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ION-EXCHANGE IN THE PRESENCE OF COMPLEX III

-USSR-

By O. Budevski and N. Krasnobayeva

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FOREWORD

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SEPARATION OF STRONTIUM FROM CALCIUM BY
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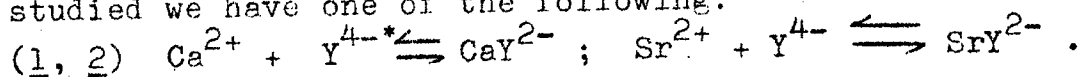
-USSR-

Following is a translation of the article entitled "Otdeleniye strontsiya ot kal'tsiya putem ionnogo obmena v prisutstvii kompleksa 3" (English version above) by O. Budevski and N. Krasnobayeva in Doklady Bolgarskoy Akademii Nauk (Reports of the Bulgarian Academy of Sciences), Vol XIII, No 1, Sofia, January/February 1960, pages 67-70.

The basic difficulty in the analytic determination of strontium is its separation from calcium. The use of the different solubilities of calcium salts from those of strontium in various solvents is not considered a precise method, especially when they are not present together in approximately equal quantities (1).

Calcium and strontium form stable complexes, in varying degree, with ethylenediaminetetraacetic acid (EDTA) in which the calcium complex is about one hundred times more stable, $pK_{Ca} = 10.96$, $pK_{Sr} = 8.63$ (2). This fact has been utilized to effect a separation of both elements, but the studies that have been carried out are very limited as concerns the feasibility of separating small amounts of strontium from large amounts of calcium (3,4).

Choosing the known conditions (pH, concentration of EDTA), it is possible to convert one of these two species (Ca^{2+}) into a complex, while the other (Sr^{2+}) remains in the form of the free ion. Recalling that complexes of cations with EDTA have negative charge, in the case being studied we have one of the following:

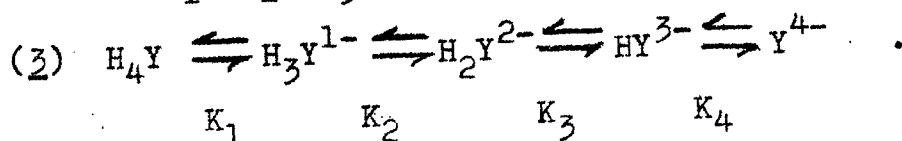


[* See Note 7 (* Y⁴⁻ here stands for the quadrivalent anion EDTA.)

CaY²⁻ will have a negative charge, whereas Sr²⁺ -- a positive charge. The passage of this solution through an ion-exchange column would effect a quantitative separation of these elements, only if the presence of the ion-exchange resin did not result in a displacement of the equilibria (1 and 2).

In a system consisting of calcium and strontium ions, EDTA, and the ion-exchange resin, one must keep in mind the following three mutually interacting equilibria:

EQUILIBRIUM No 1. Ethylenediaminetetraacetic acid is a quadrivalent acid with four dissociation constants (K₁, K₂, K₃, K₄)



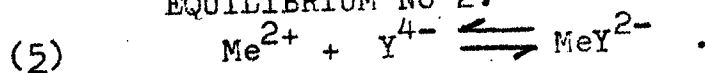
Out of all the ions that EDTA forms, only the quadrivalent anion participates in complex-formation. The ratio of the concentration of the free quadrivalent ion (Y⁴⁻) to the total concentration of EDTA (C_Y) in the solution is given by the equation

$$(4) \quad \frac{[\text{Y}^{4-}]}{C_Y} = \frac{[\text{Y}^{4-}]}{[\text{H}_4\text{Y}] + [\text{H}_3\text{Y}^{1-}] + [\text{H}_2\text{Y}^{2-}] + [\text{HY}^{3-}] + [\text{Y}^{4-}]}$$

$$= \frac{1}{\frac{[\text{H}^+]^4}{K_1 K_2 K_3 K_4} + \frac{[\text{H}^+]^3}{K_1 K_2 K_3} + \frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_1} + 1} = \frac{1}{\beta}$$

and, as is seen, depends on the hydrogen ion concentration (pH) in the solution. At pH = 12 EDTA is almost wholly dissociated (2).

EQUILIBRIUM No 2.



This equilibrium depends on the stability constants of the complexes formed

$$(6) \quad K = \frac{[\text{MeY}^{2-}]}{[\text{Me}^{2+}][\text{Y}^{4-}]}$$

Inasmuch as in order for the ion exchange to have taken place, the ratio between the free form and the bound form of the ion must be of a substantial value, then we will conditionally designate \underline{a} to stand for this ratio. From equation (6)

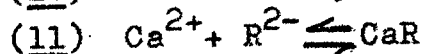
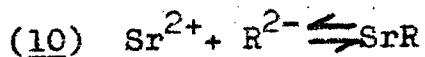
$$(7) \quad \underline{a} = \frac{[\overline{Me}^{2+}]}{[MeY^{2-}]} = \frac{1}{K[\overline{Y}^{4-}]}$$

Substituting $[\overline{Y}^{4-}]$ from equation (4), we obtain

$$(8, 9) \quad \underline{a} = \frac{\beta}{KC_Y} \quad \log \underline{a} = \log \beta - \log KC_Y$$

Equations (8) and (9) allow us to calculate the size of \underline{a} from a given value of the pH. In figure 1 the values of $\log \underline{a}$ are represented graphically in dependence on the pH value of a EDTA-containing solution of both elements. The ionic strength of the solution is not considered here. From the graph in figure 1 it is clear that the region most favorable for a separation of both elements lies near pH = 4.4, where the $\log \underline{a}_{Ca} = -1.2$, but the $\log \underline{a}_{Sr} = 1$, that is, the larger portion of the calcium is found in the anionic form (in the complex), but the strontium is in the cationic form (free ion).

EQUILIBRIUM No 3.



The third equilibrium which is established in the system under study is the adsorption of cations on the cation-exchange resin. This equilibrium plays an important role, since it can show an effect on the other two equilibria. If the adsorption forces are very large, then the region favorable to the separation of the two elements shifts to the area of high pH values, where \underline{a} has a small value for both elements. The shifting of equilibria (10) and (11) also has a considerable influence on this effect.



Fig. 1. Dependence of $\log \underline{a}$ on pH

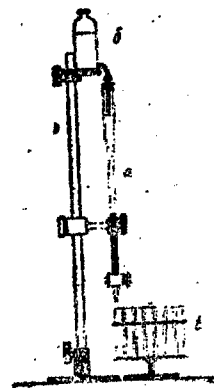


Fig. 2

From what has been stated it is clear that the effects occurring in the ion-exchange column are much too complex for one to predict exactly what the optimal value of the pH is for separation of calcium from strontium.

The goal of the present studies is the determination of precisely this optimal pH value at selected experimental conditions.

TABLE 1

Results of strontium determination in the presence of calcium

	Mg of Sr, Ca Added	Mg of Sr Found	Ratio Ca:Sr
A.	0.400 Sr 4.000 Ca	0.40 ₄	10:1
B.	0.300 Sr 7.500 Ca	0.30 ₂	25:1
C.	0.300 Sr 15.000 Ca	0.29 ₇	50:1
D.	0.300 Sr 30.000 Ca	0.30 ₄	100:1

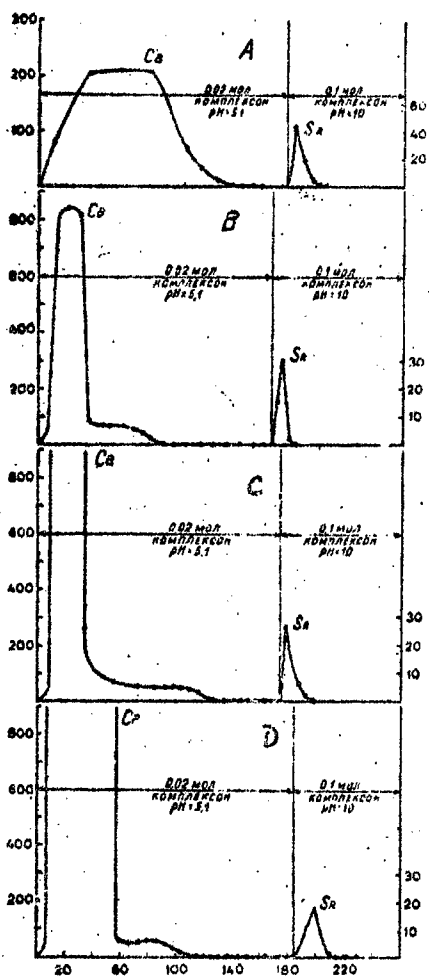


Figure 3. Washing curves of calcium and strontium. Ratio of Ca:Sr = A -- 10:1, -- 25:1, B -- 50:1, -- 100:1. The declinations of the galvanometer are

Experimental part.

A standard column a (see figure 2) was used -- length 300 mm, internal diameter 9 mm, a vessel with the washing liquid δ , and an automatic fraction collector ϵ . The collector was comprised of 18 test tubes distributed about the periphery of a disk. By means of the apparatus every five minutes the tubes changed position, at which time 10 ml had just accumulated in a tube (dropping rate -- 2 ml/minute). Measurement of the pH value is done by means of

7 /Caption to figure 3 continued/

plotted on the ordinate axes; on the abscissae -- millimeters of the wash liquid. 7 /In the figure above the words "mole" and "complex at pH ____" are repeated twice in each of the four graphs./

7 /Experimental part continued/

a glass electrode. Determination of the concentrations of calcium and strontium is obtained by means of a K. Zeiss flame photometer, Model III.

The ion-exchange resin, cationite, Wofatit F, was ground to dimensions of 0.10-0.25 mm. It was subjected to a treatment with dilute hydrochloric acid 1:1 for a period of 3-4 hours. After rinsing the resin with water it was placed in the column. The effective height of the cationite was 100 mm. In order to convert the resin into the NH_4 -form an ammoniacal solution of 0.02 M EDTA at a pH of 10 was run through the cationite.

On the basis of preliminary experiments, a pH = 5.1 ± 0.1 , at a EDTA concentration of 0.02 M, was chosen as the optimal value for separation. At lower pH values the elution of the calcium proceeds slowly at the expense of eluting liquid. Above pH = 5.4 there already exists the danger of the elution of strontium.

Studies were carried out in a series of experiments on the separation of calcium and strontium at various ratios (small quantities of strontium and large quantities of calcium). The column was prepared beforehand by passing through a 0.02 M solution of the ammonium complex at a pH = 5.1 ± 0.1 until the same pH was determined in the exiting liquid. To 2-3 ml of the solution of the calcium and strontium salts (0.3-3.0 ml) 25 ml of 0.02 M of the ammonium complex was added; by means of ammonia and hydrochloric acid a pH value of 5.1 ± 0.1 was attained. The solution was passed through the column at a dropping rate of 2 ml/minute and then the column was washed with 150-180 ml of 0.02 M of the ammonium complex at the same pH. The calcium passed quantitatively through the column, but the strontium was held back. The elution of the strontium was carried out with 20.0 ml of a 0.1 M solution of the ammonium complex at a pH = 10. Figure 3 shows the washing-out curves for calcium and strontium at various concentration ratios, while table 1 has the quantitative results of their separation.

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Beneficiation

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