

ION EXCHANGE PROCEDURES

V. SEPARATION OF BARIUM AND RADIUM*,**

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In a separations scheme under development at this laboratory, barium and radium occur together in a subgroup separated from all the other elements. With the present procedure, barium and radium, at low concentrations, may be separated from each other. It is a modification of the method of DUYCKAERTS AND LEJEUNE²; the elements are absorbed on a small column of Dowex 50 cation exchange resin and then sequentially eluted with solutions of the di-ammonium salt of ethylenediaminetetraacetic acid [(NH₄)₂H₂EDTA] of appropriate pH.

DISCUSSION

Satisfactory column separations of barium and radium have been demonstrated with cation exchange resins and ammonium citrate^{3,4} or lactate⁵ solutions as eluents. These separations are better than those obtained with non-complexing mineral acids such as HCl⁶. However, fairly concentrated citrate or lactate solutions are used and this introduces complications when removal of excess solute is needed, *e.g.*, as in subsequent determination of radium by α -counting, where essentially residue-free "plates" are desirable.

With EDTA solutions of appropriate pH, the separation factor, $D_v(\text{Ra})/D_v(\text{Ba})$, is significantly larger than for citrate or lactate.² In addition, because of the high stability of their EDTA complexes, barium and radium can be eluted with relatively dilute EDTA solutions (*e.g.* 0.01 *M*).

Optimum conditions of pH for adsorption and elution of barium and radium (at low concentration) were established by a series of column experiments with 0.01 *M* (NH₄)₂H₂EDTA solutions adjusted to the desired pH with concentrated NH₃ (14 *M*). The di-ammonium EDTA salt was used rather than the more available di-sodium salt because it can be completely removed by "flaming". Small columns (0.28 cm² × 3 cm) of Dowex 50-X8 (-400 mesh) in the ammonium-form were used. Elution positions were determined radiometrically, using ¹³³Ba and ²²⁶Ra as tracers. The Po, Pb and Bi decay products of ²²⁶Ra were removed immediately before use by passing a 2 *M* HCl solution of the tracer through a small column of Dowex-1 anion exchange resin. The HCl

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** For Part IV, see ref. 1.

solution was evaporated to dryness and the residue containing ^{220}Ra was taken up in an appropriate EDTA solution.

The results are shown in Fig. 1, a plot of $\log D_v$ vs. pH, where D_v is amount per ml bed/amount per ml solution. Barium and radium are strongly adsorbed at low pH. Adsorbability of both elements decreases rapidly with increasing pH; the functions are arbitrarily plotted as straight lines. Barium may rapidly be eluted while retaining radium near pH = 8.8 where $D_v(\text{Ba}) = \text{ca. } 1.2$ and $D_v(\text{Ra}) = \text{ca. } 9$; radium may be eluted at pH ≥ 10.0 where D_v becomes < 1 .

Our results may be compared with column experiments of DUYNCKAERTS AND LEJEUNE². From their data for 0.01 M EDTA solutions at pH 9, we compute a separation factor, $D_v(\text{Ra})/D_v(\text{Ba}) = \text{ca. } 7$ which is in reasonably good agreement with our value, $D_v(\text{Ra})/D_v(\text{Ba}) = \text{ca. } 7.5$. This rather favorable separation factor is not surprising. In the absence of complexing agents, radium is more strongly adsorbed by the resin than barium; additional improvement in separability results when EDTA solutions are employed as eluents since barium is more strongly complexed than radium by this reagent⁶.

TYPICAL SEPARATION

A typical separation of barium and radium is shown in Fig. 2. For this separation, a 0.4 ml aliquot containing ^{133}Ba and ^{220}Ra in 0.01 M EDTA (adjusted to pH 8.8 with NH_3) was added to a $0.28 \text{ cm}^2 \times 3 \text{ cm}$ column of Dowex 50-X8, -400 mesh resin in

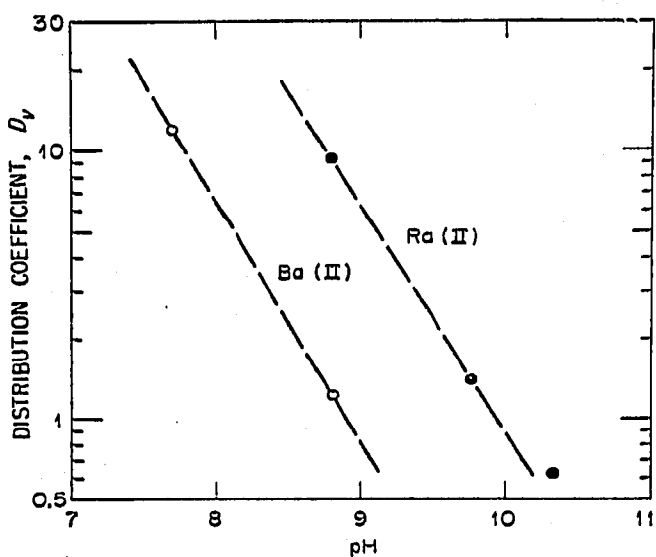


Fig. 1. Adsorption of barium and radium from 0.01 M EDTA solutions (Dowex 50-X8, NH_4^+ form, 25°).

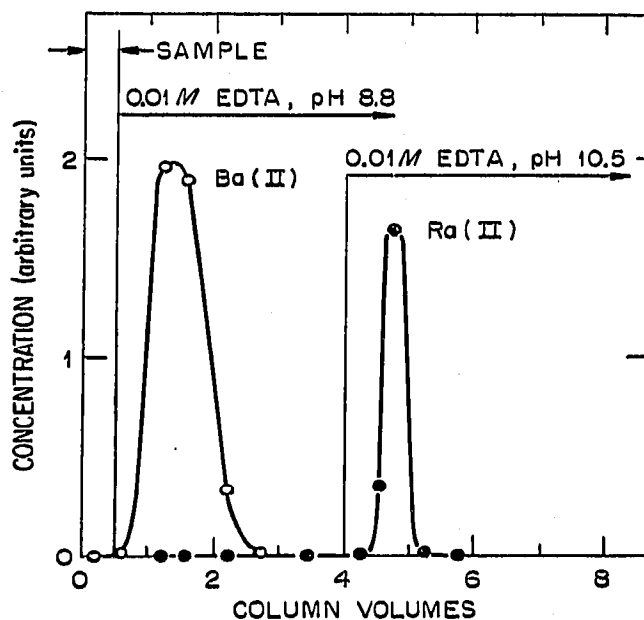


Fig. 2. Separation of barium and radium (Dowex 50-X8, $3 \text{ cm} \times 0.28 \text{ cm}^2$, 25°).

the NH_4^+ -form. The column had been pretreated with the same EDTA solution; on continued elution with this solution, Ba was removed in a sharp band with peak concentration near 2 column volumes. Radium was removed in a sharp band with 0.01 M EDTA at pH 10.5.

PROCEDURE

(a) Materials and reagents

Resin. Dowex 50-X8 (-400 mesh), hydrogen-form. The resin is converted to the NH_4^+ -form by treating it in a column with 10 column volumes (c.v.) of 1 *M* NH_4Cl . After conversion, excess NH_4Cl is washed from the bed with *ca.* 3 c.v. of distilled water. The resin is stored in water.

Apparatus. A section of plastic tubing 0.6 cm inside diameter and 12 cm in length is used to prepare the column. The tubing is pulled out to a tip at one end and a porous Teflon plug inserted to retain the resin. Additional apparatus are plastic test tubes, Teflon evaporating dishes, plastic transfer pipettes and syringes.

Column. Resin bed: $0.28 \text{ cm}^2 \times 3 \text{ cm}$; column volume – 0.85 ml.

Flow rate: *ca.* 0.6 cm/min.

Temperature: 25°.

Effluent volumes (column volumes – c.v.):

Ba fraction: 4 c.v. (3.4 ml) of Solution II;

Ra fraction: 2 c.v. (1.7 ml) of Solution III.

Solutions. (I) 1 *M* NH_4Cl ;

(II) 0.01 *M* $(\text{NH}_4)_2\text{H}_2\text{EDTA}$ – adjusted to pH 8.8 with conc. NH_3 ;

(III) 0.01 *M* $(\text{NH}_4)_2\text{H}_2\text{EDTA}$ – adjusted to pH 10.5 with conc. NH_3 .

Note: If the di-ammonium EDTA salt is not available, solutions II and III may be prepared from the di-sodium salt by cation exchange as illustrated in the following example:

A 10 ml aliquot of 0.10 *M* $\text{Na}_2\text{H}_2\text{EDTA}$ solution is passed into a $2.0 \text{ cm}^2 \times 5 \text{ cm}$ column of water-washed Dowex 50-X8 in the NH_4^+ -form. The column is washed with *ca.* 25 ml of distilled water; the effluent contains $(\text{NH}_4)_2\text{H}_2\text{EDTA}$ and has a pH of *ca.* 4.7. Water is added to give the desired EDTA concentration and then concentrated NH_3 (dropwise) is added to give the desired pH.

(b) Sample preparation

The sample containing Ba and Ra in HNO_3 is evaporated in a Teflon beaker to near dryness and the residue is taken up in *ca.* 0.4 ml of Solution II.

(c) Column operation

Resin as a slurry in water is added to the plastic column until a resin bed 3 cm in length (*ca.* 0.85 ml) is formed. The bed is pretreated with 2 c.v. of Solution II and the sample is added. Flow rate is controlled by air pressure to about 0.6 cm/min. When the sample has passed into the bed, 0.4 ml of 0.01 *M* EDTA at pH 8.8 is added as wash, followed by an additional 3 c.v. (2.5 ml) of the same solution. This removes Ba. The column is then treated with 2 c.v. (1.7 ml) of 0.01 *M* EDTA at pH 10.5 to remove Ra. The column may be regenerated with *ca.* 4 c.v. of water.

The total column operation time is about 30 min.

SUMMARY

A cation exchange procedure is described for separating barium and radium. Separation is achieved with EDTA solutions of controlled pH.

REFERENCES

- ¹ T. MURASE, E. L. LIND AND F. NELSON, *J. Chromatog.*, 14 (1964) 478.
- ² G. DUYSKAERTS AND R. LEJEUNE, *J. Chromatog.*, 3 (1960) 61.
- ³ E. R. TOMPKINS, *J. Am. Chem. Soc.*, 70 (1948) 3520.
- ⁴ W. H. POWER, H. W. KIRBY, W. C. MCGLUGGAGE, G. D. NELSON AND J. H. PAYNE, Jr., *Anal. Chem.*, 31 (1959) 1077.
- ⁵ G. M. MILTON AND W. E. GRUMMIT, *Can. J. Chem.*, 35 (1957) 541.
- ⁶ F. NELSON, R. A. DAY AND K. A. KRAUS, *J. Inorg. Nucl. Chem.*, 15 (1960) 140.

J. Chromatog., 16 (1964) 403-406