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SEPARATION OF STRONTIUM ION FROM A LARGE AMOUNT OF CALCIUM ION BY THE USE OF A MACROCYCLIC ETHER

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A small amount of Sr^{2+}(0.7∿20 mg) was simply separated from a large amount of Ca^{2+}(1.5 g) by liquid-liquid extraction using dicyclohexyl-18-crown-6 chloroform solution. Average recovery of Sr^{2+} was 97 %, and the amount of Ca^{2+} in the final strontium fraction of the separation was decreased to 10^{-4}∿10^{-5} part of the initial amount.

The separation of strontium ion from calcium ion has been of importance in determining radioactive strontium nuclides in environmental samples which often contain a large amount of calcium. This letter describes the separation of strontium ion from a large amount of calcium ion by liquid-liquid extraction with a macrocyclic ether.

Formation of complexes of metal ions with a group of macrocyclic ethers, generally known as crown ethers, and solubilization of the complex salts in organic solvents have been reported.1,2,3) In the present work the crown ether dicyclohexyl-18-crown-6 was selected for the separation on the basis of its ring size2) and stability of its complexes with Ca^{2+} and Sr^{2+} in aqueous solutions.1,2,3) In chloroform it extracted Sr^{2+} better than in toluene.

Strontium ion in aqueous solutions of pH 2.5∿7 was easily extracted by chloroform solution containing the crown ether in molar amount twice that of Sr^{2+}, when picrate was used as a counter ion of Sr(II)-complex. However, the extraction was appreciably decreased for an aqueous solution of pH 1.2: this is thought to be due to the hydrogen ion affinity of the picrate.

Acetic acid-sodium acetate(1 : 1) was used as a buffer reagent for the aqueous solution. Extraction of alkaline earth metal ions was examined at varying concentrations of the buffer reagent. The metal ions in aqueous solutions($[M^{2+}]$= 5.8 mM, [sodium picrate]= 23 mM, the buffer reagent at varying concentrations; 10 ml) were extracted by the extractant(2.9 mM dicyclohexyl-18-crown-6 chloroform solution; 40 ml). Values of extraction percentage for Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} were 2.8, 36, 100, and 100 without the buffer reagent; 2.1, 30, 100, and 99 at 0.02 M acetic acid and 0.02 M sodium acetate; and 0.7, 7.5, 98, and 98 at 0.17 M acetic acid and 0.17 M sodium acetate, respectively.

A procedure was devised for separating Sr^{2+} from a large amount of Ca^{2+}; it is shown in Fig. 1. It was applied to separate mixtures of 0.7∿20 mg Sr^{2+} and 1.5 g Ca^{2+}, and the results are shown in Table 1. Strontium ion in sample solutions was extracted more than 98 % by the single extraction in the procedure. A small amount of Ca^{2+} was extracted into the organic phase with Sr^{2+}. However, this calcium ion was removed from the organic phase by double washing with the aqueous solution described in Fig. 1. Loss of strontium ion in the organic phase by a single washing procedure was less than 1 %. Strontium ion in organic phase-3(Fig. 1) was completely transferred in aqueous phase-4.

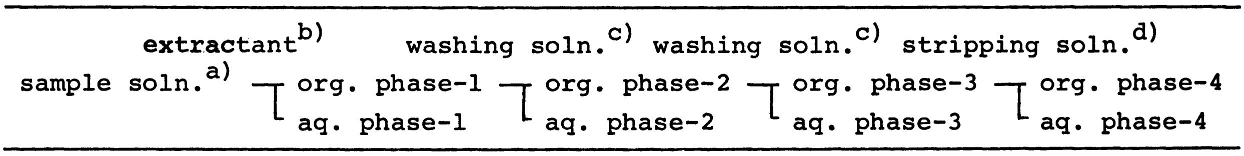

Fig. 1. Procedure for the Separation of Sr^{2+} from Ca^{2+}

a) 45 ml of 0.02 M sodium picrate – 0.055 M acetic acid – 0.055 M sodium acetate solution containing Ca and Sr ions; b) 40 ml of 0.011 M dicyclohexyl-18-crown-6 chloroform solution; c) 30 ml of 0.085 M acetic acid – 0.085 M sodium acetate – 0.015 M sodium picrate solution; d) 50 ml of 2 M ammonium chloride – 0.2 M hydrochloric acid solution.

Table 1. Results of the Separation of Sr^{2+} from Ca^{2+}

sample soln.		aq. phase-1	aq. phase-2	aq.phase-3		aq. phase-4		recovery
Ca^{2+} g	Sr^{2+} mg	Sr^{2+} mg	Sr^{2+} mg	Ca^{2+} mg	Sr^{2+} mg	Ca^{2+} mg	Sr^{2+} mg	of Sr^{2+} %
1.5	0.69[a]	0.013	0.001	2.03	0.001	0.11	0.66	96
1.5	2.2_5	0.033	0.002	1.79	0.002	0.09	2.1_3	95
1.5	$10._4$	—	0.012	1.01	0.017	0.04	$10._1$	97
1.5	$20._5$	0.02	0.09	—	0.11	0.02	$20._7$	101

a) impurity in the $CaCl_2 \cdot H_2O$ reagent used.

The extraction of Mg^{2+} was much less than that of Ca^{2+}, and hence Mg^{2+} might be easily separated from Sr^{2+}. Behavior of Ba^{2+} was similar to that of Sr^{2+}.

By this method, the average recovery of Sr^{2+} was 97 %. The amount of Ca^{2+} in the final strontium fraction of the separation was found to be $10^{-4} \sim 10^{-5}$ part of the initial amount. These results compare well with those by the usual separations hitherto reported. The procedure is more rapid than that in the chromatographic ion-exchange methods, and is easier to be carried out than that in the precipitation methods.

Experimental: The dicyclohexyl-18-crown-6 was purchased from Nippon Soda Co., and was a mixture of two isomers. It was used without any purification.

Mg^{2+}, Ca^{2+}, and Sr^{2+} in aqueous solution were determined by atomic absorption spectroscopy, and Ba^{2+} by flame photometry.

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