

International Journal of Scientific Research and Reviews

Extraction of Potassium (I) with mixed crown ether from weak acid medium and its applications

Rahul S. Patil¹ and Shivaji H. Burungale^{2*}

Yashwant rao Chavan College of Science, Karad -415124, Maharashtra, India
E-mail:shivajiburungale777@gmail.com

ABSTRACT

A novel method has been developed for the solvent extraction of Potassium (I) from 0.001M picric acid with 0.0001M 15crown-5 and B15crown-5 in nitrobenzene. Potassium (I) from the organic phase was determined flame emission spectroscopy at 767 nm. Extraction was found to be quantitative from 0.00005M picric acid. The effect of various diluents were studied like Benzene Toluene xylene Carbon

Tetrachloride Chloroform Tetrachloroethane Dichloroethane Tetrachloromethane Nitrobenzene. the concentration of 15crown-5 and B15crown-5 was varied from 0.000001M to 0.001M in nitrobenzene, it showed that optimum concentration was 0.0005M. Amongst diluents like nitrobenzene was found to be an effective diluent. Effect of stirring time, concentration of metal ion. Potassium (I) was separated from associated elements in its binary mixture with Fe(III), Li(K), Mg (II) and Ca(II). The study of Tolerance limits mostly alkali, alkaline earths, Transition metals and Lanthanide metals of various diverse ions were studied. The proposed method was applied for separation and determination of Potassium (I) in Rock and biological samples.

KEYWORDS: Liquid-liquid extraction of Potassium (I); mixed crown ether; Analysis of biological samples.

***Corresponding author**

Shivaji H. Burungale *

Yashwantrao Chavan College of Science,

Karad -415124,

Maharashtra, India

E-mail:shivajiburungale777@gmail.com

INTRODUCTION

In 1967, Charles Pedersen, who was a chemist working at DuPont, discovered a simple method of synthesizing a crown ether when he was trying to prepare a complexing agent for divalent cations.^{1,2} His strategy entailed linking two catecholate groups through one hydroxyl on each molecule. This linking defines a polydentate ligand that could partially envelop the cation and, by ionization of the phenolic hydroxyls, neutralize the bound dication. He was surprised to isolate a by-product that strongly complexed potassium cations. Citing earlier work on the dissolution of potassium in 16-crown-4,^{5,6} he realized that the cyclic polyethers represented a new class of complexing agents that were capable of binding alkali metal cations. He proceeded to report systematic studies of the synthesis and binding properties of crown ethers in a seminal series of papers. The fields of organic synthesis, phase transfer catalysts, and other emerging disciplines benefited from the discovery of crown ethers. Pedersen particularly popularized the dibenzo crown ethers.⁷

Apart from its high affinity for potassium cations, 18-crown-6 can also bind to protonated amines and form very stable complexes in both solution and the gas phase. Some amino acids, such as lysine, contain a primary amine on their side chains. Those protonated amino groups can bind to the cavity of 18-crown-6 and form stable complexes in the gas phase. Hydrogen-bonds are formed between the three hydrogen atoms of protonated amines and three oxygen atoms of 18-crown-6. These hydrogen-bonds make the complex a stable adduct. By incorporating luminescent substituents into their backbone, these compounds have proved to be sensitive ion probes, as changes in the absorption or fluorescence of the photoactive groups can be measured for very low concentrations of metal present.⁹ Some attractive examples include macrocycles, incorporating oxygen and/or nitrogen donors, that are attached to polyaromatic species such as anthracenes (via the 9 and/or 10 positions)¹⁰.

In the growing field of separation science numerous methods have been describe for the separation and determination of metals viz. Solvent extraction¹¹⁻¹⁵.

From the literature survey it is clear that no attempts were made for the extractive separation analysis of potassium (I) using synergistic extraction crown ether. Therefore it was thought worthwhile to undertake systematic investigations on the solvent extraction separation of potassium (I) with 15C5 +B15C5 with the major emphasis upon the development of new method for its separation from associated elements at trace concentration.

EXPERIMENTAL

Apparatus

A Systronic spectrophotometer, Systronic digital Flame photometer, a digital pH meter, with glass electrodes, mechanical stirrer 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), were used without further purification. All other chemicals were of AR 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 conical flask and was equilibrated with 10 ml crown ether (0.0005M) in nitrobenzene as a diluent for 5 min. on a mechanical stirrer. Two phases were allowed to separate by using separating funnel. 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 (I) was calculated from the calibration curve.

RESULTS AND DISCUSSION

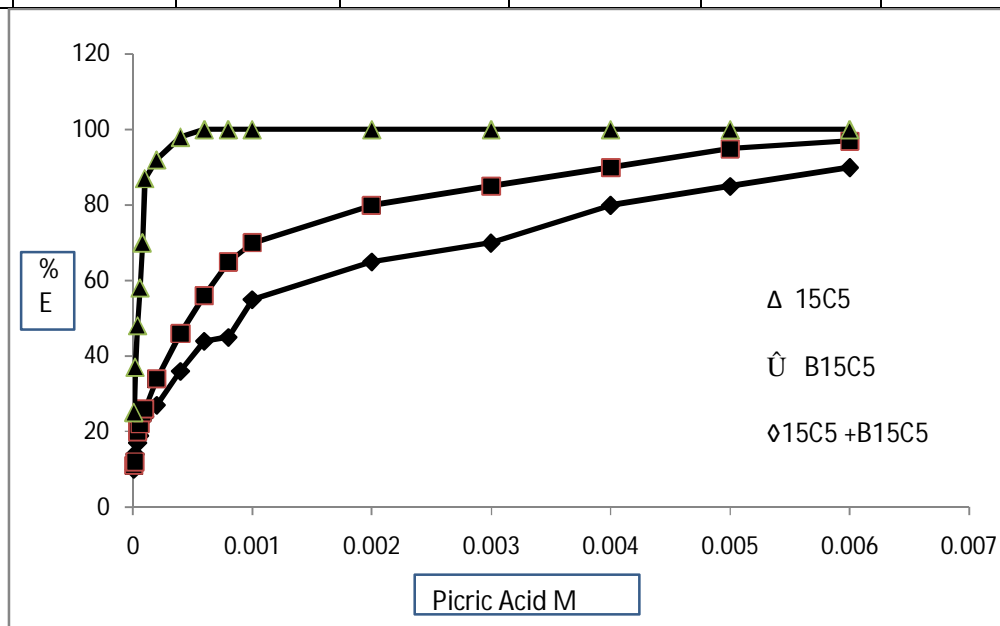
Extraction of potassium (I) as a function of picric acid Concentration with crown ethers.

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 0.0005 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 and fig-1 it is clear that amongst crown ethers not efficient extractants for the quantitative extraction of potassium(I). There was only 44% extraction of potassium(I) with 15-crown-5, 56% Benzo-15-crown-5, at 0.05 M picric acid. The extraction of potassium (I) was quantitatively increased with the mixture of 15crown-5 and B15crown-5 in nitrobenzene from 0.001-0.05 M picric acid. Further extraction studies of potassium (I) was carried out with 0.001M 15C5 +B15C5 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 HNO₃ Crown Ether-0.0005M in Nitrobenzene

| Picric Acid M | Potassium(I) Extraction % | | | | | |
|---------------|---------------------------|----------------------|----------|----------------------|----------------|----------------------|
| | 15C5 %E | Distribution Ratio D | B15C5 %E | Distribution Ratio D | 15C5 +B15C5 %E | Distribution Ratio D |
| 0.00001 | 10 | 0.11 | 11 | 0.12 | 25 | 0.33 |
| 0.00002 | 14 | 0.16 | 12 | 0.13 | 37 | 0.59 |
| 0.00004 | 17 | 0.20 | 20 | 0.25 | 48 | 0.92 |
| 0.00006 | 19 | 0.23 | 22 | 0.28 | 58 | 1.20 |
| 0.00008 | 23 | 0.29 | 25 | 0.33 | 70 | 2.33 |
| 0.0001 | 24 | 0.31 | 26 | 0.35 | 87 | 6.69 |
| 0.0002 | 27 | 0.36 | 34 | 0.51 | 98 | 49 |
| 0.0004 | 36 | 0.56 | 46 | 0.85 | 100 | ∞ |
| 0.0006 | 44 | 0.78 | 56 | 1.27 | 100 | ∞ |
| 0.0008 | 45 | 0.81 | 65 | 1.85 | 100 | ∞ |
| 0.001 | 55 | 1.22 | 70 | 2.33 | 100 | ∞ |



Effect of varying Concentration of 15C5 +B15C5

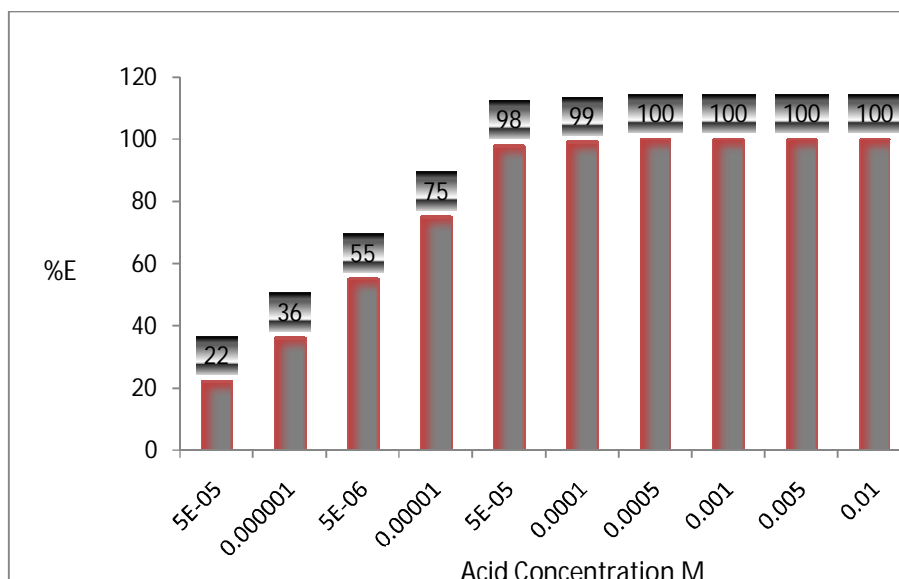
In order to ascertain the optimum concentration of 15C5 +B15C5 required for the quantitative extraction of potassium (I), the extraction studies were performed with a range of picric acid of 0.001 M with varying the concentration of 15C5 +B15C5 in nitrobenzene. The concentration of 15C5 +B15C5 was varied from 0.00005-0.01M. 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 15C5 +B15C5 concentration and was quantitative from 0.0001 – 0.01M 15C5 +B15C5. Further extraction

studies of potassium (I) was carried out using 10 ml of 0.005M 15C5 +B15C5in nitrobenzene as a diluent.

Table-2Effect of varying Concentration of 15C5 +B15C5

| 15C5 +B15C5 Conc.M | Extraction %E | Distribution ratio D |
|-----------------------|------------------|-------------------------|
| 0.00005 | 22 | 0.28 |
| 0.000001 | 36 | 0.82 |
| 0.000005 | 55 | 1.22 |
| 0.00001 | 75 | 3 |
| 0.00005 | 98 | 3 |
| 0.0001 | 99 | 99 |
| 0.0005 | 100 | ∞ |
| 0.001 | 100 | ∞ |
| 0.005 | 100 | ∞ |
| 0.01 | 100 | ∞ |

Fig-1Effect of varying Concentration of 15C5 +B15C5

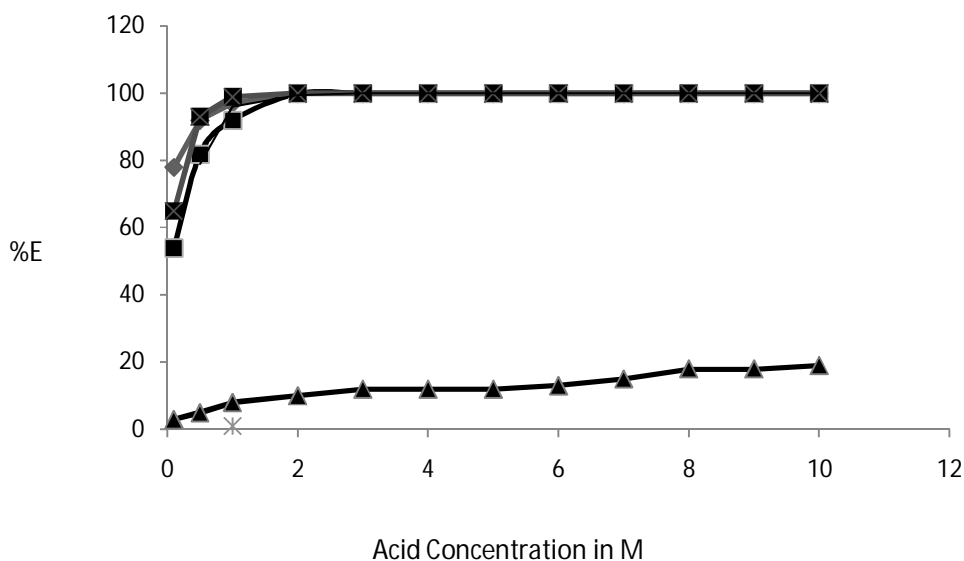


Effect of Various of Stripping Agents

After extraction of potassium (I) from 0.001 M picric acid with 0.001M 15C5 +B15C5in 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 0.1-10M.The stripping of potassium was quantitative with 2.0-10M nitric, perchloric acid ,hydrochloric acidand 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-3

Table -3 Effects of Stripping Agents
Potassium (I) -100 µg, Crown Ether-0.001M in Nitrobenzene, 0.001M Picric Acid

| Conc Molar | % Stripping Agents | | | | |
|---------------|--------------------|-------------------|-----|----------------------|-----|
| | HNO ₃ | HClO ₄ | HBr | CH ₃ COOH | HCl |
| 0.1 | 78 | 54 | 85 | 03 | 65 |
| 0.5 | 92 | 82 | 90 | 05 | 93 |
| 1 | 97 | 92 | 100 | 08 | 99 |
| 2 | 100 | 100 | 100 | 10 | 100 |
| 3 | 100 | 100 | 100 | 12 | 100 |
| 4 | 100 | 100 | 100 | 12 | 100 |
| 5 | 100 | 100 | 100 | 12 | 100 |
| 6 | 100 | 100 | 100 | 13 | 100 |
| 7 | 100 | 100 | 100 | 15 | 100 |
| 8 | 100 | 100 | 100 | 18 | 100 |
| 9 | 100 | 100 | - | 18 | 100 |
| 10 | 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 15C5 +B15C5 in various solvents such as benzene, toluene, xylene, carbon tetra chloride, 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 from nitrobenzene as diluent. The results of extraction studies are shown in Table- 4

Table -4 Effect of various Diluents

Potassium (I) -100 µg, 15C5 +B15C5 0.001M, 0.001M Picric Acid, Strippant 2.0M HNO₃

| 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)

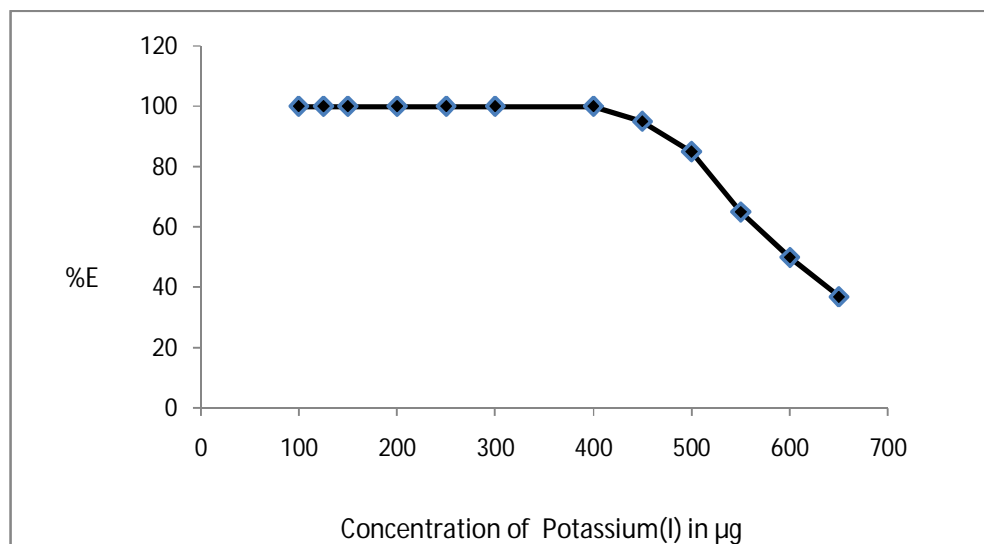
Potassium (I) was extracted with 10 ml of 0.001m dicyclohexano-18-crown-6 from 0.001M picric acid using nitrobenzene as a diluent. The Potassium (I) was varied from 25- 300µg per 10 ml. it was found that 10ml of 0.001M 15C5 +B15C5solution was adequate to extract potassium(I) quantitatively up to 200µgper 10 ml of sample solution. The results are shown in table-5.

Table-5 Effect of varying Concentration of potassium (I)

15C5 +B15C5 0.001M, 0.001M Picric Acid, Strippant 2.0M HNO₃

| Potassium (I) µg | Extraction % | Distribution Ratio D |
|------------------|--------------|----------------------|
| 100 | 100 | ∞ |
| 125 | 100 | ∞ |
| 150 | 100 | ∞ |
| 200 | 100 | ∞ |
| 250 | 100 | ∞ |
| 300 | 100 | ∞ |
| 400 | 100 | ∞ |
| 450 | 95 | 19 |
| 500 | 85 | 5.66 |
| 550 | 65 | 1.85 |
| 600 | 50 | 1.00 |
| 650 | 37 | 0.58 |

Fig-2 Effect of varying Concentration of potassium (I)



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 15C5 +B15C5 in nitrobenzene from 0.001M picric acid in the presence of a various diverse ions. The tolerance limit was set at the amount of foreign ions required to cause a $\pm 2\%$ 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 6

Table-6 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 ₂ O | 0.2 |
| Na ⁺ | NaCl | 25 | Sb ³⁺ | SbCl ₃ | 0.3 |
| Rb ⁺ | RbCl | 0.5 | Y ³⁺ | Y(NO ₃) ₃ | 0.5 |
| Cs ⁺ | CsCl | 0.1 | Zr ⁴⁺ | Zr(NO ₃) ₄ .4H ₂ O | 0.6 |
| Be ²⁺ | BeSO ₄ .4H ₂ O | 0.3 | V ⁴⁺ | VO ₂ .4H ₂ O | 0.8 |
| Mg ²⁺ | MgCl ₂ .6H ₂ O | 30 | Th ⁴⁺ | Th(NO ₃) ₄ | 0.9 |
| Ca ²⁺ | CaCl ₂ | 15 | U ⁶⁺ | UO ₂ (NO ₃) ₂ .6H ₂ O | 1 |
| Sr ²⁺ | Sr(NO ₃) ₂ | 20 | Cr ⁶⁺ | K ₂ Cr ₂ O ₇ | 0.7 |
| Ba ²⁺ | Ba(NO ₃) ₂ | 20 | Mo ⁶⁺ | (NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O | 0.6 |
| Cu ²⁺ | CuCl ₂ .2H ₂ O | 20 | W ⁶⁺ | Na ₂ WO ₄ .4H ₂ O | 35 |
| Ni ²⁺ | NiCl ₂ .6H ₂ O | 25 | C ⁻ | HCl | 25 |
| Mn ²⁺ | MnCl ₂ .4H ₂ O | 50 | Br ⁻ | HBr | 10 |
| Zn ²⁺ | ZnCl ₂ | 40 | SCN ⁻ | NaSCN | 75 |
| Pb ²⁺ | Pb(NO ₃) ₂ | 10 | ClO ₄ | ClO ₄ | 20 |
| Fe ³⁺ | FeCl ₃ .6H ₂ O | 16 | CH ₃ COO ⁻ | CH ₃ COOH | 35 |
| Cr ³⁺ | Cr(NO ₃) ₃ .9 H ₂ O | 50 | Tartrate | Tartaric acid | 25 |
| Al ³⁺ | Al(NO ₃) ₃ .9 H ₂ O | 45 | EDTA | EDTA | 35 |
| La ³⁺ | LaCl ₃ | 35 | Ascorbate | Ascorbic acid | 5 |

Separation of potassium (I) from multicomponent Mixtures

Potassium (I) was extracted from 0.001M picric acid with 0.001M 15C5 +B15C5 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 15C5 +B15C5 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 15C5 +B15C5 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 0.001M 15C5 +B15C5 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-7

Table .7 Separation of potassium (I) from Multicomponent Mixtures

| No | Mixture | Taken μg | Found μg | Recovery % | Extractants | Stripping agents |
|----|---------|---------------------|---------------------|------------|----------------------------|---------------------|
| 1 | Fe(III) | 100 | 100 | 100 | 15C5 +B15C5,8MHCl | 1M HNO ₃ |
| | K(I) | 100 | 100 | 100 | 15C5+B15C50.01MPicric acid | 1M HNO ₃ |
| | Li(I) | 100 | 100 | 100 | Aqueous Phase | ----- |
| 2 | Fe(III) | 100 | 100 | 100 | 15C5 +B15C5,8MHCl | 1M HNO ₃ |
| | K(I) | 100 | 100 | 100 | 15C5+B15C50.01MPicric acid | 1M HNO ₃ |
| | Be(II) | 100 | 100 | 100 | Aqueous Phase | ----- |
| 3 | Fe(III) | 100 | 100 | 100 | 15C5 +B15C5,8MHCl | 1M HNO ₃ |
| | K(I) | 100 | 100 | 100 | 15C5+B15C50.01MPicric acid | 1M HNO ₃ |
| | Mg(II) | 100 | 100 | 100 | Aqueous Phase | ----- |
| 4 | Fe(III) | 100 | 100 | 100 | 15C5 +B15C5,8MHCl | 1M HNO ₃ |
| | K(I) | 100 | 100 | 100 | 15C5+B15C50.01MPicric acid | 1M HNO ₃ |
| | Ca(II) | 100 | 100 | 100 | Aqueous Phase | ----- |

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- 8

Table-8 Analysis of Rock and Biological Sample

| Sr.No. | Sample | % K ₂ O | |
|--------|-------------|--------------------|-------|
| | 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 |

| Sr.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 |

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, reproducible and adds significantly to the use of crown ethers as extractants for the separation of potassium(I).

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