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CHEMICAL TECHNOLOGY DIVISION

LABORATORY SECTION

LABORATORY DEVELOPMENT OF AN ION EXCHANGE RALA PROCESS

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1.0 Abstract

This report presents the laboratory development of an ion exchange process for the purification of radioactive barium.



2.0 Introduction

Multi-kilocurie quantities of pure radio barium are produced at ORNL by a precipitation process consisting of the following steps:

- (1) separation of the barium from the slug dissolver solution by co-precipitation with lead sulfate;
- (2) conversion by metathesis of the barium-lead sulfate to carbonate by boiling with concentrated potassium carbonate;
- (3) dissolution of the carbonate in acid, and removal of the lead by electrolysis;
- (4) final purification by precipitation of barium chloride from ether-hydrochloric acid solution. The barium yield has averaged only 67% and the product has not consistently met purity requirements. A survey⁽¹⁾ of the present processing equipment indicated that considerable alterations would be necessary in order to increase the yield of this process.

The ion exchange processes described in this report were developed to replace the purification steps following the lead sulfate precipitation. Ion exchange processes offer the following advantages: (1) ease of remote control; (2) reduction in time cycle with the attendant increase in yield as a result of less product decay; (3) increased purity of product; (4) high yield.

Development work is projected to evaluate the feasibility of separating barium directly from slug dissolver solution by an ion exchange process. This was suggested by previous investigators in 1945⁽⁵⁾. The new resins available today may make this procedure very advantageous.

3.0 Summary

The Acetate-Citrate, Versene, and Alkali-Citrate ion exchange processes have been developed for the purification of radio barium. Laboratory and Semi-Works⁽²⁾ demonstration runs on the first two processes showed good reproducibility, product yield of the order of 98%, and a product purity which met or exceeded specifications. The overall process time for both processes was approximately 27 hours. No adverse radiation effects were noted in three runs made at the 600-3000 curie (6000 gross beta curies) level⁽⁴⁾ in specially designed equipment⁽³⁾. Although the Alkali-Citrate Process proved satisfactory in the laboratory, it was never pilot planted due to lack of suitable equipment.

The Acetate-Citrate Process was designed to replace the electrolysis and ether hydrochloride precipitation steps in the present process. The process steps are:

- (1) Adjust the dilute acid solution of the metathesis cake to 0.5 M in sodium acetate and pass it through an ion exchange resin column where the barium and most of the other cations are adsorbed.
- (2) The contaminants, lead, iron, chromium, nickel, rare earths, strontium and sodium are removed selectively from the column by washing the resin with eluting agents such as sodium hydroxide, sodium citrate, and hydrochloric acid.
- (3) The product barium is eluted in 6 M nitric acid and the solution evaporated to dryness.

Summary (continued)

The Versene[‡] Process would replace the metathesis, electrolysis, and ether-hydrochloride precipitation steps with a two column ion exchange process. The advantages of this process are: (1) elimination of the metathesis step which has proved to be unreliable under process conditions. The 10-15 hours process time needed for metathesis is also saved, resulting in a 3-4% increase in yield as a result of less barium decay; (2) the level of radiation could be much higher using the Versene Process rather than the Acetate-Citrate Process since in the former process a large fraction of the gross activity is never adsorbed on the resin column. The process steps are:

- (1) The lead-barium sulfate cake is dissolved in Versene at pH 6.0-6.5 and the solution passed through the metathesis substitute* resin column where the barium is adsorbed while the sulfate ion passes through. Most of the iron, lead, and fission products which are present as anion complexes also pass through.
- (2) The impure barium is removed from the M.S. column by a solution of Versene at pH 11.0. The impure product solution is readjusted to pH 4.0 - 4.3 and passed through a smaller purification column, where the barium is readsorbed.

[‡] ethylene diamine tetra acetic acid
* hereafter abbreviated as M.S.



Summary (continued)

- (3) The strontium and any remaining iron, chromium, nickel, and lead are selectively eluted with pH 6.3 Versene. The sodium is eluted with hydrochloric acid.
- (4) The barium is eluted in 6 M nitric acid and the solution evaporated to dryness.

Dowex 50 has been chosen over IRC-50 and IR-105 as the process resin because of its marked stability to strong acids and alkali, minimum swelling characteristics, high capacity, and lack of capacity - pH interdependence.

4.0 Acetate-Citrate Process

In the present process, the barium is separated from the dissolver solution by co-precipitation with lead sulfate, the sulfate cake converted to carbonate by metathesis, and the latter subsequently dissolved in dilute nitric acid. The Acetate-Citrate Process uses this solution as its starting point and eliminates the electrolytic removal of lead and the ether-hydrochloride removal of strontium and other impurities. Table 4.0-1 shows complete results of several representative runs. (See flowsheet Figure 4.0-1.)

4.1 Product Adsorption

4.11 Equilibrium Data

The development of an ion exchange separation process requires an intimate knowledge of the equilibrium distribution coefficients of the cations involved in the resin-complexing agent system.

The resin-aqueous phase distribution coefficients, K_d , for barium, lead, iron, nickel, strontium, and chromium were determined for citrate, oxalate, and acetate complexing systems at pH's varying from 1.7 to 7.8 using Dowex 50 as the resin phase (see Table 4.11). Since it was not possible to obtain tracer activity for all of these cations, these equilibria were determined in systems sufficiently high in cation molarity to ensure accurate colorimetric analyses. Although K_d is known to vary with cation concentration when this concentration is greater than 10^{-3} M(6), these values are suitable for rough comparison. The procedure employed consisted of shaking 5 ml of resin, previously saturated with cation, with 25 ml of solution for 2 hours. The equilibrium distribution coefficient was calculated as:

$$K_d = \frac{\text{mg cation/ml resin}}{\text{mg cation/ml solution}} .$$

The process data derived from these experiments are as follows:

- (1) The oxalates of the cations involved are too insoluble for a process requiring macro amounts of material.

Equilibrium Data (continued)

- (2) Iron is strongly complexed by citrate at pH 3.0 but not at pH 7.8. Consequently, it may be separated from barium by selective elution at pH 3.0. Nickel, chromium, strontium, and barium, however, are complexed more strongly by citrate at higher pH values. Since the distribution coefficient of barium is the highest, that is, the barium citrate complex is the weakest, the other cations are easily separated from the barium by selective elution.
- (3) Lead is highly complexed by, and soluble in, sodium hydroxide and sodium acetate. Since the sodium hydroxide has little effect on barium, it can be used effectively to separate lead from barium. Citrate complexes lead⁽⁷⁾ and barium but is not suitable for their separation in macro amounts due to the limited solubility of lead citrate.
- (4) Iron was found to be irreversible in the acetate system; that is, when complexed as the basic acetate at pH 6.0, K_d (Fe) is low, where as, K_d (Fe) is very high when the iron is adsorbed on the resin first and then equilibrated with pH 6.0 acetate solution.

Another series of distribution coefficients was run to determine the optimum pH and citrate concentration for separation of barium and strontium.

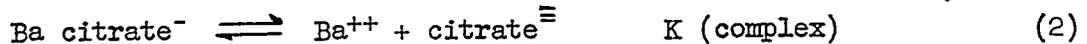
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Equilibrium Data (continued)

In this series, weighed amounts of air dried sodium resin were shaken for 24 hours with 25 ml of sodium citrate solutions which were varied from 0.1 to 0.5 M and from pH 6.0 to 9.0. The solutions were 10^{-3} M in barium and strontium (plus tracer) and were analyzed radio-chemically before and after equilibration. The weight of resin was adjusted so that approximately one-half of the material was adsorbed. Thus the analyses by difference would have the optimum accuracy. The weight of sodium on the resin was known and the percent moisture was determined by oven drying. K_d was calculated as:

$$K_d = \frac{\text{cts/gm oven dried, H}^+, \text{resin}}{\text{cts/ml solution}}$$

In Figures 4.11- 1, 2, and 3 $\log K_d$ (Ba), (Sr) is plotted v.s. the equilibrium pH. The decrease of K_d with increase of pH and citrate molarity is predicted from equation (4) which was derived from equations (1), (2), and (3) where R denotes resin:



$$K_d = \frac{\text{Ba R}_2}{\text{Ba citrate}^-} = \left[\frac{K(\text{exchange})K(\text{complex})}{K_1, K_2, K_3} \right] \left[\frac{(\text{NaR})^2 (\text{H})^3}{(\text{Na}^+)^2 (\text{H}_3 \text{ citrate})} \right] \quad (4)$$

The Ba H-citrate complex is assumed to be negligible since the H-citrate⁼ concentration decreases rapidly at pH's higher than 6.0.

Equilibrium Data (continued)

Also the ratio of the two complex constants is known to be⁽⁸⁾:

$$\frac{K (\text{complex Ba citrate}^-)}{K (\text{complex Ba H citrate})} = \frac{5.0 \times 10^{-3}}{10^{-1}} = 5.0 \times 10^{-2}$$

Actually there is little difference between pH 8 and 9 in this system since the citric acid is over 99% dissociated at pH 8.0⁽⁹⁾.

The results of these experiments showed that the separation factors, $K_d (\text{Ba})/(\text{Sr})$, increased from approximately 7 to 10 as the citrate molarity increased from 0.1 M to 0.5 M at constant pH. Very little, if any, increase was found as the pH increased from 6.0 to 9.0 at constant citrate molarity.

Similar experiments with IRC-50 resin showed much lower separation factors with the same trend (see Figures 4.11 - 4, 5, 6). That is, the separation factor increased from 2 to 3 with increasing citrate concentration but exhibited little pH dependence. K_d , however, showed an enormous increase with pH, rising by a factor of 50 in the case of the 0.1 M citrate as the pH increased from 6.0 to 9.3. All of the quantities in equation (4) are the same in both the Dowex 50 resin and IRC-50 resin systems except K (exchange) and NaR. NaR, the resin capacity, is constant for Dowex 50 as the pH is increased from 6 to 9, while for IRC-50 it increases by approximately a factor of 2 (see Figure 4.11-7). This could account for only a four fold increase in K_d . Kunin and Barry⁽¹⁰⁾ studied the exchange between

Equilibrium Data (continued)

alkaline earth hydroxides and sodium at a high pH using IRC-50 resin and attributed the high alkaline earth exchange constants to chelate bonding. The large change in K_d noted above is, therefore, attributed to a change in K (exchange) due to the formation at higher pH's of a chelate ring between the alkaline earths and the neighboring carboxyl groups present in this resin. The evidence indicates that only alternate carboxyl groups are ionized at low pH values preventing the formation of a chelate ring until neighboring carboxyl ionization takes place at higher pH values.

The low separation factor for barium and strontium, and other considerations, eliminate IRC-50 as a process resin (see Section 7.0).

4.12 Column Specifications

The resin column bed height necessary for the Acetate-Citrate Process was determined empirically to be 7". The laboratory column employed was 7" x 0.55". This represented approximately 1/30 of the full scale process column which measured 7" x 3". The process resin was 60-100 mesh Dowex 50, which had been converted to the sodium form with concentrated sodium nitrate and water washed prior to start up. The hydrogen form cannot be used as the pH of the feed would be lowered as the cations displaced the H^+ ions. The ammonium form is also unsatisfactory because the ammonium ions would cause precipitation of lead hydroxide during the elution of lead with sodium hydroxide.

Column Specifications (continued)

All flow rates were held to 0.7 ± 0.2 ml/cm² column cross section/minute.

The amount of radiation in the effluent was measured by passing the liquid through a spiral located under a Geiger tube. The Geiger impulses activated a counting rate scaler and were recorded automatically on a Speedomax chart as an elution curve (see Flowsheet Figure 2.0-1).

4.13 Feed Make Up

The dilute (0.2 M) nitric acid solution obtained by dissolution of the carbonate metathesis cake is made 0.5 M in sodium acetate and passed through the resin column where essentially all of the cations are adsorbed except iron, of which approximately 90% passes through as the ferric basic acetate complex. This feed solution for a full scale run contains 85 gm. of lead, 1.0 gm. of barium, up to 1 gm. of iron, and lesser amounts of chromium, nickel, and strontium. Fifty to ninety percent of the strontium is removed in the preceding lead-barium sulfate precipitation step⁽¹¹⁾.

It is known that lead will displace barium from the resin⁽⁷⁾, so it is necessary to add a complexing agent to the feed which will complex the lead more strongly than the barium, effectively reducing the ionic lead concentration. Thus the barium will be caught near the top of the column. The relative degree of barium and lead acetate complex formation

Feed Make Up (continued)

is shown by their K_d 's of 8.9 and 1.3 (see Table 4.11) and their chromatographic separation by acetate elution (see Figure 4.13-1). Sodium citrate has been suggested as a complexing agent for such a feed solution(7), but its use is not feasible due to the low solubility of lead citrate.

Subsequently, Versene has been found to be a very desirable feed complexing agent. It has been shown that at pH 6.0, the barium and strontium are adsorbed on the resin while essentially all of the lead, iron, and other impurities are complexed and pass through the bed (see Table 4.0-1).

4.2 Contaminant Elution

In the following steps, all of the contaminants are selectively removed from the resin by passing a suitable complexing agent through the column until finally only H^+ and Ba remain adsorbed (see Table 4.0-1).

Lead Elution

The lead (approximately 85 grams) is selectively eluted as the plumbite anion with 0.5 M sodium hydroxide. The distribution coefficient in such a system is very low. Thus lead removal is efficient and complete. Other amphoteric trace impurities such as chromium and niobium are also removed.

Iron

The bulk of the iron is complexed by the acetate feed and never adsorbs on the resin. The small amount that does adsorb is removed by elution

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Contaminant Elution (continued)

with 0.5 M sodium citrate pH 3. (Note the low $K_d(\text{Fe})$ in Table 4.11.)

It is well known that the rare earths, zirconium and niobium are efficiently eluted by pH 3.0 citrate.⁽¹²⁾ The barium loss in this step is negligible as the barium is not appreciably complexed by citrate until the pH is greater than 3.5⁽⁵⁾.

Strontium Elution

Strontium is selectively eluted with 0.1 M, pH 9.0, sodium citrate. Separations of barium and strontium by citrate elution have been made by previous investigators at pH's ranging from 5.0 to 7.8 and citrate molarities from 0.2 to 0.5 M⁽⁵⁾ (12) (13). As described in Section 4.11, the highest separation factor for this system was found at 0.5 M citrate, pH 9. In practice, however, 0.1 M citrate is used so that the strontium will be eluted more slowly, contributing to more rigid process control. Any traces of nickel, chromium, or lead present at this point should also be selectively removed because they are all more strongly complexed than barium or strontium.

The number of theoretical plates the strontium passes through in the Acetate-Citrate Process has been calculated as 13, using the empirical

Contaminant Elution (continued)

Matheson formula:

$$p = \frac{2C (C + 1)}{W^2}$$

Where p = no. of theoretical plates,

W = half width of the elution curve at height

1/e when the curve is plotted as effluent cation concentration v.s. column volumes of eluting agent.

C = no. of column volumes of elutrate at the mid-point of the elution curve.

Column volume = volume of void space in resin bed.

When the feed complexing agent was Versene, however, (see Section 3.13) the number of plates in the strontium-citrate elution curve was calculated to be 43, indicating that the strontium (and barium) were caught much higher on the resin column in this case and then passed through more separation plates.

Sodium Elution

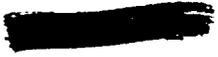
The sodium is selectively removed from the resin with a small volume of 6 M hydrochloric acid. The barium being di-valent is much more strongly held than the sodium so that no appreciable amount of barium is lost. Sulfuric acid has been used successfully and, although it is more desirable from a corrosion standpoint, its use was abandoned when indications of sulfate were found in the final product.

4.3 Elution of Product

At this point in the process, everything except barium has been removed from the column and the resin converted to the H^+ form. The barium is eluted quantitatively with 6 M nitric acid and the solution evaporated to dryness.

The relative ability of 6 M nitric acid, 6 M hydrochloric acid, and 2 M nitric acid for barium elution was determined. The results indicated that 6 M nitric acid removed barium from a column in 1/8 the volume required by 6 M hydrochloric acid due to the complexing action of the nitrate ion with barium (see Figure 4.3-1). This experiment also shows the reason that a considerable amount of 6 M hydrochloric acid can be used for selective sodium elution without appreciable barium loss.

The product purity specification defines the maximum milligram amounts of impurities that may be present. For convenience in process development with synthetic solutions, these specifications have been converted to a percentage basis. Example: the largest amount of iron that has been found by analysis of actual process solutions corresponding to the ion exchange feed solution is 1,000 mg. Since the product specification for iron is 10 mg, the percent specification is 1%.



Product Purity Specifications per Kilocurie Batch

	<u>In mg</u>	<u>Percentage Basis</u>
Lead	50	0.06
Iron	10	1.0
Chromium	5	1.7
Nickel	5	1.7
Radio Strontium	100 curies	2.0 if feed contains 5000 curies of strontium

The sodium specification is 1.5 gms for a batch containing less than 2 gms of barium and strontium or an approximate ratio of Na/Ba = 1.

The product analyses listed in Table 4.0-1 either meet or are lower than these specifications.

5.0 Alkali-Citrate Process

5.1 Dissolution of the Sulfate Cake

In the Alkali-Citrate Process, the lead-barium sulfate cake is dissolved in 6 M sodium hydroxide and subsequently diluted to 0.5 M. An alternate starting point would be the dilute nitric acid solution of the metathesis cake which would be brought to 0.5 M in sodium hydroxide.

Table 5.1-1 shows the results of several representative runs. (See Flow-sheet Figure 5.1-1.)

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Dissolution of the Sulfate Cake (continued)

The sodium hydroxide must be free from carbonate and in addition, all alkaline operations must be performed in air free from carbon dioxide to prevent the precipitation of insoluble barium carbonate. All process water used in this system should be freshly boiled to remove dissolved carbon dioxide.

It is known that lead sulfate is quite soluble in strong sodium hydroxide and it has been shown by tracer experiments that the solubility of freshly precipitated barium sulfate in 6 M sodium hydroxide (carbonate free) is at least 42 mg/100 ml of solution at room temperature.

5.2 Hydrous Oxide Removal

Small amounts of iron, chromium, and nickel present as impurities would be precipitated as hydrous oxides in the sodium hydroxide and removed by centrifugation.

Hydrous ferric oxide is known to be an excellent scavenging agent. Therefore an investigation was made to determine the barium losses during this separation. J. D. Kurbitov et. al⁽¹⁴⁾ have shown that the highest adsorption of strontium by hydrous ferric oxide was 8 atoms of strontium per 1000 atoms of iron, corresponding to approximately 1%, if the strontium and iron were present in equal amounts. He also established the pH dependence of the system by showing that radium is carried by hydrous ferric

Hydrous Oxide Removal (continued)

oxide above but not below pH 6.0. These results have been confirmed and amplified for the barium, strontium, and lead system under consideration, showing that:

- (1) Greater than 90% of the barium and strontium was carried by hydrous ferric oxide when the former were present in tracer concentrations only.
- (2) Carrying was greatly inhibited by the presence of macro amounts of either barium or lead and that when all the ions were present in their maximum expected amounts, 2 to 5% of the barium was carried.
- (3) Any lead oxidized by peroxide and precipitated as lead dioxide carried appreciable quantities of barium. The peroxide could come from decomposition of water by radiation.
- (4) Washing the hydrous oxides with ammonium nitrate, pH 5, reduced the amount of barium carried to approximately 0.1%.

Representative results from these experiments are shown in Table 5.2-1.



5.3 Product Adsorption

5.31 Column Specifications

The column used in the Alkali-Citrate Process development was 1.5 cm by 10 cm containing Dowex 50 resin, 100-200 mesh, in the sodium form. This represented approximately 1/30 of a full scale process column which would measure 3" in diameter with the same height of 10 cm. Flow rates were held to 0.7 ± 0.2 ml/cm² of column cross section/minute.

5.32 Adsorption Theory

The effluent from the centrifuge contains lead as the plumbite anion complex, sulfate anion, barium, strontium and traces of impurities in a solution 0.5 M in sodium hydroxide.

As this solution passes through the cation exchange resin, only the cations are caught, effecting an efficient separation of the barium and strontium from the anion lead and sulfate. The column is then washed with a small amount of 0.5 M sodium hydroxide followed by a water wash to displace the feed solution from resin bed.

5.4 Contaminant Elution

The strontium is selectively eluted with 0.1 M sodium citrate pH 9, and the sodium with 6 M hydrochloric acid as in the Acetate-Citrate Process (see Section 4.2).

5.5 Product Elution

At this point only barium remains on the column. It is eluted in 6 M nitric acid and the solution evaporated to dryness.

5.6 Comparison Of The Alkali-Citrate And Acetate-Citrate Processes

Product analyses indicate that the Alkali-Citrate Process is equal chemically to the Acetate-Citrate Process and would eliminate the undesirable metathesis step. The overall saving in the process time is estimated at 20 hours. This process was never pilot planted on full scale, however, because of equipment complexity.

6.0 Versene Process

The Versene Process is designed to replace the metathesis, electrolysis, and ether-hydrochloride steps of the present process by a two column ion exchange process. Briefly, the Versene Process consists of dissolution of the barium-lead sulfate cake in Versene and passing the resulting solution through the M.S. resin column where the cations are adsorbed but sulfate and other anions pass through. The cations are then removed and re-adsorbed on the small "purification" column for barium purification and volume reduction. Table 6.0-1 shows the results of several representative runs. (See flowsheet Figure 6.0-1.)

6.1 Sulfate Cake Dissolution

The lead-barium sulfate cake is dissolved in 0.1 M Versene at a pH of 6.0-6.5. This dissolution takes place in a few minutes and is complete. Versene accomplishes this dissolution by complexing (formation of a chelate ring) the ionic barium and reversing the following equilibrium:



Similarly, the other cations, lead, iron, chromium, nickel, and strontium are complexed and held in solution. The amount of Versene needed to dissolve a full scale RaLa sulfate cake containing the maximum expected impurities was determined empirically. Including an 18% excess, the amount was 7.2 liters of 0.1 M Versene for a batch containing 85 gms of lead, 1 gm of barium, 0.1 gm strontium as their sulfates, and 1, 0.3, 0.2 gms, respectively, of iron, chromium and nickel at pH 6.0 to 6.5.

6.2 M.S. Resin Column

Laboratory scouting runs showed that a resin column measuring 0.67" x 10" was necessary to quantitatively adsorb the barium in a Versene-RaLa feed on a 1/36 process scale. To insure complete barium adsorption, the column height was increased to 20" so that the laboratory column dimensions were 0.67" x 20" while full scale dimensions are 4" x 20". The resin used was sodium form Dowex 50, 60-100 mesh. The effluent gross activity was monitored as in the Acetate-Citrate Process (see Section 4.12 flowsheet Figure 6.0-1).

6.21 Equilibrium Data

The dissociation constants for the alkaline earth complexes in the Versene system were determined by Schwarzenbach and Ackermann⁽¹⁵⁾.

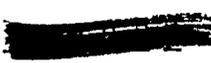
It is not practical to use these constants in a quantitative sense for the solutions in question, however, because of the great sensitivity of the constants to foreign ions.

The complexing action of Versene is very pH dependent. At high pH the complexes are strong, decreasing with pH so that there is little complexing action at pH 4.0 while at pH 3.0 to 3.5 the Versene acid precipitates.

The barium-Versene complex starts to break down at pH values below 7.0. The elements of interest in the RaLa process are listed in increasing order of complex strength at pH 6.3 as follows:

Ba < Sr < Ca << Fe, Cr, Ni, Pb, Rare Earths

The variation of the distribution coefficient, K_d , of barium and strontium with pH was determined for synthetic feed Versene solutions v.s. Dowex 50 resin. The two solutions were 0.065 and 0.13 M in Versene and contained lead, iron, chromium, and nickel but no sulfate. In set I, the amount of Versene was just sufficient to prevent the precipitation of the hydrous oxides. Thus, the bulk of the Versene was complexed by the lead, and its effect on barium and strontium was small. In set II, however, the barium and strontium distribution coefficients decreased



Equilibrium Data (continued)

by factors greater than 100 as the pH changed from 5 to 7. K_d was calculated as:

$$K_d = \frac{\text{cts/gm oven dry H}^+ \text{ resin}}{\text{cts/ml solution}}$$

(See Figure 6.21-1.)

6.22 Product Adsorption: Separation from Sulfate

The solution obtained by dissolving the sulfate cake in Versene is passed through the M.S. column at a pH of 6.0 to 6.5. At this pH the barium is weakly complexed so that it is quantitatively adsorbed on the resin. About 30 to 50% of the strontium is also adsorbed, while the bulk of the iron, chromium, nickel, lead, and rare earths pass on through as the Versene complexes along with the anion sulfate. The column is then washed with water to remove all traces of sulfate.

6.23 Impure Product Elution

The barium, strontium, and small amounts of impurities are removed from this column in a small volume of 0.23 M Versene at pH 11.0. This elution is efficient and quantitative due to the strong complexes formed at high pH values.

6.3 Purification Column

6.31 Column Specifications

The first laboratory column used was 0.67 cm by 3" representing 1/20 of the process scale. Adequate barium-strontium separation was not obtained so the height was increased to 7". Sodium form, 60-100 mesh, Dowex 50, resin was used in this column also. The effluent gross activity was monitored as in the Acetate-Citrate Process (see Section 4.12, also Figure 6.0-1).

6.32 Product Adsorption

The Versene solution containing the barium product eluted from the M.S. column is adjusted from pH 11 to 4.0-4.3 with nitric acid and passed through the product column. At this pH the complexing action of Versene is very small so that essentially all of the cations are adsorbed at the top of the column leaving the rest of the column free for chromatographic contaminant separation. The column is then washed with water to displace the feed solution.

6.33 Impurity Elution

Strontium Elution

The column is washed with 0.03 M, pH 6.3 Versene. As strontium is complexed more strongly than barium, it is selectively eluted leaving the barium on the column. Any traces of iron, lead, chromium, or nickel left in the system will also be removed for the same reason.

Impurity Elution (continued)

Sodium Elution

The sodium is removed from the column by elution with 1 M hydrochloric acid. At this molarity of acid, the sodium is easily removed with negligible barium loss (see Section 4.2).

6.34 Product Elution

At this point the resin contains only barium and H^+ . The barium is removed in 6 M nitric acid. Analyses listed in Table 6.0-1 show that the product meets the purity requirements.

6.4 Comparison of Versene and Acetate-Citrate Processes

The advantages of the Versene Process are:

- (1) The elimination of the metathesis step which has been shown to be unreliable in process operations over the last four years. Direct solution in Versene offers a distinct advantage in process reliability.
- (2) An estimated 10 to 15 hours of process time will be saved by using the Versene Process. This time saving represents approximately a 2-3% increase in barium yield as a result of reduced barium decay.

Comparison of Versene and Acetate-Citrate Processes (continued)

- (3) The resin and solution will be subjected to much less concentrated radiation in the Versene Process because the bulk of the rare earths and strontium pass through the first column in the complex form and are never adsorbed in concentrated bands as in the Acetate-Citrate Process. Since the overall time cycle is lower, any radiation damage will also be less.

7.0 Evaluation of IRC-50 Resin.

As seen in the preceding processes, the purification of barium is carried out in the pH range 6.0-9.0. This pH range is known to be optimum for IRC-50 resin so that an effort was made to evaluate this resin.

The outstanding advantage of IRC-50 for barium purification is its ease of regeneration with strong acids. That is, the carboxyl exchange groups being weak acid groups exhibit a strong preference for H^+ ions. Thus the barium product can be eluted in an amount of acid roughly equivalent to the resin capacity. As a result the volume of acid to be evaporated prior to product shipment would be greatly reduced. The resistance of IRC-50 to strong acids and bases is known to be high, in fact, about the same as Dowex 50.

NS

Evaluation of IRC-50 Resin (continued)

The disadvantages of IRC-50 listed below proved to be so great that its projected use in a final purification column has been abandoned. Indications are, however, that the use of this resin would be advantageous for separation of barium from uranium (see Section 10.0).

- (1) IRC-50 resin swells 50% as it changes from the H^+ form to the Na^+ form so that the sodium hydroxide regenerant must be passed up through the resin bed to prevent the resin from packing and breaking the column as the resin expands. Any changes in pH during processing cause a change in volume and capacity of the resin (see Figure 4.11-7).
- (2) The rate of diffusion is known to be slower for IRC-50⁽¹⁰⁾ resin than for the Dowex 50 type resin. Therefore slower flowrates are necessary.
- (3) The separation factor, $K_d(Ba)/K_d(Sr)$, was found to be roughly a factor of 3 less for the IRC-50 resin-citrate system than for the Dowex 50-citrate system (see Section 4.11). The separation of barium and strontium using a column of IRC-50 resin and citrate elution proved to be inefficient.
- (4) As a final step in barium purification, it is necessary to separate the sodium and barium by selectively eluting the sodium from the resin with hydrochloric acid, leaving the barium on the

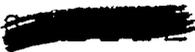


Evaluation of IRC-50 Resin (continued)

resin (see Section 6.33). However, with IRC-50 resin, hydrochloric acid quantitatively removes both the barium and sodium due to the marked affinity of the resin carboxyl groups for the H^+ ion. An attempt was made to overcome this difficulty by washing the resin with sodium acetate solutions buffered to pH 4.0 or 4.3. At this pH the bulk of the carboxyl groups should be holding on to barium only since barium is held much more strongly than sodium and there is not enough resin capacity (ionized carboxyl groups) to hold both. Column experiments to prove this theory were not successful, presumably because it is difficult to reach true equilibrium conditions when the diffusion rate is low.

8.0 Impurity Removal by Anion Exchange

An effort was made to reduce the Acetate-Citrate Process time cycle by passing the acetate feed (see Section 4.13) through an anion exchange column to remove the iron, chromium, nickel, and lead contaminants prior to adsorption of the barium on the regular column. It was found that 80-90% of these impurities could be removed by passing an acetate feed solution at pH 6.0 through a column of IR4B anion resin. The barium, being present as a cation, should not be adsorbed in this system. It



Impurity Removal by Anion Exchange (continued)

was found, however, that the barium yields were very erratic, ranging from 15 to 85%. It was felt that further work on this system was not justified.

Three possible mechanisms to explain these results are as follows:

- (1) that anion acetate complexes, such as basic ferric acetate, are formed and adsorbed as such;
- (2) that the hydrous oxides or acetates are adsorbed as colloids; or
- (3) that the weak base IR4B resin is sufficiently hydrolyzed at pH 6.0, so that the impurities are precipitated in and on the resin as their hydroxides. These hydrous oxides could carry barium, accounting for the erratic barium yields. The last mechanism is probably the best explanation as the results could not be repeated using the strong base Dowex A-2 anion resin.

9.0 Upflow Resin Column Development

An attempt was made to develop an upflow resin column for use in the RaLa Process so that if gas were formed as a result of water decomposition from radiation, the bubbles could escape and thus not block the column. An investigation of bed expansion as a function of resin mesh size and upflow rate was made. Resin sizes smaller than 200-240 mesh were found to be impractical. A resin bed was prepared for further study containing known

[REDACTED]

Upflow Resin Column Development (continued)

percentages of resin with mesh size varying from 40 to 240 and where the bed expansion was 25% for a flow rate of 0.56 cc/cm²/min. The theory of such a column is that in upflow operations the larger resin particles remain at the bottom and, in general, each particle assumes a position relative to its size. Thus the bed would not "churn" and a chromatographic separation would be made possible. Duplicate runs made on upflow and down flow columns to separate barium and strontium under flow sheet conditions by citrate elution showed that the product barium obtained in the upflow column contained 14.4% of the strontium while the product barium from down flow operation contained only 0.13% of the Sr.

Although these results are considered to be very encouraging and could undoubtedly be improved, further development was deferred until it could be determined if gassing was to be a major problem in high radiation level resin columns.

10.0 Separation of Barium from Dissolver Solution

In the present process, the barium is separated from the uranium and fission products in the slug dissolver solution by co-precipitation with lead. Previous investigators⁽⁵⁾ have shown that this separation can be done efficiently by ion exchange using IR-1 resin. It is proposed to re-evaluate the efficiency of these two processes in the light of the improved high capacity resins available today.

Separation of Barium from Dissolver Solution (continued)

For example, it has been shown that in the IRC-50 resin system, the barium distribution coefficient increases tremendously with pH (see Figures 4.11 - 4, 5, 6). It is evident that use of a complexing agent, such as bicarbonate, to complex and hold the uranium in solution at a high pH would make use of the most favorable barium distribution coefficient. Although barium bicarbonate is soluble, calculations have shown that at pH 7.8 the equilibrium carbonate concentration would be just high enough to precipitate barium carbonate in aqueous solution. The true solubility of barium carbonate in the system of interest will be determined accurately.

11.0 Acknowledgement

Appreciation is expressed for the advice Dr. G. E. Boyd has given on basic ion exchange theory and also for his time spent in identification by absorption and decay techniques of unknown activity peaks in the elution curves (see Figure 4.0-1).

Table 4.0-1

¹⁴⁰Ba Purification by the Acetate-Citrate Process and a Versene Modification

Conditions:

Column: 0.55" diameter x 7" height
 Resin: Na⁺ Form Dowex 50, 100-200 mesh
 Flow Rate = 0.55 ml/cm²/min

Feed: 2.824 gms Pb 35 mg, Ba, Ba tracer
 6.2 mg Ni 3.3 mg, Sr, Sr tracer
 32.8 mg Fe (328.0 mg Fe in Run Ba-34)
 Runs Ba-31 to 34 - 0.5 M in Na Acetate
 Runs Ba-35 to 37 - 0.06 M in Versene; pH 6.0
 Total Volume = 233 ml

(Quantities Represent 1/30 Full Chemical Scale under Maximum Conditions of Impurity)

Washes: I - Pb Elution - 0.5 M NaOH; 200 ml
 II - Fe Elution - 0.5 M Na Citrate, pH 3; 166 ml
 III - Sr Elution - 0.1 M Na Citrate, pH 9; 300-500 ml
 IV - Na Elution - 6 N H₂SO₄, 30-50 ml
 Product Elution - 200 ml 6 N HNO₃

Run No.	Feed Effluent			Waste Analyses (%)						Product Analyses**						Ba Material Balance
	Ba	Fe	Pb	Ba	NaOH	Pb	Ba	NaCit pH 3	Fe	NaCit pH 9	Ba	H ₂ SO ₄	Ba	Sr	Pb	
Ba-31	0.5	92	6.3	0.44	0.1	2.7	0.1	3.6	103	0.4	0.4	96	0.14	<0.02	1.14	97.6
Ba-32	0.02	122	145	0.005	0.012	5.3	**	0.082	91	0.008	0.008	106	56*	0.02	<0.04	121.1
Ba-33	0.03	74.3	80	0.004	0.42	3.3	2.3	1.45	34	0.023	0.023	102.4	0.67	0.06	-	104.3
Ba-34	0.22	76.5	21.36	0.12	41.02	0.10	1.23	1.15	101.4	0.36	0.36	96.6	0.1-1.0	<0.049	-	98.55
Ba-35	0.29	91	186	0.04	0.67	0.24	**	0.54	108.7	0.08	0.08	110	0.04	0.02	1.39	112.3
Ba-36	0.1	97	162	0.35	0.08	0.04	ca 5.0	0.097	13	0.033	0.033	104.1	76.2*	<0.02	<0.58	105.5
Ba-37	0.031	47	156	0.006	0.09	0.04	0.7	0.12	87.4	2.9	2.9	91	<0.17	<0.02	1.69	94.1

* Poor separation of Ba and Sr obtained when insufficient pH 9 NaCit was used as result of recorder breakdown.

** Fe, Ni, and Cr were not detectable by colorimetric analysis

≠ See Section 4.2 for comparison of HCl v.s. H₂SO₄

Table 4.11

Distribution Coefficients of Ba¹⁴⁰ and Contaminants Between
Dowex 50 and Possible Eluting Agents

Conditions: 5 ml of resin, previously saturated with cation,
was shaken for 2 hours with 25 ml of eluting agent.

$$\text{Distribution Coefficient} = K_d = \frac{\text{mg of cation/ml resin}}{\text{mg of cation/ml solution}}$$

Distribution Coefficients							
Cation	0.5 M Citric Acid pH 1.7	0.5 M Ammonium Citrate pH 3.0	0.5 M Ammonium Citrate pH 7.6	0.4 M Oxalic Acid pH 0.78	0.4 M Ammonium Oxalate pH 3.0	0.4 M Ammonium Oxalate pH 7.8	1.0 M Ammonium Acetate pH 6.0
Ni ⁺²	147	8.3	7.2x10 ⁻²	ppt.	ppt.	ppt.	2.4
Sr ⁺²	81.9	15.7	ppt.	ppt.	ppt.	ppt.	6.5
Fe ⁺³	13.1	2.0	101	2.3x10 ⁻²	2.0x10 ⁻²	1.1	21.2
Cr ⁺³	61	10	0.17	28	7.0	3.8	0.22
Ba ⁺²	263.	24.8	ppt.	266	ppt.	ppt.	8.9
Pb ⁺²	Very High	ppt.	ppt.	ppt.	ppt.	ppt.	1.3

The distribution coefficient for Ba was 265 under the following conditions:

<u>Resin</u>	<u>Eluting Agent</u>
5 ml sodium Resin	0.5 M NaOH 5 mg/ml Pb as PbO ₂ ⁼ 0.05 mg/ml Ba ⁺² Tracer Ba

Table 5.1-1

Separation of Barium from Lead and Strontium by An

Alkali-Citrate Ion Exchange Process

Conditions:

Column: Diameter: 1.4 cm
 Height: 10 cm
 Resin: Na⁺ Form Dowex 50; 140-200 mesh
 Flow Rate: 0.5 ml/cm²/min.

Feed: 0.5 M NaOH(CO₃⁼Free) containing:
 1 gm Pb as PbO₂⁼
 10 mg Ba + Ba tracer
 1 mg Sr + Sr tracer (Ba-9 and 11, only)
 Total volume = 202 ml; (3000 ml for Ba-7)

Washes: I, for Pb removal: 30 ml 0.5 M NaOH(CO₃⁼Free); 30 ml H₂O
 II, for Sr removal: see table below

Elution of Ba product: 6 N HNO₃

Run No.	Effluent and Wash I % Ba	Wash II		Product Ba			Ba Material Balance		
		Composition	% Sr	% Pb	% Ba	% Sr		% Pb	% Ba
Ba-11	0.08	15 ml 0.5 M Na Citrate pH 7.8	86.5	-	0.97	6.7	-	107.8	108.8
Ba-7	0.3	"	-	8 x 10 ⁻⁴	1.4	-	<0.003	94.2	95.7
Ba-5	0.15	150 ml 0.1 M Na Citrate pH 9	-	<0.15	0.14	-	<0.10	>99	-
Ba-9	0.01	"	103	<0.2	0.34	0.11	<0.04	94.3	94.6

Table 5.2-1

Carrying of Ba and Sr by the Oxides of Fe and Pb

Conditions: NaOH (CO₃⁻ Free) and boiled H₂O - used in all precipitations, dilutions, and washes. Cations precipitated from 0.25 M NaOH (CO₃⁻ Free), pH 11.3 in all cases.

Feed: Feed Volume = 40 ml

Washes: All precipitates washed with 3-15 ml volumes 0.5 M NaOH (CO₃⁻ Free) followed by 1-30 ml volume of H₂O before proceeding as follows:

Run XVII: Use 2-15 ml volumes 0.5 M NH₄NO₃, pH 5, washes; then 30 ml H₂O

Runs XVIII and XIX: Use 3-15 ml volumes 0.5 M NH₄NO₃, pH 5, washes; then 30 ml H₂O

All precipitates were dissolved in 3 N HNO₃ for final analysis

Run No.	Cation Concentrations in Feed Solutions	% Ba		Carried by ppt.	% Sr		Carried by ppt.
		In NaOH Wash	In NH ₄ NO ₃ Wash		In NaOH Wash	NH ₄ NO ₃ (pH 5) Wash	
I	200 mg Fe; 0.45 mg Cr; 0.34 mg Ni; 1.88 mg Ba; 0.22 mg Sr; 207 mg Pb	-	-	2.5	-	-	7-10
I-C	Same as Run I + 0.1 M H ₂ O ₂	-	-	50	-	-	39
III	201.7 mg Pb, 0.1 M H ₂ O ₂ + Ba and Sr tracer	56	-	44	63.2	-	36.8
VII	1.0 mg Fe + Ba and Sr tracer	9.95	-	90.1	16.4	-	83.3
XVII	1.0 mg Fe + Ba and Sr tracer	-	-	-	18.2	78.9	3.2
XVIII	1.0 mg Fe + 10 mg "cold" Ba + Ba tracer	94.4	4.54	0.97	98.8	1.03	0.07
XIX	1.0 mg Fe + 100.5 mg Pb + 10 mg "cold" Ba + Ba tracer	99.3	0.56	0.10	99.6	0.33	0.02

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Table 6.0-1
Two Column Versene Process for Ba¹⁴⁰ Purification

Conditions:

Columns: Resin - Na⁺ Form Dowex 50, 100-200-Mesh
Dimensions - M.S.* Column = 0.67" diam. x 20" hgt.
Purification Column - 0.67" diam. x 7" hgt.

Procedure:

M.S. Column: Feed - 1/36 full RaLa chemical scale under conditions of maximum impurity:

2236 mg Pb ⁺²	} Precipitated as	22.0 mg Fe ⁺³	
29.7 mg Ba ⁺²		sulfates and dissolved +	5.7 mg Ni ⁺²
3.2 mg Sr ⁺²		in Versene	8.3 mg Cr ⁺³
Ba-Sr Tracer			

Total Volume - 200 ml, 0.10 M in Versene, pH 6.0 - 6.5

Impure Product eluted in 0.25 M Versene, pH 11

Purification Column: Feed - Impure product from M.S. column adjusted to pH 4.0-4.5; vol. = 300 ml.

Eluting Agents: Sr Elution - 250-300 ml 0.07 M Versene, pH 6.3 followed by 75 ml H₂O
Na Elution - 250 ml 0.5 M HCl; followed by 100 ml H₂O (V-19 and 20)
Ba Product - 200 ml 1.0 M HCl; followed by 100 ml H₂O (V-21)
Ba Product - 200 ml 6 N HNO₃

Run No.	M.S. Column				Purification Column							Ba Material Balance			
	Waste Analysis				Impure Product			Waste Analysis (%)					Product Analysis**		
	Ba	Sr	Fe	Pb	% Ba	% Sr	F.E.#	Ba	Sr	HCl	Ba		Sr	Pb	Na/Ba
V-19	0.73	79.3	65.6	136	105	0.6	0.78	17.9	1.8	96.1	0.76	<0.02	12	100.01	
V-20	4.1	76.3	72.6	147	108	<0.32	<1.12	18.44	4.79	101.1	<0.29	<0.04	7.05	<105.4	
V-21	2.5	85	63	154	110	0.1	0.2	6.0	0.7	97	0.3	<0.06	0	100.5	

* Metathesis Substitute

** Fe, Ni, and Cr were not detectable by spectro-photometric analysis

Feed effluent

SECRET

Figure 4.0-1

Flowsheet: Acetate-Citrate Process for Purification
of Barium by Ion Exchange

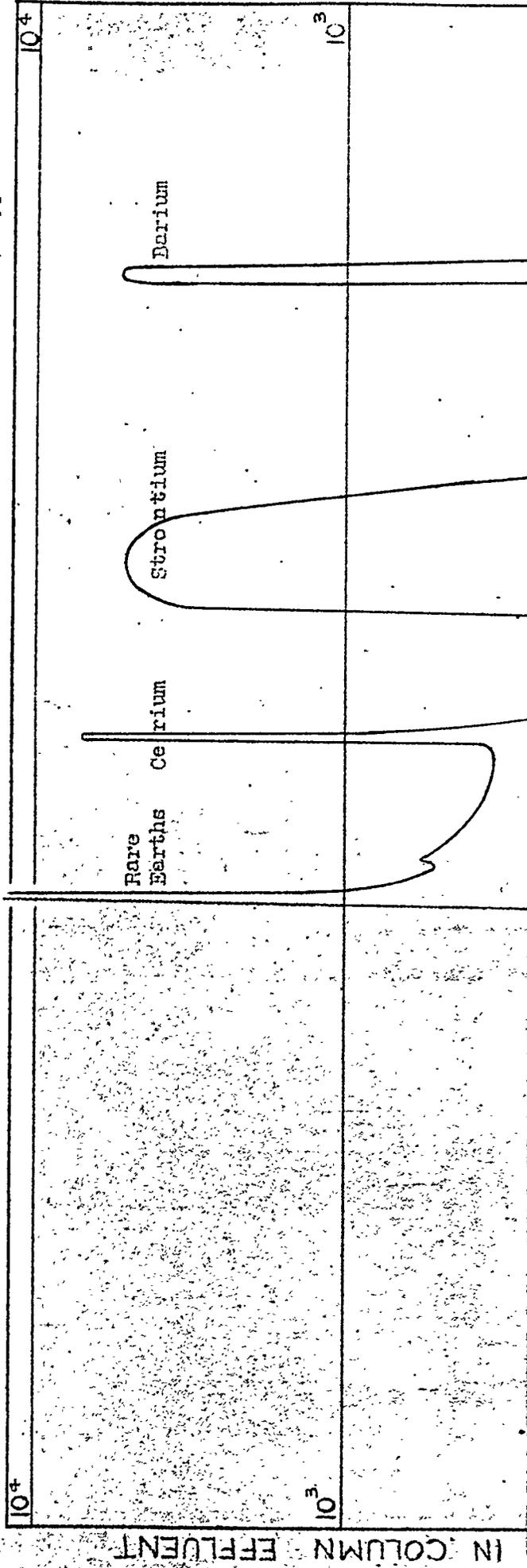
(Full process scale)

Resin Column: 3"x7", sodium form, 60-100 mesh, "Dowex 50" Resin
 Flowrate: 0.7 ± 0.2 ml/min/cm² column cross section
 Feed: 0.5 M sodium acetate, 0.2 M HNO₃
 87 gms lead

Approximately 1.0 gm barium, and 0.1 gm strontium
 Small amount of iron, chromium, nickel

Over all process time: 27 hours

Eluting Agent	Volume (Liters)	Cumulative Volume (Liters)	Column Effluent
Feed (as above)	10	10	Bulk of iron
Water Wash	2	12	-
Sodium Hydroxide, 0.5 M	10	22	Lead, chromium
Water Wash	2	24	-
Sodium Citrate 0.5 M, PH 3.0	5	29	Iron, Rare Earths, Zirconium, Niobium
Sodium Citrate, 0.1 M, PH 9.0	13	42	Strontium, Nickel, Chromium
Water Wash	2	44	-
Hydrochloric Acid 6 M	2.5	46.5	Sodium
Water Wash	2	48.5	-
Nitric Acid 6 M	5	53.5	Barium Product



	Volume (Liters)	Carbons Eluted from Column
Feed (as above)	10	Dulk of iron
Water Wash	2	-
Sodium Hydroxide, 0.5 M	10	Lead, chromium
Water Wash	2	-
Sodium Citrate 0.5 M, pH 3.0	5	Iron, Rare Earths, Zirconium, Niobium
Sodium Citrate, 0.1 M, pH 9.0	13	Strontium, Nickel, Chromium
Water Wash	2	-
Hydrochloric Acid 6 M	2.5	Sodium
Water Wash	2	-
Nitric Acid 6 M	5	Barium Product

FIG. 4.11-1

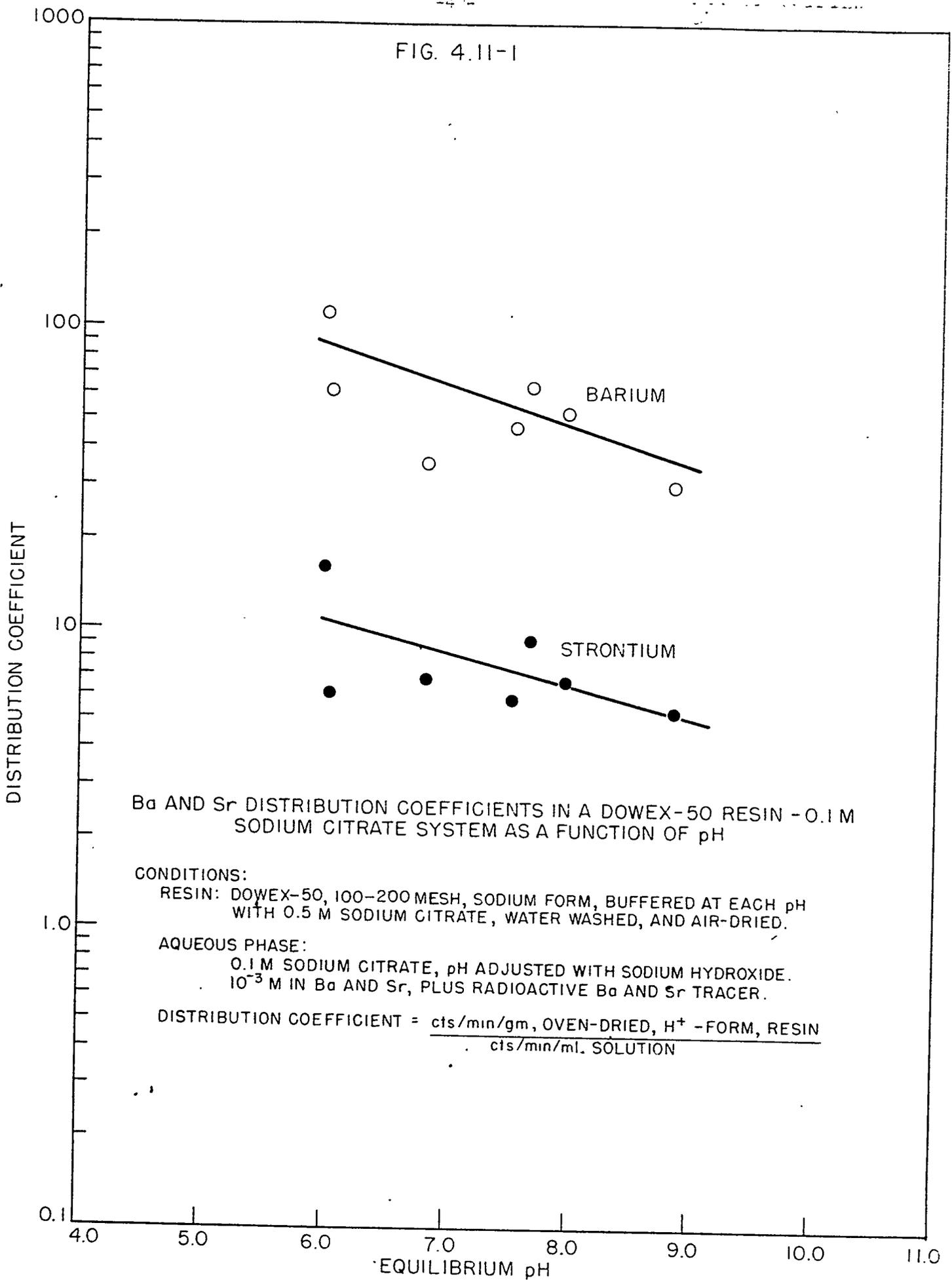


FIG. 4.11-2

Ba AND Sr DISTRIBUTION COEFFICIENTS IN A DOWEX-50 RESIN-0.3 M SODIUM CITRATE SYSTEM AS A FUNCTION OF pH

CONDITIONS:

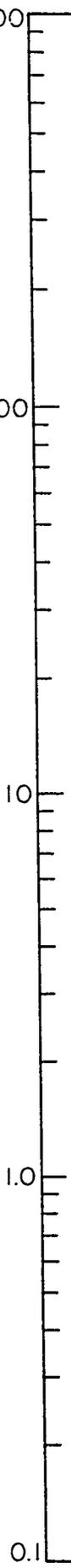
RESIN: DOWEX-50, 100-200 MESH; SODIUM FORM, BUFFERED AT EACH pH WITH 0.5 M SODIUM CITRATE, WATER WASHED, AND AIR-DRIED.

AQUEOUS PHASE:

0.3 M SODIUM CITRATE, pH ADJUSTED WITH SODIUM HYDROXIDE. 10^{-3} M IN Ba AND Sr, PLUS RADIOACTIVE Ba AND Sr TRACER.

$$\text{DISTRIBUTION COEFFICIENT} = \frac{\text{cts/min/gm, OVEN-DRIED, H}^+\text{-FORM, RESIN}}{\text{cts/min/ml SOLUTION}}$$

DISTRIBUTION COEFFICIENT



EQUILIBRIUM pH

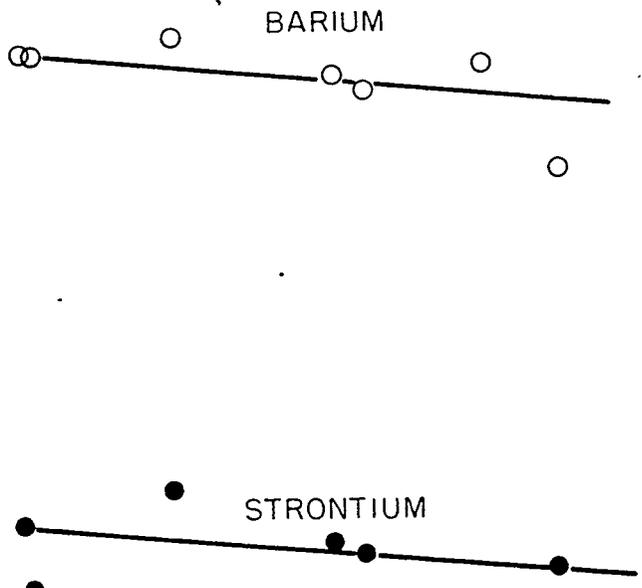


FIG 4.11-3

Ba AND Sr DISTRIBUTION COEFFICIENTS IN A DOWEX-50 RESIN-0.5 M SODIUM CITRATE SYSTEM AS A FUNCTION OF pH

CONDITIONS:

RESIN: DOWEX-50, 100-200 MESH; SODIUM FORM, BUFFERED AT EACH pH WITH 0.5 M SODIUM CITRATE, WATER WASHED, AND AIR-DRIED.

AQUEOUS PHASE:

0.5 M SODIUM CITRATE, pH ADJUSTED WITH SODIUM HYDROXIDE.
 10^{-3} M IN: Ba AND Sr, PLUS RADIOACTIVE Ba AND Sr TRACER.

$$\text{DISTRIBUTION COEFFICIENT} = \frac{\text{cts/min/gm, OVEN-DRIED, H}^+\text{-FORM, RESIN}}{\text{cts/min/ml. SOLUTION}}$$

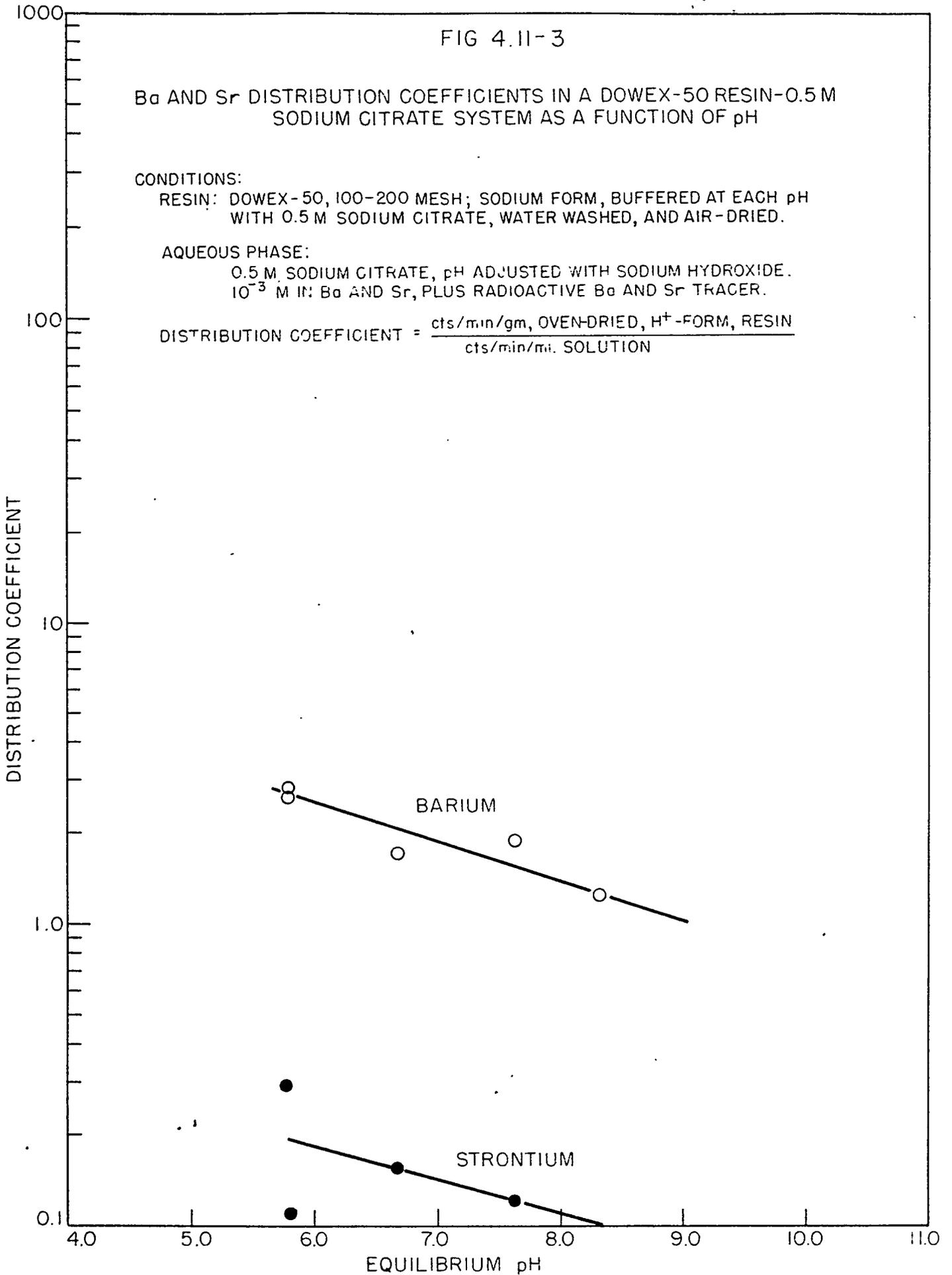


FIG 4.11-4

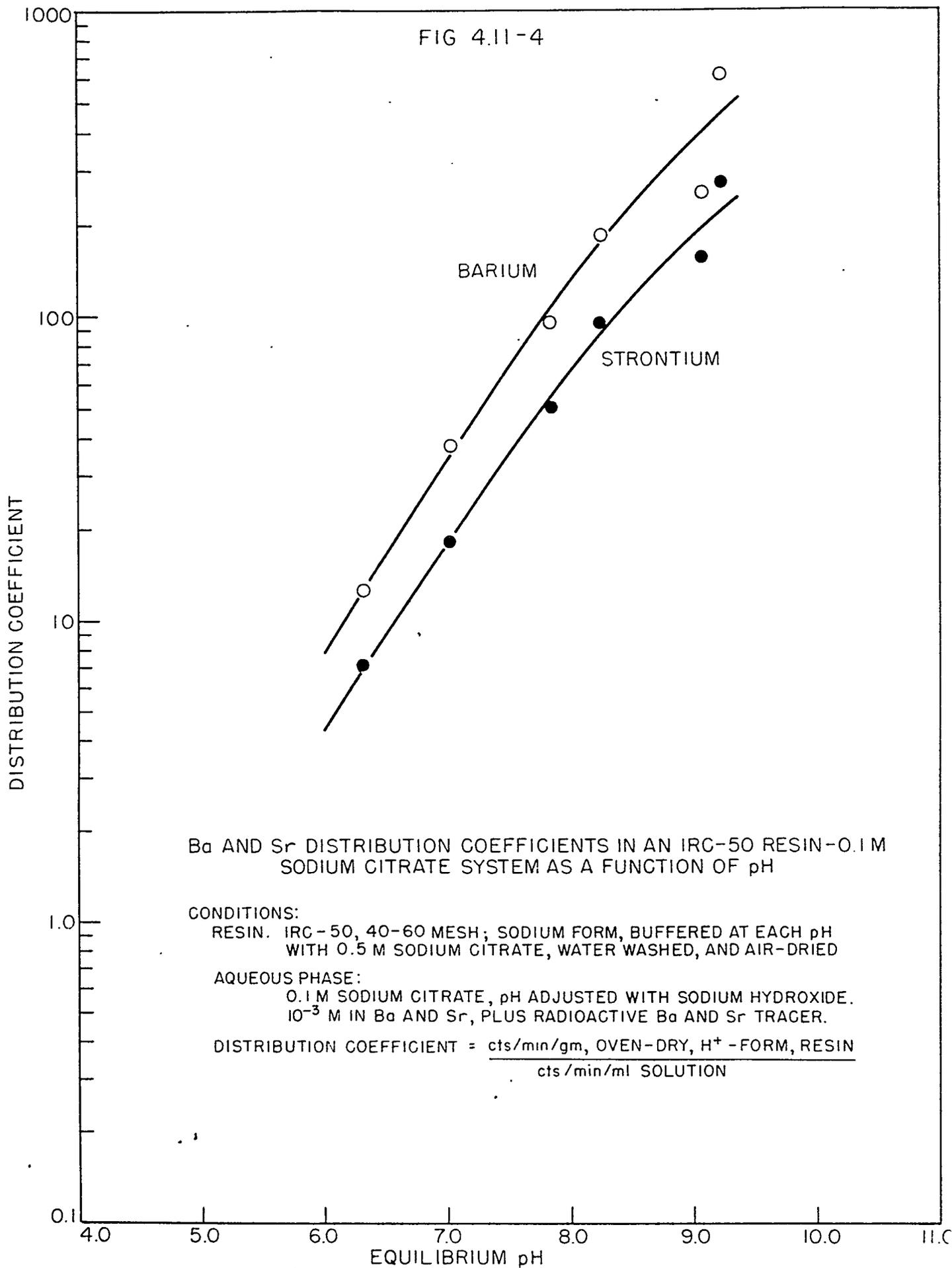


FIG. 4.11-5

Ba AND Sr DISTRIBUTION COEFFICIENTS IN AN IRC-50 RESIN-0.3 M SODIUM CITRATE SYSTEM AS A FUNCTION OF pH

CONDITIONS:

RESIN: IRC-50, 40-60 MESH; SODIUM FORM, BUFFERED AT EACH pH WITH 0.5 M SODIUM CITRATE, WATER WASHED, AND AIR-DRIED.

AQUEOUS PHASE:

0.3 M SODIUM CITRATE, pH ADJUSTED WITH SODIUM HYDROXIDE. 10^{-3} M IN Ba AND Sr, PLUS RADIOACTIVE Ba AND Sr TRACER.

$$\text{DISTRIBUTION COEFFICIENT} = \frac{\text{cts/min/gm, OVEN-DRY, H}^+ \text{ FORM, RESIN}}{\text{cts/min/ml SOLUTION}}$$

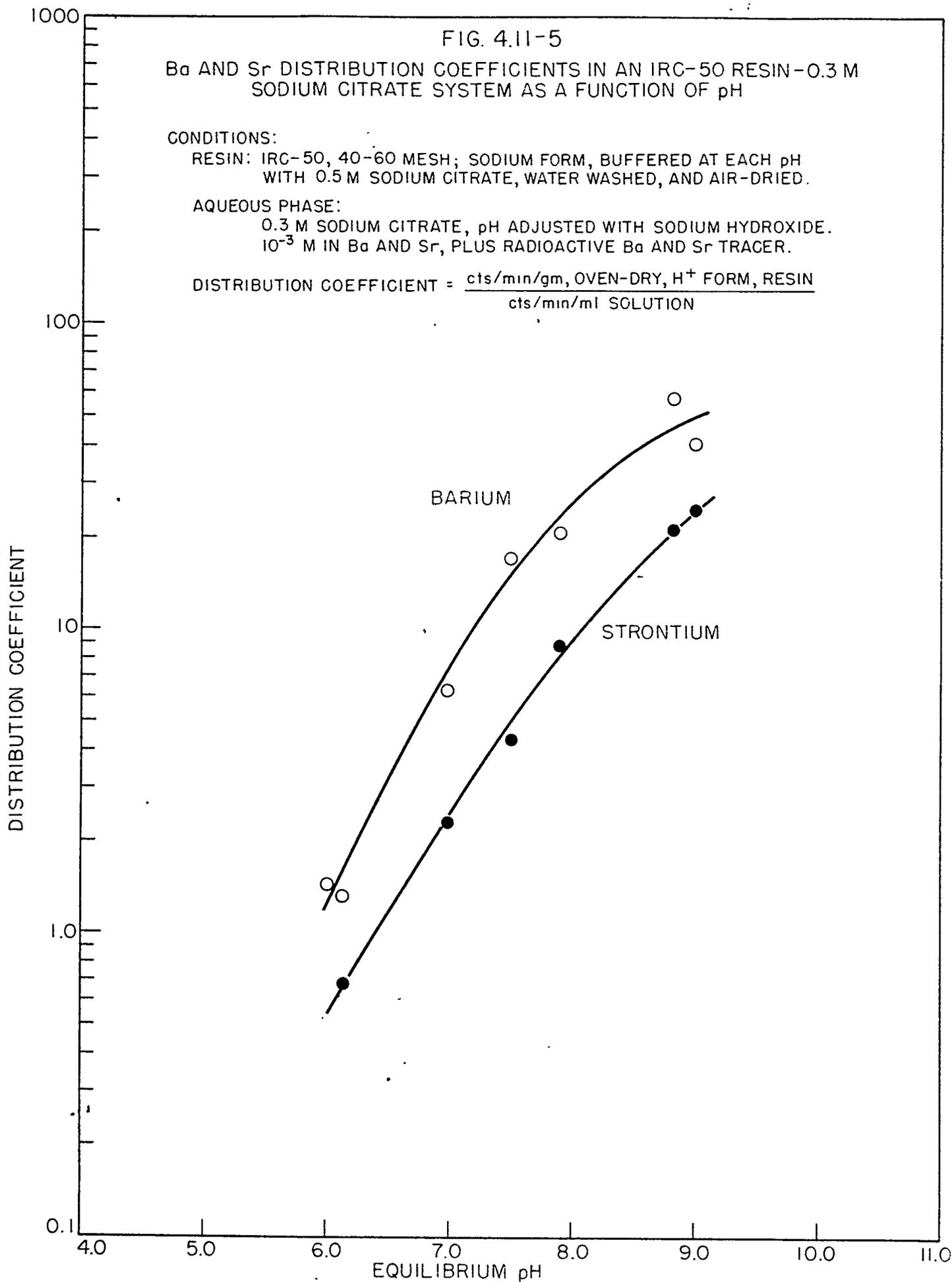


FIG. 4.11-6

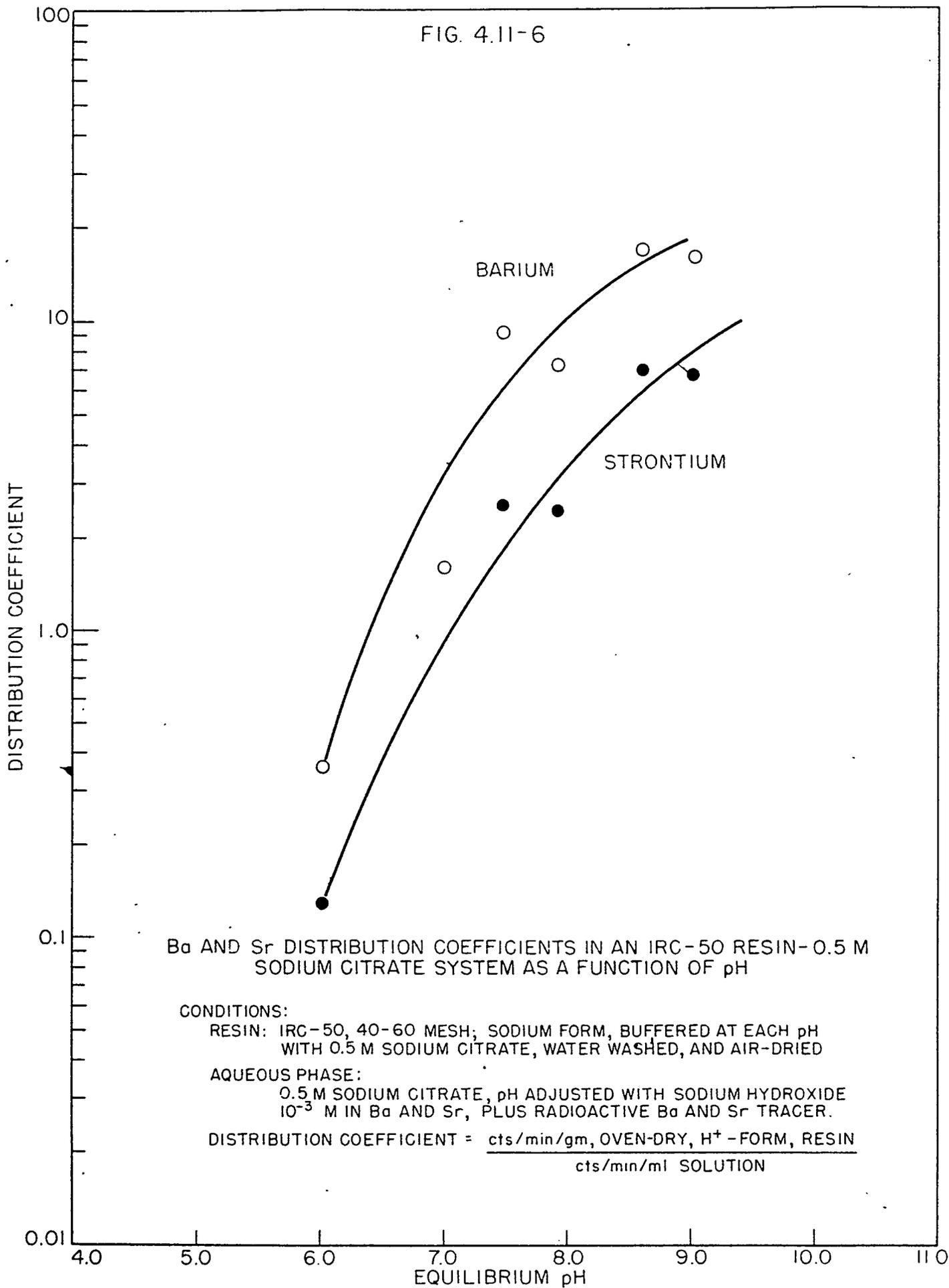


FIG. 4.11-7

SODIUM CAPACITY OF IRC-50" RESIN AS A FUNCTION OF pH

CONDITIONS:

COLUMN: 2.38 gms. OVEN DRY H⁺ FORM RESIN

ACTIVATION: (1) DOWN-FLOW - 25 ml. 1.0 M HCl; 10 ml H₂O

(2) UP-FLOW - 1.0 M NaOH UNTIL EFFLUENT IS ALKALINE + 20 ml EXCESS.

(3) DOWN-FLOW - 50 ml. H₂O

WASH(DOWN-FLOW): (1) 1.0 M Na ACETATE BUFFER SOLUTION UNTIL EFFLUENT EQUALS FEED pH.

(2) 50 ml. H₂O

Na ELUTION: 20 ml. 1.0 M HCl

PRODUCT: EVAPORATE TO DRYNESS AT 110°C AND WEIGH AS NaCl.

SODIUM CAPACITY: mg./2.38 gms. RESIN (H⁺ FORM, OVEN DRY)

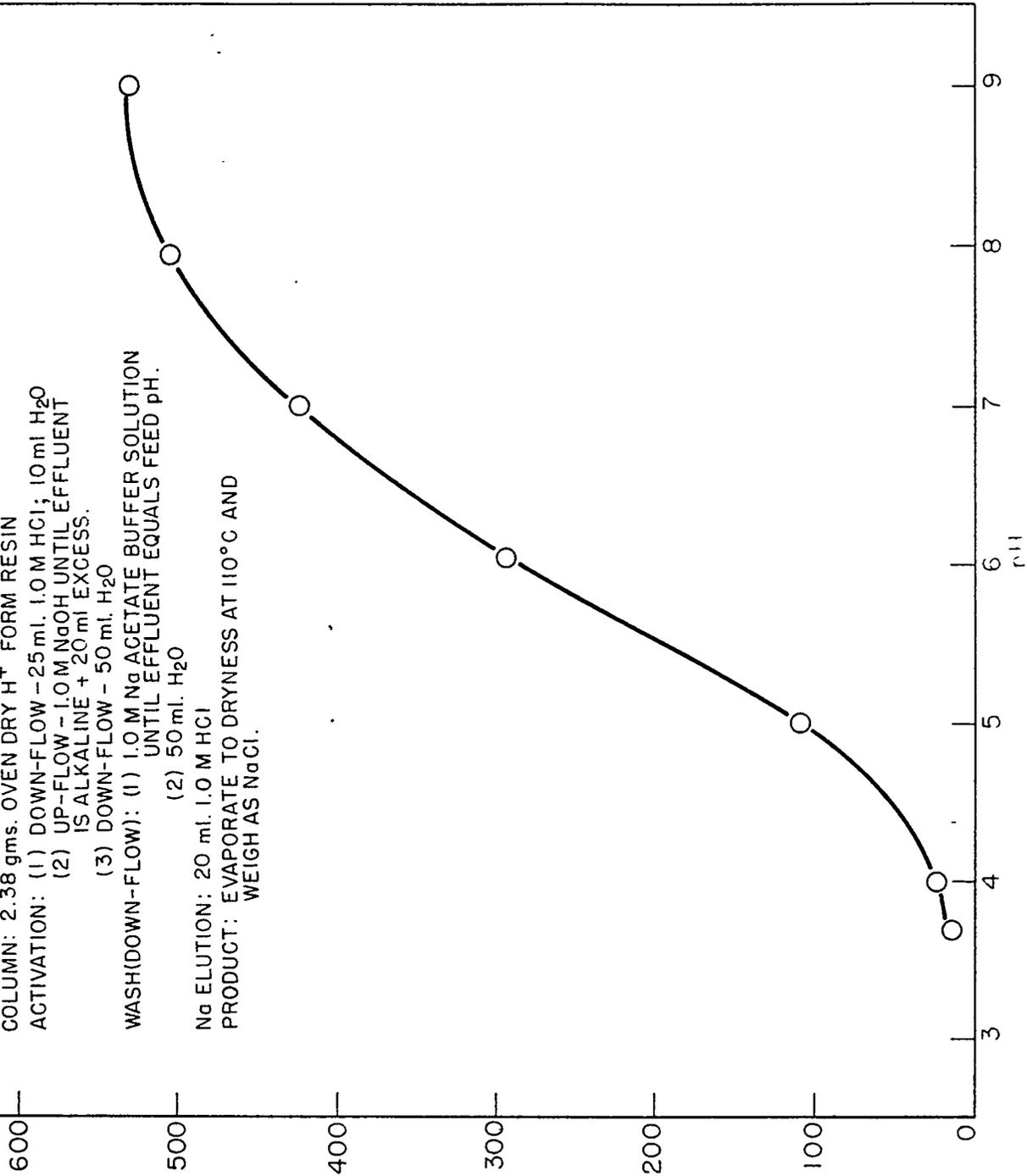


FIG. 4.13-1

SEPARATION OF Ba AND Pb BY ELUTION WITH 1.0 M
SODIUM ACETATE - RUN IR-10

FEED: 713 mg Pb^{+2} + 100 mg Ba^{+2}

CONDITIONS: IR-105 RESIN, 40-60 MESH

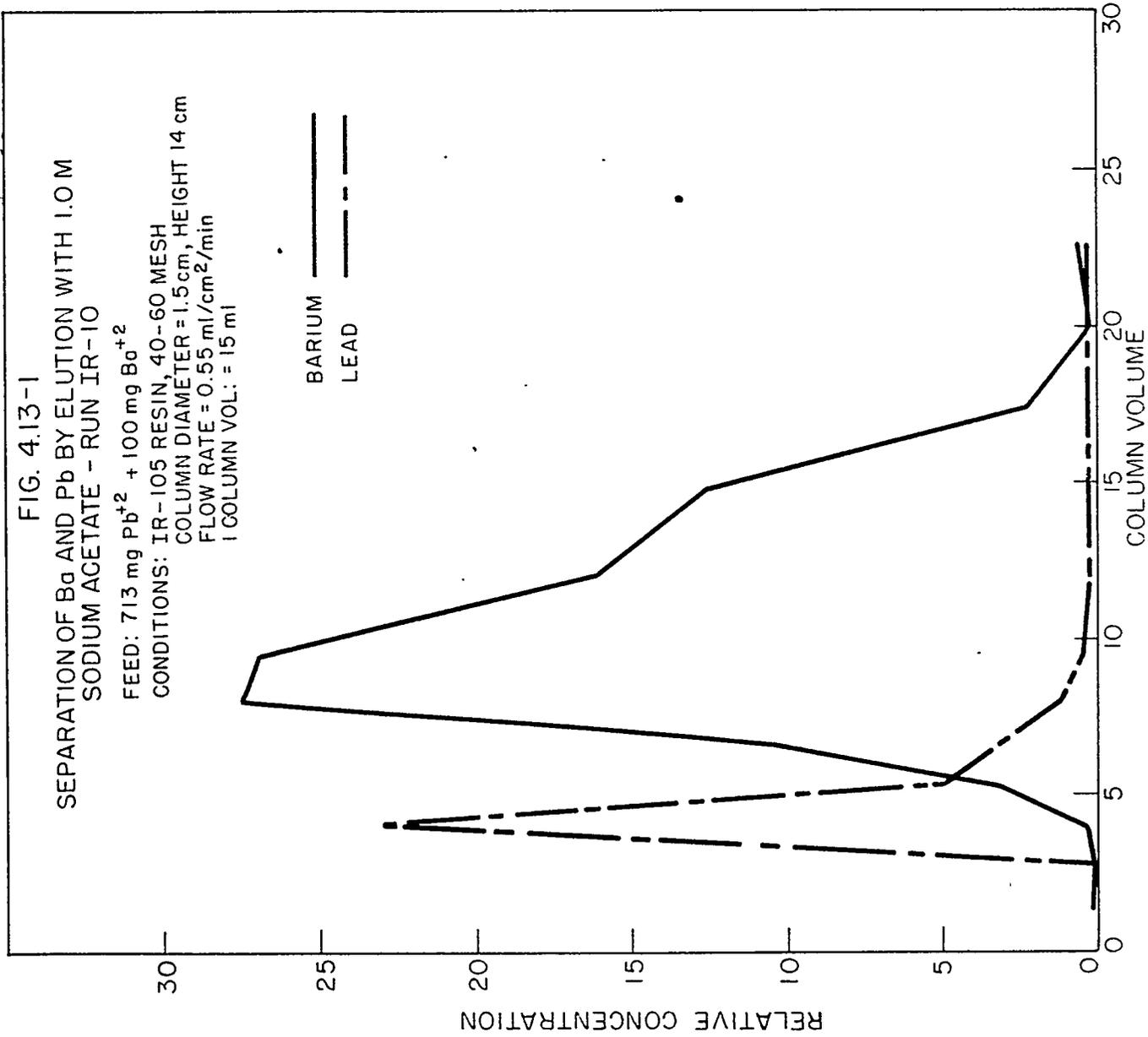
COLUMN DIAMETER = 1.5 cm, HEIGHT 14 cm

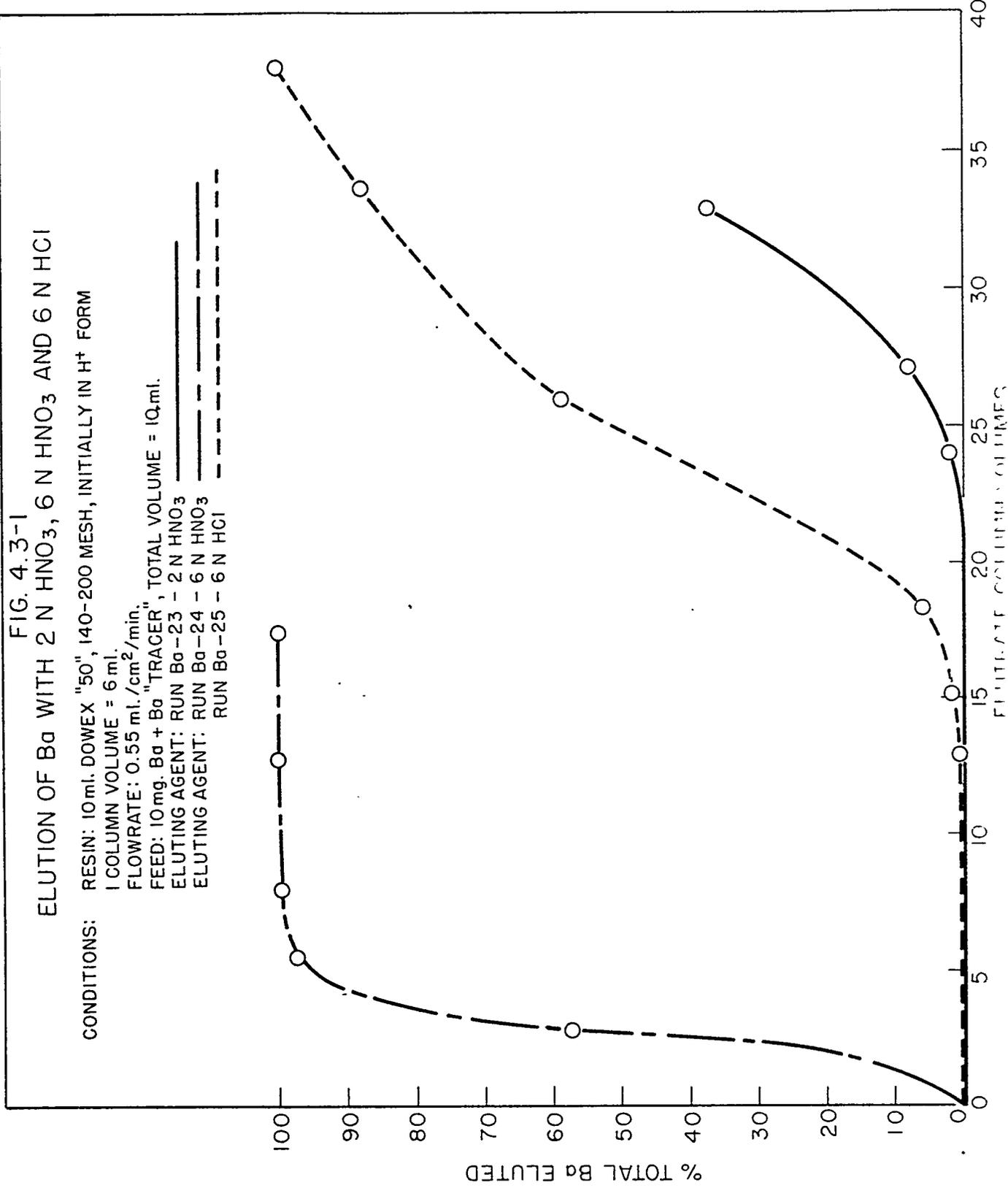
FLOW RATE = 0.55 ml/cm²/min

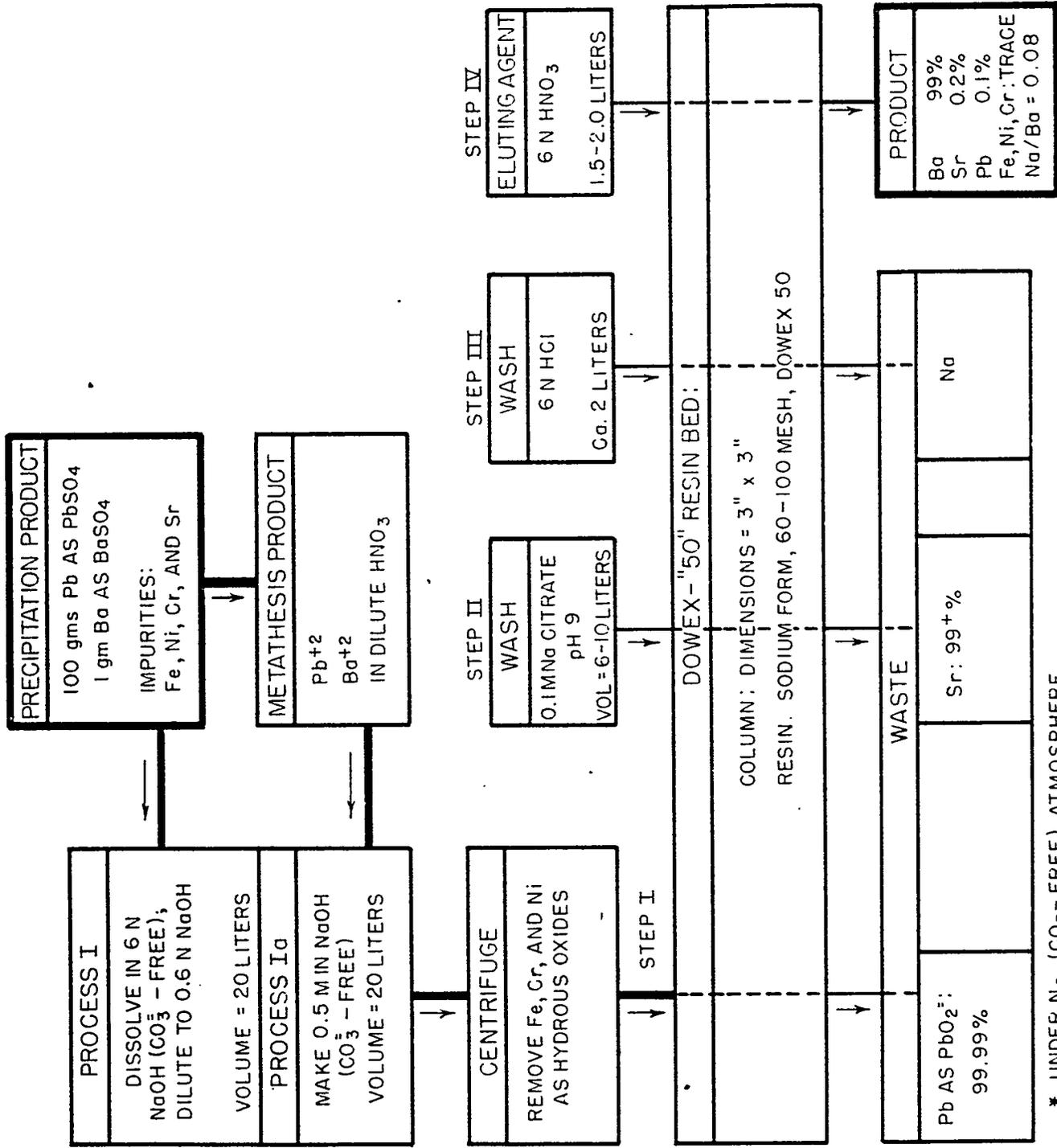
COLUMN VOL: = 15 ml

BARIUM

LEAD







* UNDER N₂ (CO₃ - FREE) ATMOSPHERE

Figure 6.0-1

Flowsheet: Versene Process for the Purification of Barium by Ion Exchange
 (full process scale)

M. S. Column: 4" x 20", 60-100 mesh, sodium form, Dowex 50 resin
 Purification Column: 3" x 7", 60-100 mesh, sodium form, Dowex 50 resin
 Flow Rate: 0.7 + 0.2 ml/min/cm² column cross section area

Feed: 87 grams lead, and approximately 1.0 gram barium and 0.1 gram strontium as their sulfates dissolved in 0.1 M, pH 6.0 - 6.5, Versene (ethylene diamine tetra acetic acid). Small amount of iron, chromium, nickel.

Overall process time: 27 hours

M. S. Column		Purification Column		Column Effluent
Eluting Agent	Volume (liters)	Cumulative Volume (liters)		Cations Eluted from Column
Feed (as above)	10	10		Lead, Iron, Chromium, nickel, rare earths, 50-90% strontium
Water Wash	3	13		
Versene, 0.23 M, pH 11.0	3	16		Impure Barium product
Water Wash	3	19		
Purification Column			Dilute to 10 liters Adjust to pH 4.0-4.3	
Feed	10	31		rare earths
Water Wash	2	33		
Versene, 0.03 M, pH 6.3	11	44		strontium, balance of other impurities
Water Wash	2	46		
Hydrochloric Acid 1 M	6	52		sodium
Water Wash	2	54		
Nitric Acid 6 M	5	59		barium product

RELATIVE RADIOACTIVITY IN COLUMN EFFLUENT

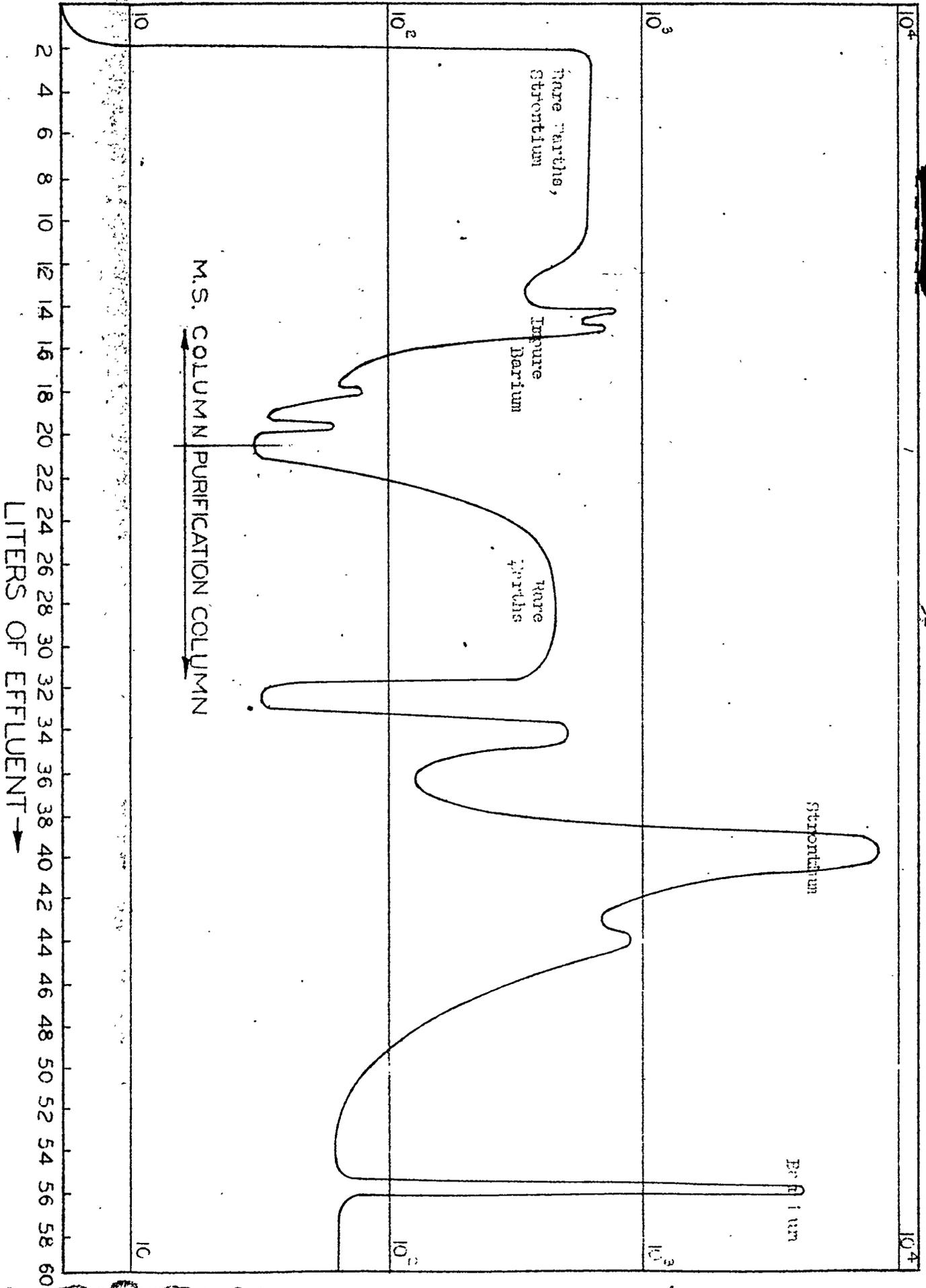
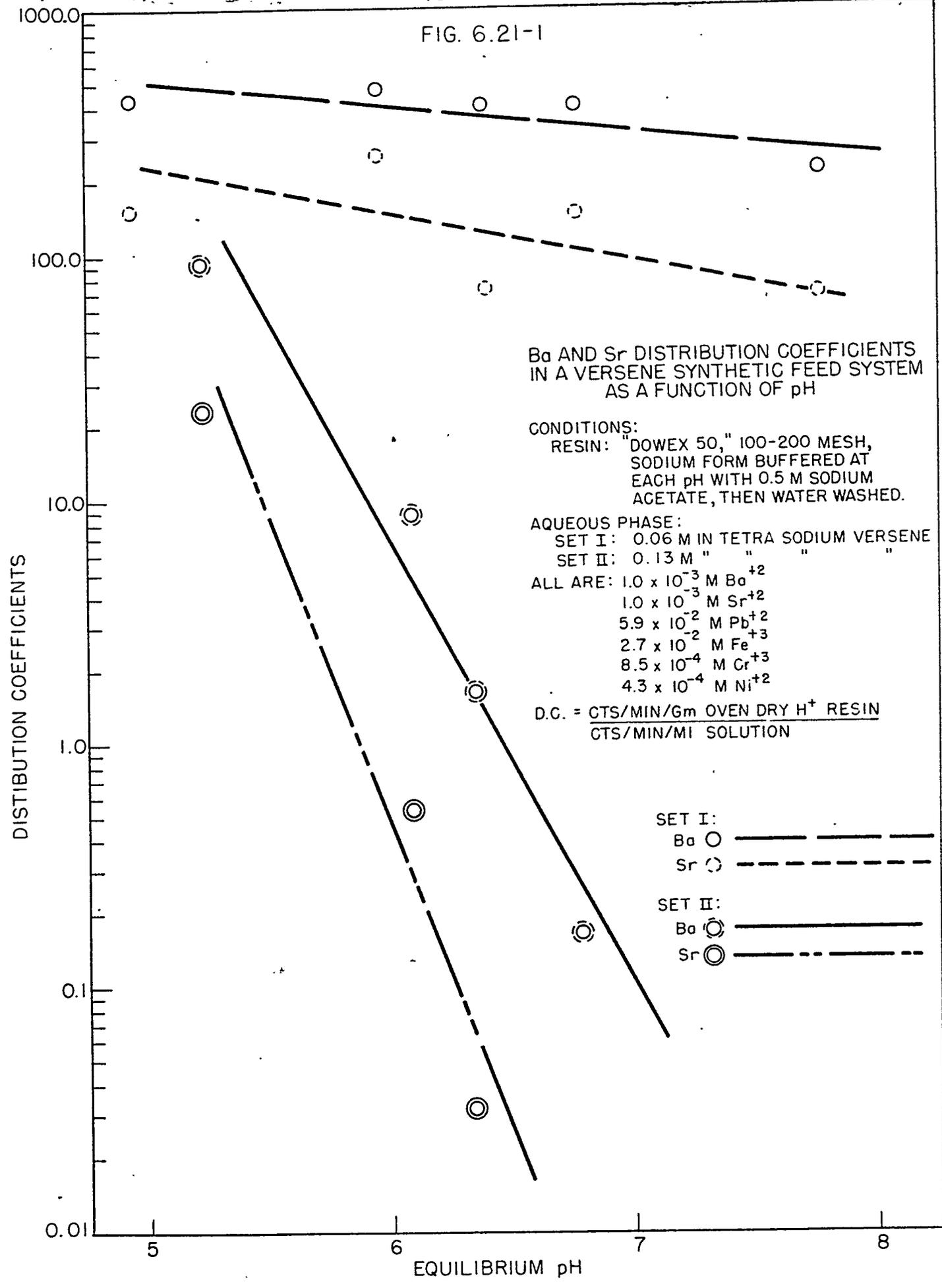


FIG. 6.21-1



Ba AND Sr DISTRIBUTION COEFFICIENTS
IN A VERSENE SYNTHETIC FEED SYSTEM
AS A FUNCTION OF pH

CONDITIONS:
RESIN: "DOWEX 50," 100-200 MESH,
SODIUM FORM BUFFERED AT
EACH pH WITH 0.5 M SODIUM
ACETATE, THEN WATER WASHED.

AQUEOUS PHASE:
SET I: 0.06 M IN TETRA SODIUM VERSENE
SET II: 0.13 M " " " "

ALL ARE: 1.0×10^{-3} M Ba⁺²
 1.0×10^{-3} M Sr⁺²
 5.9×10^{-2} M Pb⁺²
 2.7×10^{-2} M Fe⁺³
 8.5×10^{-4} M Cr⁺³
 4.3×10^{-4} M Ni⁺²

$$D.C. = \frac{QTS/MIN/Gm \text{ OVEN DRY } H^+ \text{ RESIN}}{QTS/MIN/MI \text{ SOLUTION}}$$

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