

PAPER CHROMATOGRAPHY OF INORGANIC IONS
IN NITRATE MEDIAIII. SEPARATION OF CALCIUM, STRONTIUM, BARIUM
AND RADIUM

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The separation of the alkaline earth elements by paper chromatography in nitric acid media was investigated by ELBEIH *et al.*¹, who used collidine as organic solvent, and by NAKANO², who used a mixture of HCl and HNO₃ in methyl alcohol.

The alkaline earths associate with the nitrate ion to form complexes with different stabilities³. Nitrate media should therefore be useful for chromatographic separations of 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 No. 1 paper, which was placed in a closed chamber for ascending development. The eluting solvents were treated beforehand with appropriate nitrate solutions and development was carried out at room temperature for about 16 hours.

The separation of Ca-Sr-Ba was investigated with about 0.2 mg of each cation. Calcium was detected by spraying an alcoholic solution of 8-hydroxyquinoline in ammoniacal medium; the spots obtained became fluorescent on irradiation with ultraviolet light. Strontium and barium were identified with potassium rhodizonate, red spots being obtained.

Separations of barium and radium were investigated at the tracer level by using carrier-free ¹⁴⁰Ba (β , γ , $T_{1/2} = 12.8$ days) and ²²⁸Ra (MsTh I, β , γ , 6.14 years) as isotopes. Both isotopes were obtained from the Atomic Energy Research Establishment, Harwell, England.

After development the strip of paper was scanned with a Geiger-Müller counter. The measurements were made some days after the development in order to attain the transient equilibrium between the tracers and their radioactive descendants, which are ¹⁴⁰La (β , γ , 40 h period) and ²²⁸Ac (β , γ , 6.13 h period). The separations of ¹⁴⁰Ba-²²⁸Ra were also checked by measurement of the γ ray spectra of the isotopes in a single channel spectrometer with Na I (Tl) crystal.

RESULTS

(a) Separation of Ca-Sr-Ba

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

TABLE I

Organic phase	LiNO ₃ molarity	HNO ₃ molarity	R_F		
			Ca	Sr	Ba
Amyl alc.	7	8	0.043	0	0
Butanol	9	0.5	0.182	0.062	0
Butanol	7	8	—	0	0
Butanol	7	2	—	0.033	0
Propanol	9	0.5	0.8	0.6	0.402-0.04
Propanol	7	2	0.71	0.47	0.33 -0.074
Propanol	7	—	0.648	0.495	0.33 -0
Propanol	4	0.5	0.616	0.385	0.19 -0
Isopropyl 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
Acetone	3	0.5	0.575	0.540	0.406-0.066
	<u>Al(NO₃)₃</u>				
Butanol	Satur.	0.5	0.142	0.056	0
Propanol	Satur.	0.5	—	0.18	0.094-0

(b) Double spot formation with barium

As can be observed in Table I, barium nitrate yields a double spot when the development is carried out with low molecular weight solvents. Similar results were obtained by using solvents saturated with $\text{Al}(\text{NO}_3)_3$ instead of LiNO_3 .

Since the formation of double spots was observed with different samples of $\text{Ba}(\text{NO}_3)_2$ and also when acid-washed paper was used 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 has been observed by several authors in various 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 explanation, as well as others, for the formation of multiple spots has been discussed in a recent review⁷.

A remarkable aspect of the double spot formation of Ba in nitrate media was observed when the concentration of the cation Ba^{2+} was varied. The chromatograms reproduced in Fig. 1, obtained with a mixture of propanol (80%) and an 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 $2 \cdot 10^{-4}$ mg two peaks are observed ($R_F = 0$ and $R_F = 0.4$). At about 10^{-4} mg the two peaks join and a "comet" is observed. With smaller amounts of barium only a single peak is observed ($R_F = 0.4$). The concentration of barium in the peak is thus dependent on the initial concentration of the cation.

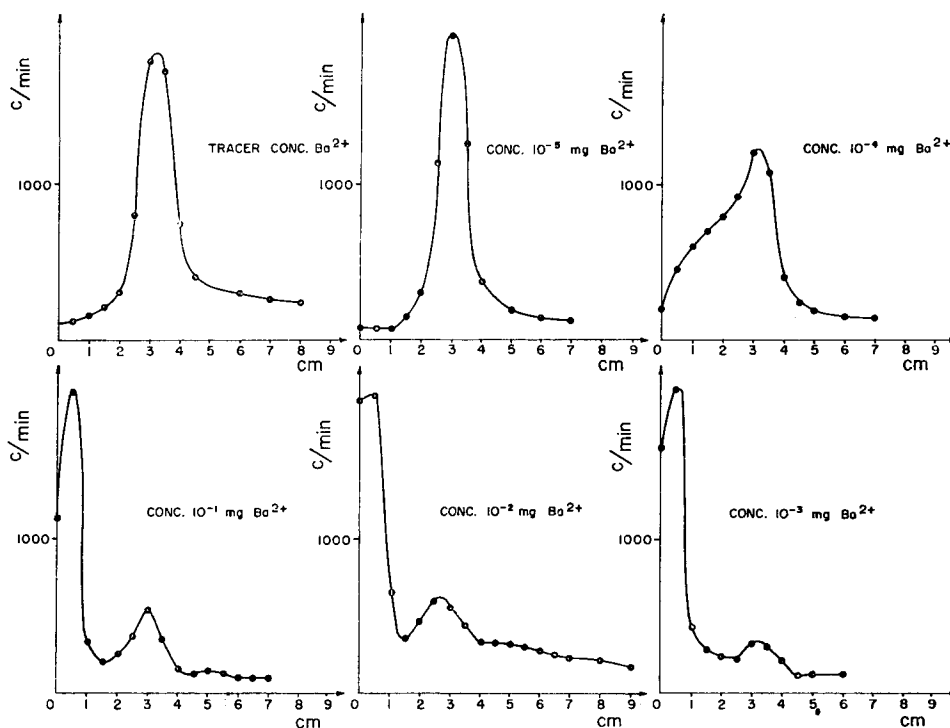
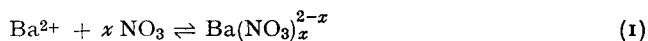


Fig. 1.

This behaviour cannot be explained by assuming that the double spots are due to the formation of barium complexes possessing different R_F values, such as:



The equilibrium constant for this reaction is:

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

where F is the activity coefficient ratio of the species. At constant $[\text{NO}_3^-]$, F can be assumed as constant and we have:

$$\frac{[\text{Ba}(\text{NO}_3)_x^{2-x}]}{[\text{Ba}^{2+}]} = K' \quad (3)$$

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 are of the opinion that further investigations are required in order to explain the anomalies observed in the chromatographic behaviour of barium.

(c) *Separation of Ba-Ra*

As was observed with the other systems, the chromatographic separation 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 Fig. 2. This chromatogram was obtained with propanol (80 %) and an aqueous solution of HNO_3 (2 M) and LiNO_3 (4 M). Trace amounts of the elements were employed by using ^{228}Ra (MsTh I) and ^{140}Ba as radioactive isotopes. All other conditions were similar to those used in the separation Ca-Sr-Ba.

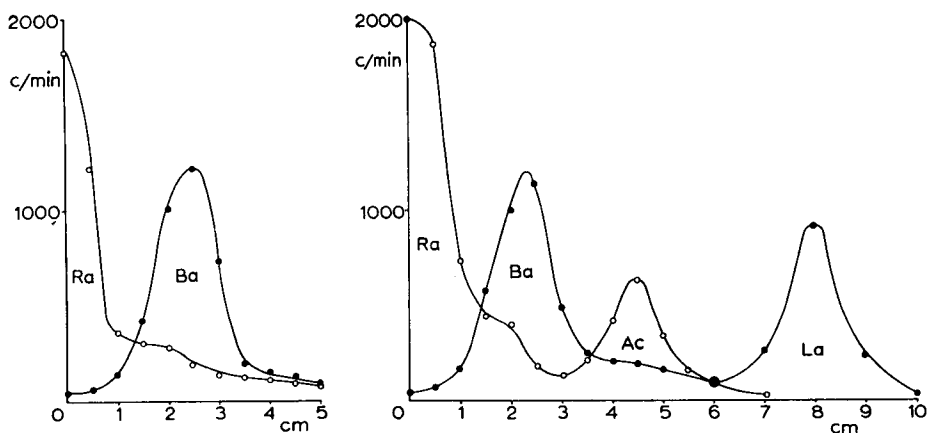


Fig. 2.

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

Since the R_F values of Ac ($R_F = 0.25$) and La ($R_F = 0.47$) differ considerably from those of Ra and Ba respectively, the method is useful for the purification of these radioactive elements by paper chromatography, as is illustrated in Fig. 2.

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SUMMARY

The separation of Ca-Sr-Ba was achieved by paper chromatography using concentrat-

ed nitrate solutions with propanol as solvent. Ba yields double spots with some organic solvents.

The method enables a separation of Ba and Ra in trace amounts and is useful for the radiochemical purification of ^{140}Ba and ^{226}Ra sources.

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