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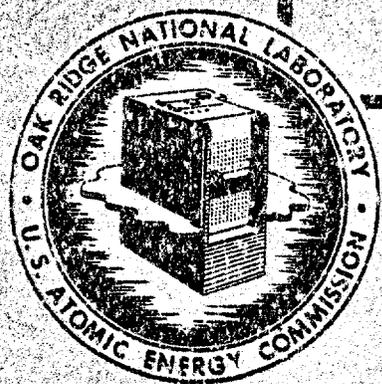
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LABORATORY DEVELOPMENT OF THE  
VERSENE PROCESS FOR THE  
PURIFICATION OF RADIOBARIUM  
ION EXCHANGE



OAK RIDGE NATIONAL LABORATORY

OPERATED BY

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Title: Laboratory Development of the Versene Process for the Purification of Radiobarium

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Abstract: This report presents the laboratory development of the Versene and Nickel-Versene ion exchange processes for the purification of radioactive barium. Ion exchange is an improvement to ease of remote operations, increased purity of product, and higher yield. (Versene is ethylenediamine tetra acetic acid).

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LABORATORY SECTION

LABORATORY DEVELOPMENT OF THE VERSENE PROCESS FOR THE  
PURIFICATION OF RADIOBARIUM BY ION EXCHANGE

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1.0 Abstract

This report presents the laboratory development of the Versene and Nickel-Versene ion exchange processes for the purification of radioactive barium.

2.0 Introduction

Multi-kilocurie quantities of pure radio barium are produced at ORNL by the RaLa Process<sup>(1,4)</sup>, 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<sup>(3)</sup> of the present processing equipment indicated that several alterations were desirable in order to increase the efficiency 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) increased purity of product; and (3) high yield.

Two ion exchange processes for the purification of radio barium were described in a previous report<sup>(2)</sup>. The success of the first process, the Acetate Citrate Process, depended on the complete removal of all sulfate by the metathesis step. Pilot Plant runs<sup>(5)</sup> showed, however, that up to 0.5% of the sulfate remained in the system and interfered with subsequent processing. In the second process, the metathesis step was eliminated by dissolving the sulfate cake in Versene (ethylenediamine tetra acetic acid). This process

Introduction (continued)

was not satisfactory since it was limited to a total of one gram of barium and strontium ( $3 - 4 \times 10^3$  curies). The ion exchange processes described in this report were developed to handle up to 2 grams each of barium and strontium while utilizing a single ion exchange column.

The radiation stability of Dowex 50 resin at the kilocurie process level has been demonstrated previously<sup>(6)</sup>.

3.0 Summary

The Versene Process was developed for the purification of 15,000 curie batches of radiobarium. This process employs ethylene diamine tetra acetic acid, a chelating agent sold under the trade name Versene, for the selective separation of impurities from barium by ion exchange. The Versene Process was designed to follow the metathesis step and replace the purification steps in the current procedure (see flowsheet, Figure I). Laboratory demonstration runs, performed on a 1/20 chemical, and tracer radiochemical scale, showed good reproducibility with barium yields greater than 98%; in all cases product purity met or exceeded specifications. The overall operating time, including 4 hours for product evaporation, was 20 hours. The process steps are:

- (1) Add Versene to the dilute acid solution of the metathesis cake, adjust the pH to 6.2 - 6.5, and pass the solution through a column of sodium form Dowex 50 resin. The barium is adsorbed while the bulk of the contaminants, which include approximately 50% of the gross beta activity, pass through.
- ~~SECRET~~

Summary (continued)

(2) The column is washed first with pH 6.3 Versene to selectively remove the small amount of contaminants present and then with dilute hydrochloric acid to remove the sodium.

(3) The pure barium is eluted with 6M nitric acid and the solution evaporated to dryness. An alternate method for the concentration of the barium product is precipitation from 85% nitric acid.

The Nickel-Versene Process, a modified form of the Versene Process, was developed to replace both the metathesis and purification steps with a one column ion exchange process. Several demonstration runs produced a product of adequate purity in yields greater than 95%. The results were not acceptable in all cases, however, indicating that this process lacks reliability in its present state of development. The overall operating time is approximately 28 hours.

The process steps are:

(1) Convert the Dowex 50 resin to the nickel form with a citric acid-nickel solution adjusted to pH 2.3 (not included in process time).

(2) Dissolve the barium-lead sulfate cake in Versene at pH 6.5 and pass the solution through the resin column. All of the sulfate and the bulk of the nickel and lead pass out in the waste effluent while the barium and strontium are adsorbed.

(3) Selectively elute the impurities with Versene at pH's 5.5 and 6.3

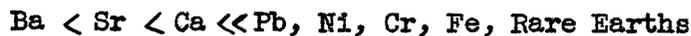
Summary (continued)

- (4) Elute the sodium with dilute hydrochloric acid.
- (5) Elute the pure barium in 6M nitric acid and evaporate the solution to dryness.

4.0 Solubility of Barium, Strontium, and Lead Sulfates in Versene

The projected use of Versene for the purification of barium by ion exchange necessitated a comprehensive study of the solubility of barium, strontium, and lead sulfates in Versene.

The chemistry of Versene has been studied by Schwarzenbach and Ackermann<sup>(7)</sup> who determined the dissociation constants for the alkaline earth Versene complexes. These constants could not be applied to the system of interest in a quantitative sense however, because of their great sensitivity to foreign ions and total ionic strength. The Bersworth Chemical Company<sup>(8)</sup> has presented data on Versene showing titration curves, complex formation as a function of pH, and other information of general interest. The elements of interest in the RaLa Process are listed as follows in increasing order of complex strength at pH 6.3:



The complexing action of Versene is pH dependent. This was illustrated for the Dowex 50 resin - Versene system by a plot of the distribution coefficients of barium and strontium as a function of pH, where the distribution coefficients decreased by a factor of 100 as the pH increased from 5.0 to 7.0<sup>(2)</sup>.

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Solubility of Barium, Strontium, and Lead Sulfates in Versene (continued)

The solubility data presented below were determined by shaking graduated cylinders, containing known quantities of materials, end over end for 24 hours at  $24^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , then centrifuging the solutions and sampling the clear supernate for analysis. It should be noted that barium solubility values greater than 85% were erratic since they lie in the range of super-saturation. In this portion of the curves, dotted lines were drawn through the best available data.

The solubility of barium sulfate in a constant amount of Versene was plotted as a function of pH (See Figure 2). It is seen that the degree of complex formation drops off markedly below a pH of 8. The general shape of this curve is similar for all cations. The main variations are the pH at which the break occurs and the relative ordinate values, the latter being a function of the individual complex constants. The break occurs at about pH 6.3 for strontium and at 5.5 for calcium<sup>(8)</sup>.

The solubility of barium, strontium, and lead in the Versene feed solution was determined at pH's 6.2, 6.4 and 6.5 as a function of sulfate concentration. For convenience in interpreting results, the sulfate concentration was also expressed as the percent of sulfate cake metathesized to carbonate (see Figure 3). The results show that the barium, strontium, and lead will be completely soluble in the pH range 6.2 - 6.5 even though the removal of sulfate by metathesis is only 95% complete. In two analogous experiments the solubility of barium, strontium, and lead was determined at pH's 6.0 and 6.5 as a function of Versene concentration under conditions of 90% metathesis (see Figure 4).

Solubility of Barium, Strontium, and Lead Sulfates in Versene (continued)

Both of these experiments show that the lead and strontium are completely soluble under conditions where the barium solubility is still very low. This, of course, is a reflection of the difference in their complex constants.

The characteristic difference in complex constants for these cations was illustrated over a greater range of conditions by determining the solubilities of these cations first as a function of Versene concentration at pH 10 (Figure 5) and then as a function of pH at constant Versene concentration (Figure 6). In each case the sulfate concentration was constant and stoichiometrically equal to the barium, strontium, and lead. It is immediately apparent that the lead Versenate complex is so strong that essentially no barium and strontium are dissolved (complexed) until the lead is completely in solution. In a similar experiment the amount of Versene necessary to dissolve the lead, barium, and strontium sulfate cake at pH's 6.2 and 6.4 was determined by plotting the solubility of the cations as a function of Versene concentration (Figure 7). The results show that 4.8 moles of Versene in 15.2 liters of solution are required at pH 6.4 to dissolve the sulfate cake on full process scale.

The mass of barium and strontium in the RaLa system will vary depending on the number of curies to be produced. Therefore, it is of interest to know the amount of Versene required to dissolve a sulfate cake composed of 87 gm of lead and an amount of barium and strontium which varies from 0.5 gm to 2.0 gm each. The results of such a determination are plotted in Figure 8 and show that the concentration of Versene required increases almost linearly with the total mass of barium and strontium present even though the amount of lead remains

constant and is present in a 20-80 fold mole excess.

## 5.0 Versene Process

The present process for the production of radioactive barium is as follows:

- (1) co-precipitation of lead and barium sulfate from the acid slug solution;
- (2) conversion of the sulfate precipitate to the carbonate by metathesis with potassium carbonate;
- (3) dissolution of the carbonate precipitate in acid and removal of the lead by electrolysis;
- (4) evaporation to dryness;
- (5) precipitation of barium chloride from an ether hydrochloric acid solution; and
- (6) precipitation of barium nitrate from a fuming nitric acid solution.

The Versene Process would replace the steps following the metathesis with an ion exchange purification procedure. Flowsheets for the present process and the proposed ion exchange process are shown in Figures 1 and 9. The detailed results of representative ion exchange demonstration runs are given in Table I.

## 5.1 Product Adsorption

### 5.11 Column Specifications

Laboratory demonstration runs were performed on a resin column 25" in height by 0.67" in diameter which represented 1/20 of full process scale. A column 25" x 3" containing 177 cu. in. or 2.9 liters of resin is recommended for full scale operations. The resin should be measured under water as the settled volume of the hydrogen form, since under these conditions the resin assumes its maximum volume.

The process resin was 60 - 100 mesh Dowex 50 (Nalcite HCR). Analysis of commercial Dowex 50, as received, showed that it contains approximately 0.5 mg

Column Specifications (continued)

of iron per ml of resin in addition to other metallic impurities and organic decomposition products. The iron is evidently precipitated in the resin matrix during production and therefore is not exchangeable in the ordinary sense. Since the iron tended to dribble out in all process solutions including the product, vigorous pretreatment of the resin was necessary. Three cycles of alternate washing with 5 column volumes each of 6M nitric acid and concentrated sodium nitrate reduced the iron content of the resin to such an extent that the iron appearing in the product barium did not exceed specifications. An order for C.P. resin has been placed with Dow Chemical Company. The use of a pure resin will eliminate the pretreatment steps and ensure product purity. Prior to start-up, the resin should be converted to the sodium form with concentrated sodium nitrate, buffered with 0.1M sodium versenate at pH 6.4, and washed with water.

The flow rate for the feed and wash solutions was 1.2 ml/cm<sup>2</sup> column cross section/min, while the flow rate for the eluting solutions was 0.7 ± 0.2 ml/cm<sup>2</sup> column cross section/min.

The amount of radiation in the effluent was measured by passing the liquid through a maze located under a thin mica end window Geiger tube. The Geiger impulses activated a count rate scaler and were recorded automatically on a Brown recorder as an elution curve (see Figure 9). 

5.12 Feed Make-Up

The Versene Process uses the 8 liter (full scale) dilute nitric acid solution of the metathesis cake as its starting point (see Table 2). The column feed is made up as follows: Add to the above solution with agitation one liter of Fe-3-Specific solution\* followed by two liters of 0.5M tetra sodium Versenate\*\*, adjust the pH to 6.2 to 6.5 with nitric acid using the titration curve shown in Figure 10 as a guide; and bring the final volume up to 12 liters with water. This feed is passed through the resin column where the barium is adsorbed while the bulk of the impurities pass through in the waste effluent.

The approximate analysis of the metathesis cake solution listed in Table 2 shows that the sulfate content is high enough to precipitate a large portion of the barium. Therefore, Versene is added to complex the barium and hold it in solution. Since barium is the most weakly complexed cation of those of interest in this system (see Section 4.0), the barium is preferentially adsorbed when the feed passes through the resin column.

The amount of iron which can be complexed by a given amount of Versene drops off rapidly as the pH increases due to the low solubility product of ferric hydroxide. The complete solution of iron is assured by adding

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\* 80 ml of Fe-3-Specific diluted to 1 liter with water. Fe-3-Specific is a 48% solution of diethanol glycine.

\*\* Ethylene diamine tetra acetic acid (pharmaceutical grade) neutralized to pH 10 with sodium hydroxide.

Feed Make-up (continued)

Fe-3-Specific to the acid metathesis cake solution. This material complexes iron very strongly at pH's up to 12 but has little effect on the alkaline earths. The slight complexing effect of Fe-3-Specific on alkaline earths is attributed to glycine, a trace impurity. Care must be taken to complex the iron completely before the pH rises above 3.0, since the rate of redissolution of ferric hydroxide by complexing agents is extremely slow.

In full scale operation, the slug dissolution is performed in two batches, and the subsequent sulfate precipitation is likewise done in two steps. The lead loss in the first batch precipitation has not been precisely determined, but is estimated at 20%<sup>(1,2,6)</sup>. This loss is rectified by adding this amount of lead to the second batch precipitation. Variations in lead loss will result in either an excess or a deficiency of lead in the sulfate cake. A large lead excess in the Versene feed would selectively complex most of the Versene, thus permitting barium sulfate to precipitate; on the other hand, a large lead deficiency would leave too much Versene free to complex the barium, hence the barium would pass through the column in the waste effluent without adsorbing on the resin. The versatility of the Versene Process was demonstrated by runs in which a 20% excess and a 20% deficiency of lead were used in the feed solution. The barium losses in each case were less than 2% (see Table 1).

5.2 Contaminant Elution

The bulk of the contaminants are separated from the barium during the

Contaminant Elution (continued)

feed step and pass through the column in the waste effluent. Approximately 10% of the strontium, however, is caught on the bottom of the column along with trace amounts of the other impurities. These impurities are selectively eluted with 0.07 M sodium Versenate at pH 6.3.

At this point in the process only barium and sodium remain on the column. The sodium is selectively eluted with 1M hydrochloric acid solution. This separation is easily effected since the di-valent barium is adsorbed much more strongly than the mono-valent sodium.

5.3 Product Elution

The pure barium product is eluted with 6M nitric acid. As a concentration step, the product solution can be evaporated or the barium precipitated as the nitrate from 85% nitric acid and recovered by filtration. The product produced by the ion exchange method meets the specifications listed in Table 3 (see Table 1 for representative runs).

6.0 The Nickel-Versene Process

The Versene Process described in the preceding sections replaces only the purification steps following the metathesis step in the current process. A variation of this procedure, the Nickel-Versene process, was developed to replace both the metathesis and purification steps with a one column ion exchange process by the dissolution of the sulfate cake in Versene and subsequent purification by ion exchange. The elimination of these steps by a two

The Nickel-Versene Process (continued)

column ion exchange process has been reported.<sup>(2)</sup> The capacity of this process, however, was limited to a total of one gm. of barium and strontium equivalent to 3000 curies as compared to a 4 gm. or 15,000 curie capacity in the Nickel-Versene Process. A relatively high concentration of Versene is required for the dissolution of the sulfate cake (see Figure 8). Since the size of a resin column needed to adsorb the barium from a Versene solution increases tremendously with an increase in Versene concentration, it was necessary to develop a method for the adsorption of barium in which the column size would be relatively small and thus consistent with chromatographic practices and shielding criteria. The reduction in column size was accomplished by using resin in the nickel form to adsorb the barium. The bulk of the nickel is desorbed during the feed operation and passes out of the column in the waste effluent with the sulfate and other impurities. The adsorbed barium is then purified by selective elution.

The development of this process is not complete. Although barium yields greater than 95% and of adequate purity were obtained in demonstration runs, the final conditions for consistent operation have not been determined. Representative runs are listed in Table 4 (see flowsheet, Figure 11).

It should be noted, that without further development, the nickel form adsorption column could be effectively employed at the 15,000 curie level as the preliminary separation column in a two column process.

The sulfate cake for a 15,000 curie operation would contain 2 gm each of

The Nickel-Versene Process (continued)

barium and strontium and 87 gm of lead as their sulfates, plus lesser amounts of iron, chromium, nickel, and fission products. The action of Versene and Fe-3-Specific in complexing these cations and dissolving the precipitate was discussed in Section 4.0 and 5.12.

As the feed passes through the nickel resin bed the nickel is desorbed and selectively complexed by the Versene, thus effectively breaking the barium Versene complex and leaving the barium free to adsorb. This phenomenon is a result of the large differences in the complex constants of barium and nickel. If the nickel concentration in the resin phase is too high, all the Versene will be complexed by the nickel, allowing the precipitation of barium and lead sulfates in the resin column. Conversely, if the nickel concentration in the resin phase is too low, the barium-Versene complex will not be broken in which case the barium cannot adsorb on the resin and will pass through as loss in the waste effluent, (see Section 6.1 for preparation of nickel resin). The size of the column was chosen such that 6 - 10 inches of nickel resin remain at the bottom of the column at the end of the feed operation. A scanning technique, using an ionization chamber, showed that the radioactivity (barium, strontium, and rare earths) was concentrated in a 5" band directly above the remaining nickel resin.

The net result of the feed operation is the use of the upper portion of the column to replace the metathesis step, that is to separate the sulfate from the barium. At the same time the lower portion of the column is available for

The Nickel-Versene Process (continued)

the chromatographic purification of the barium. It should be noted that if the nickel resin column is to be used only for the simple recovery of barium or other cations from a complexing system or for separation of cations from anions, the resin column height can be reduced by approximately 10". In this case the barium would be purified on a second resin column. A schematic sketch of the feed operation is presented in Figure 12.

6.1 Column Specifications

Laboratory development runs were performed on a resin column 0.67" in diameter and at heights varying from 32" to 42", the latter figure representing 1/40 of full process scale. The recommended column dimensions for full process scale are 4" in diameter by 47" in height containing 590 cu. in. or 9.67 liters of resin. The resin should be measured under water as the settled hydrogen form, since under these conditions the resin assumes its maximum volume.

The process resin was 60-100 mesh Dowex 50 (Nalcite HCR) which had been converted to the nickel form by treatment with an excess of nickel citrate solution. This solution was 0.25M in both nickel and citrate and was adjusted to pH 6.3 by the addition of sodium hydroxide to a nickel nitrate-citric acid solution. Under these conditions, the equilibrium concentration of nickel in the resin is 2.0 m.e.q./ml. The nickel concentration in the resin is too low (1.7 m.e.q./ml) when the pH of the nickel citrate solution is 2.5, and too

Column Specifications (continued)

high (3.0 m.e.q./ml) when 0.25M nickel nitrate is used in the absence of citrate (see Section 6.12 for a discussion of the importance of the nickel concentration in the resin phase).

The flow rates and automatic activity monitoring equipment were similar to those described in Section 5.11.

6.12 Feed Make-up

The Nickel Versene Process uses as its starting point the sulfate cake obtained by the co-precipitation of barium and lead sulfate. The cake is dissolved in 16 liters (full scale) of an aqueous solution containing 4.95 moles of tetra sodium Versenate and 40 ml of Fe-3-Specific. The pH is then adjusted to 6.5 with nitric acid and the solution passed through the nickel column where the barium is adsorbed while the sulfate, the bulk of the nickel, and about 50% of the lead pass out of the column in the waste effluent.

6.2 Contaminant Elution

Nickel, lead, and the rare earths are selectively eluted by washing the column with 0.07M sodium Versenate at pH 5.5. This operation clears the bottom of the column for the chromatographic separation of strontium from the barium (see Figure 11).

The strontium is selectively eluted by washing the column with 0.07M

Contaminant Elution (continued)

sodium Versenate at pH 6.3 until the activity in the eluate has reached a minimum. The barium losses during this elution were erratic as a result of non-equilibrium conditions in the feed adsorption step, (see Table 4, Runs V-69 to V-73). The column height will be increased to 42 inches in an attempt to counter-balance this effect. If these conditions do not produce successful reproducible results, it will be concluded that the adsorption and purification steps should be performed on separate columns, that is a two column process.

An effort was made to eliminate the pH 6.3 elution by increasing the volume of pH 5.5 elutriant to the point where the strontium is eluted with the nickel and lead. The barium-strontium separation was neither satisfactory nor reproducible under these conditions, (see Table 3, Runs V-74 to V-85).

At this point in the process, only barium and sodium remain on the column. The sodium is selectively eluted with 1M hydrochloric acid. The amounts of sodium contained in the products listed in Table 3 are high but can be lowered to meet specifications by the passage of additional hydrochloric acid.

6.3 Product Elution

Pure barium is eluted from the column with 6 M nitric acid and concentrated by evaporation or by precipitation as barium nitrate from 85% nitric acid. The product produced by evaporation meets the specifications listed in Table 3 with the exception of sodium (see 6.2) and nickel. Both the nickel and sodium would be eliminated in the precipitation from 85% nitric acid. The

Product Elution (continued)

presence of nickel in the product eluate can probably be avoided by a closer approach to equilibrium conditions. The use of a slower flowrate would allow the nickel to diffuse out of the resin quantitatively (see Table 4 for representative runs).

  
R. E. Blanco

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Table 1

Purification of Barium by the Versene Process

Conditions:

Feed: 1/20 full RaLa chemical scale under maximum conditions of impurity

100 mg Ba<sup>+2</sup> + Ba "Tracer"  
 100 mg Sr<sup>+2</sup> + Sr "Tracer"  
 44.0 mg Fe<sup>+3</sup>  
 16.6 mg Cr<sup>+3</sup>  
 11.4 mg Ni  
 Pb<sup>++</sup> Run #1 = 4.35 gm = normal amount  
 Run #2 = 5.22 gm = 20% excess  
 Run #3 = 3.48 gm = 20% deficiency

4.0 ml Fe-3 - Specific  
 0.05 mole tetra sodium Versenate  
 SO<sub>4</sub> = 5 mg% 99.5% Metathesis  
 Total volume = 600 ml, pH 6.4

Column: Bed: 0.67" x 25", 60-100 mesh, Dowex 50 measured under water as H<sup>+</sup> form.  
 Activation: a) Clean with 3 cycles of 6M HNO<sub>3</sub> followed by con. NaNO<sub>3</sub>, 150 ml. each  
 b) Buffer with 0.1M sodium Versenate, pH 6.4 until effluent is also pH 6.4  
 c) Wash with 200 ml H<sub>2</sub>O

Elution Steps: a) Strontium: 0.07M sodium Versenate, pH 6.3; 150 - 200 ml; 200 ml H<sub>2</sub>O wash.  
 b) Sodium: 1.0M HCl; 200 - 385 ml; 200 ml H<sub>2</sub>O wash.  
 c) Barium product: 400 ml 6N HNO<sub>3</sub>

Run No.	Waste Analyses (% Barium)		Product Analyses						Ba Material Balance (%)		
	Feed Effluent	Strontium Eluate	Sodium Eluate	Ba %	Sr %	mg Fe	mg Ni	Cr		Pb	(gm)± Na
1	0.034	0.00	0.086	101.79	0.64	< 0.14	< 0.14	< 0.14	< 0.99	1.04	101.91
2	0.09	0.03	0.00	94.19	0.48	0.5	0.1	< 0.1	< 0.7	1.23	94.30
3	0.02	0.04	0.04	92.87	1.29	0.33	0.12	< 0.12	< 0.84	2.13	92.97

+ Use of additional 1M HCl will lower mass of sodium present to meet new specifications.

Table 2

Approximate Composition of Nitric Acid Solution of Metathesis Cake

Component	Amount
Barium	1.2 gm/10,000 Curies
Strontium	1.4 gm/10,000 Curies
Iron	1.0 gm
Nickel	300 mg
Chromium	200 mg
Lead	87 gm
Sulfate	0.2-0.4 gm = 99.5 - 99.0% Metathesis
Sodium	-

Table 3

RaLa Product Specifications

The quantities listed represent the maximum amounts of impurities which may be present per batch of RaLa product and are independent of the curie content.

Component	Specification	
	Before Jan. 1951	After Jan. 1951
Barium } Strontium }	6 gm. Total (100 Curies Sr )	2 gm. Total (100 Curies Sr)
Iron	10 mg	500 mg
Nickel	10 mg	10 mg
Chromium	10 mg	10 mg
Lead	50 mg	200 mg
Sulfate	None	None
Sodium	10 gm	1.5 gm



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Drawing # 11540

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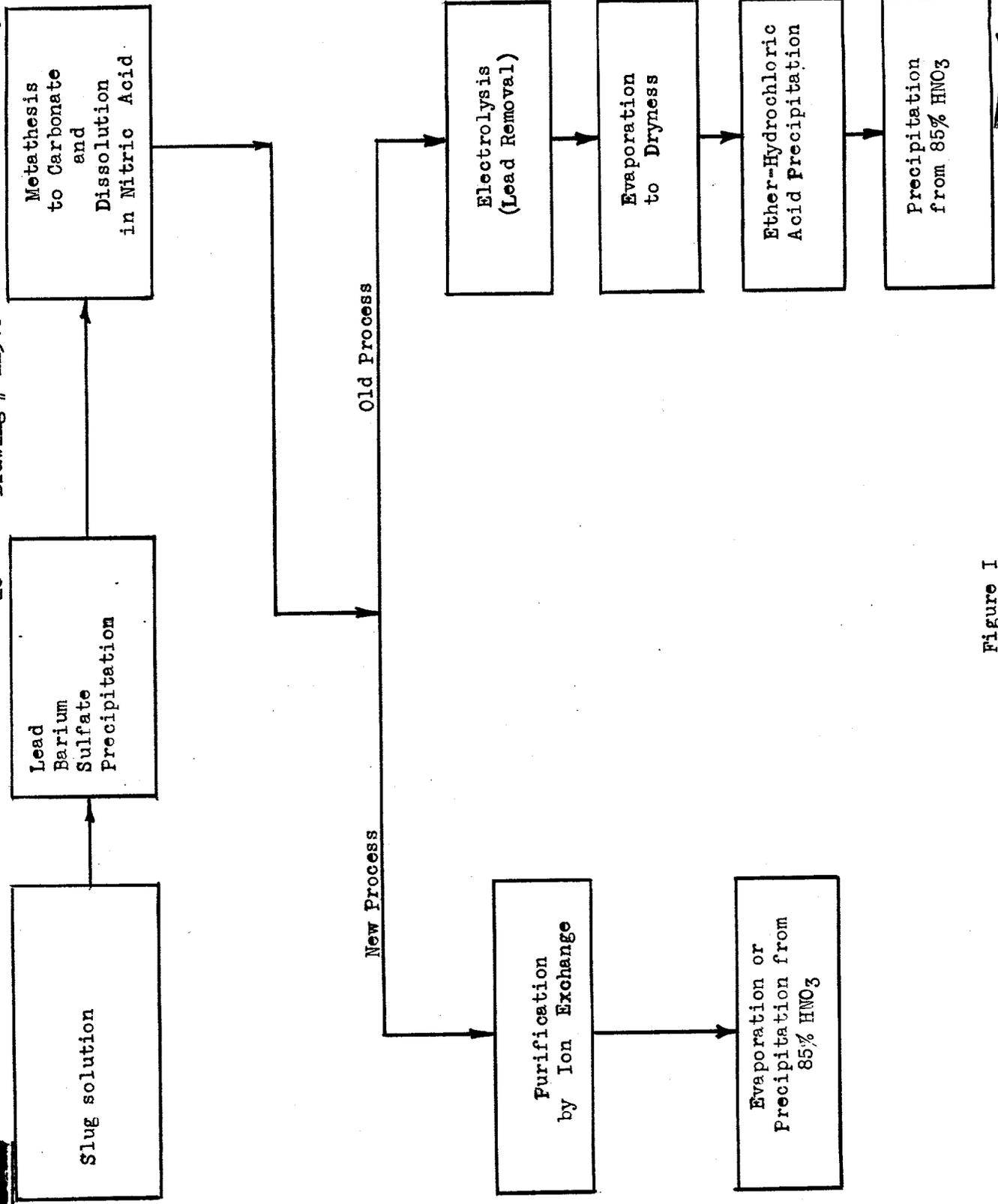


Figure I  
Ra La Process

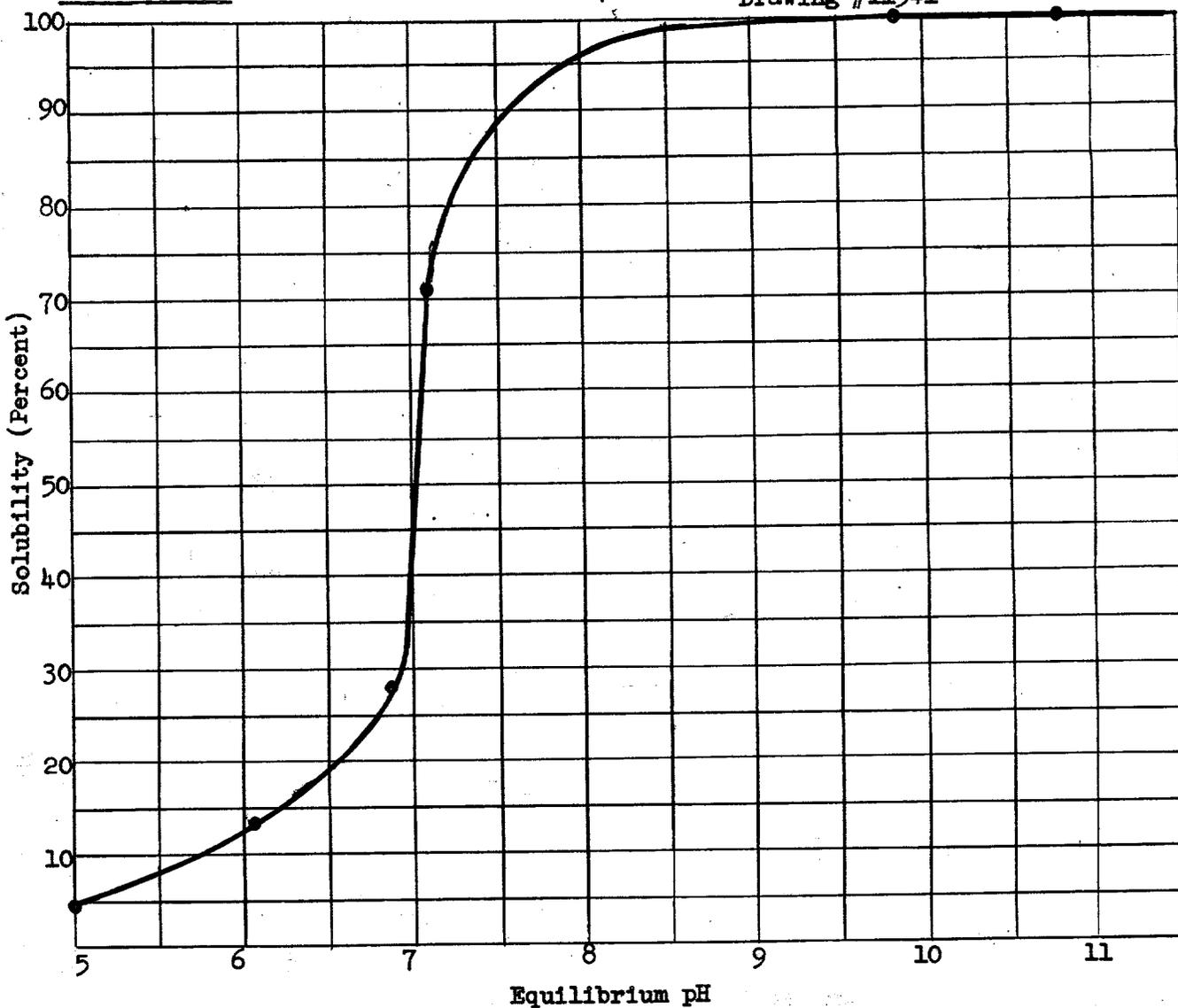


FIGURE 2

SOLUBILITY OF BARIUM SULFATE IN VERSENE AS A  
FUNCTION OF PH

Conditions:

Feed: 10 mg. Ba as  $\text{BaSO}_4$ , plus Ba tracer  
0.402 millimoles Versene  
Volume = 40.-53.0 ml.

Procedure: Shake 24 hrs; centrifuge and sample supernate.

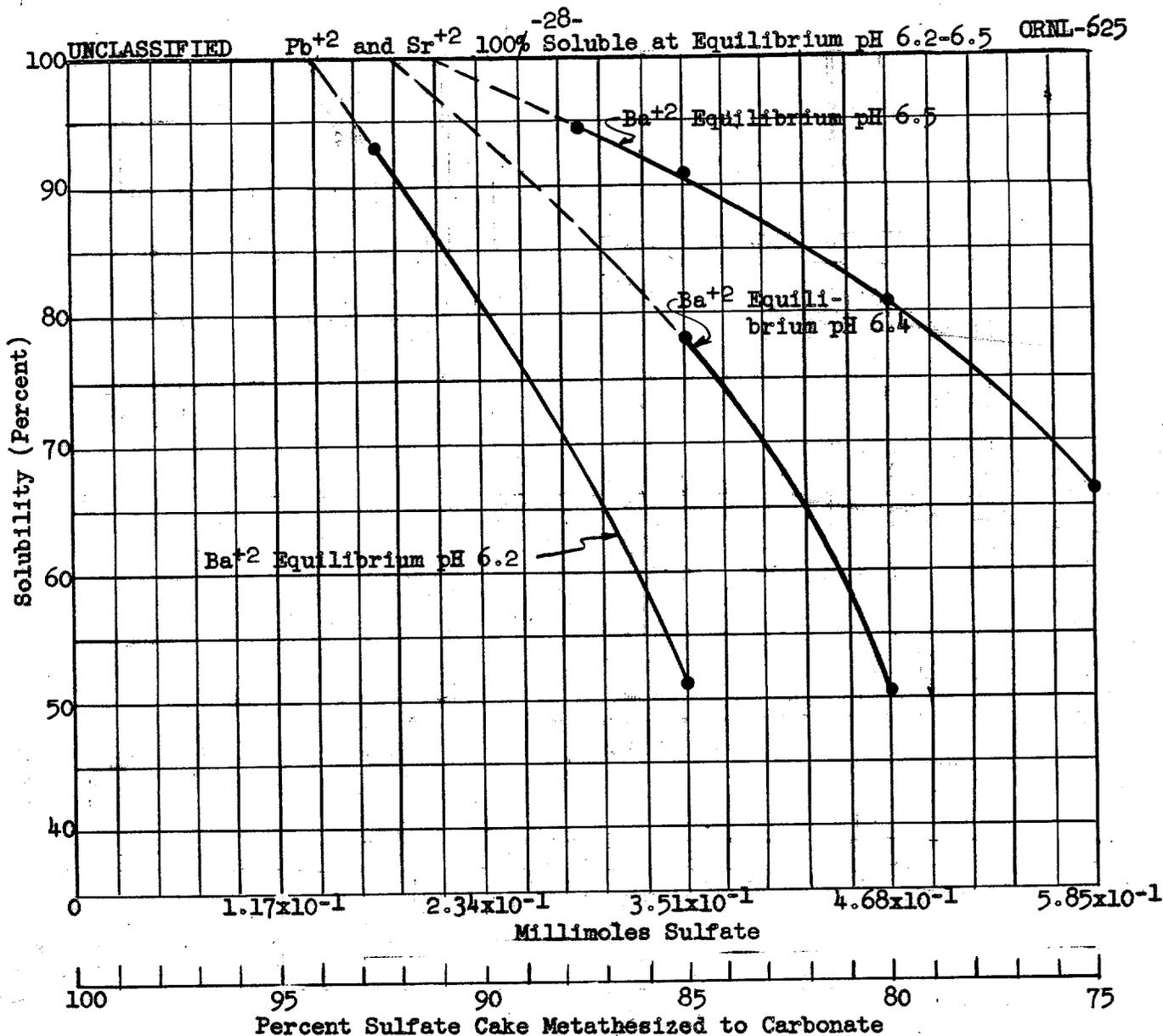


Figure 3

Drawing #11542

SOLUBILITY OF BARIUM, STRONTIUM AND LEAD SULFATES IN  
0.13M VERSENE AS A FUNCTION OF PH AND COMPLETE-  
NESS OF METATHESIS

Conditions:

Feed: 1/200 full chemical scale:

10 mg. Ba <sup>2+</sup> + tracer	4.5 mg Fe <sup>3+</sup>
10 mg. Sr <sup>2+</sup> + tracer	1.6 mg Cr <sup>3+</sup>
446 mg Pb <sup>2+</sup>	1.1 mg Ni <sup>2+</sup>

5.0 Millimoles Versene

0.2 ml. Fe-3, Specific

2.34 Millimoles sulfate = 0 Metathesis = Stiochiometric  
equivalent of Ba, Sr and Pb  
volume = 40 ml

Procedure: Shake 24 hrs., centrifuge; sample supernate

NOTE: Solubility values greater than 85% are erratic since they lie in the range of supersaturation.

UNCLASSIFIED

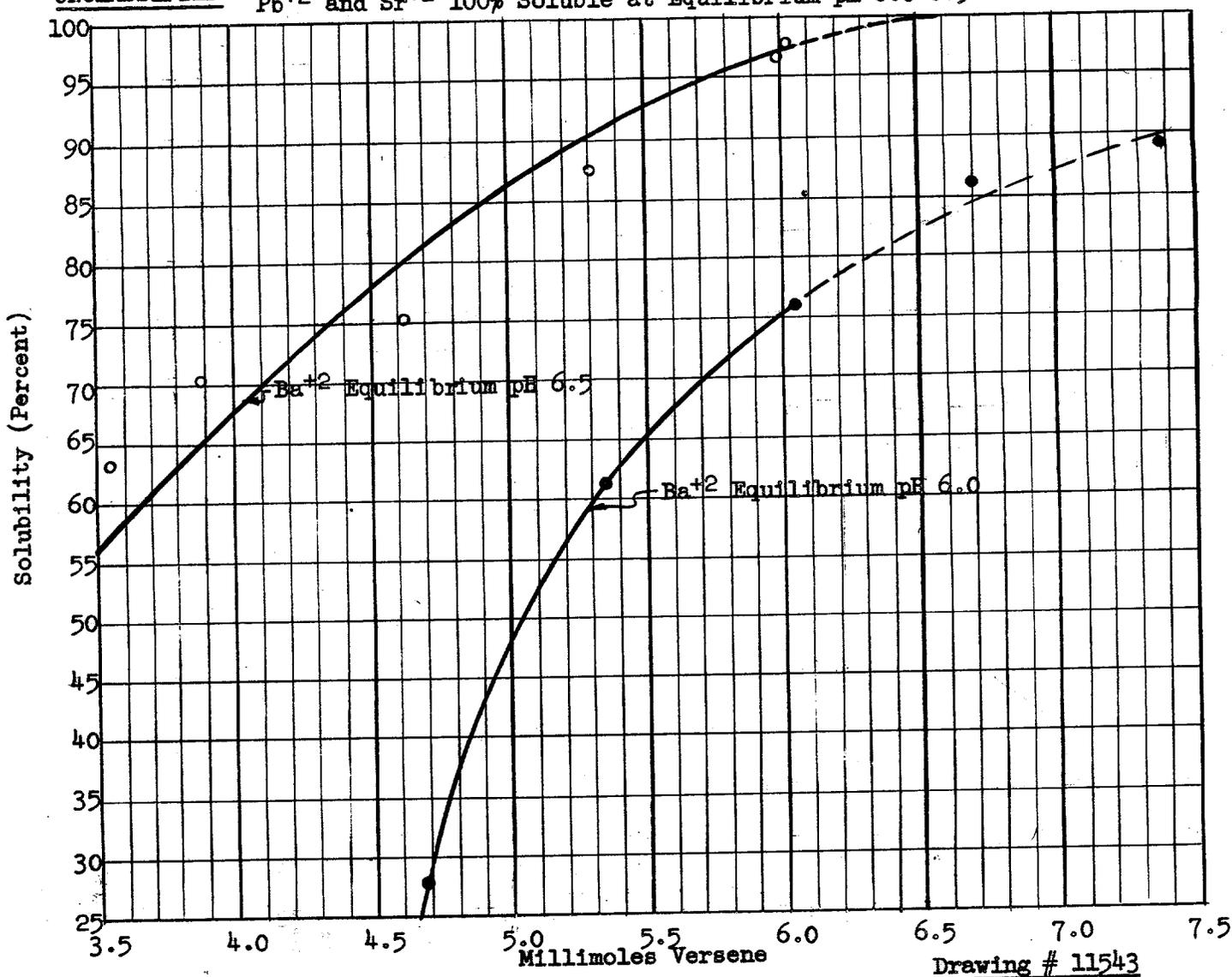


FIGURE 4

SOLUBILITY OF BARIUM, STRONTIUM, AND LEAD SULFATES AT PH 6.0 AND 6.5 AS A FUNCTION OF VERSENE CONCENTRATION UNDER CONDITIONS OF 90% METATHESIS

Conditions:

Feed: 1/200 full chemical scale:

10 mg. Ba<sup>+2</sup> + tracer10 mg Sr<sup>+2</sup> + tracer446 mg Pb<sup>+2</sup>0.234 millimoles SO<sub>4</sub>  $\approx$   $\frac{1}{10}$  stoichiometric equivalent of Ba<sup>+2</sup>, Sr<sup>+2</sup>, and Pb<sup>+2</sup>

Volume = 40.0 -50.0 ml.

Procedure: Shake 24 hrs; centrifuge; sample supernate.

NOTE: Solubility values greater than 85% are erratic since they lie in the range of supersaturation.

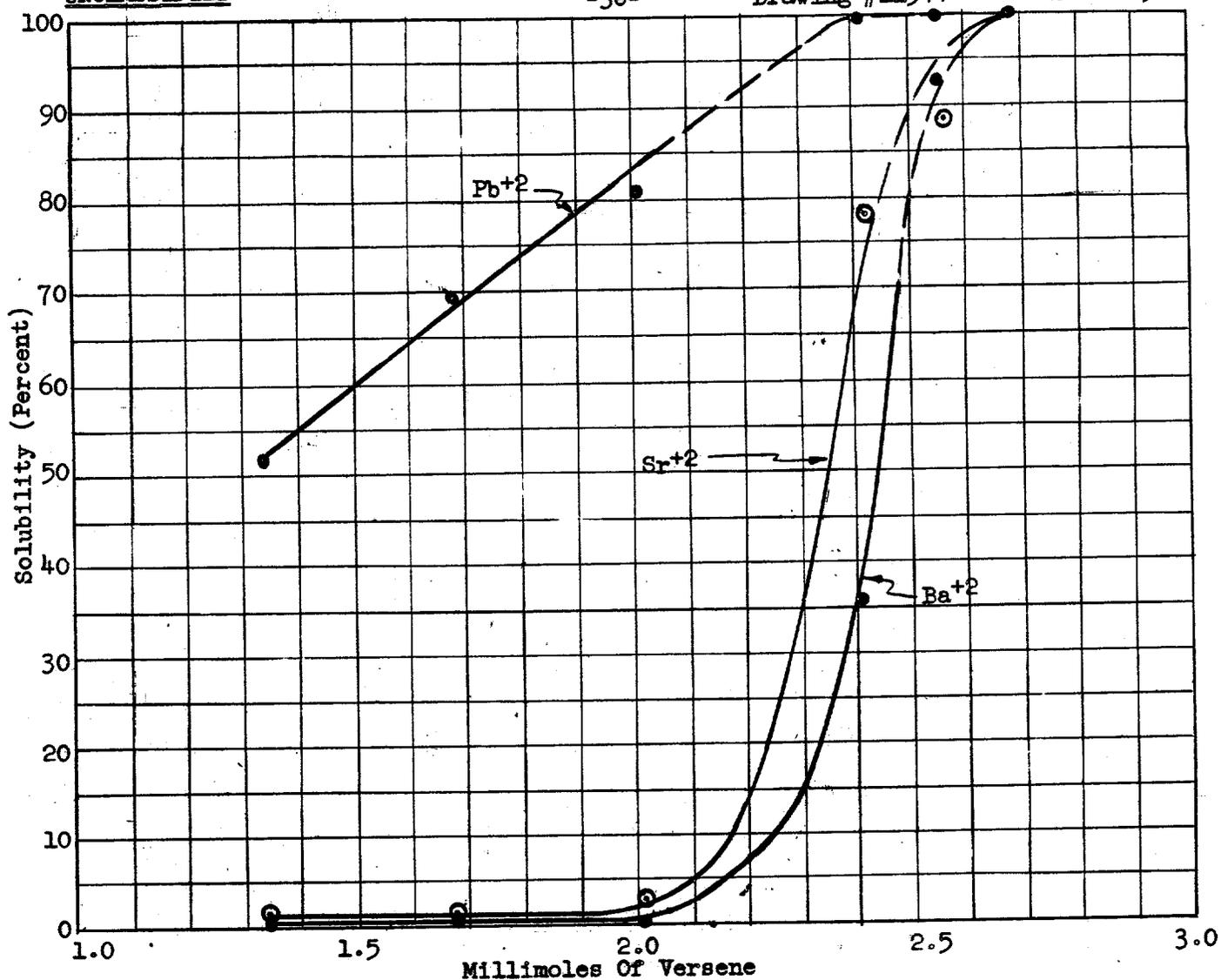


Figure 5

SOLUBILITY OF BARIUM, STRONTIUM, AND LEAD SULFATES AT  
PH 10 AS A FUNCTION OF VERSENE CONCENTRATION

Conditions:

Feed: 1/200 full chemical scale:  
 10 mg. Ba as BaSO<sub>4</sub> + tracer  
 10 mg Sr as SrSO<sub>4</sub> + tracer  
 446 mg Pb as PbSO<sub>4</sub>

Volume= 40.0 - 51.0 ml.  
 Equilibrium pH Range: 9.8-10.6

Procedure: Shake 24 hrs.; centrifuge; sample supernate.

NOTE: Solubility values greater than 85% are erratic since they lie in the range of superaturation.

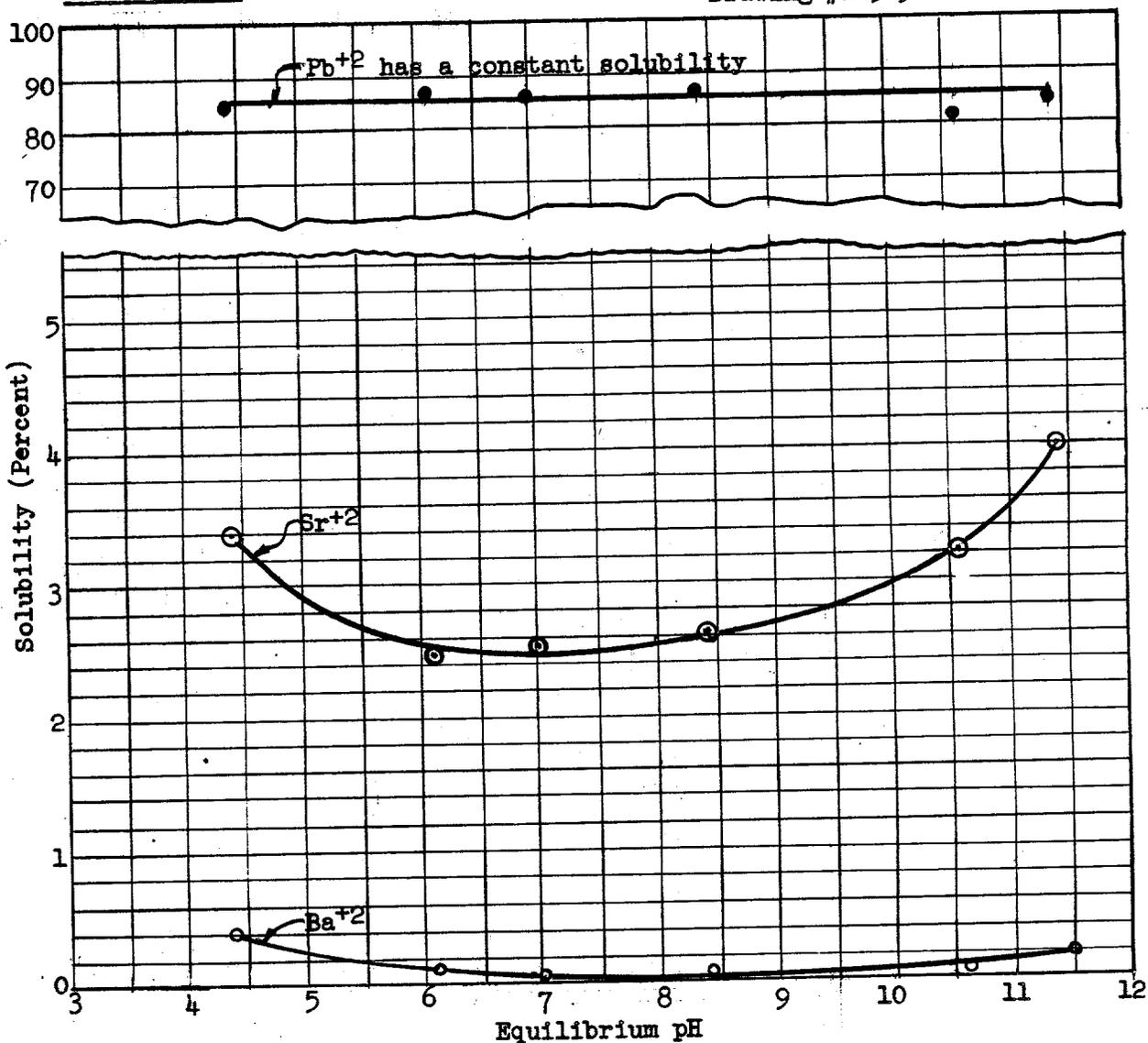


Figure 6

SOLUBILITY OF BARIUM, STRONTIUM, AND LEAD SULFATES  
IN VERSENE AS A FUNCTION OF PH

Conditions: Feed:  $\frac{1}{200}$  full chemical scale:  
 10 mg. Ba as  $\text{BaSO}_4$  + Ba tracer  
 10 mg. Sr as  $\text{SrSO}_4$  + Sr tracer  
 446 mg. Pb as  $\text{PbSO}_4$   
 4.4 mg.  $\text{Fe}^{+3}$   
 1.1 mg.  $\text{Ni}^{+2}$   
 1.6 mg.  $\text{Cr}^{+3}$   
 2.01 millimoles Versene (Insufficient to complex all the  $\text{Pb}^{+2}$ )

Volume = 40.0-51.0 ml.

Procedure: Shake 24 hrs.; centrifuge; sample supernate.

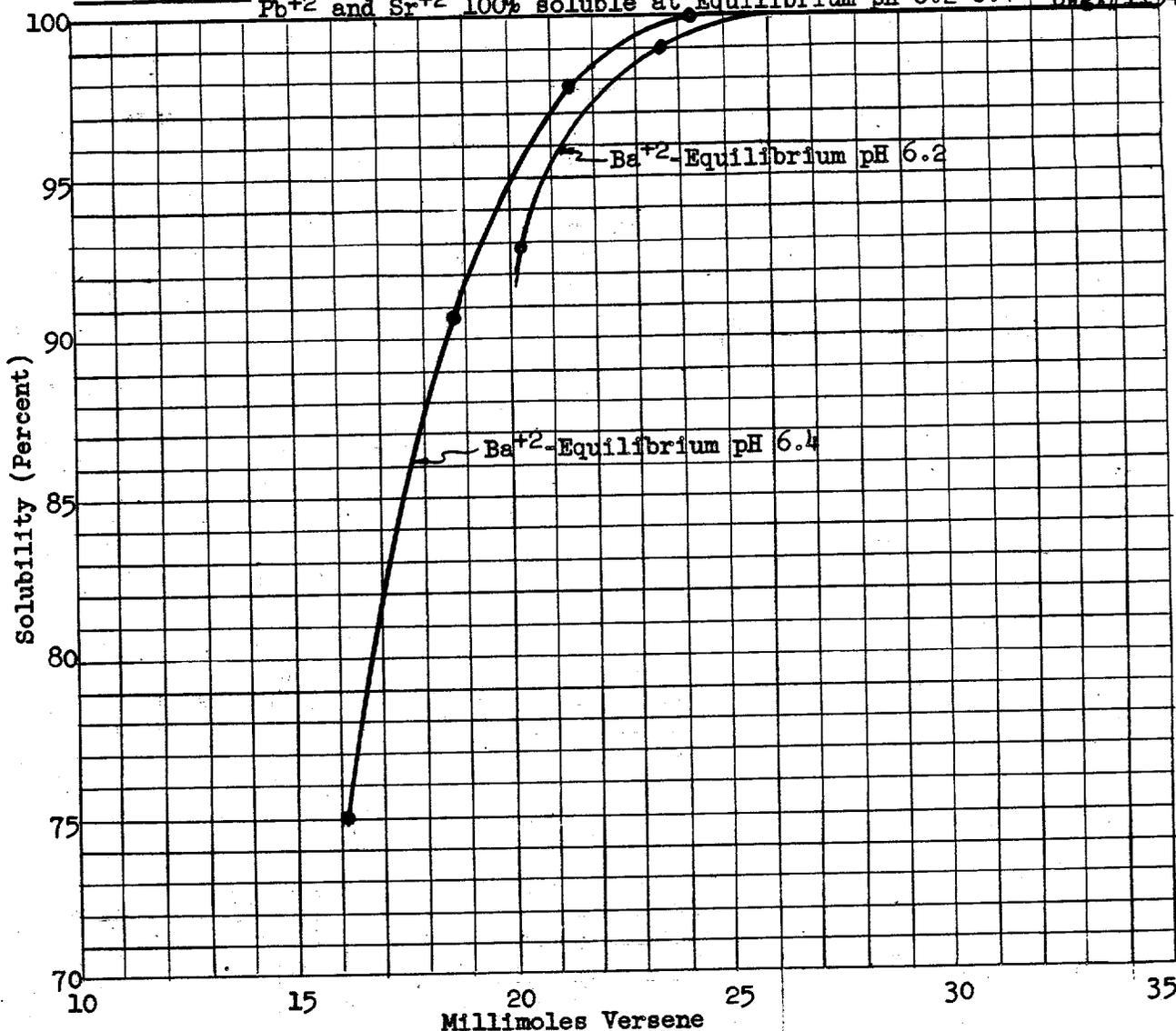


Figure 7

SOLUBILITY OF BARIUM, STRONTIUM AND LEAD SULFATES AT  
PH 6.4 AND 6.2 AS A FUNCTION OF VERSENE CONCENTRATION  
UNDER CONDITIONS OF NO METATHESIS

Conditions:

Feed: 1/200 full chemical scale:

10 mg. Ba as BaSO<sub>4</sub> + Ba tracer10 mg. Sr as SrSO<sub>4</sub> + Sr tracer446 mg. Pb as PbSO<sub>4</sub>

Volume = 76.0 ml.

Procedure: Shake 24 hrs.; centrifuge; sample supernate.

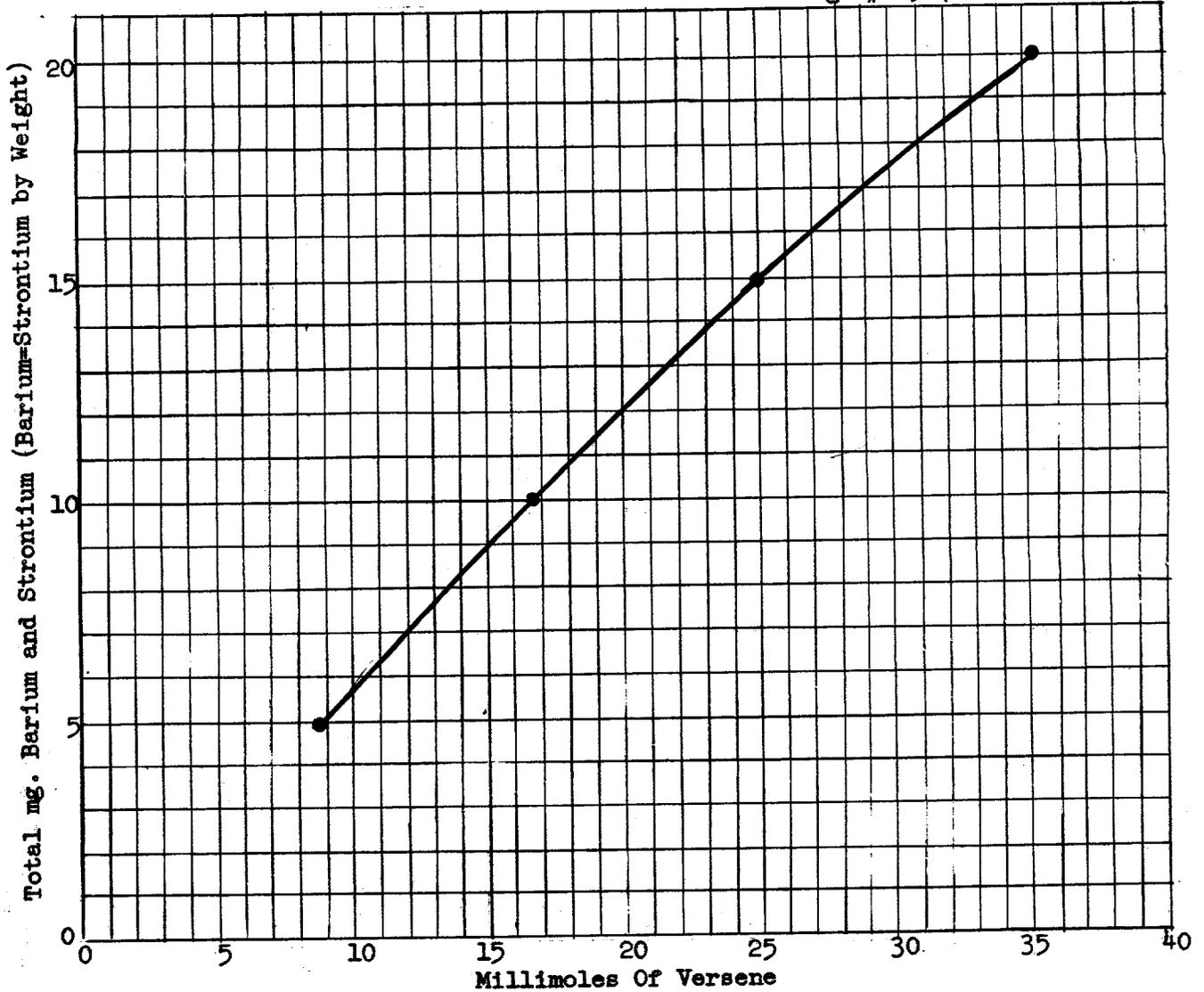


Figure 8

AMOUNT OF VERSENE REQUIRED TO DISSOLVE THE SULFATE CAKE  
AS A FUNCTION OF TOTAL WEIGHT OF BARIUM  
AND STRONTIUM

Conditions:

Feed: 1/200 full chemical scale:

2.5-10.0 mg. Ba as  $BaSO_4$  + Ba tracer

2.5-10.0 mg. Sr as  $SrSO_4$  + Sr tracer

434.9 mg. Pb as  $PbSO_4$

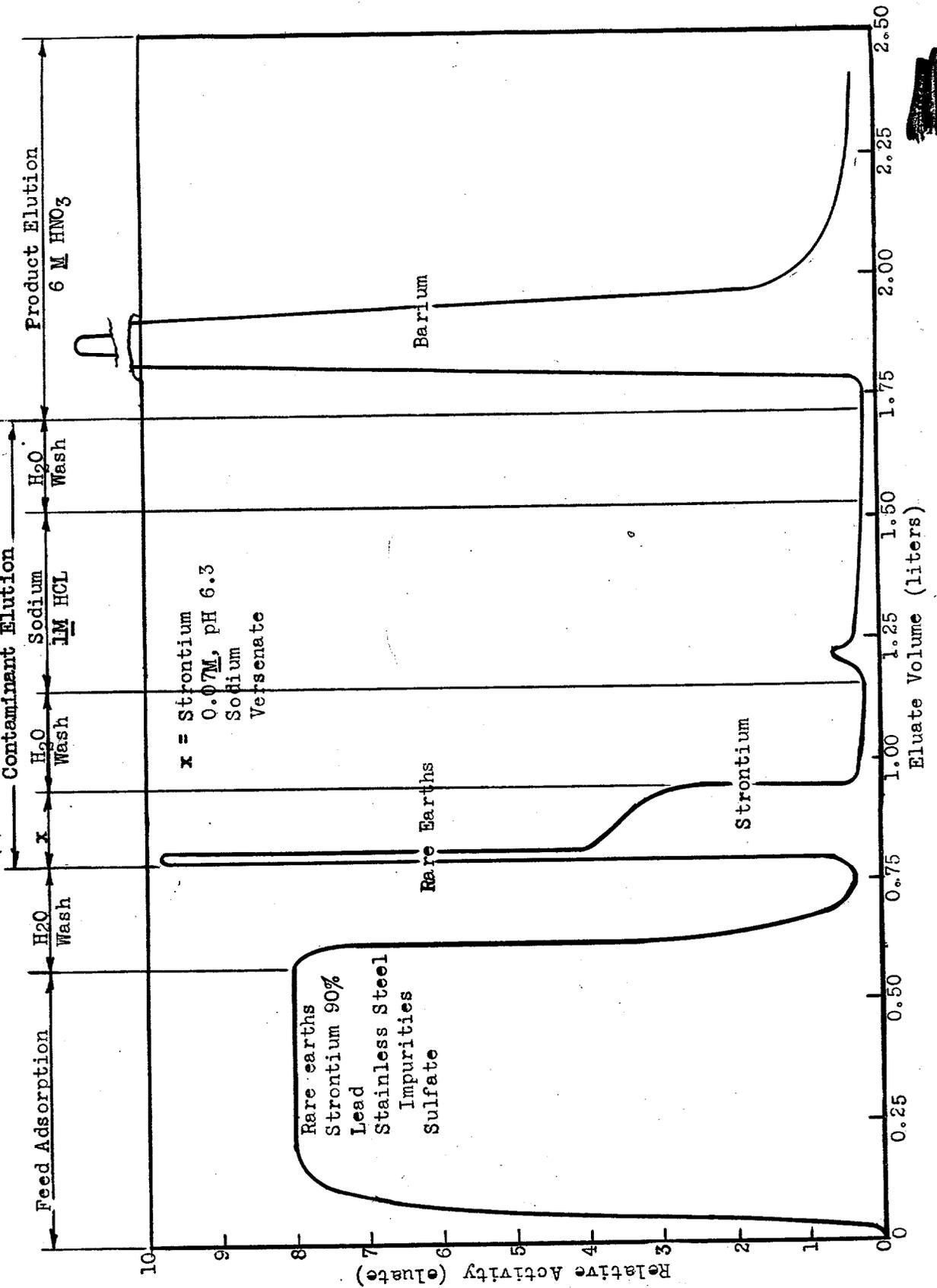
Volume = 80.0 ml.

Equilibrium pH: 6.5

Procedure: Shake 24 hrs.; centrifuge; sample supernate

Figure 9 -34-

PROFILE OF THE RADIOACTIVITY CONTENT OF THE COLUMN ELUATE DURING THE REVERSE ION EXCHANGE PROCESS (1/20 full process scale---see table 1)



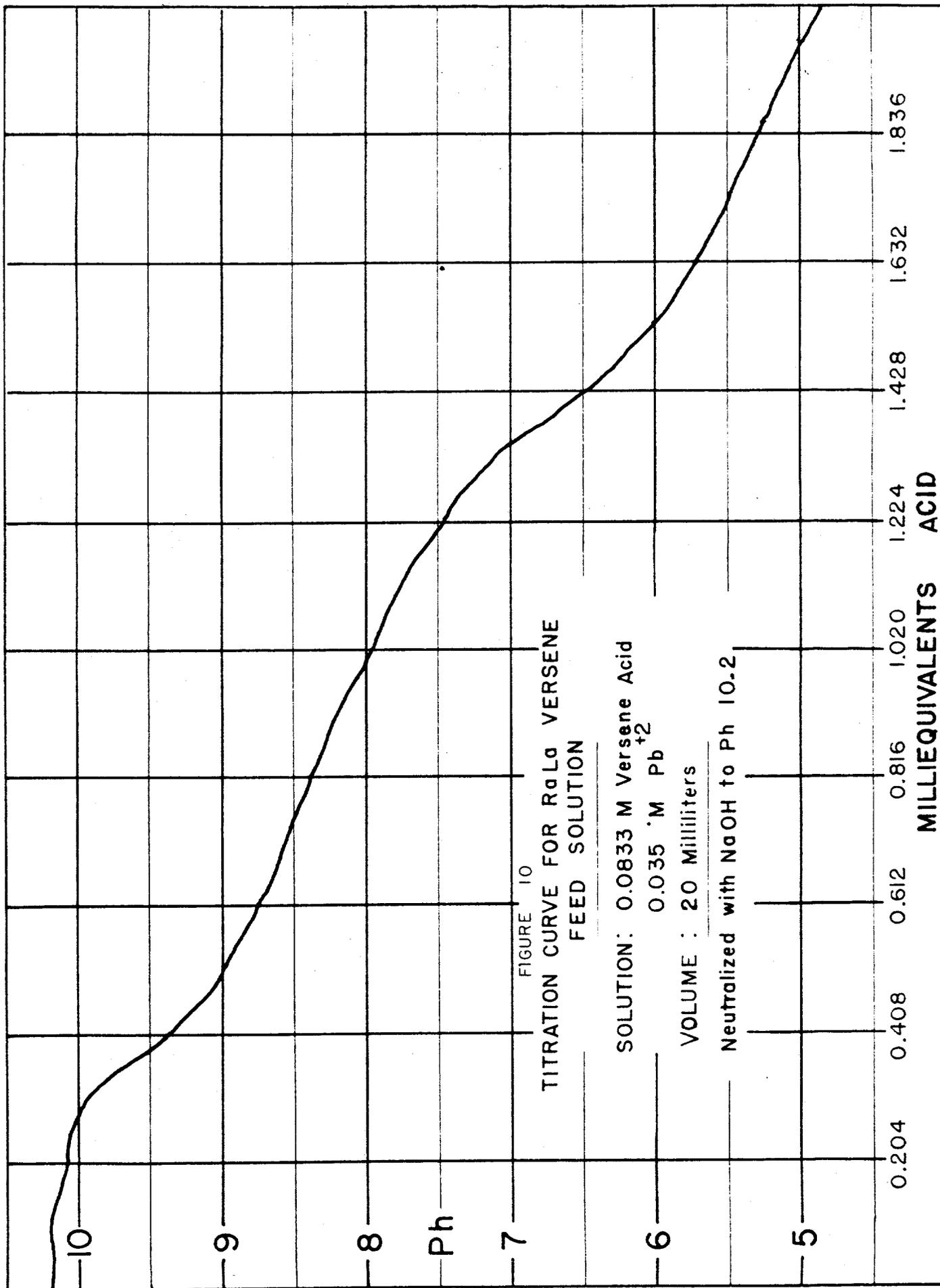
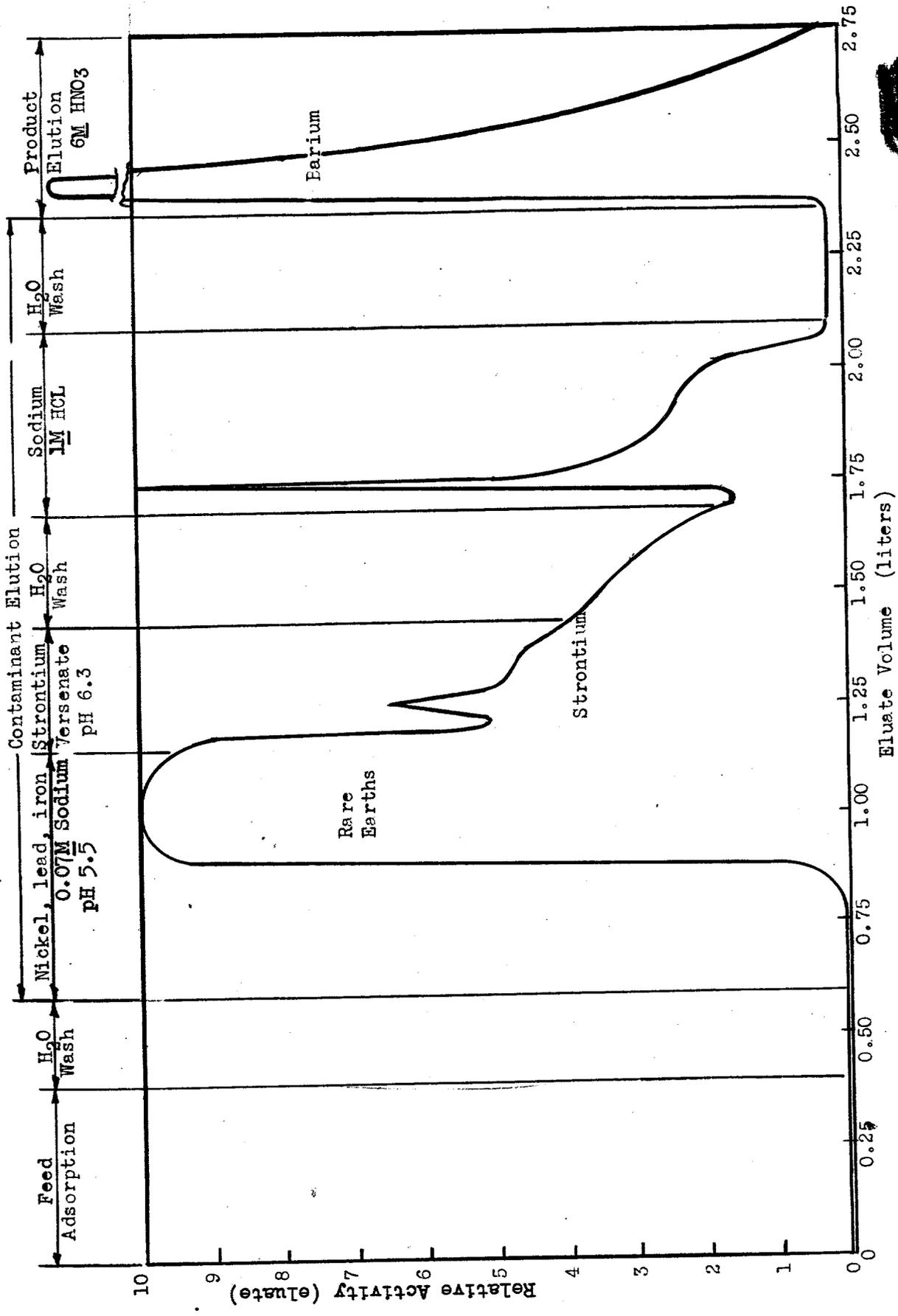


FIGURE 10  
TITRATION CURVE FOR RaLa VERSENE  
FEED SOLUTION

SOLUTION: 0.0833 M Versene Acid  
0.035 M Pb<sup>+2</sup>  
VOLUME : 20 Milliliters  
Neutralized with NaOH to Ph 10.2

Figure 11  
PROFILE OF THE RADIOACTIVITY CONTENT OF THE COLUMN ELUATE  
DURING THE NICKEL-VERSENE ION EXCHANGE PROCESS  
(Run V-69--1/40 full process scale--see table 3)

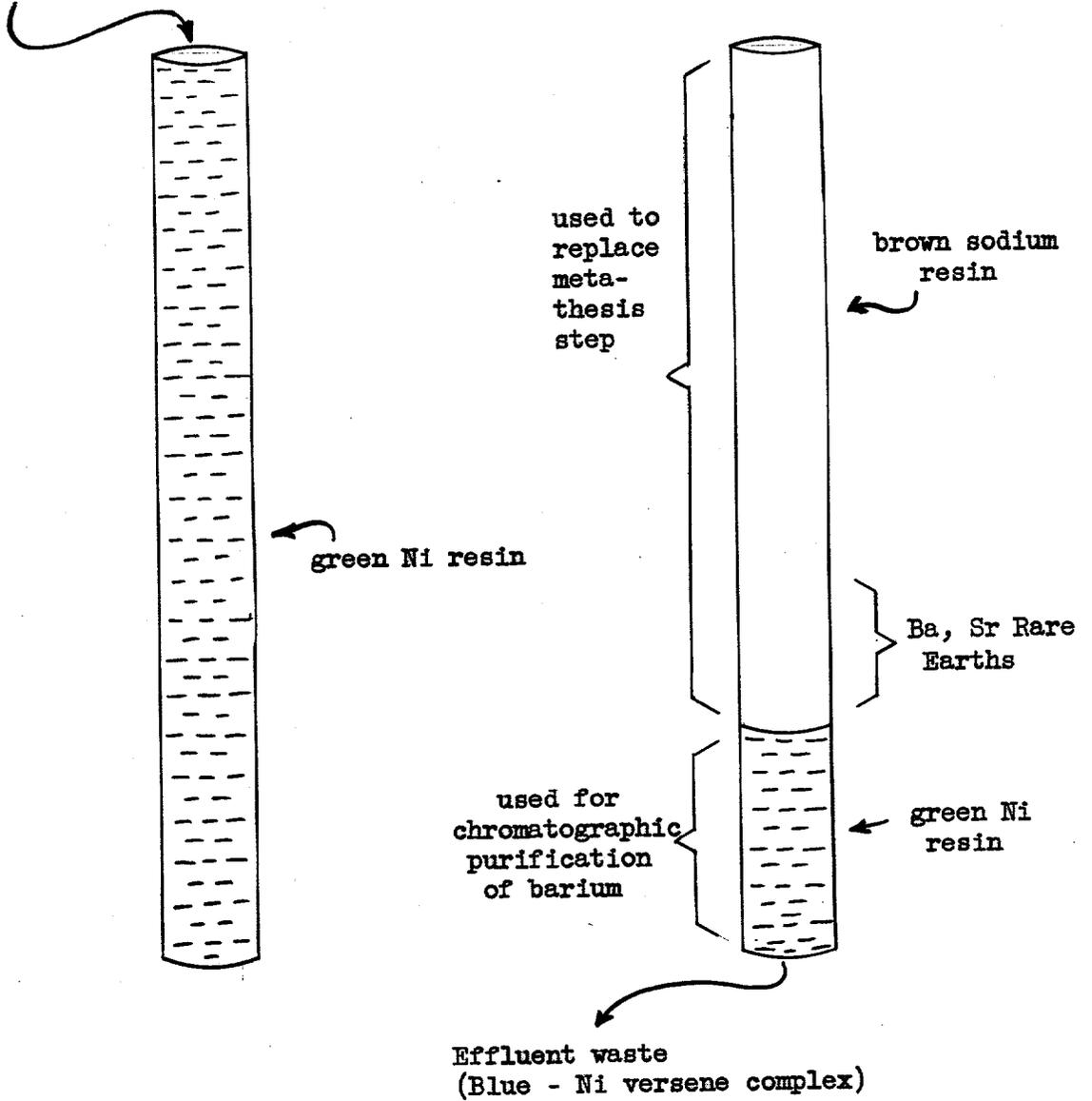


Schematic Diagram of Feed Operation  
in the Nickel Versene Process

Before Feed Operation

After Feed Operation

Feed  
(Violet, Fe, Cr, Ni Versene Complexes)



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by (Author) R.E. Blanco & A.H. Kibbey Dated 7-30-51  
Title or Description Laboratory Development of the Versene Process for the Purification of Radiobarium by Ion Exchange  
has been changed to: Declassified by authority of\* Tid 1148  
Our records indicate you have copy(ies): 17 Series: A

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