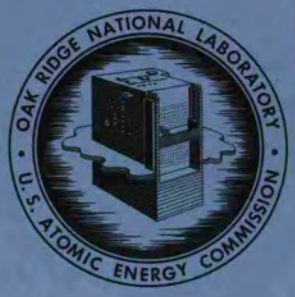

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SEPARATION OF STRONTIUM AND BARIUM BY CATION EXCHANGE USING POLYAMINEPOLYCARBOXYLIC ACIDS AS ELUANTS

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ISOTOPES DEVELOPMENT CENTER

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ISOTOPES DIVISION

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G. S. Wamanacharya*

ABSTRACT

Strontium and barium were separated on a cation-exchange column using 2-hydroxyethylethylenediaminetriacetic acid (HEDTA) and diethylenetriaminepentaacetic acid (DTPA) as eluants. Separations were equally good but not as fast as with citric acid, the eluant now used; however, the polyaminepolycarboxylic acids were more easily removed from the product.

INTRODUCTION

The use of polyaminepolycarboxylic acids as eluants in the cation-exchange separation of barium and strontium was studied in an attempt to find an easier separation method. In the process now used, ([1]) with citric acid as the eluant, the citric acid is removed from the product by another small cation-exchange column and the final product is converted to the chloride with hydrochloric acid. If polyaminepolycarboxylic acids are used, they can be easily and completely destroyed by fuming HNO_3 and the ion-exchange concentration step can be avoided.

The use of polyaminepolycarboxylic acids was investigated because of the extensive use of ethylenediaminetetraacetic acid (EDTA) as a chelating agent in the determination of metal concentrations by complexometric titrations and as an eluting agent for various cations on ion-exchange columns. The low solubility of the free acid is, however, a serious disadvantage in the separation procedures. Diethylenetriaminepentaacetic acid (DTPA), which is more soluble than EDTA in water and whose interaction with divalent metal ions and rare earth ions has been studied by many workers, ([2-5]) has been used as an eluting

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agent ([6]) for the purification of ^{147}Pm. The interaction of 2-hydroxyethylethylenediaminetriacetic acid (HEDTA) with iron, divalent metal ions, and rare earths has also been studied, ([7-12]) and HEDTA has been used as an eluant for many divalent metal cations and rare earths. ([13-14])

The more soluble the polyaminepolycarboxylic acid is in water, the more useful it is as an eluant in ion-exchange work, since the free acid has less tendency to precipitate on the column. On this basis, DTPA is better than EDTA or 1,2-cyclohexylenedinitrilotetraacetic acid (CHDNTA), and HEDTA is better than DTPA. After these factors were considered, it was decided that HEDTA and DTPA were good possibilities for the ion-exchange separation of fission-product strontium and barium.

The formation of anionic complexes of divalent metal ions with DTPA is explained ([2]), in general, by the reactions

$$H_5A + M^{2} + 4OH^- \longrightarrow MHA^{2-} + 4H_2O$$

and

$$MHA^{2-} + OH^- \longrightarrow MA^{3-} + H_2O$$

where A^{5-} represents the DTPA anion and M^{2+} the metal cation. Thus the negatively charged metal complexes MHA^{2-} and MA^{3-} are selectively eluted from a cation resin column at different alkaline pH's of DTPA solutions.

It is reported, ([11]) that the sparingly soluble neutral species RCh (where R is the rare earth metal cation and Ch is the chelating anion) combines with an equivalent amount of base to form a new complex species of the type $RChOH^-$, based on the buffering properties and solubility of rare earth HEDTA complexes in a base. Thus it may be these negatively charged metal complexes that cause the elements to move down the cation resin column when water solutions of HEDTA are used as eluants at alkaline pH's.

EXPERIMENTAL

Equipment

Two glass columns were used (Fig. 1), one with 10 mm dia and 8 cm height (column volume, 5.5 ml) at room temperature and the other with 5 mm dia and 20 cm height (column volume, 3.92 ml) used at higher temperatures maintained by circulating hot water through the jacket.

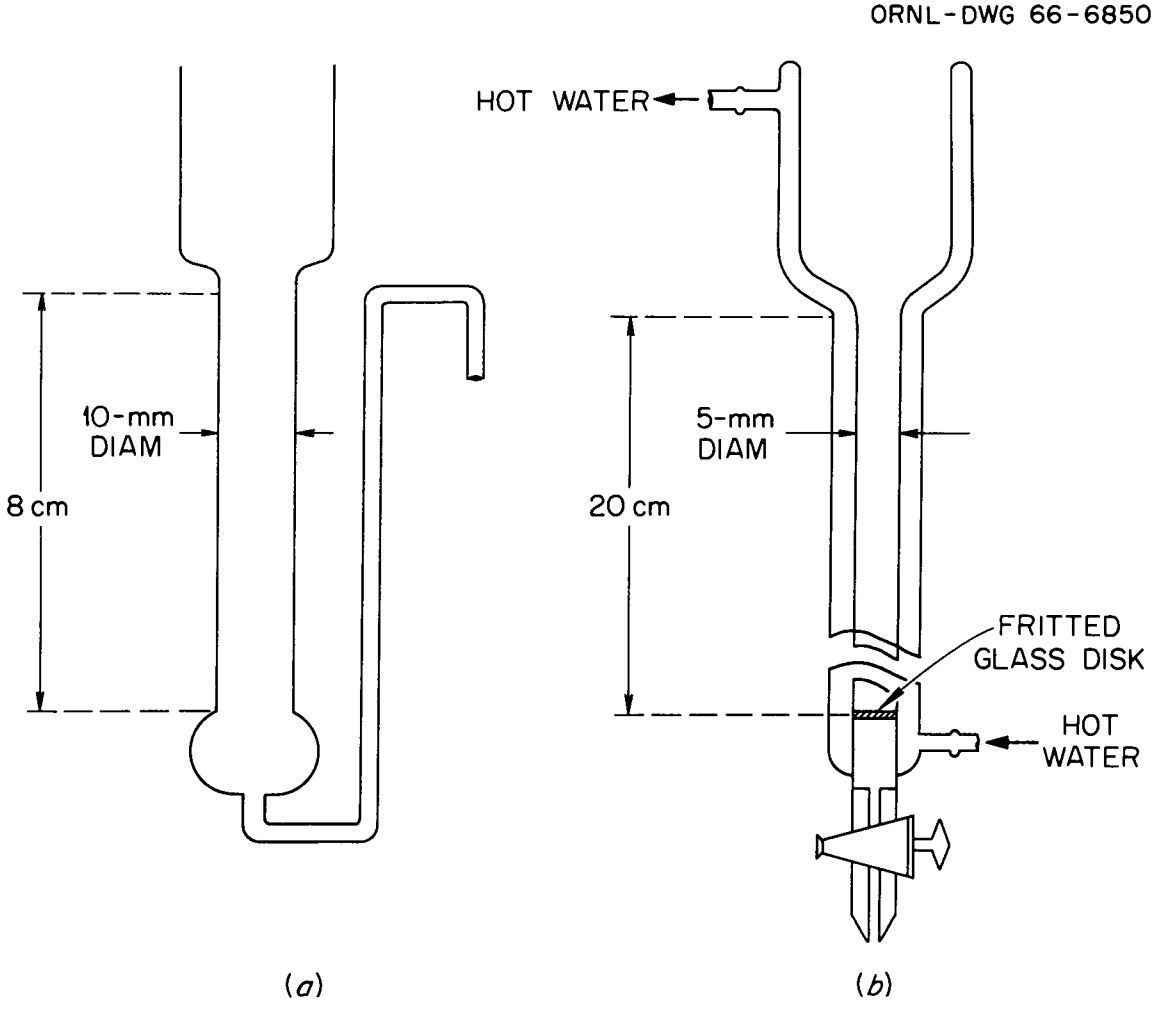

Fig. 1. Ion-Exchange Columns Used in Strontium-Barium Separation: (a) at Room Temperature, (b) at Elevated Temperature.

Chemicals

Dowex 50-X16, 50-100 mesh, in the hydrogen form was used throughout the experiment, since it has been found at ORNL that the best strontium-barium separations are obtained with it.

Strontium and barium were first traced with 1 mc each of ^{85}Sr and ^{133}Ba. However, the count rate of some fractions was very high, and therefore 50 μc of ^{85}Sr and 30 μc of ^{133}Ba were used in subsequent runs. The specific activity of the ^{85}Sr was ~10 curies/g and that of ^{133}Ba was ~1 curie/g. No carriers were added.

The eluants were 0.5% aqueous solutions of HEDTA and DTPA at pH values between 7 and 10, with the actual pH being controlled by addition of ammonia and measured to ± 0.05 pH unit by a Corning pH meter, Model 12. For comparison, 0.2 M citric acid at pH 5.8 was also used. Below pH 7 the elements moved very slowly, and at pH 9 or higher, separations were not good, although the elements moved rapidly.

Procedure

The columns were filled with the regenerated resin and washed with ~25 ml of water. The ^{85}Sr and ^{133}Ba solutions were sorbed on the column at a flow rate of ~0.5 ml/min. The column was then washed with 20 ml of water and the elution was started. The radioactivity was followed by a radiation probe. Until the activity was about an inch above the bottom of the column, the effluent was collected in bulk; afterwards, fractions of ~16 ml each (~3 column volumes) were collected and analyzed by a gamma spectrometer. With each eluant, when all the strontium had been eluted from the column, the pH was raised 1 to 1.5 units to elute the barium rapidly.

The column used for operation at elevated temperature was prepared by passing 4 column volumes of a degassed eluant through the column before hot water was run into the jacket. It was found, however, that the pH of the eluants is decreased to ≤ 7 by the degassing. Hence operation of the columns at elevated temperatures with ammoniacal eluants was unsuccessful.

Each fraction was examined by a gamma spectrometer with a NaI(Tl) crystal. The presence or absence of the 0.36-Mev peak for ^{133}Ba and the 0.514-Mev peak for ^{85}Sr was taken as the criterion for identification of the fractions. Gross gamma counts at 4 volts base line were taken for 0.5 min for each fraction, and the counts per milliliter were plotted against the column volumes to get the elution curve.

DISCUSSION OF RESULTS

The results (Table 1) show that best separations are obtained using 0.5% HEDTA water solutions at pH 8.5 and 0.5% DTPA water sclutions at pH 7.5. The pH seems to be critical for this separation; at pH values 0.5 unit below the best ones, the radioactivities moved very slowly, and at 0.5 unit higher, they moved rapidly but separation was poor.

Table 1. Effect of Eluant Concentration and pH on the Separation of Strontium and Barium on Dowex 50-X16 Resin

	Conc., %	pH	Remarks	Col Vol
DTPA	0.5	7.0	Elements moved very slowly	
	0.5	7.5	Separation very good; pH raised to 9.2 for quick Ba elution	60
	0.5	8.0	Separation not good though elements moved rapidly	
	1.0	7.5	Separation fairly good; Sr band narrow but Ba band broad	20
HEDTA	0.5	7.5	Elements moved very slowly	
	0.5	8.5	Separation very good; pH raised to 10.2 for quick Ba elution	46
	0.5	9.0	Separation not good	
	1.0	8.5	Separation not good	38
Citric acid	0.2 M	5.8	Separation not good at room temp.	<5

In the elution with 0.5% HEDTA at pH 8.5 (Fig. 2), strontium first appeared in the effluent after ~46 column volumes of eluant had passed through. Another 46 column volumes were required for its complete removal while barium required 33 column volumes after raising the pH to 10.2. By comparison, when 0.2 M citric acid was used for elution at pH 5.8 (Fig. 2), strontium appeared in the first 5 column volumes. Up to 8 column volumes, strontium was pure but from column volumes 11 to 33 strontium and barium were eluted together. Subsequent barium fractions were pure. About 50 column volumes were required for complete removal of both elements.

In elution with 0.5% DTPA at pH 7.5 (Fig. 3), strontium appeared in the effluent after 60 column volumes and was eluted completely with another 35 column volumes; barium was eluted in 30 column volumes even at the higher pH 9.2. With 1.0% DTPA at pH 7.5, the elements moved more rapidly; strontium started coming off the column after 20 column volumes and was completely eluted in only 9 to 10 column volumes. Barium followed strontium closely, and at the same pH, 45 column volumes were required for its complete removal. At a higher pH it would have been eluted more rapidly.

The large number of column volumes eluted before the strontium appears in the effluent is due[14] to the peculiar property of HEDTA to be sorbed on the resin column in the form of H_5V^{2+} where V represents HEDTA. James[15] has shown that the H_5V^{2+} band grows as the elution proceeds and that the initial eluate is pure water. As the growing band of H_5V^{2+} passes off the column, the eluate becomes an aqueous solution of pure HEDTA which is twice as concentrated as the eluant. A similar phenomenon is also observed[16] with DTPA.

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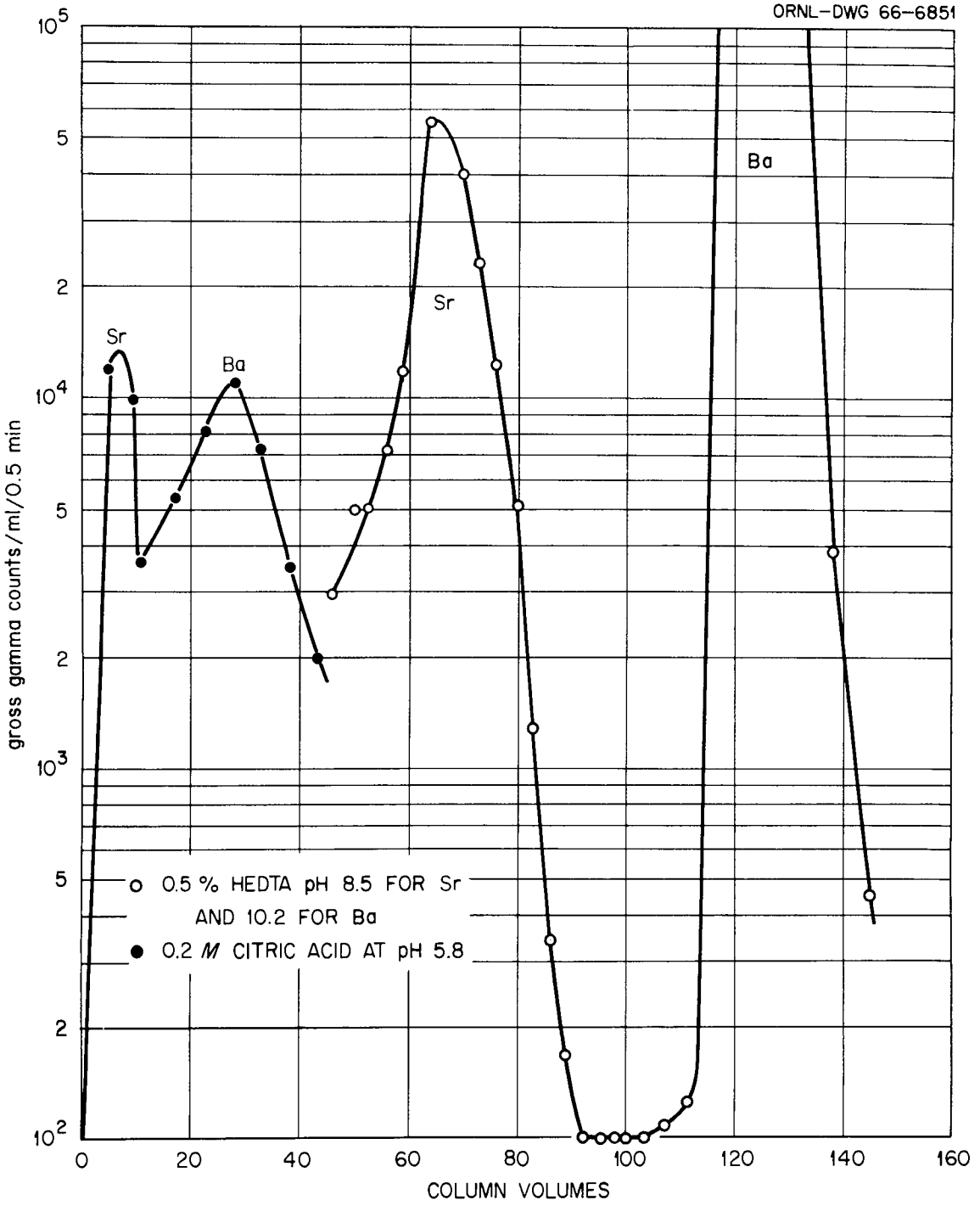

Fig. 2. HEDTA and Citric Acid Elution Curves for Strontium and Barium.

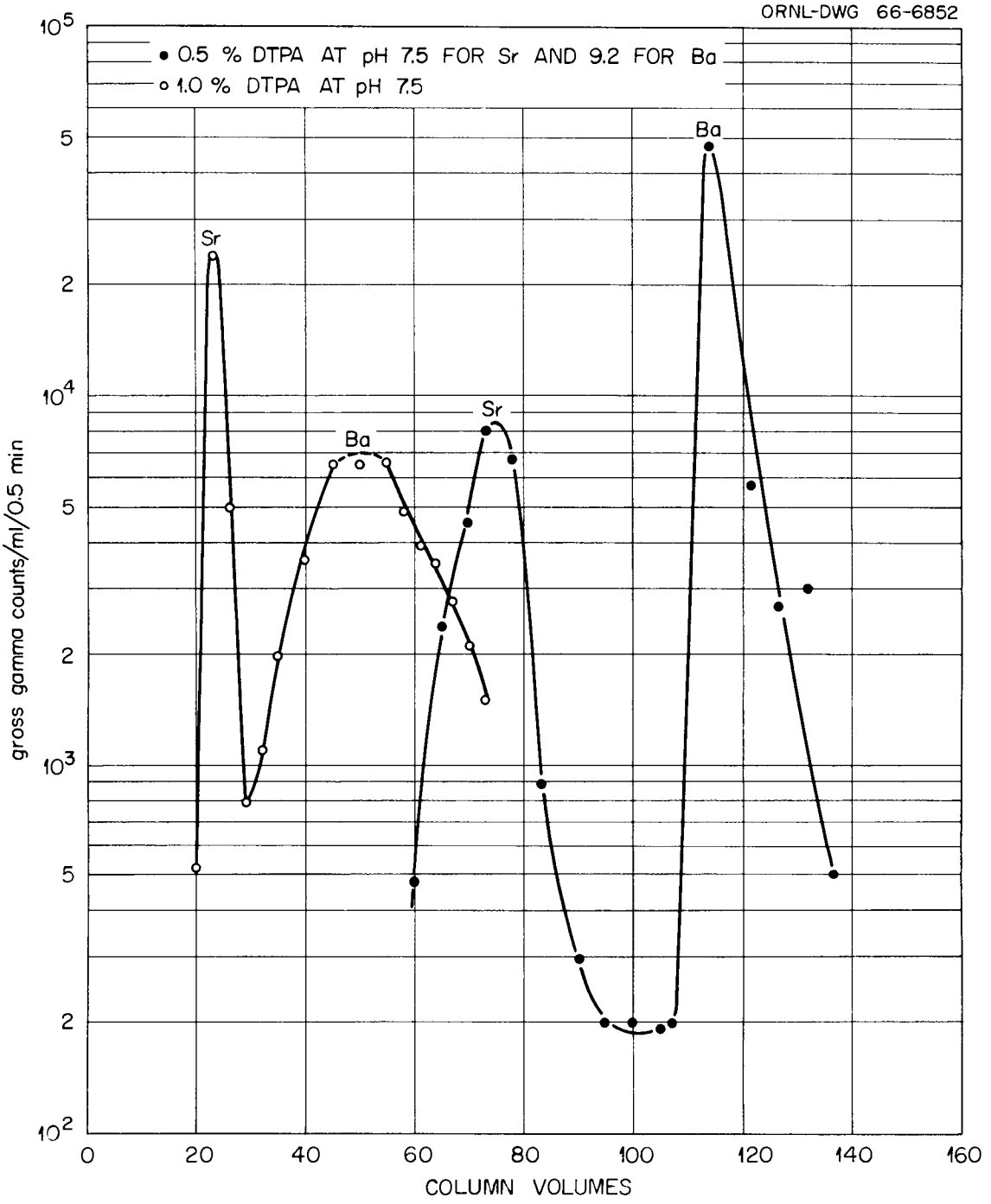

Fig. 3. DTPA Elution Curves for Strontium and Barium.

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