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PAPER CHROMATOGRAPHY OF INORGANIC IONS

IN NITRATE MEDIA

III - SEPARATION OF CALCIUM STRONTIUM, BARIUM AND RADIUM

by

M. C. Levi and J. Danon

CENTRO BRASILEIRO DE PESQUISAS FÍSICAS

Av. Wenceslau Braz, 71

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PAPER CHROMATOGRAPHY OF INORGANIC IONS
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III - SEPARATION OF CALCIUM STRONTIUM, BARIUM AND RADIUM

M. C. Levi and J. Danon

Centro Brasileiro de Pesquisas Físicas

Rio de Janeiro, E. G., Brazil

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The separation of the alkali earth elements by paper chromatography in nitric acid media was investigated by Elbeih¹ and all¹ using colidine as organic solvent and by S. Nakano² with a mixture of HCl and HNO₃ in methyl alcohol.

The alkali earths associate with the nitrate ion forming complexes with different stabilities³. Nitrate media should therefore be useful for chromatographic separations among these elements, particularly at high nitrate concentrations as was observed in other systems^{4,5}.

Experimental

Small aliquots of about 0.02 ml of the samples were applied to a strip of Whatman paper n° 1 which was placed in a closed chamber for ascending development. The eluting solvents were previously conditioned with appropriate nitrate solutions and the development was made in about 16 hours at room temperature.

The separation between Ca-Sr-Ba was investigated with about 0.2 mgs of each cation. Calcium was detected by spraying an alcoholic solution of 8-hydroxyquinoline in ammoniacal media; the spots obtained became fluorescent on irradiation with ultra-violet light. Strontium and Barium were identified with potassium rodizonate giving red spots.

Separations between barium and radium were investigated at the tracer level by using carrier-free Ba^{140} (beta, gamma, $T_{1/2} = 12.8$ d) and Ra^{228} (MsThI, beta, gamma, 6.14 years) as isotopes. Both isotopes were obtained from Harwell.

After development the strip of paper was scanned with a G. M. counter. The measurements were made some days after the development in order to attain the transient equilibrium between the tracers and their radioactive descendents which are La^{140} (beta, gamma, 40 h. period) and Ac^{228} (beta, gamma, 6,13 h period). The separations between Ba^{140} - Ra^{228} were also controlled by measurements of the gamma-ray spectra of the isotopes in a single channel spectrometer with NaI(Tl) crystal.

Results

a. Separation between Ca-Sr-Ba

Table 1 gives the values of R_f obtained with different organic solvents at different $\text{LiNO}_3 + \text{HNO}_3$ concentrations. It is observed that larger differences between the R_f 's of these elements were obtained with the more concentrated nitrate solutions. The R_f 's are strongly dependent on the nature of the organic solvent. The value of R_f was found to decrease with the increase in the molecular weight of the alcohols investigated. Better separations were obtained with lower alcohols such as ethyl alcohol or with diethyl ketone.

b. Double spot formation with barium

As can be observed in table 1, barium nitrate yields double spot when the development is made with low mol. weight solvents. Similar results were obtained by using saturated $\text{Al}(\text{NO}_3)_3$ in the place of LiNO_3 .

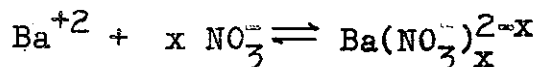
Since the formation of double spots was observed with different samples of $\text{Ba}(\text{NO}_3)_2$ and by using acid-washed paper it cannot be attributed to the presence of impurities in the solution or in the paper.

The formation of multiple spots of a given element was observed by several authors's in different systems⁶. The existence of more than one spot is generally attributed to the formation of stable complexes of the element in the media investigated.

This and other interpretations for the multiple spots formation have been discussed in a recent review ⁷.

A remarkable aspect of the double spot formation of Ba in nitrate media was observed by varying the concentration of the cation Ba^{++} . The chromatograms reproduced in fig. 1, obtained with a mixture of propanol (80%) and aqueous solution (20%) of $LiNO_3$ (7M) and HNO_3 (2M), show that the double spot formation is a function of the initial concentration of barium. With amounts of barium higher than $2 \cdot 10^{-4}$ mgs two peaks are observed ($R_f = 0$ and $R_f \approx 0.4$). At about 10^{-4} mgs the two peaks joint and a "comet" is observed. At lower amounts of barium only a single peak is observed ($R_f \approx 0.4$) The concentration of barium in the peaks is thus dependent on the initial concentration of the cation.

This behaviour cannot be explained by assuming that the double spots are due to the formation of barium complexes with different values for R_f , such as



The equilibrium constant for this reaction is

$$K = \frac{[Ba(NO_3)_x^{2-x}]}{[Ba^{+2}][NO_3^-]^x} \cdot \Gamma$$

where Γ is the activity coefficient ratio of the species. At constant $[NO_3^-]$, Γ can be assumed as constant and we have:

$$\frac{[\text{Ba}(\text{NO}_3)_x]^{2-x}}{[\text{Ba}^{+2}]} = K'$$

The relation between the concentration of barium in the two peaks should thus be independent of the initial concentration of the cation, if only mononuclear barium nitrate complexes are formed. We think that further investigations are required in order to explain the anomalies observed in the chromatographic behaviour of barium.

c. Separation between barium and radium

As was observed with the other systems the chromatographic separations of barium and radium in HNO_3 media with propanol as organic solvent is not efficient.

The addition of LiNO_3 to the HNO_3 solution greatly improves the separation, as is shown in figure 2. This chromatogram was obtained with propanol (80%) and aqueous solution of HNO_3 (2M) and LiNO_3 (4M). Trace amounts of the elements were employed by using Ra^{228} (Ms Th I) and Ba^{140} as radioactive isotopes. All other conditions were similar to those used in the Ca & Ba separations.

It is important to observe that the separation cannot be effected with larger amounts of barium ($> 10^{-7}$ grs), since this element gives two spots, the first one with $R_f = 0$, equal to that of radium in trace amounts.

Since the values of R_f for Ac ($R_f = 0,25$) and La ($R_f = 0,47$)

differ largely from that of Ra and Ba respectively, the method is useful for the purification of these radioactive elements by paper chromatography as is illustrated in figure.

ACKNOWLEDGMENT

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TABLE I

ORGANIC PHASE	LiNO ₃ MOLARITY	HNO ₃ MOLARITY	Rf		
			Ca	Sr	Ba
Amyl alc.	7	8	0,017	0	0
Butanol	9	0,5	0,182	0,062	0
"	7	8	-	0	0
"	7	2	-	0,033	0
Propanol	9	0,5	0,8	0,6	0,402 - 0,04
"	7	2	0,71	0,47	0,33 - 0,074
"	7	-	0,648	0,495	0,33 - 0
"	4	0,5	0,616	0,385	0,19 - 0
Isopropy alc.	7	2	-	-	0,212 - 0
Ethanol	7	2	0,7	0,425	0,233 - 0,039
Ether	7	2	-	-	0
Acetone	3	2	0,688	0,537	0,356 - 0,073
"	3	0,5	0,575	0,540	0,406 - 0,066
Butanol	Al(NO ₃) ₃				
	Satur.	0,5	0,142	0,056	0
Propanol	Satur.	0,5	-	0,18	0,094 - 0

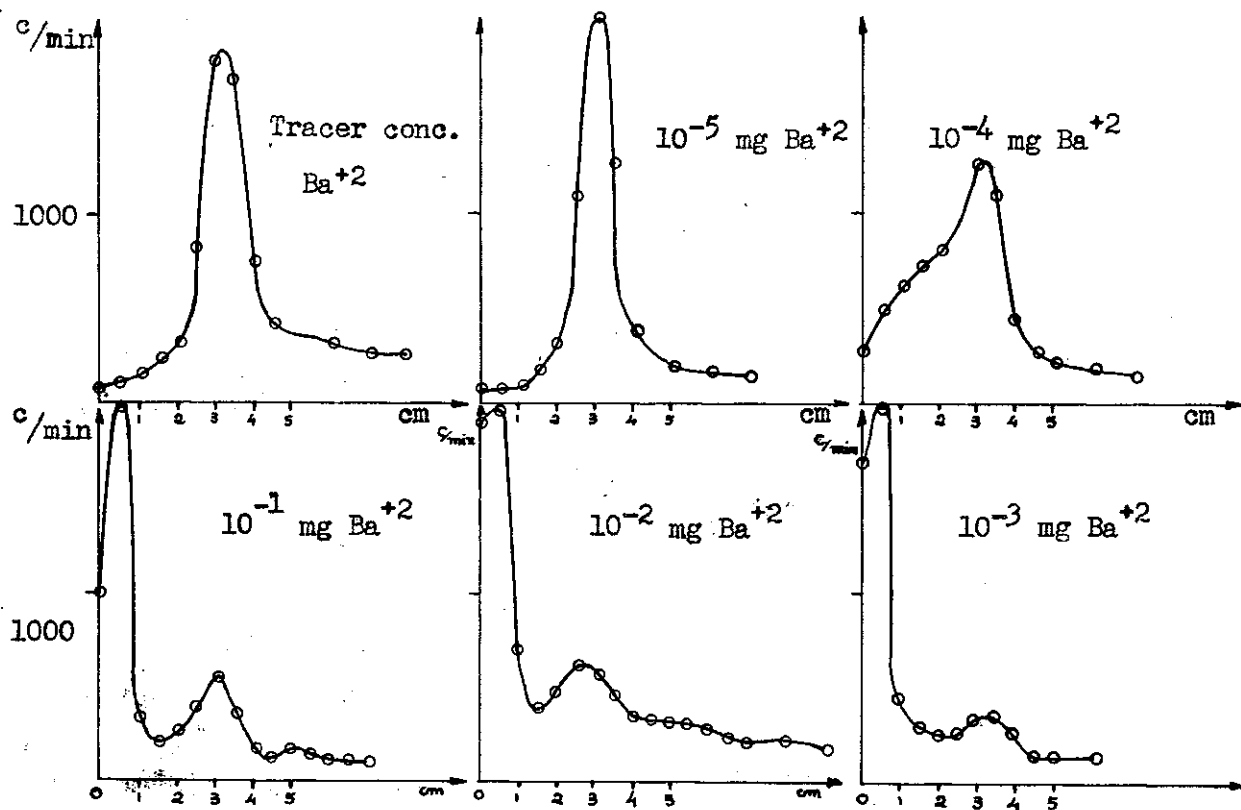


Fig. 1

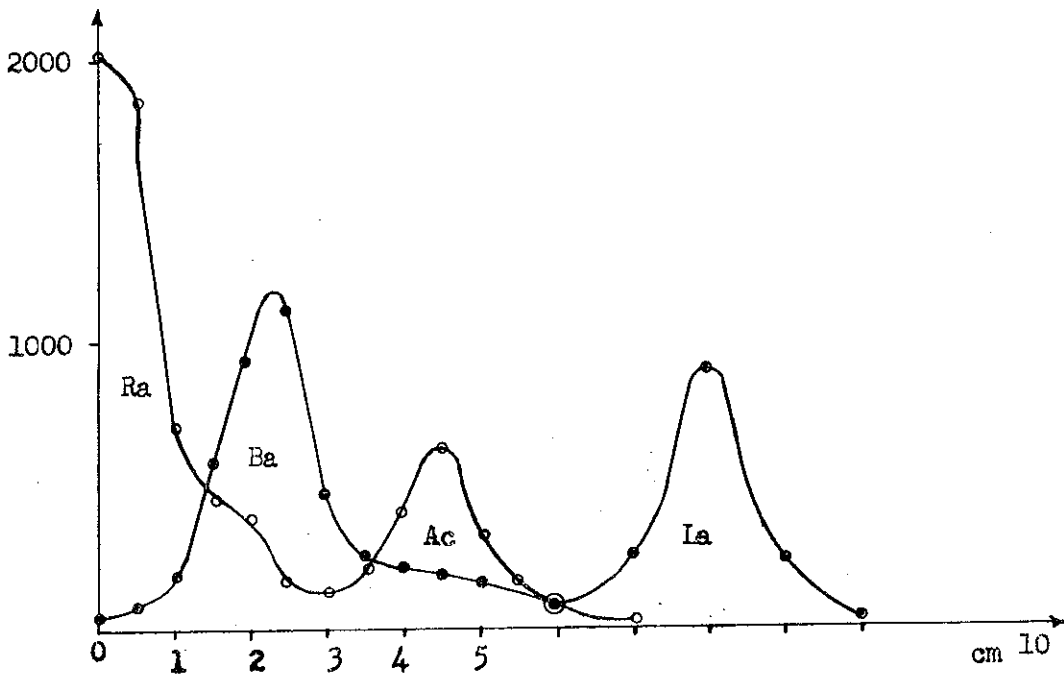
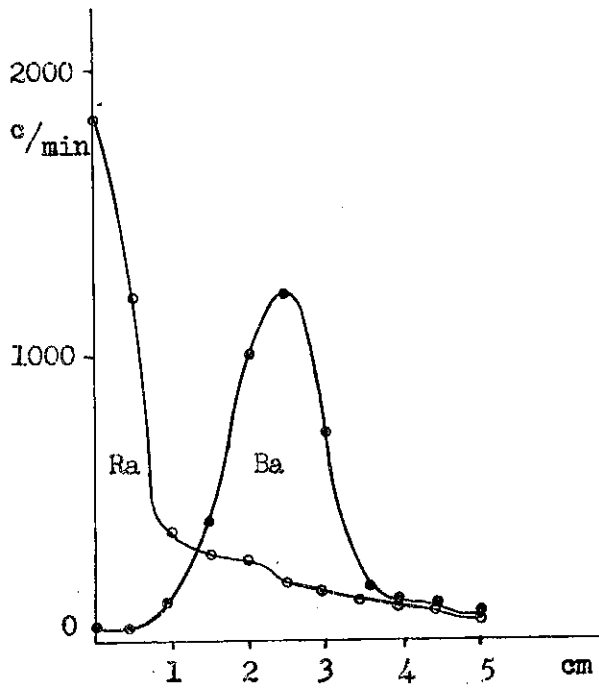


Fig. 2