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MEMORANDUM

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DECONTAMINATION OF DISSOLVED SALT SOLUTION FROM TANK 19F USING DUOLITE CS-100 & AMBERLITE IRC-718 RESINS

INTRODUCTION

The high level alkaline waste generated at SRP is separated and stored as solid and liquid fractions in underground tanks. In the proposed flowsheet for the Defense Waste Processing Facility (DWPF), the solid fraction (sludge) will be sent to a glass melter for fixation in a borosilicate glass matrix (DWPF - Stage I). The liquid fraction (supernate) will be processed through ion exchange columns where the major radioactive isotopes (Cs^{137} and Sr^{90}) are removed (DWPF - Stage II). This report describes a demonstration of ion exchange decontamination of defense waste from Tank 19F in the High Level Caves (HLC).

In the past few years, extensive data[1,2,3,4] has been accumulated on the removal of cesium and strontium from synthetic supernate solutions via ion exchange processes. In this study actual SRP liquid supernate solutions were processed to refine and verify these synthetic solution studies. The main objectives were: (1) confirm high decontamination factors (DF's) for cesium-137 and strontium-90 using Duolite CS-100 and Amberlite IRC-718 ion exchange resins, (2) obtain DF's for other minor radioactive isotopes such as plutonium, technetium and ruthenium, (3) provide ion

exchange elutriant containing cesium-137, strontium-90 and other radioactive isotopes for "hot" melter studies, (4) determine the quality of the decontaminated salt solution and (5) provide actual decontaminated salt solution for saltcrete development programs.

SUMMARY

o   Operation of the DWPF Stage II (Ion-Exchange) flowsheet was successfully demonstrated in a HLC facility.

o   Actual decontaminated salt was prepared to support further saltcrete development efforts.

o   Actual ion-exchange elutriants were obtained for "hot" melter studies.

o   Unusually good decontamination of cesium-137 was observed. About 105 column volumes (CV's) of Tank 19F waste was processed using Duolite CS-100 resin at $\sim 10^5$ DF or higher. (TDS specifications - 40 CV at 10^4 DF)

o   The Amberlite IRC-718 resin was able to provide a DF of 10^3 at approximately 35 CV. (TDS specifications - 40 CV at 10^3 DF)

o   The decontaminated salt solution meets TDS requirements.[1] The only major radioactive isotopes remaining were ruthenium-106 and technetium-99.

o   As expected, the current ion exchange process does not remove any significant quantity of ruthenium-106 or technetium-99.

o   The overall DF for Pu is estimated at ~ 10 to 20. Very low Pu in the feed makes accurate estimation of DF questionable.

o   Slightly alkaline water is recommended for ion-exchange column rinsing to prevent accidental removal of cesium and strontium by acidified water due to CO_2 adsorption.

o   A 20% increase in sand filter capacity was demonstrated by backwashing with water instead of filtered supernate.

DETAIL EXPERIMENTAL RESULTS

A.   Process Overview

Removal of cesium and strontium from the synthetic supernate has been studied extensively.[1,2,3,4] Ion exchange processes have been identified as the most suitable method for removing trace amounts of cesium and strontium. Significant improvements have been made in the past few years, and the latest version of the ion exchange flowsheet was used in this HLC study. The ion exchange columns were packed with Duolite

CS-100 for cesium-137 adsorption and Amberlite IRC-718 for strontium-90 adsorption. The elutriant for both columns was dilute formic acid. The advantages of this latest flowsheet are summarized below[2]:

(1) Duolite CS-100 has Cs capacity better than the older Duolite ARC-359 resin.

(2) Duolite CS-100 is effective in partially removing strontium and thus reducing the Sr load to the Amberlite IRC-718 column.

(3) Elution of cesium from the Duolite CS-100 and strontium from Amberlite IRC-718 using dilute formic acid is simplier than using ammonium carbonate elution for Duolite ARC-359 and EDTA elution for Amberlite IRC-718 resin as recommended in older flowsheets.

The Integrated Supernate Processing Facility (ISPF) is a very flexible facility in the HLC for processing actual SRP high level liquid waste.[5] This facility was used to perform the following process steps on a sample of Tank 19F dissolved salt solution:

1. Supernate sample receipt and characterization

2. Agglomeration/gravity settling

3. Sand filtration/filter backwash

4. Cesium ion exchange

5. Strontium ion exchange

6. Ion exchange elution and concentration

7. Decontaminated salt solution recovery and characterization

B. The As-Received Dissolved Salt Solution

High level liquid waste, according to the TDS[1], consists of (1) supernate above salt cake, (2) aluminum dissolver solution, (3) sludge wash solution concentrate, and (4) dissolved salt cake solution. Because this was the first run in this facility, only dissolved salt cake solution from Tank 19F was used. The composition of the as-received dissolved salt solution is given in Table 1A. The total sodium ion and free hydroxide concentrations were typical but the cesium-137 and strontium-90 radioactivity were almost two orders of magnetude lower than the TDS values.[1]

C. Gravity Settling

The purpose of gravity settling and sand filtration is to reduce the suspended solids in the ion exchange feed to 1 ppm

or less to avoid pluggage of the ion exchange columns. The gravity settling and sand filtration were carried out according to TDS[1] conditions.

In gravity settling, a starch solution (8% Flojel-60) coagulant was used as a settling aid (1 ml of 8% Flojel-60 per 1000 ml of feed). The agglomeration of undissolved solids was carried out at 60°C with gentle air sparging. The mixture was allowed to settle overnight at room temperature before sand filtration was started. A clear solution was obtained until the gravity settler dip-leg was lowered to within 1 to 2 inches of the tank bottom, indicating the volume of the settler solids was approximately 12% of the original liquid volume. The composition of the clarified solution after gravity settling is given in Table 1B. As expected, the gravity settling step did not change the composition of the feed. (A small dilution effect was caused by residual water left over during the hot checkout test.)

D. Sand Filtration

Backwash

The sand filtration was carried out at 1.2 gpm/ft^2 using an anionic polyelectrolyte solution Versa TL 700 (0.07 ppm) as a filtration aid. The filtration reduced the suspended solids to less than detection limit (<7 ppm). Forty liters of supernate were filtered with no observed pressure drop changes across the sand filters. The composition of the filtered solution is given in Table 1C. Comparison of feed composition before and after filtration indicated that a 20% dilution occurred because the sand filters were full of water from previous hot checkout tests.

After filtration, the sand filters were successfully backwashed with water instead of filtered supernate solution. As expected, no aluminum hydroxide precipitation was formed. This modification will give an ∿20% increase in the overall capacity of the sand filters. The composition of the filter backwash solution is given in Table 1D. Comparison of the as-received feed and the filter backwash solution shows that their compositions were roughly proportional to each other with no preferentially absorption by the sand filters.

E. Regeneration of Ion Exchange Resin

The Duolite CS-100 resin was received in hydrogen form from the vendor. Before it was used for removing cesium from the feed, it was converted to sodium form using a 0.5M NaOH solution at 1.5 CV/hr. The completion of regeneration can be followed readily by measuring the conductivity of the regenerant. Figure 1 gives the conductivity of the regenerant as a function of regeneration column volumes after it had gone

through the cesium columns. At the start, the conductivity
was low because most of the sodium ions in the regenerant
were removed by the Duolite CS-100 resin. When most of the
resin was converted to sodium form, the sodium ions passed
through the column and gave a high conductivity reading equal
to the regenerant feed conductivity.

F. Cs Ion Exchange

The column test of Duolite CS-100 resin in removing cesium-
137 from Tank 19F dissolved salt solution was unusually good.
About 105 CV of salt solution was processed through the columns
before cesium breakthrough occurred and the decontaminated
salt had a DF $\sim 10^5$, Figure 2. This better than expected Cs
performance was the result of a low cesium concentration in
the feed. The feed from Tank 19F contained only 2 X 10^{-5}M Cs
instead of 2 X 10^{-4}M used in most of the previous synthetic
studies. (Synthetic studies have shown that the K_d for cesium
increases from about 160 to 270 as its concentration is reduced
from 1 X 10^{-4} to 1 X 10^{-5}M.[2]) Since the cesium concentration
from the other waste tanks is expected to be in $\sim 10^{-4}$ range,
a breakthrough value of 105 CV should not be considered as a
typical value, but it does confirm the process sensitivity to
cesium concentration.

G. Sr Ion Exchange

The DF for strontium-90 before breakthrough occurred at ~ 35
CV was 10^3, see Figure 3. The data for strontium-90 in Figure
3 scattered considerably more than the cesium data. This
scattering of strontium-90 data occurred because the strontium-
90 in the feed was low and after ion exchange it was near the
analytical detection limit. In future tests, strontium-85, a
gamma emitter, will be added to the feed to improve the accuracy
of the strontium breakthrough data.

H. Decontaminated Salt Solution

The only radioactive isotopes found in the decontaminated salt
solution are: cesium-137, strontium-90, ruthenium-106 and
technetium-99. The radioactivities of the decontaminated salt
solution meets the requirements set forth in the TDS.[1] Table
2 gives a breakdown of major radioactivities except strontium-
90. Strontium-90 is omitted because it broke through well
ahead of cesium-137 in this experiment. Comparison of ruthenium-
106 and technetium-99 radioactivities in the feed and the
decontaminated solution reveals that both radionuclides are
not retained by Duolite CS-100 or Amberlite IRC-718. Since
ruthenium-106 and technetium-99 radioactivities are in the
order of 10^4 d/m/ml, any attempts to reduce cesium-137 and
strontium-90 to less than 10^4 d/m/ml is meaningless, unless
other means are developed to remove ruthenium-106 and technetium-
99.

A good estimation of DF for plutonium was not possible because the plutonium in the feed was only $\sim$2 X 10^3 d/m/ml which is about the limits of plutonium detection. Examination of the data accumulated so far indicated that DF for Pu was $\sim$10 to 20.

I.   Ion-Exchange Rinse & Elution

The relative radioactivities of cesium-137 in the rinse solution after the first and the second cesium column are given in Figure 4. The relative radioactivity is defined as the ratio of radioactivity in the rinse solution to the radioactivity at the end of the loading cycle. It can be seen that the relative cesium-137 radioactivity after the second cesium column is higher than at the end of supernate loading. Absorption of CO_2 may produce enough acidity in water to start removing the adsorbed cesium-137 from the resin. To avoid this possibility of contaminating the decontaminated solution, a slightly causticized water should be used for the first rinse. This point is particularly important for Duolite CS-100 because even a very dilute acid such as 0.1M formic acid is able to remove all cesium from the resin.[6]

The conductivity of the elutriant during elution as a function of elutriant column volumes is given in Figure 5. As expected, the curve is bell-shaped. At the start of elution, the con-ductivity was low because the conductivity cell was exposed to deionized water. As formic acid was removing Na^+ and Cs^+ from the resin, the conductivity increased. At the end of elution, the conductivity dropped to that of a 0.4M formic acid.

Figure 6 shows the aluminate ion concentration at the bottom of first cesium, second cesium, and strontium columns as a function of the column volume of rinse water used. At the end of the first rinse about 8 column volumes of rinse water were used. It can be seen that the residual supernate in the first and the second cesium columns were completely removed. How-ever, there was still substantial amounts of supernate remaining in the strontium column as indicated by aluminum analysis. The incomplete rinsing of the strontium column was also indicated by the sodium analysis at the beginning of strontium elution, see Figure 8. The sodium concentration at the beginning of strontium elution, unlike cesium elution in Figure 7, cannot be extrapolated to zero. To avoid this kind of incomplete rinse, we need to extend the rinse cycle from 8 CV to at least 12 CV.

We were able to elute the second cesium columns to almost background level with 21 CV of 0.4M formic acid. However, after the column had set for a few days, the eluate in the column contained about 8 times the cesium background radio-activity. The cesium elution as a function of column volumes is given in Figure 9. The elution required significantly more column volumes than the single column test because of

backmixing in the overhead void volume on the top of the second column. This effect is magnified because Duolite CS-100 shrinks ∿25% during elution by formic acid creating overhead void volume. Careful column design is required to reduce this backmix effect.

Strontium is more difficult to elute than cesium. Only about half of strontium is removed after 10 CV of 0.4M formic acid has passed through the column. About the same amount of strontium was removed when the strontium column was further eluted with 10 CV of 2M formic acid.

The elution data for cesium and strontium indicated that a longer than expected elution time may be required. This long elution cycle plus the need of a sodium/cesium split will make the utilization time for ion exchange a smaller portion of the total cycle time.

LML:lmn

REFERENCES

1. "Preliminary Technical Data Summary for the Defense Waste Processing Facility - Stage 2," DOE Report DPSTD-80-39, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina.

2. R. M. Wallace, "The Basis of an Improved DWPF Ion-Exchange Process: Absorption of Cesium on Weak Acid Phenolic Acid Resin, Duolite CS-100 and S-761 and Elution With Formic Acid," DOE Report DPST-80-453, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina, July 1, 1980.

3. L. L. Kilpatrick, "Strontium Removal from Synthetic Supernate Using Amberlite IRC-718," DOE Report DPST-80-680, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina, December 16, 1980.

4. M. A. Ebra, "Effect of Resin Particle Size on the Absorption of Cesium on Duolite CS-100, A Weak Phenolic Acid," DOE Report DPST-80-641, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina, November 7, 1980.

5. P. K. Baumgarten, "Process Description Integrated Supernate Processing Facility," DOE Report DPST-80-710, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina, December 12, 1980.

6. M. A. Ebra, "Effect of Formic Acid Elutriant Concentration on Cesium Elution from Duolite CS-100," DOE Report DPST-81-212, Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina, January 12, 1981.

Table 1A

DISSOLVED SALT SOLUTION FROM TANK 19F - BEFORE GRAVITY SETTLING

A. Major Radioactive Isotopes

Cs-137	1.0×10^8	d/m/ml
Sr-90	1.3×10^5	d/m/ml
Ru-106	1×10^4	d/m/ml
Tc-99	3.5×10^4	d/m/ml
Pu	$\sim 10^3$	d/m/ml

B. Chemical Composition

Na^+	5.9M	$SO_4^=$	0.26M
NO_3^-	3.6M	$CO_3^=$	0.10M
OH^-	1.4M	Cl^-	0.005M
AlO_2^-	0.62M	F^-	0.024M
K^+	0.024M	NO_2^-	0.14M
$C_2O_4^=$	2×10^{-3}M	Sp. Gr.	1.30
Cs^+	2×10^{-5}M	I^-	ND

C. Suspended Solids ~ 200 ppm

Table 1B

DISSOLVED SALT SOLUTION FROM TANK 19F - AFTER GRAVITY SETTLING

A.   Major Radioactive Isotopes

Cs-137	9.0×10^{7}	d/m/ml
Sr-90	-	d/m/ml
Ru-106	-	d/m/ml
Tc-99	-	d/m/ml
Pu	-	d/m/ml

B.   Chemical Composition

Na^{+}	5.4M	$SO_4^{=}$	-
NO_3^{-}	-	NO_2^{-}	-
AlO_2^{-}	-	$CO_3^{=}$	-
OH^{-}	1.4M	F^{-}	-
K^{+}	0.018M	Cl^{-}	-
$C_2O_4^{=}$	-		-

Table 1C

<u>DISSOLVED SALT SOLUTION FROM TANK 19F – AFTER SAND FILTRATION</u>

A. Major Radioactive Isotopes

Cs-137	7×10^7	d/m/ml
Sr-90	1×10^5	d/m/ml
Ru-106	1×10^4	d/m/ml
Tc-99	3.2×10^4	d/m/ml
Pu	$\sim 10^3$	d/m/ml

B. Chemical Compositions

Na^+	4.5M	$SO_4^=$	0.2M
NO_3^-	2.7M	NO_2^-	0.1M
AlO_2^-	0.4M	$CO_3^=$	0.1M
OH^-	1.1M	F^-	0.023M
K^+	0.015M	Cl^-	0.005M
$C_2O_4^=$	2×10^{-3}M	I^-	<7ppm

Suspended Solid Not Detected (Detection Limit 7 ppm)

Table 1D

SAND FILTER BACKWASH SOLUTION FROM TANK 19F RUN

A. Radioactive Isotopes

Cs-137 9.5×10^5 d/m/ml

Sr-90 1.4×10^3 d/m/ml

B. Chemical Compositions

Na^+ 0.045M

OH^- <0.001M

K^+ 2×10^{-4}M

TABLE 2.   RADIOACTIVITIES OF THE DECONTAMINATED SALT SOLUTION

Radionuclides	Radioactivities	
	nCi/ml	d/m/ml
Cs^{137}	0.22	494
Ru^{106}	3.83	8500
Tc^{99}	14.4	32000
Sb^{125}	0.03	67

Specific Gravity = 1.24

Figure 1. The Conductivity of Regenerant After Going Through the CS-100 Columns Using 0.5M NaOH

Conductivity, mS

Regeneration in Column Volumes
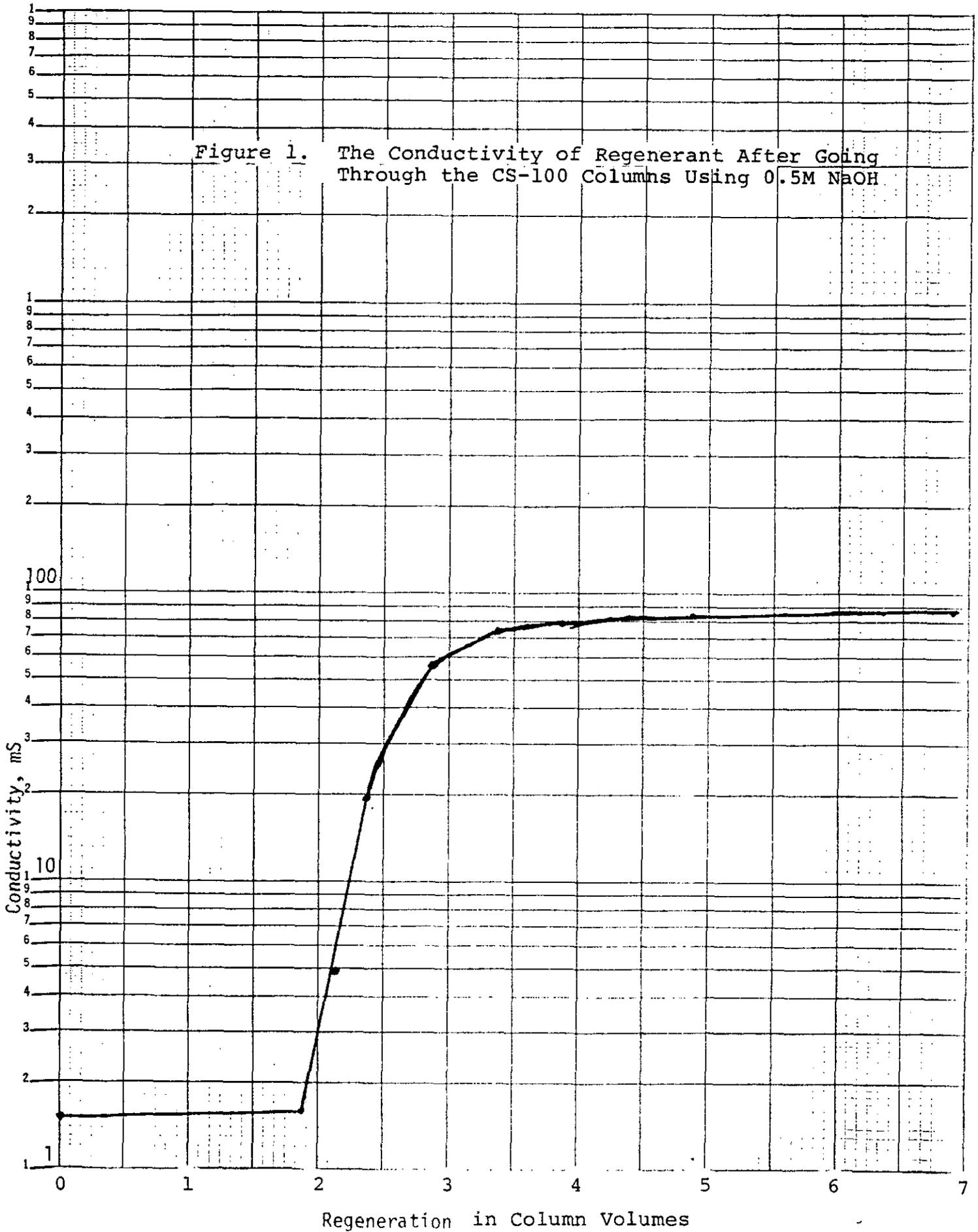
Figure 2. Decontamination of 19F Dissolved Salt Cake Solution by CS-100, Cs-137
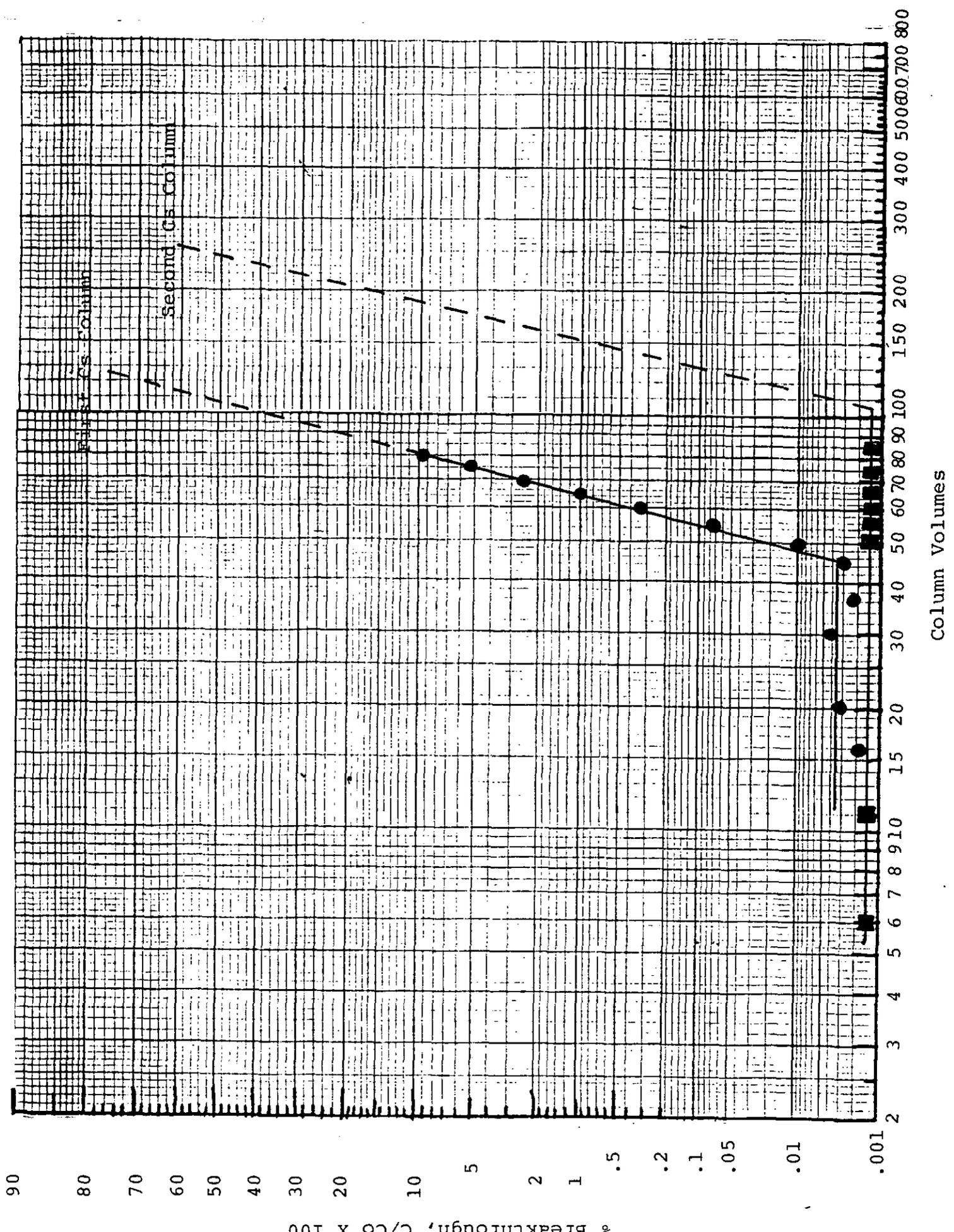
Figure 3. Decontamination of Sr-90 from the 19F Dissolved Salt Cake by Amberlite IRC-718
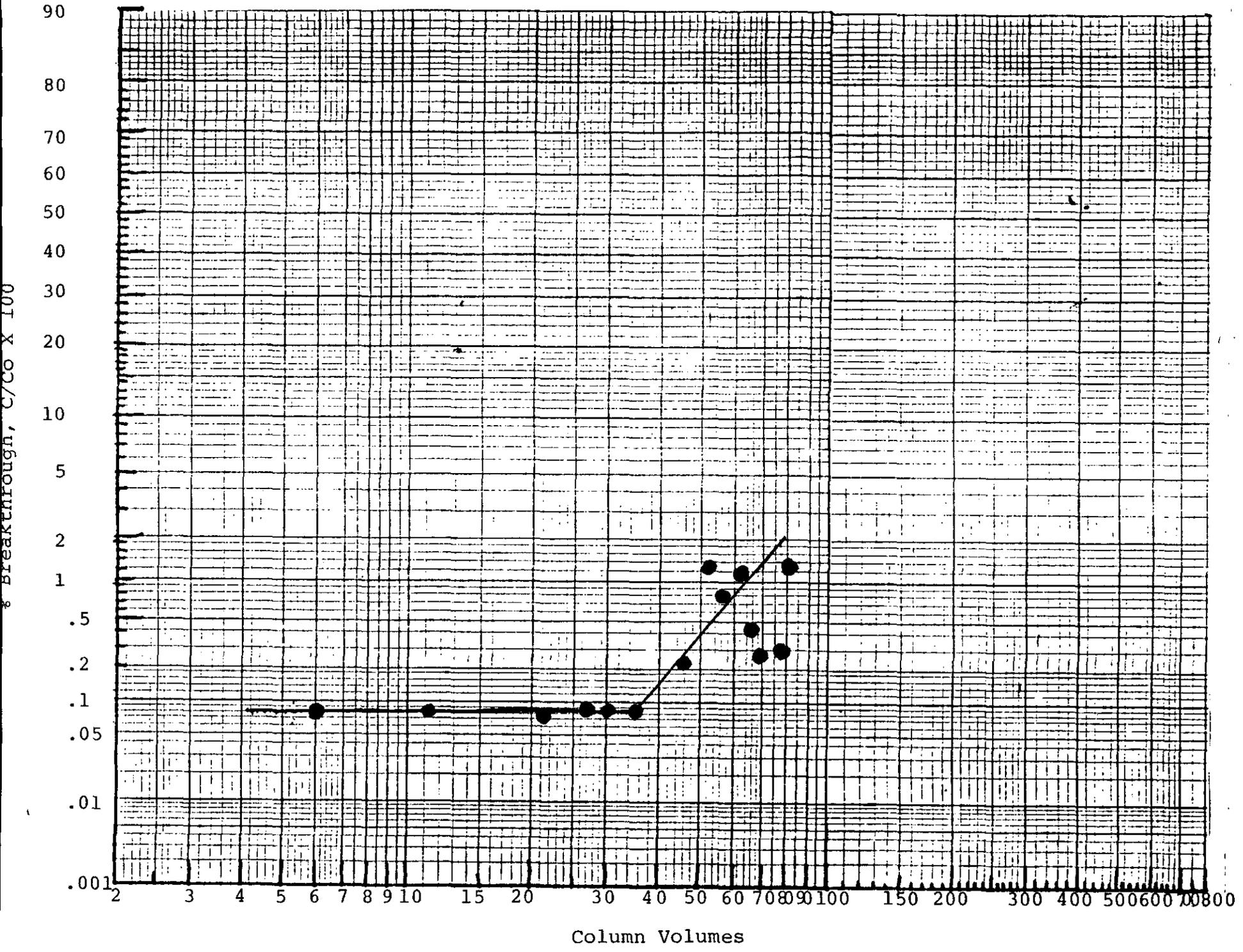
Figure 4. Cs^{137} Radioactivity in the Rinse Solution as a Function of CV

Second Cesium Column

First Cesium Column

Percent of Cs137 Activity in the Rinse as a Function of CV
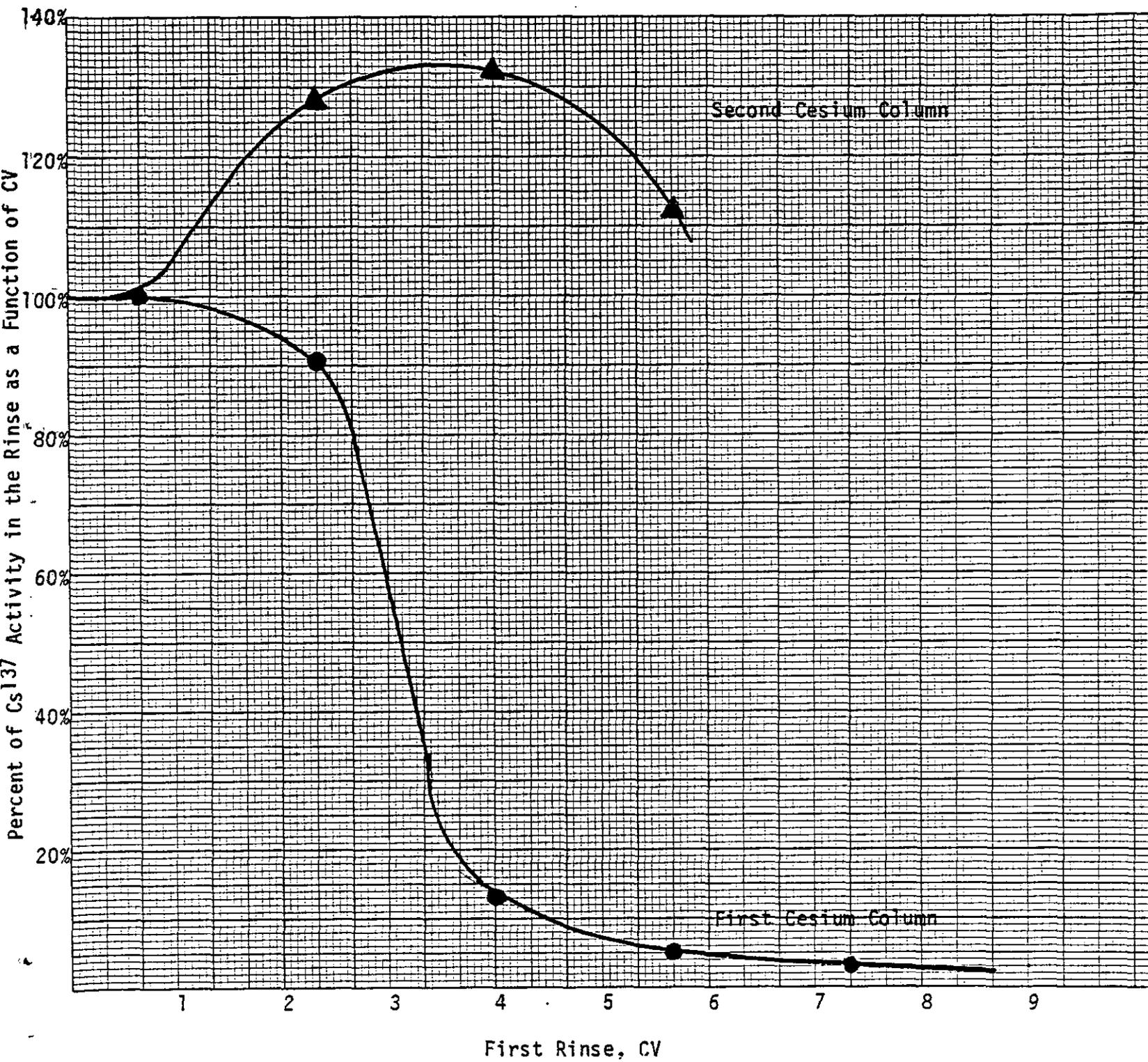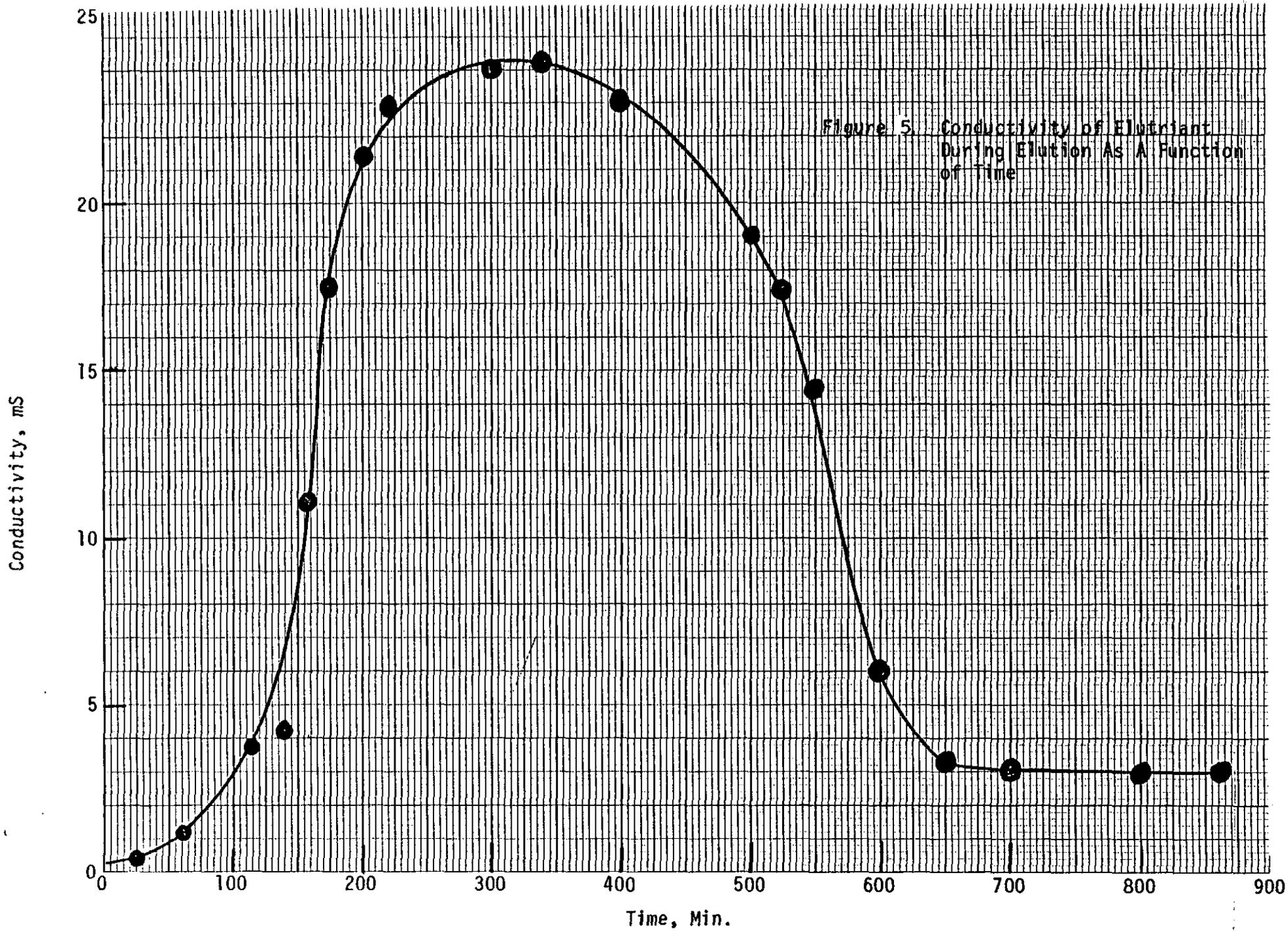
First Rinse, CV

Figure 5. Conductivity of Elutriant During Elution As A Function of Time

Figure 6. The Concentration of Aluminate in the First Rinse at the Bottom of First Cesium, second cesium and strontium column as a function of Rinse Water Column Volume
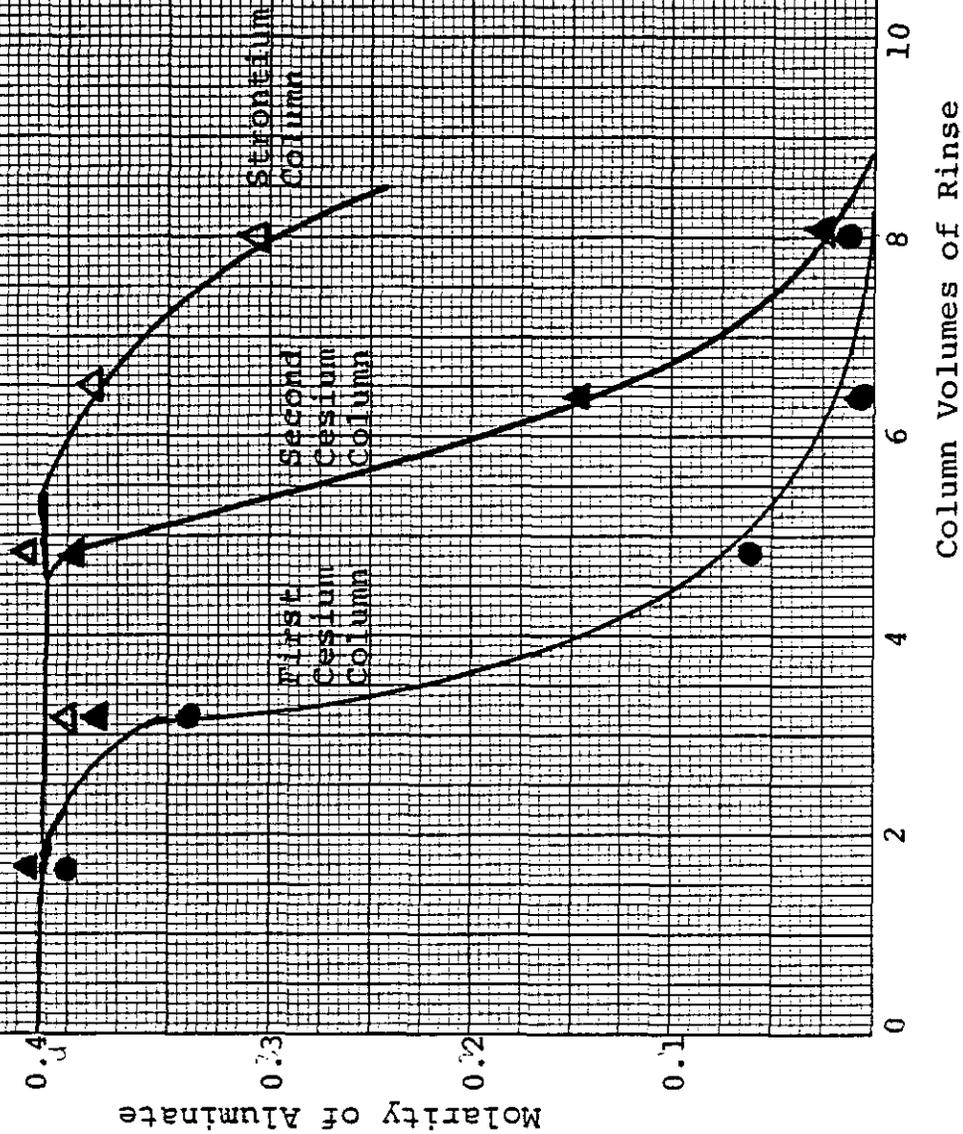
Figure 7. Sodium Ion Concentration at the Top of the First and the Second Cesium Column During Elution

▲ First Cesium Column

● Second Cesium Column

Molarity of Sodium Concentration in the Eluate, Cesium Column
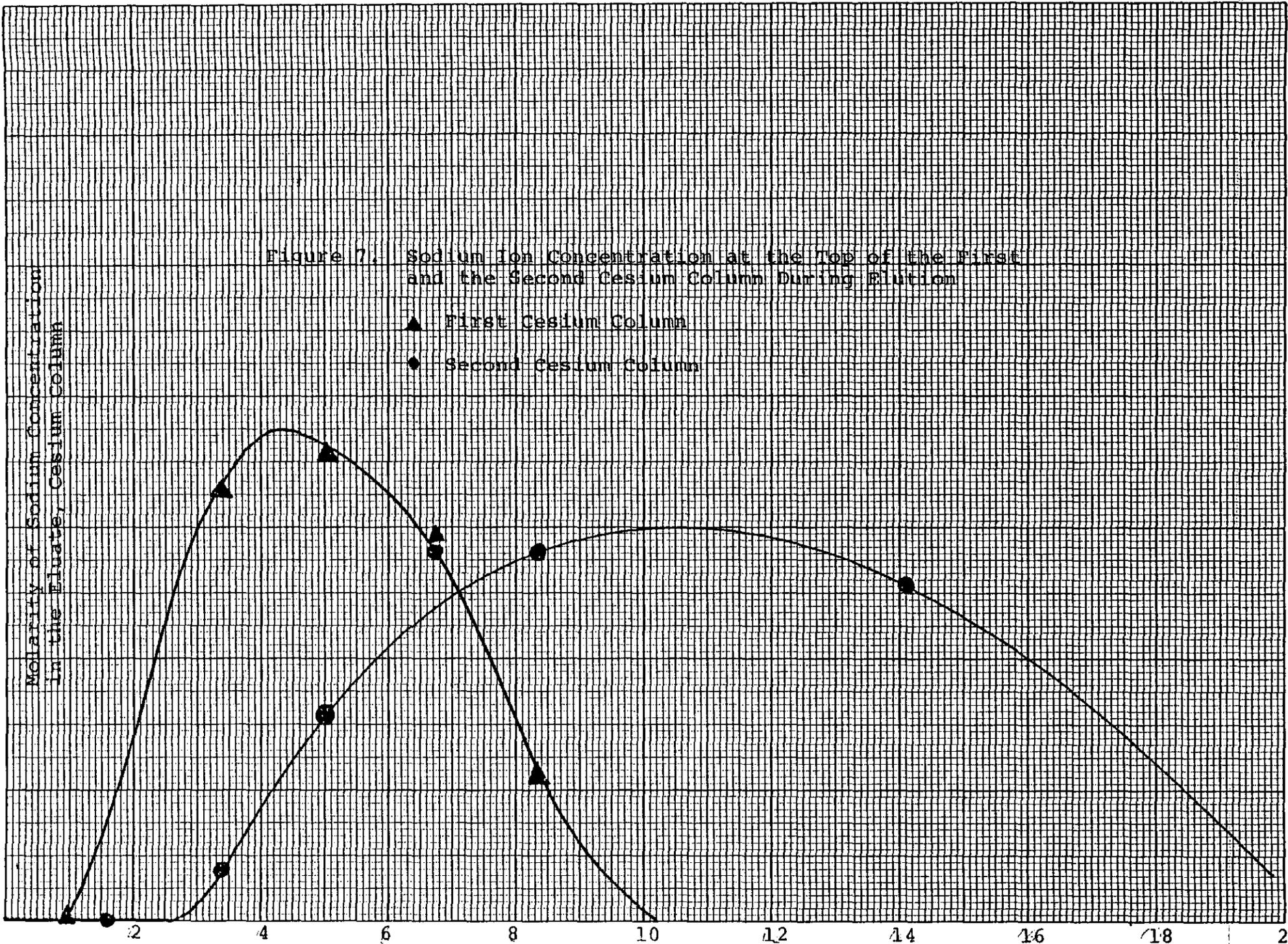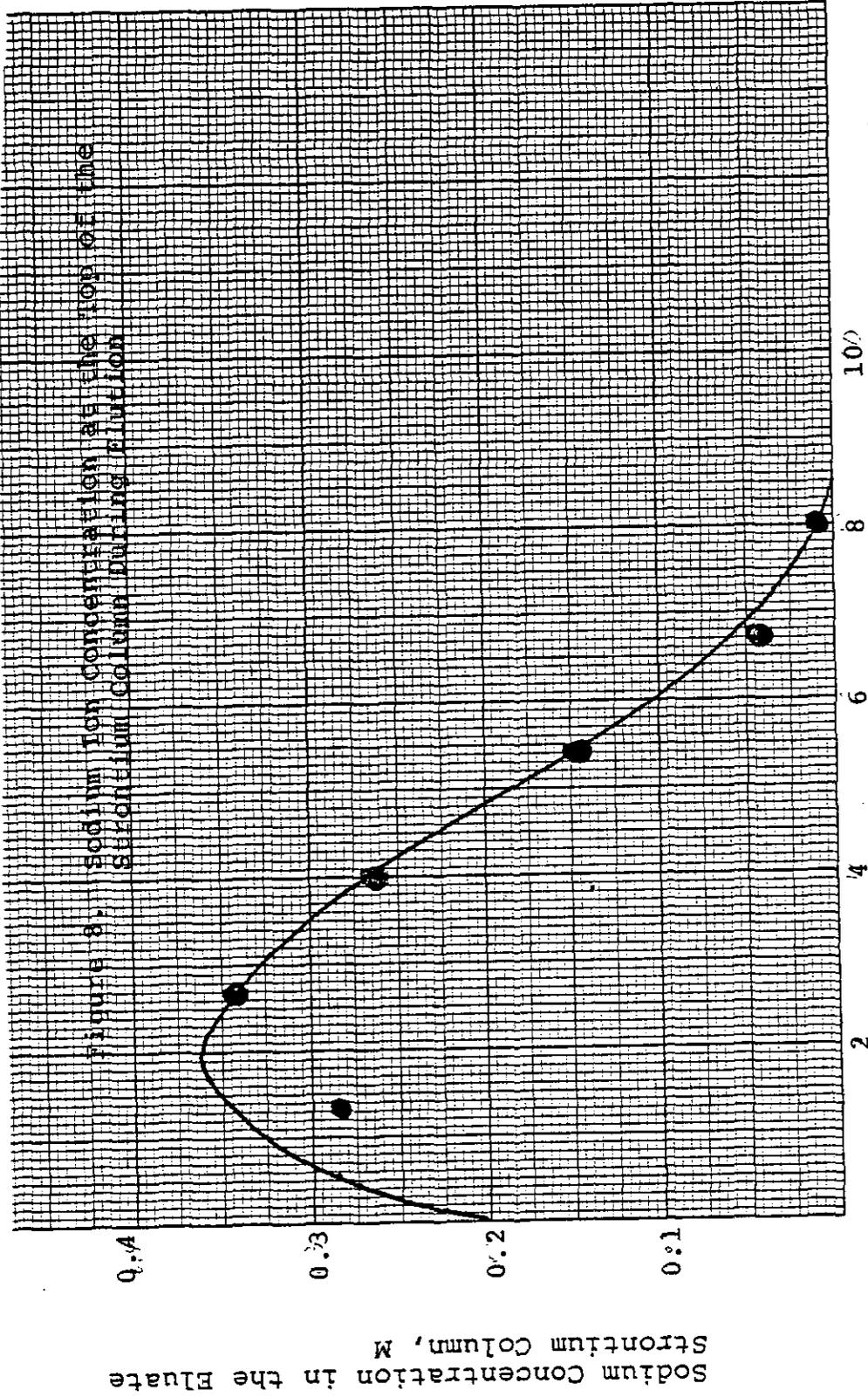
Column Volumes of Elution

Figure 8. Sodium Ion Concentration at the Top of the
Strontium Column During elution

Column Volumes of Elution

Sodium Concentration in the Eluate
Strontium Column, M

Figure 9. Percent and Accumulated Percent of Cesium Eluted from the Column Using 0.4M Formic Acid as an Eluriant