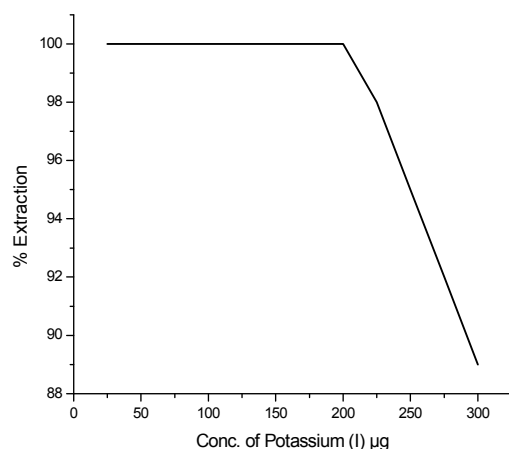
Period of Equilibration

Potassium (I) was extracted with 10 ml of 0.001m dicyclohexano-18-crown-6 from 0.001M picric acid using nitrobenzene as a diluent. The period of equilibration was varied from 1-30 minutes on the wrist action flask shaker. It was observed that the extraction of potassium (I) was quantitatively in minutes of equilibration. To ensure complete extraction of potassium (I), the period of equilibration employed was 2 minutes

Separation of Potassium (I) from Binary Mixtures

Potassium (I) was extracted with 10 ml of 0.001m dicyclohexano-18-crown-6 in nitrobenzene from 0.001M picric acid in the presence of a various diverse ions. The tolerance limit was set at the amount of foregn ions required to cause a ± 2% error in the recovery of potassium (I). Amongst s block cations, rubidium(I), cesium(I), strontium (II),and barium(II) were co-extracted along with potassium (I), strontium (II), and barium(II) showed low tolerance limit. All the s- block cations showed high tolerance limit. Amongst d block cations, showed high tolerance limit. All the s- block cations showed high tolerance limit. Most of the p- block cations showed high tolerance limit except lead (II) which showed low tolerance limit. The results of separation of potassium (I) from binary mixtures are shown in Table 7

Separation of potassium (I) from multicomponent Mixtures

Potassium (I) was extracted from 0.001M picric acid with 0.001M DC18C6. Under these set conditions there was no extraction of iron (III), uranium (VI) and molybdenum (VI) but from 8.0 M hydrochloric acid there was quantitatively extraction of iron(III) with dicyclohexano-18-crown-6, Uranium(VI)was quantitatively extracted with dibenzo-18-crown-6 from 8.0 M hydrochloric acid while molybdenum(VI)was quantitatively extracted with dibenzo-18-crown-6 from 8.0 M hydrochloric acid whereas potassium(I) was not extracted. Most of the geological samples contain iron hence its separation from other trace elements is important. The separation of iron (III), potassium (I) and other elements is achieved as follows. When a mixture containing iron(III), potassium(I) and lithium (I) was extracted with 0.001M dicyclohexano-18-crown-6 in nitrobenzene from 8.0 M hydrochloric acid, Iron was extracted quantitatively leaving behind potassium(I) and in aqueous phase. The aqueous phase after evaporating was treated with water and extracted 0.001Mdicyclohexano-18-crown-6 in nitrobenzene from 0.001M picric acid . Under these set conditions potassium(I) was extracted while lithium(I) remained in the aqueous phase. Iron and potassium from the respective organic phases were stripped with 2.0M nitric acid. The separation of potassium from iron and other cations was accomplished by following similar methodology Table-8

Table 7. Separation of Potassium (I) from Binary Mixtures

Ions	Added as	Tolerance Limit(mg)	Ions	Added as	Tolerance Limit (mg)
Li^+	LiCl	35	Ce^{3+}	$CeCl_3.6H_2O$	0.1
Na^+	NaCl	25	Sb^{3+}	$SbCl_3$	0.1
Rb^+	RbCl	0.5	Y^{3+}	$Y(NO_3)_3$	0.5
Cs^+	CsCl	0.1	Zr^{4+}	$Zr(NO_3)4.4H_2O$	0.3
Be^{2+}	$BeSO_4.4H_2O$	0.3	V^{4+}	$VOSO_4.4H_2O$	0.5
Mg^{2+}	$MgCl_2.6H_2O$	30	Th^{4+}	$Th(NO_3)_4$	0.5
Ca^{2+}	$CaCl_2$	15	U^{6+}	$UO_2(NO_3)_2.6H_2O$	1
Sr^{2+}	$Sr(NO_3)_2$	20	Cr^{6+}	$K_2Cr_2O_7$	0.5
Ba^{2+}	$Ba(NO_3)_2$	20	Mo^{6+}	$(NH_4)_6Mo_7O_{24}.4H_2O$	0.5
Cu^{2+}	$CuCl_2.2H_2O$		W^{6+}	$Na_2WO_4.4H_2O$	30
Ni^{2+}	$NiCl_2.6H_2O$		C^-	HCl	15
Mn^{2+}	$MnCl_2.4H2O$		Br^-	HBr	10
Zn^{2+}	$ZnCl_2$		SCN^-	NaSCN	75
Pb^{2+}	$Pb(NO_3)_2$		$ClO4$	ClO_4	
Fe^{3+}	$FeCl_3.6H_2O$		$CH3COO^-$	CH_3COOH	35
Cr^{3+}	$Cr(NO_3)_3.9\ H_2O$		Tartrate	Tartaric acid	25
Al^{3+}	$Al(NO_3)_3.9\ H_2O$		EDTA	EDTA	35
La^{3+}	$LaCl_3$		Ascorbate	Ascorbic acid	5

Table 8. Separation of potassium (I) from multicomponent Mixtures

S.No	Mixture	Taken µg	Foundµg	Recovery %	Extractants	Stripping agents
1	Fe(III)	100	100	100	DC18C6,8MHCl	$2M\ HNO_3$
	K(I)	100	100	100	DC18C6,0.01MPicric acid	$2M\ HNO_3$
	Li(I)	100	100	100	Aqueous Phase	-----
2	Fe(III)	100	100	100	DC18C6,8MHCl	$2M\ HNO_3$
	K(I)	100	100	100	DC18C6,0.01MPicric acid	$2M\ HNO_3$
	Be(II)	100	100	100	Aqueous Phase	-----
3	Fe(III)	100	100	100	DC18C6,8MHCl	$2M\ HNO_3$
	K(I)	100	100	100	DC18C6,0.01MPicric acid	$2M\ HNO_3$
	Mg(II)	100	100	100	Aqueous Phase	-----
4	Fe(III)	100	100	100	DC18C6,8MHCl	$2M\ HNO_3$
	K(I)	100	100	100	DC18C6,0.01MPicric acid	$2M\ HNO_3$
	Ca(II)	100	100	100	Aqueous Phase	-----
5	U(VI)	100	100	100	DB24C8,8MHCl	$2M\ HNO_3$
	K(I)	100	100	100	DC18C6,0.01MPicric acid	$2M\ HNO_3$
	Li(I)	100	100	100	Aqueous Phase	-----
6	U(VI)	100	100	100	DB24C8,8MHCl	$2M\ HNO_3$
	K(I)	100	100	100	DC18C6,0.01MPicric acid	$2M\ HNO_3$
	Be(II)	100	100	100	Aqueous Phase	-----
7	U(VI)	100	100	100	DB24C8,8MHCl	$2M\ HNO_3$
	K(I)	100	100	100	DC18C6,0.01MPicric acid	$2M\ HNO_3$
	Th(IV)	100	100	100	Aqueous Phase	-----
8	U(VI)	100	100	100	DB24C8,8MHCl	$2M\ HNO_3$
	K(I)	100	100	100	DC18C6,0.01MPicric acid	$2M\ HNO_3$
	Ce(III)	100	100	100	Aqueous Phase	-----

Table 9. Application to the Analysis of Potassium (I) from various Samples

S.No.	Sample	% K_2O	
	Rock Sample	Present	Found
1	KC-11	2.1	2.0
2	KC-12	3.98	3.96
3	KC-13	4.8	4.75
4	SY-II	4.51	4.50
5	USGS-G_2	4.52	4.50

S.No.	Sample	K Meq/lit	
	Biological Sample	Present	Found
1	Blood Serum-1	4.9	4.85
2	Blood Serum-2	4.6	4.5
3	Milk-1	72	71.8
4	Milk-2	75	74.5

Application to the Analysis of Potassium (I) from various

Samples

The proposed method was applied for determination of potassium (I) in standard rocks samples, blood serum and milk. The results are shown in Table- 9

Conclusion

The important feature of the developed method is that it permits the separation of potassium (I) at trace level concentration. The concentration of crown ether required is very low. It is possible to separate potassium (I) from iron(III),

lithium (I), beryllium (II), calcium (II), magnesium (II) thorium (IV), effectively. The method was extended to the analysis of potassium (I) in various standard rock samples, blood serum and milk samples yielding excellent results. The method is simple, rapid, selective, and reproducible and adds significantly to the use of crown ethers as extractants for the separation of potassium (I).

REFERENCES

Danesi, P.R., Meider-gorincan, H., Chiorzia, R., Scibona, G., 1975. *J. Inorg.Nucl. Chem*. 37 1479–1483.

Healy, T.V. J. *Inorg.Nucl. Chem*., 30 1025 1968.

Iwachido, T., Sadakane, A and Toeia, KBull, *Chem.Soc. Jpn*., 51629 1978.

Kedar, W e., Sheppard, J.C. and Wilson, A.S., *J. Inorg.Nucl. Chem*., 12327 19660.

Kim, Jung Suk, Lee, Chang Heon, Han, Sun Ho, Su, Moo Yul, 1997. Talanta 45, 437–444.

Koshima, H., Onishi, H., 1993. Anal. Sci.9, 141–142.

Mayers, K.T., 1980. *Inorg.Nucl.Chem.Lett*. 16 (6), 329–330.

Medal, A.S. Gomis, D.B. and Alvarez, J.R.G. Talanta 28, 425 1981.

Moore, F.L., 1969. Anal. Chem. 41 (12), 1658–1661.

Rabie, K.A., 1996. Third Conf. on Peaceful Uses of Atomic Energy, Damascus, pp. 355–360.

Sadakane, AIwachido, T., and Toeia, K *Bull,Chem.Soc. Jpn*., 48 60 1975.

Suniyashi, H Nakahara, Kand Ueno K., I. Talanta 24, 763 1977.

Takeda, Y., 1984. In: Vögle, F., Weber, E. (Eds.), Topics in Current Chemistry, 121. Springer Verlag, New York.

Takedd, Y. and Goto, H.Bull,Chem.Soc. Jpn., 52 1920 1979.

Tang, J., Wai, C.M., 1989a. Analyst 114, 451–453.37 (6), 1479–1483.

Vogel, A. I. A text book of quantitative Inorganic analysis 3rdEdn p. 561 Longman London 1975

Zamani, Abbas Ali, Yaftian, Mohammad Reza, 2004. Sep. *Purif. Technol*. 40, 115–121.

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