Solvent extraction separation of barium(II) from associated elements using 15-crown-5 from picrate medium

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A simple extraction method has been developed for separation of barium(II) from picric acid medium using 15-crown-5. Barium(II) has been quantitatively extracted from 0.001-0.05 M picric acid with 0.002-0.01 M 15-crown-5 in nitrobenzene as a diluent. From the organic phase barium(II) has been quantitatively stripped with 0.5-10 M HNO₃ and HCl and 10 M HClO₄. Separation of barium has been carried out from a number of elements in binary and multicomponent mixtures. Most of the elements from s-block, p-block and d-block show high tolerance limit. The method has been extended for the determination of barium(II) in various rock samples.

Barium has attracted considerable attention because it is one of the major constituent of fission products. It is also found in a number of rocks. Therefore the determination of barium(II) in environmental samples such as rocks, minerals, marine organisms and bone is important. However, the environmental samples often contain large amount of calcium(II) and other alkaline earth metals which may cause spectral interference. Therefore, for the precise determination, it is essential to separate barium(II) from other elements. The classical methods involve selective precipitation either as insoluble sulfate or chromate. These methods are applicable only when the concentration of barium(II) is in milligram concentrations. In solvent extraction methods benzoylacetone and dibenzoylethane have been used as extractants but the extraction of barium(II) is very poor. The extraction of barium(II) has been carried out in alkaline media using thenoyltrifluoroacetone, bis-2-ethylhexyl phosphoric acid, hexafluoroacetylatedone, however no attempts have been made to separate barium(II) from the associated elements. Crown ethers like 18-crown-6(ref. 7, 8), dibenzo-18-crown-6(ref. 9), dibenzo-24-crown-8(ref. 10) have been used for the study of extraction constant and stability constant. The separation of barium(II) from other alkaline earths was achieved with dibenzo-18-crown-6 and 18-crown-6 (ref. 11). The stability of strontium(II) and barium(II) has been reported with 18-crown-6 from picrate solution. The substoichiometric ion-pair extraction of barium with cryptand-2.2.2 and 18-crown-6 has also been carried out using picrate as a counter anion. Spectrophotometric investigation of complex formation of barium(II) and calcium(II) with aza-15-crown-5 has also been carried out.

We report in this note the solvent extraction separation studies of barium(II) and its separation from the associated elements using 15-crown-5. The method developed is simple and allows extraction at trace levels. Barium(II) can be separated very effectively from associated elements in multicomponent mixtures. The developed method has also been extended for the determination of barium(II) in a number of certified rock samples.

Experimental

A Zeiss spectrophotometer, a digital pH meter, with glass and calomel electrodes, a digital flame photometer, a wrist action flask shaker and 125 ml separating funnels were used.

Stock solution of barium(II)(1.00 mg/ml) was prepared by dissolving 1.90 g of barium nitrate(AnalaR grade, BDH) in 1000 ml of distilled, deionised water and standardized gravimetrically. A solution containing 100 µg/ml of barium(II) was prepared by appropriate dilution of the standard stock solution.

Solutions of crown ethers were prepared from 15-crown-5, benzo-15-crown-5, 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6, dicycloclohexano-18-crown-6, dibenzo-24-crown-8 and dicycloclohexano-24-crown-8 (Aldrich,USA) without further purification.

Picric acid solution (0.05 M) was prepared by dissolving 2.846 g of picric acid in 250 ml of distilled, deionised water.
General procedure

To an aliquot containing 100 μg barium(II), picric acid was added so as to have a concentration of 0.00001-0.05 M in a total volume of 10 ml. The solution was then transferred to a separating funnel and equilibrated with 10 ml of 0.001 M suitable crown ether with nitrobenzene as the diluent, for 10 min on a wrist action flask shaker. The two phases were allowed to settle and separate. Barium(II) was stripped from the organic phase with 10 ml of 2 M nitric acid and was determined spectrophotometrically with Sulphonazo-III at 640 nm. The concentration of barium(II) was calculated from a calibration graph.

Results and discussion

According to hard-soft acid base rule, soft acid prefers soft base, barium(II) being soft acid its extraction is favored with picric acid which is a soft base. In order to ascertain the optimum concentration of picric acid required for the quantitative extraction of barium, experiments were performed by extracting barium with various crown ethers (0.005 M) in nitrobenzene as the diluent and varying the picric acid concentration from 0.00001-0.05 M. It was found that with 15C5, barium(II) was quantitatively (100%) extracted from 0.001-0.05 M picric acid. With B15C5 and DC24C8, the extraction was quantitative from 0.004-0.05 M picric acid. The extraction of barium was also quantitative with B18C6, DC18C6 and DB24C8 from 0.008-0.05 M picric acid. With DB18C6, the extraction of barium(II) was quantitative from 0.01-0.05 M picric acid. For further extraction studies of barium(II) 15-crown-5 was selected. The extraction of barium(II) was studied for 0.005 M 15-crown-5 in nitrobenzene by varying the concentration of picric acid in the concentration range of 0.00002-0.05 M. It was observed that the extraction of barium was 15% at 0.00002 M and increased with increase in picric acid concentration being 40% at 0.00008 M, 82% at 0.0004 M, 98% at 0.0008 M and quantitative from 0.001-0.05 M picric acid. For further work, 0.001 M of picric acid was used.

In order to ascertain the optimum concentration of 15-crown-5, extractions were carried out from 0.001 M picric acid by varying the concentration of 15-crown-5 in the concentration range of 0.0001-0.01 M using nitrobenzene as a diluent. Barium(II) was extracted to the extent of 37% at 0.0001 M. The extraction of barium(II) increased with increase in 15-crown-5 concentration. The extraction was 50% at 0.0002 M, 67% at 0.0004 M, 94% at 0.001 M and quantitative from 0.002-0.01 M. Further extraction studies of barium were carried out using 10 ml of 0.005 M 15-crown-5 in nitrobenzene.

The extraction of barium(II) was studied using 0.001 M picric acid with 0.005 M 15-crown-5 with various solvents such as benzene, toluene, xylene, carbon tetrachloride, chloroform, dichloromethane, dichloroethane and nitrobenzene. The phase volume ratio was maintained at unity. The studies revealed that the extraction of barium(II) was 24% with benzene, 13% with toluene and xylene, 8% with carbon tetrachloride, 18% with chloroform and 20% with dichloromethane and dichloroethane. The extraction was quantitative only with nitrobenzene. Further extraction studies were carried out using nitrobenzene as the diluent.

Barium(II) was extracted with 0.001 M picric acid using 15-crown-5 0.005 M in nitrobenzene as a diluent. The equilibration period was varied in the range of 1-30 min. It was observed that the extraction of barium was quantitative with 1 min of equilibration.

After extraction under the above conditions, barium(II) was stripped from the organic phase with various stripping agents such as nitric acid, hydrochloric acid, hydrobromic acid, perchloric acid and acetic acid in the concentration range of 0.1-10 M (0.1-8 M in the case of HBr). The stripping of barium(II) was quantitative with 0.5-10 M HNO₃ and HCl and 10 M HClO₄. Hydrobromic acid and acetic acid were found to be an inefficient strippants. For further studies 2 M HNO₃ was used as a strippant.

Plots of log D versus log [15C5] at fixed picric acid concentration (0.001 M) and log D versus log [picric acid] at fixed 15C5 concentration (0.005 M) were linear. The slopes were found to be 1.20 and 2.10 respectively, indicating that the extracted species is probably 1:1:2 in composition, with respect to barium:15C5:picrate.

Separation of barium(II) from synthetic mixtures

Barium(II) was extracted with 0.005 M 15-crown-5 in nitrobenzene from 0.001 M picric from binary mixtures with several ions. The tolerance limit was set at the amount of foreign ions required to cause a ± 2%
error. Amongst s-block elements, potassium(I), rubidium(I) and cesium(I) showed extraction along with barium(II), thus showing low tolerance limit. Lithium(I) and other alkaline earth metal ions were not extracted and showed very high tolerance limit. Lead(II) showed partial extraction along with barium(II). Most of the p-block and d-block elements were tolerated in high proportions. The anions of inorganic and organic acids were tolerated in higher concentrations.

Under the optimum conditions there was no extraction of iron(III). From 7M hydrochloric acid however there was quantitative extraction of iron(III) with 15-crown-5 in nitrobenzene while barium(II) was not extracted. This behavior, exhibited by 15-crown-5 with different anions, has been exploited for the separation of barium(II), iron(III) and other ions in multicomponent mixtures.

A mixture of iron(III), barium(II) and X [X = Be(II), Li(I), Mg(II), Ca(II), La(III), Y(III) or Th(IV)] was separated by extracting iron(III) from 7M hydrochloric acid with 0.005 M 15-crown-5, while barium(II) and X remained in the aqueous phase. After evaporating the aqueous phase, the residue was treated with water and barium(II) was extracted with 0.005 M 15-crown-5 from 0.001 M picric acid leaving behind X in the aqueous phase. Iron(III) and barium(II) from the respective organic phases were stripped with 2M nitric acid. The separation of barium(II) and iron(III) from other elements in multicomponent mixtures was accomplished by following similar methodology.

Barium(II) was also separated from rubidium(I) and other elements as follows: When a mixture containing rubidium(I), barium(II) and X [X = Be(II), Li(I), Mg(II), Ca(II), La(III), Y(III) or Th(IV)] was extracted from 0.001M picric acid with 0.005 M 15-crown-5 in nitrobenzene as diluent. Under these conditions rubidium(I) and barium(II) were extracted leaving behind X in the aqueous phase. From the organic phase rubidium(I) was first stripped out with 2M perchloric acid. Under this condition barium(II) was not stripped because of formation of extractable perchlorate complex which was then stripped out with 2M nitric acid.

The separation of barium(II), rubidium(I) from other elements in multicomponent mixtures was accomplished by following similar methodology.

**Analysis of barium(II) in rock samples**

The proposed method was applied for determination of barium(II) in standard rock samples such as KC-11, KC-12 and syenite rock (SY-II). The samples were brought into solution by following the procedure described earlier 15. From the sample solution iron(III) was first separated as per the procedure described above in multicomponent mixture separation. After separation of iron(III), the sample solution was treated as per the general procedure and barium(II) content was determined. The amount of barium(II) found in KC-11 rock sample was 488 ppm as against the certified value of 491 ppm and in KC-12 rock, the amount of barium(II) found was 1605 ppm as against the certified value of 1600 ppm. In syenite rock sample barium was found to be 462 ppm as against the certified value of 460 ppm. In basaltic-BR sample the barium was found to be 1040 ppm as against the certified value of 1050 ppm. These results clearly establish that the present method can conveniently be used to analyze barium(II) in rock samples.

**References**