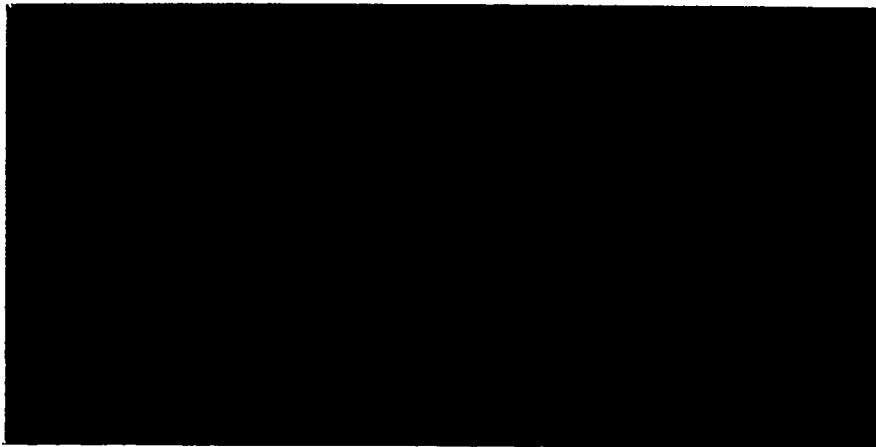


CIC-14 REPORT COLLECTION
REPRODUCTION
COPY

C.3

LOS ALAMOS SCIENTIFIC LABORATORY

OF THE UNIVERSITY OF CALIFORNIA
LOS ALAMOS, NEW MEXICO

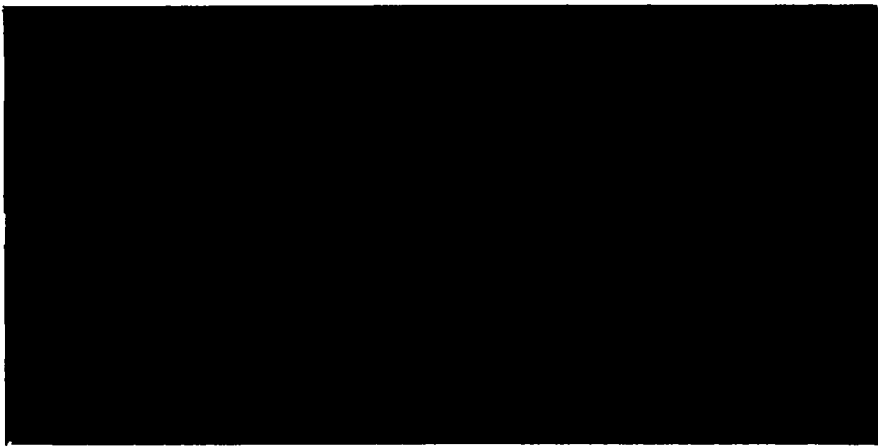


CONTRACT W-7405-ENG. 36 WITH THE
U.S. ATOMIC ENERGY COMMISSION

LOS ALAMOS NATL. LAB. LIBS.



3 9338 00353 5860



e. 5

LOS ALAMOS SCIENTIFIC LABORATORY
of the
UNIVERSITY OF CALIFORNIA

Report written:
November 1955

Report distributed: MAY 21 1956

LA-1975

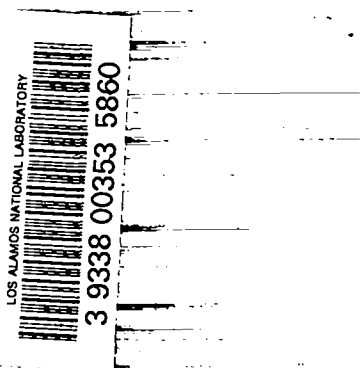
PURIFICATION OF GRAM AMOUNTS OF AMERICIUM

Work done by:

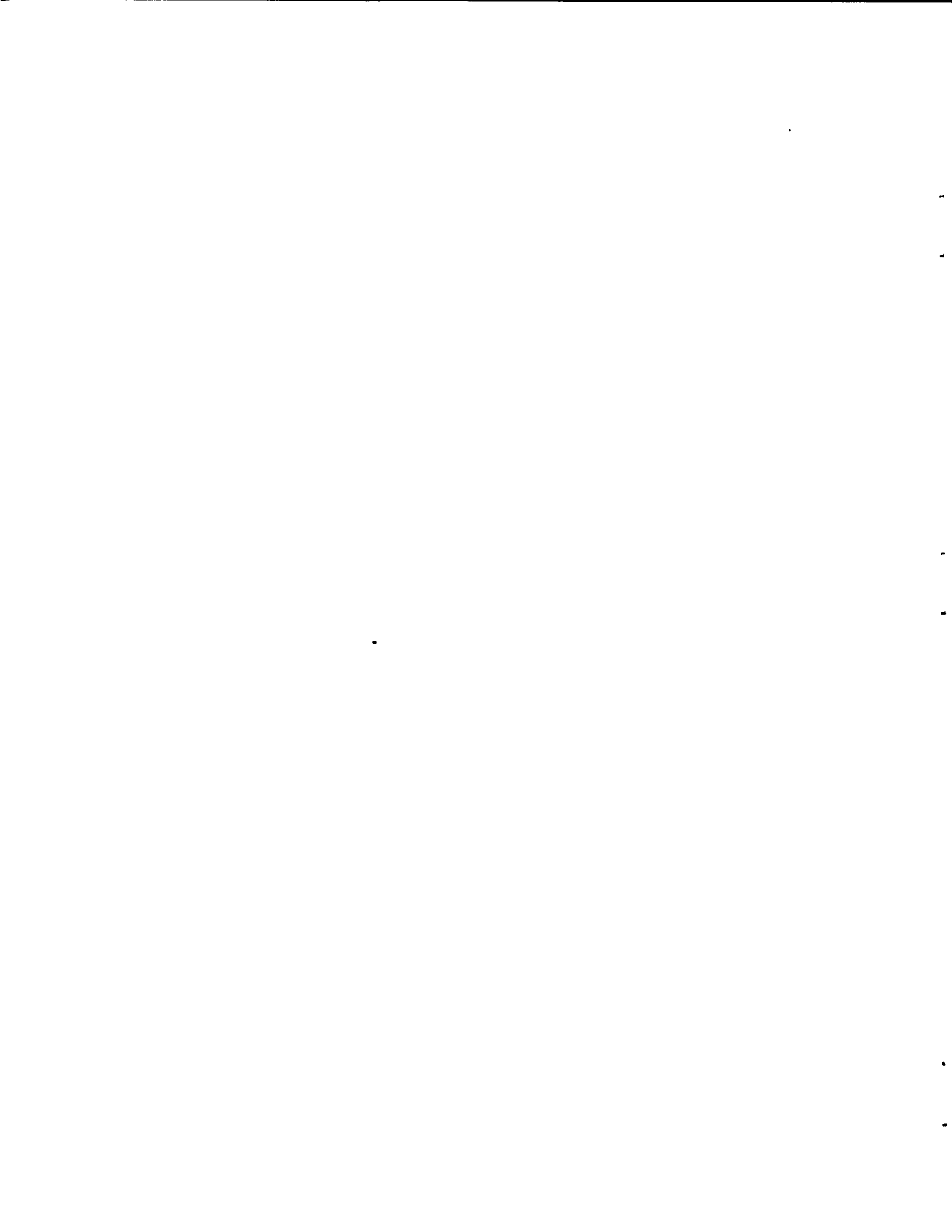
D. E. Armstrong
L. B. Asprey
J. S. Coleman
T. K. Keenan
L. E. LaMar
R. A. Penneman

Report written by:

J. S. Coleman



CHEMISTRY
(Distributed according to
TID-4500, 11th edition)

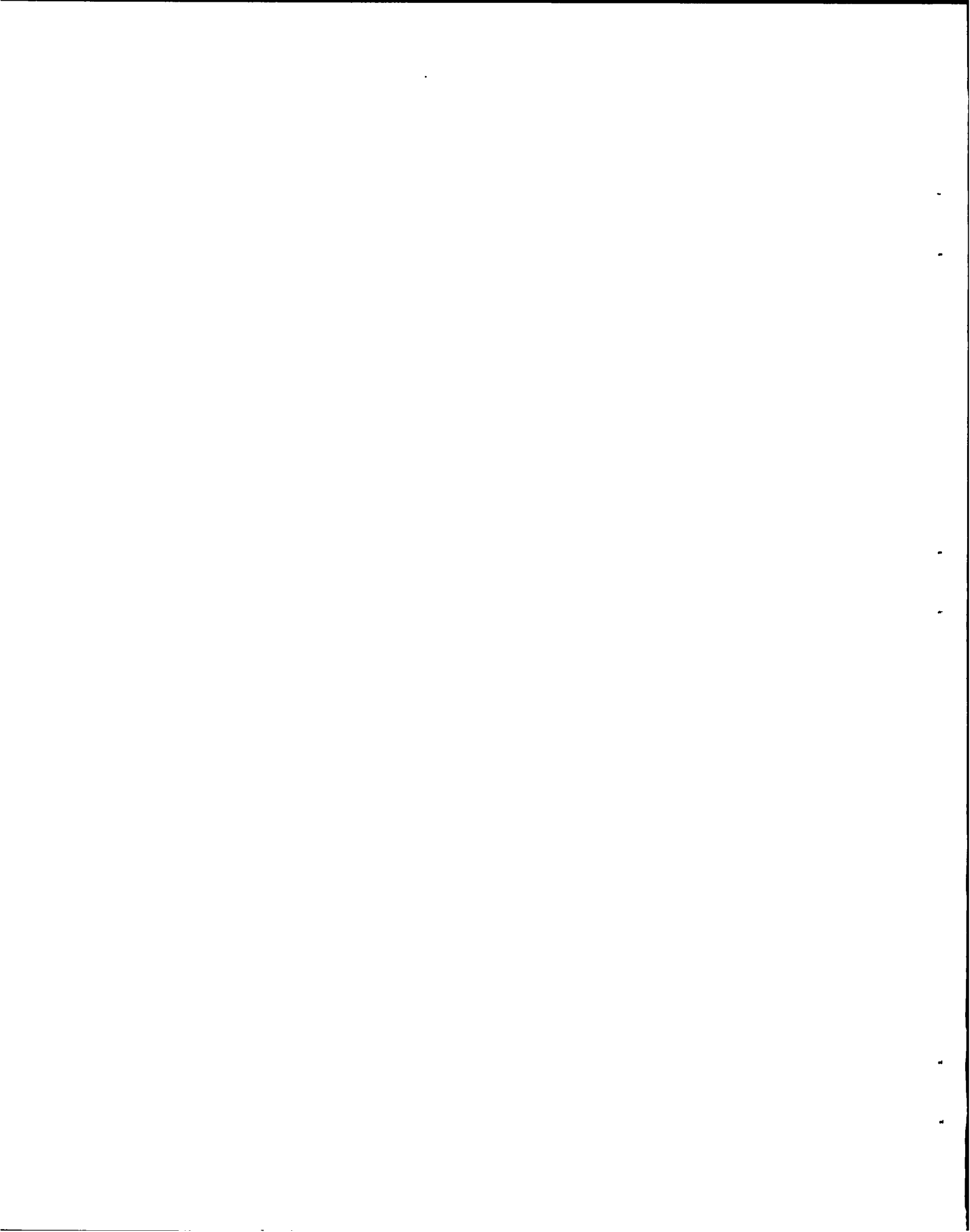


ABSTRACT

Methods of americium purification are discussed under three classifications: ion exchange, solvent extraction, and precipitation. Two new ion-exchanger processes for the separation of americium from rare earths are described in detail. The first involves absorption of rare earths and americium on a column of hydrogen-form cation exchanger, followed by elution with 0.1% ammonium citrate, pH 8. The second utilizes the marked tendency of strongly basic anion exchangers to absorb americium in preference to the rare earths from ammonium thiocyanate solutions. Solvent extraction with tri-butyl-phosphate is recommended for gross decontamination of americium crudes, and oxidation-reduction cycles suitable for final purification of americium concentrates are outlined.

ACKNOWLEDGMENTS

We are indebted to O. Simi for spectrographic analyses, and to F. H. Kruse and W. Takei for assistance in carrying out some of the initial purification.



CONTENTS

Abstract..... 3
Acknowledgments..... 3
1. Introduction..... 7
2. Precipitation Methods..... 9
3. Solvent Extraction Methods..... 13
4. Ion Exchange Methods..... 15
 4.1 Ammonium Citrate-Cation Exchanger Process..... 20
 4.2 Ammonium Thiocyanate-Anion Exchanger Process..... 29

100-100000

100-100000

-
-
-
-
-
-

1. INTRODUCTION

A dozen years have now passed since the first positive identification of americium,¹ and a variety of procedures for its isolation have been published. References to methods in the current literature are given in a recent review by Penneman and Asprey.² The availability of gram amounts of americium is sufficiently new so that procedures designed for these comparatively large quantities have previously received no mention. The major current sources of americium contain a very wide variety of contaminants, often including large amounts of rare earths, so that extensive modification of the older processes has been found desirable.

This report is intended to collect and summarize the various procedures which we have found most useful for the purification of americium. In addition, it describes in working detail the two ion-exchanger processes we recently applied to the separation of several grams of americium from a kilogram of rare earths. The first of these processes is

1. G. T. Seaborg, R. A. James, and L. O. Morgan, Paper 22.1 in Trans-uranium Elements, Seaborg, Katz, and Manning, editors, Div. IV, Vol. 14B, Book II, National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, 1949.
2. R. A. Penneman and L. B. Asprey, Paper UN-838, International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955.

patterned closely after one used by Spedding and Powell³ for large-scale separation of rare earths. The second depends on the anion-exchange absorption of americium from aqueous NH_4SCN solutions, which is in striking contrast to the behavior of the rare earths. This latter process is similar in principle to the many schemes for the separation of metals which utilize selective absorption by anion exchangers from hydrochloric acid solutions, as reported, for example, by Kraus, Nelson, and Smith.⁴

The americium isotope used in this work, Am^{241} , emits gammas of energies up to 0.37 Mev with the most common component being 0.060 Mev.⁵ As a result, the course of the americium during purification procedures may be readily followed with a gamma survey meter. In the ion-exchange processes, for example, we have typically made frequent scans of the columns with appropriately shielded probes to determine the distribution of the americium on the column, and have monitored the effluent tubes to guide collection of fractions. Precautions against hand and body exposure must, of course, be taken, and we have found 1/8 inch lead sheet or 1/4 inch photographic lead glass sufficient and convenient for this purpose.

3. F. H. Spedding and J. E. Powell, J. Am. Chem. Soc. 76, 2545 (1954).

4. K. A. Kraus, F. Nelson, and G. W. Smith, J. Phys. Chem. 58, 11 (1954).

5. P. P. Day, Phys. Rev. 97, 689 (1955).

2. PRECIPITATION METHODS

In general, trivalent americium forms insoluble compounds with reagents which precipitate the trivalent rare earths, e.g., oxalate, hydroxide, and iodate. On the other hand, the higher oxidation states of americium show little similarity to the trivalent rare earths; the least soluble compounds which have been characterized are the alkali metal americyl(V) carbonates.⁶ The purification scheme which has been found most useful for separating americium from equal or smaller amounts of impurities is shown in Fig. 1. The various precipitates of Fig. 1 are usually easily separable by centrifugation, with the exception of the sulfide-insoluble impurities which most often require filtration for adequate separation. Separation of fluoride-insoluble impurities from solutions containing hexavalent americium must be carried out rapidly because of the high ($\sim 4\%$ per hour) self-reduction rate due to the alpha radiation from the isotope commonly used, Am^{241} .⁷ Exclusion of chloride ion, which reduces AmO_2^{++} , is likewise essential.

Although the purification scheme of Fig. 1 is sufficient for removal from americium of all commonly encountered impurities, it has not been found applicable to concentration of americium from very impure stocks. In such cases, much of the americium hydroxide will not dissolve in carbonate, and no satisfactory alternative procedure for

6. J. P. Nigon, R. A. Penneman, E. Staritzky, T. K. Keenan and L. B. Asprey, J. Phys. Chem. 58, 403 (1954).

7. L. B. Asprey and S. E. Stephenou, AECU-924 (1950).

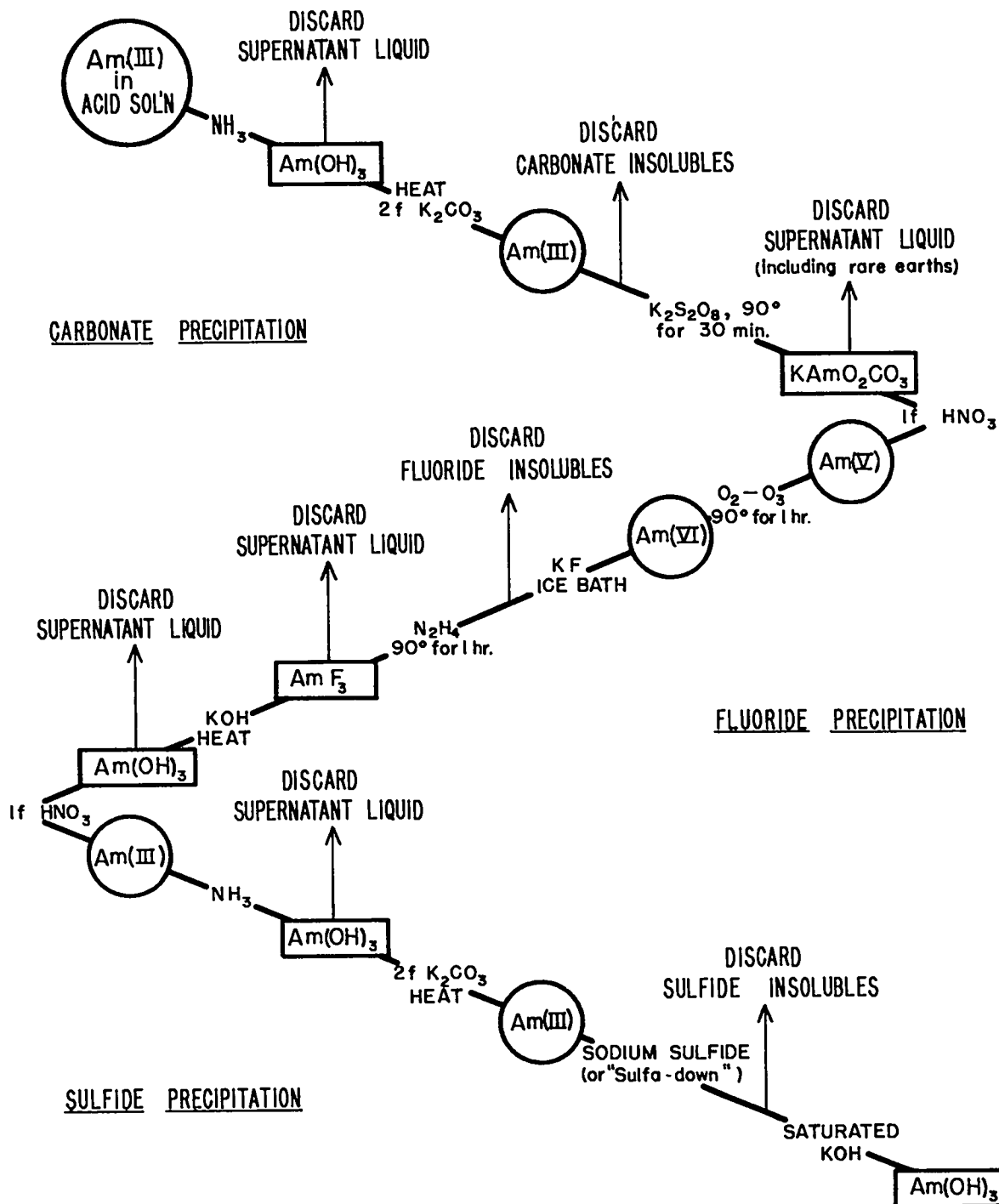


Fig. 1 A purification scheme for americium involving an oxidation-reduction cycle.

oxidation of the americium has been found. Electrolytic oxidation, for example, has been attempted with various impure stocks but has never proved useful. The nature and amounts of impurities for which the techniques of Fig. 1 are not effective have not been well established. In general, however, if leaching of an impure americium hydroxide precipitate with potassium carbonate has failed to bring the americium into solution, procedures completely different from those of Fig. 1 have been used to lower the ratio of impurities to americium.

Moderately large amounts of impurities such as calcium, iron, and nickel may be conveniently removed by oxalate precipitation, followed by metathesis to the hydroxide and finally by prolonged washing with ammonium nitrate (see Fig. 2). Washing the mixed hydroxides with 2f NH_4NO_3 removes calcium with only negligible americium loss and is continued until the wash gives a negative test for calcium. The voluminous hydroxide precipitate formed by direct addition of caustic or ammonia to crude stocks is difficult to filter and wash on a many-liter scale. The oxalate precipitates, conversely, are dense, crystalline, and easily filterable, but are not readily soluble in dilute acid (i.e., 1f HNO_3). Fortunately, the product of the metathesis of Fig. 2 (which may retain some oxalate as an integral part of the precipitate) remains both dense and easily filterable and dissolves readily in acid. Treatment with 0.1N base is continued, in practice, until a material completely soluble in dilute acid is obtained. Use of concentrated NaOH should be avoided. The scheme of Fig. 2 does not remove significant amounts of rare earth impurities.

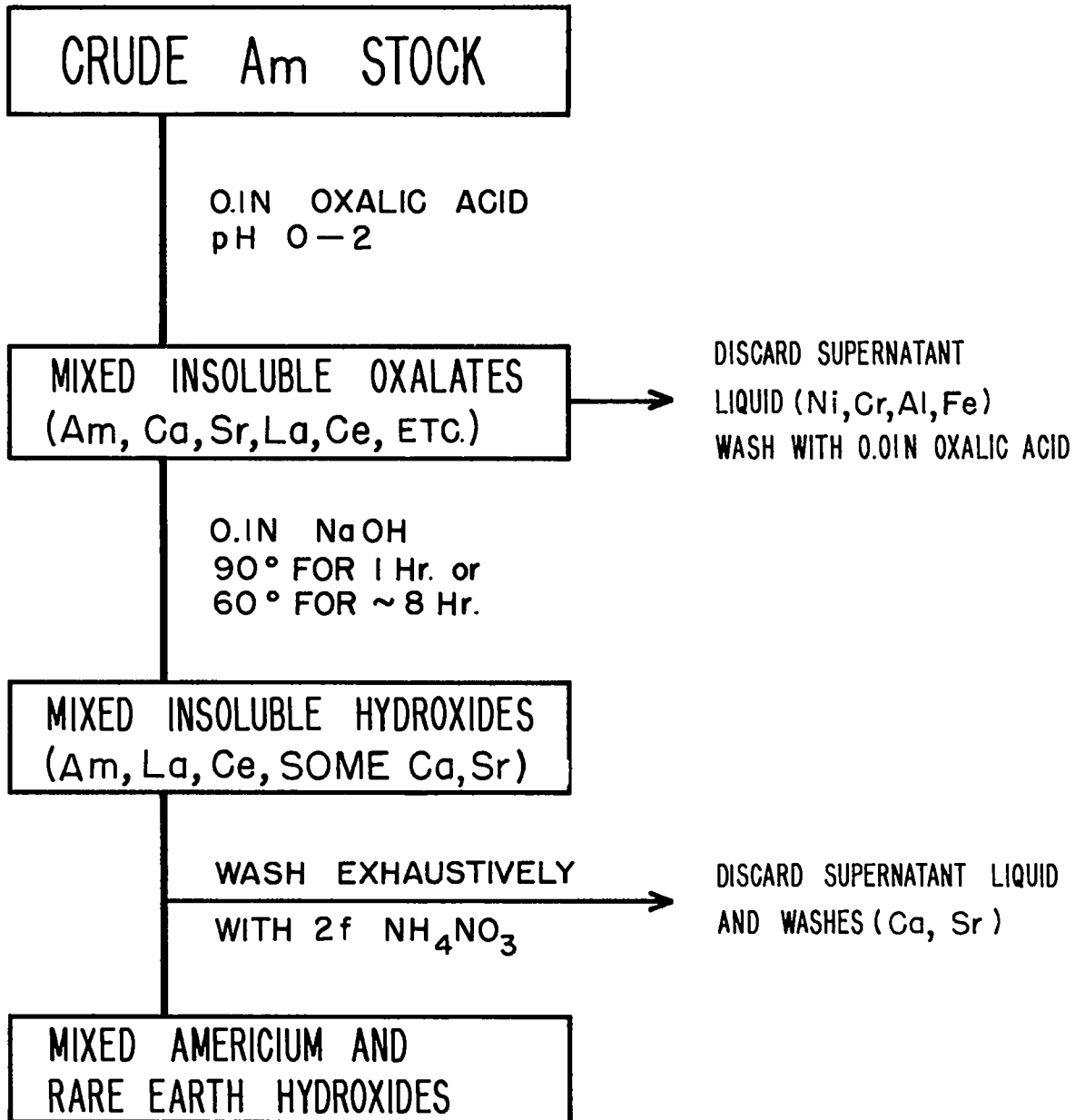


Fig. 2 Oxalate precipitation process for americium purification.

Homogeneous precipitation of mixed rare earths and americium oxalates using methyl or ethyl oxalate can, however, be used for separating americium from rare earths. For example, homogeneous oxalate precipitation of 95% of the americium from a lanthanum-americium mixture leaves about 50% of the lanthanum in solution.⁸ The elements Ca, Ba, Sr, Mg, Pb, Bi, Al, Fe, Cr, and Mn are all more efficiently removed by homogeneous oxalate precipitations than is lanthanum.

3. SOLVENT EXTRACTION METHODS

Americium extracts readily into tri-n-butyl phosphate (TBP) from concentrated nitrate solutions of low acid concentration ($\text{pH} < 1$). Solvent extraction with 30% TBP-70% Gulf BT* (by volume) has been used here routinely as the primary purification step for gross decontamination from the alkaline earths. Prior to use, the TBP solutions were scrubbed with sodium carbonate to remove hydrolysis products. Typically, feed solutions have been extracted batchwise, the americium has been stripped from the solvent with water, and the extraction has been repeated on the first aqueous concentrates after salting with aluminum nitrate. Acidity and salt concentration have been adjusted on the basis of small-scale experiments to give americium extraction coefficients, E (organic/aqueous), of 6 to 10. Under the conditions used, little or no separation

*A kerosene type hydrocarbon sold by Gulf Refining Company.

8. J. A. Hermann, AECD-3637 (1953).

from rare earths was achieved.

Walsh⁹ has recently measured the distribution of americium between nitrate solutions and TBP-Gulf BT mixtures as a function of the concentrations of sodium nitrate, nitric acid, and TBP. He has also observed that at fixed stoichiometric concentration of nitrate ion, the effectiveness of sodium nitrate, calcium nitrate, and aluminum nitrate as salting agents increase strikingly in the order given (see Table I).

TABLE I EFFECTIVENESS OF SALTING AGENTS*

Salt	Concentration, M	Am molarity ratio (33% TBP/aqueous solution)
NaNO ₃	5	3
Ca(NO ₃) ₂	2.5	30
Al(NO ₃) ₃	1.67	100

*Based on data supplied by K. A. Walsh.

Suttle and Poskanzer¹⁰ have reported measurements of the distribution of nitric acid, calcium nitrate, and lanthanum nitrate between 33% TBP-67% n-hexane and aqueous solutions containing all three of these components. The extraction coefficient, E, for lanthanum decreases sharply with increasing acid concentration, but the ratio of the extrac-

9. K. A. Walsh, Paper 270, Nuclear Engineering and Science Congress, Cleveland, 1955.

10. J. F. Suttle and A. Poskanzer, LA report (in preparation).

tion coefficient for lanthanum to that for calcium decreases only slowly with increasing acid. In particular, at 0.1f nitric acid and 3.2f calcium nitrate, E_{La} equals 25 and E_{Ca} equals 0.016.

Americium may be separated quantitatively from plutonium by the extraction of plutonium(IV) cupferrate using chloroform.¹¹ Preliminary tests of extraction of >0.004f americium using thenoyltrifluoroacetone as the chelating agent have resulted in formation of a copious precipitate, presumably a radiation-induced decomposition product of the TTA.

4. ION EXCHANGE METHODS

One of the first aspects of the chemistry of americium to be studied was its behavior in systems involving cation exchangers and ammonium citrate.¹² Since that time the use of a variety of eluants in addition to ammonium citrate has been studied, chiefly for separating tracer amounts of americium from similar amounts of the rare earths and curium.^{13,14} With all the organic acids studied, the americium is eluted in the midst of the rare earths at about the same position as promethium.

11. J. P. Nigon and R. A. Penneman, Report AECU-1006.

12. S. G. Thompson, L. O. Morgan, R. A. James, and I. Perlman, Paper 19.1 in Transuranium Elements, Seaborg, Katz, and Manning, editors, Div. IV, Vol. 14B, Book II, National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, 1949.

13. L. Wish, E. C. Freiling, L. R. Bunney, J. Am. Chem. Soc. 76, 3444 (1954).

14. R. M. Diamond, K. Street, and G. T. Seaborg, J. Am. Chem. Soc. 76, 1461 (1954).

With 12*M* hydrochloric acid as eluant, however, americium is eluted before even the heaviest of the rare earths.¹⁴

The behavior of americium in systems involving anion exchangers has received considerably less attention. W. W. T. Crane¹⁵ has reported that americium is much more readily extracted into anion exchanger from saturated lithium chloride than is lanthanum. This method has been used here for the separation of 1 gram of americium from 100 grams of lanthanum and smaller amounts of other impurities. A very satisfactory purification was obtained, but neutron tolerance was exceeded many times as a result of the reaction of alpha particles with lithium. Thus, the method cannot be recommended for use with gram amounts of Am²⁴¹. Floating of the anion exchanger in the denser lithium chloride solution was an added difficulty.

The methods referred to and, in fact, all the ion-exchanger techniques for americium purification previously reported in the literature have employed the method of column operation known as elution analysis. An alternative method, known as displacement analysis, has been found by Spedding, Powell, and co-workers to be superior for separation of kilogram quantities of rare earths.^{3,16} Since we have used both methods, a brief discussion of the advantages and limitations of each will be given before the particular processes used here are described.

15. W. W. T. Crane, private communication; also see K. A. Kraus, F. Nelson, F. B. Clough, and R. C. Carlston, *J. Am. Chem. Soc.* 77, 1391 (1955).

16. F. H. Spedding and J. E. Powell, Iowa State College Report ISC-349.

In both methods, the ions to be separated (M_1 and M_2) are first absorbed in a band at the top of a column of granular ion exchange resin. In elution analysis, an eluant is then passed through to move ions M_1 and M_2 down the column, but at different average rates. For the case of linear absorption isotherms, the rates of movement of the concentration maxima for M_1 and M_2 are constant (but different), so that the volumes of effluent collected at the two points of maximum concentration in the effluent are each simply proportional to the volume of ion exchanger used in the column. The fraction of effluent in which a given level of cross contamination occurs, however, is inversely proportional to the number of "theoretical plates".¹⁷ Hence, at constant temperature, flow rate, column diameter, and resin particle size, the volume of cross-contaminated effluent will be inversely proportional to the length of the column used. If moderately large amounts of material are to be separated, so that absorption isotherms are no longer linear, the distributions of the ions on the column will be skewed, and the amount of effluent cross-contamination increased. A high ratio of ion exchanger to absorbate will ordinarily be required for difficult separations, and the degree of separation may be increased by lengthening the column.

Quite different considerations apply in the design of ion exchanger processes operating under the conditions of displacement analysis. For elution analysis, the initial cationic form (B) of the organic cation

¹⁷. W. Mayer and E. R. Tompkins, J. Am. Chem. Soc. 69, 2866 (1947).

exchanger is normally the same as the cation (A) of the eluant, e.g., NH_4^+ -form resin and elution with a solution of an ammonium salt. To obtain displacement analysis, A and B must be different, and chosen so that, in the presence of the eluant anion, the affinities for the resin of ions A, M_1 and M_2 are all greater than that of ion B. For example, if the eluant is ammonium citrate, and M_1 and M_2 represent lanthanum and americium, then the conditions for displacement analysis are fulfilled if B is hydrogen ion, for in the presence of citrate, the ammonium, lanthanum, and americium ions readily displace hydrogen ions. The distributions of ions M_1 and M_2 no longer become Gaussian, nor does each substance become continually more and more spread out as it is eluted down the column. Instead, each substance forms, after a time, an equilibrium band of constant length which is calculable, in principle, from knowledge of the various ionic equilibria involved. Further, the band containing ion M_1 will be distinct from, but immediately adjacent to, that for ion M_2 . There is no point in increasing the length of the column beyond a certain characteristic minimum, because after the bands are fully developed they will move unchanged down the column in head-to-tail fashion with a region of overlap determined, in part, by tilting and irregularities of the band fronts, but otherwise invariant. The effect of this region of overlap may be minimized by using sufficiently large amounts of material and sufficiently narrow columns so that the length of each band is great compared to the length of the overlap region.

4.1 Ammonium Citrate-Cation Exchanger Process

The procedures developed by Spedding and Powell^{3,16} for separation of adjacent rare earths using high pH citrate elution from sulfonated polystyrene cation exchanger have been adapted to the separation of about 4.5 grams of americium from the major part of about a kilogram of the lighter rare earths. Considerable difficulty was encountered at first with precipitation in the resin bed and, as a result, the overall yield of purified material was held to about 80%. Operating conditions which avoid this trouble have now been discovered and are outlined in Section 4.1.4c.

4.1.1 Feed Composition and Prior Treatment

The americium-rich feed was originally contained in about 80 liters of nitrate slurry containing considerable amounts of calcium, magnesium, lanthanum, iron, sodium, aluminum, strontium, lead, and bismuth. Gross decontamination was obtained by solvent extraction with tributyl phosphate as described in Section 3. Mixed americium and rare earth oxalates were then precipitated, metathesized to the hydroxides, and washed with NH_4NO_3 as hydroxide sequestering agent (see Fig. 2). The resulting hydroxide was dissolved in hydrochloric acid and diluted to give 4 liters of solution about 0.2f in HCl, 0.0045f in Am, and with total normality of 4.2. The major impurities were lanthanum (~800 grams) and cerium (~50 grams). Subsequent to the first production run, the remaining stock was passed through chloride-form anion resin to remove unknown

In the displacement analysis of multicomponent systems, separation is thus necessarily incomplete between those substances which form adjacent bands, but can be complete between those forming non-adjacent bands. Essentially no separation is to be expected with tracer amounts (with which elution analysis operates most smoothly). The linear rate of movement of the band front during displacement analysis is simply equal to the flow of eluant (in equivalents per unit time) divided by the resin capacity (in equivalents per unit length of column). The time of appearance of M_1 in the effluent can, as a result, be calculated very easily and precisely.

Displacement analysis is often the more efficient method for handling large amounts of materials, particularly for separation of two or more similar components, each of which is considered valuable. For isolation of americium from kilogram amounts of impurities, the most efficient ion-exchanger process would involve the highly selective extraction of americium into the exchanger, with the great bulk of impurities passing immediately through the column. The americium could then be separated from the remaining lower levels of impurities through elution analysis, and the amount of resin required to maintain a low percentage loading of the column would not be oppressive. However, if the only convenient separation is one in which bulk impurities are absorbed along with the americium, displacement analysis may prove considerably more efficient than elution analysis.

components which caused precipitation upon dilution of this stock with water.

4.1.2 Materials

The ion exchanger used was Dowex-50, a sulfonated styrene-divinylbenzene copolymer. The nominal divinylbenzene content was given as 8% and the particle size as 60 to 100 mesh. The resin was water graded with a water to resin ratio $> 5/1$ until the settling rate was 7 to 8 inches per minute. About 15% of the graded resin was coarser than 60 mesh. The resin capacity was determined to be 2.0 meq./ml. of packed bed volume.

Analytical reagent grade chemicals were used throughout.

4.1.3 Apparatus

The major part of the apparatus consisted of one 6-inch and one 2-inch inside diameter Pyrex pipe, each 5 feet in length. These were mounted vertically, and contained water-settled Dowex-50 resin (50 to 100 mesh) to a height of 70 cm. in the 6-inch column and 100 cm. in the 2-inch column. Two 60-gallon stainless steel tanks fed solution to the column through 1/4-inch stainless steel lines. Two 60-gallon stainless steel floor tanks collected the eluant from the column through 5/16-inch Tygon tubing. The solution was readjusted to pH 8 in these last two tanks and then vacuum lifted to the feed tanks directly overhead. Solenoid valves allowed control of the lifting operation from the floor. A system of valves allowed use of any combination of the feed and floor

tanks with each column, and a rotameter indicated the flow rate of the feed solution.

The americium stock was diluted in a hood, vacuum-lifted to an 18-liter bottle, and siphoned directly onto the 6-inch column. The bottle and the two columns with connecting valves were enclosed and the enclosure connected to the house air duct to prevent contamination of the laboratory air. A view of the columns is shown in Fig. 3. After the first run, solutions were introduced into the 6-inch column through a closed end, 1/2-inch stainless steel tube with eight 40-mil holes spaced around the tube circumference. This "shower head" avoided cavitation of the resin bed, and produced very uniform flow patterns.

4.1.4 Procedure

a. Preparation of Columns

Resin was slurried into each column, converted to the ammonium form with 5% ammonium citrate to remove impurities, and reconverted to the hydrogen form with 2% sulfuric acid. After backwashing with water, the column was filled with 0.2f hydrochloric acid.

b. Loading of 6-Inch Column

About 1/3 of the stock was taken for each of three production runs. After filtration and dilution with 0.2f HCl to 15 liters, the aliquot of stock was siphoned onto the 6-inch column at a linear flow rate of $2 \text{ cm.}^3/\text{cm.}^2\text{-min.}$ (i.e., 2 cm./min.), and water was subsequently passed through until the effluent gave a negative test for chloride.

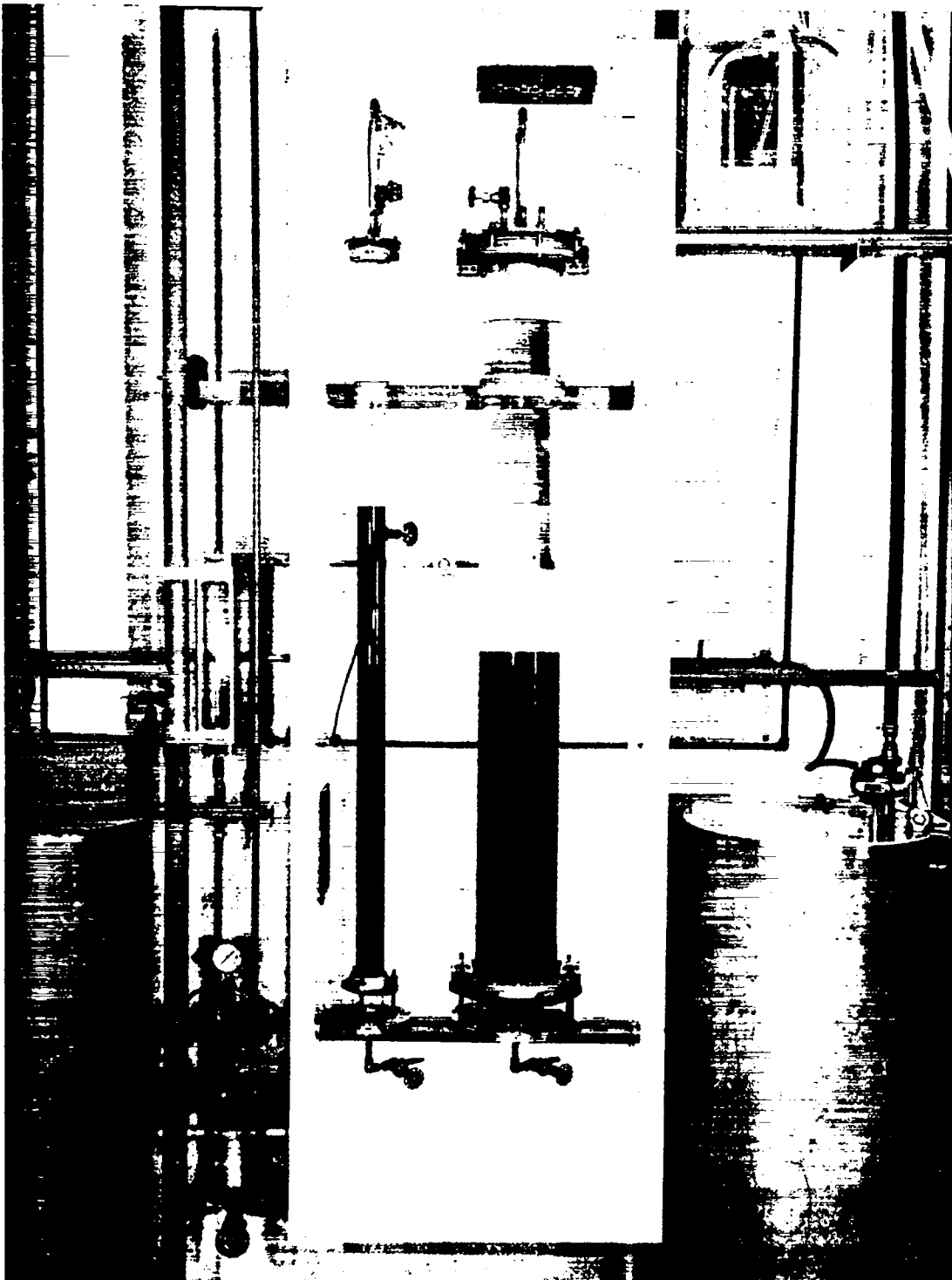


Fig. 3 Ion exchange columns.

c. Elution of Americium

One-tenth percent citric acid, containing 0.2% phenol as preservative and adjusted to pH 8.0 with ammonium hydroxide, was used as eluant. Due to the large volume of eluant required (~100 liters per liter resin), the citrate effluent was readjusted to pH 8 and recycled until the americium appeared in the effluent. In the first run a precipitate formed near the top of the 6-inch column during the elution with ammonium citrate, and in the second near the top of the 2-inch column (see Section 4.1.5). This phenomenon was avoided in the third run by careful choice of flow rates. The effective head (12 feet of water) was insufficient to give desirably high flow rates when the 6-inch and 2-inch columns were coupled. Therefore, partially evacuated 44-liter carboys were connected to the base of the 2-inch column and used as receiving vessels. By this technique high flow rates were achieved during the passage of americium from the 6-inch column onto the 2-inch column. In this final run, the eluant flow rate was maintained at about 6.5 cm./min. until the americium band as followed with a gamma survey meter was about 10 cm. from the bottom of the 6-inch column. The flow rate was then cut to 2.8 cm./min. to sharpen the bands. When americium began to appear in the effluent from the 6-inch column, the flow was diverted through the 2-inch column and maintained at 3 gallons/hour (or 1 cm./min. for the 6-inch and 9 cm./min. for the 2-inch column) until the americium band reached a point about 10 cm. above the bottom of the smaller column. The flow was then cut to 1 gallon/hour and finally to 0.5 gallon/hour

as the americium appeared in the final effluent.

4.1.5 Precipitate Formation in the Columns

Spedding and Powell³ have found that insoluble rare earth complexes, identified as $\text{RCit}\cdot 2\text{H}_2\text{O}$, may form with eluant pH above 6.0 and initial loads in excess of about 1.2 grams of rare earth per square centimeter cross-section of resin bed. However, with initial linear flow rates of 5 to 8 cm./min. they report loads of 40 grams/cm.² of the heavier rare earths could be eluted without precipitation.

In no case did we observe a visible precipitate, but in the first two runs a portion of the activity remained behind in a stationary band, while the remaining activity moved down the column in normal fashion. Although initial flow rates above 5 cm./min. were used in both cases, the marked irregularity of the band front (which is visible) in the first run may have indicated irregular flow patterns, and hence regions in the column of much slower flow. This was corrected before the remaining runs by use of the "shower head" described in Section 4.1.3 for introduction of solution onto the 6-inch column. The precipitation at the top of the 2-inch column during the second run is less easily rationalized, but may have resulted from the presence of about a liter of 0.1% citric acid in the resin-free space below the larger column at the time the americium first came off this column. At any rate, the difficulty was avoided by tripling the flow rate during the movement of the americium from one column to the other.

The success of high flow rates for avoiding precipitation is probably

due to the slowness of displacement of lanthanum ions in the resin phase by ammonium ions. Passage of ammonium citrate through a sufficiently long column of lanthanum-form resin will, of course, tend toward replacement of all the ammonium ions in solution by an equivalent number of lanthanum ions. Evidently, starting with 0.1% ammonium citrate, pH 8, the lanthanum will precipitate somewhere between lanthanum to citrate ratios of 1/1 and 1/2 (the latter being the ratio in the solution phase of the equilibrium band).³ The critical precipitation ratio may be considered exceeded only after passage of the eluant through a fixed number of "theoretical plates" of resin in the rare earth form. Increasing the flow rate acts to boost the height per theoretical plate.

4.1.6 Results

Americium-rich fractions from each run were combined and found to contain ~2.5 grams of americium, about 10 grams of cerium, and smaller amounts of other impurities. Another gram of americium was collected in other solutions, including some of high lanthanum content obtained during the slow and difficult dissolution of the column precipitates. A total of about 100 grams of lanthanum and cerium remained in this fraction.

Figures 4 and 5 are drawn from the results of the third run and show the contaminating elements in the americium-rich effluent, the rate of band movement, and a profile obtained by gamma survey of the americium on the 2-inch column. The two richest fractions collected (total volume = 5.3 liters) contained 97% of the americium. Since the cerium band was

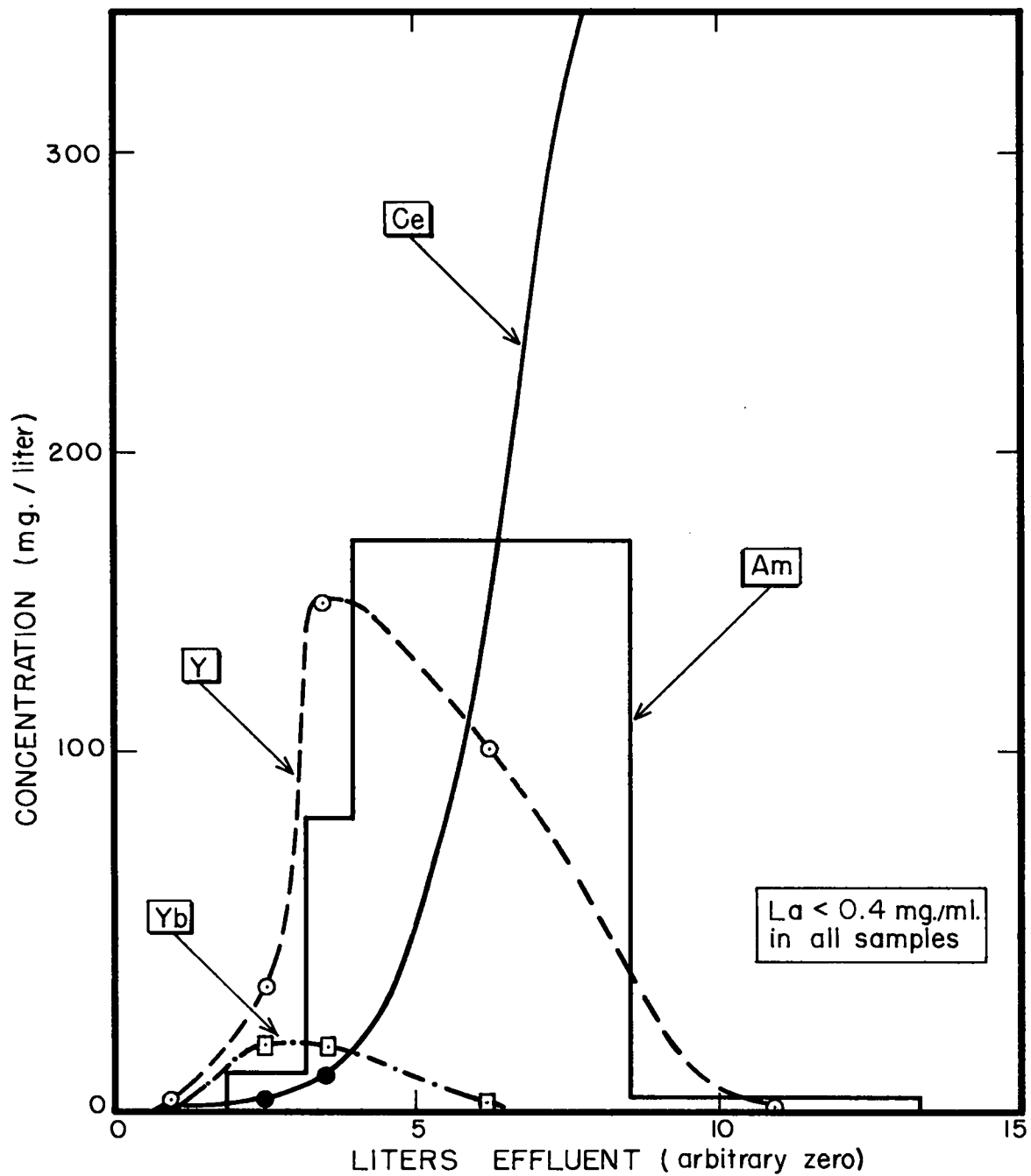


Fig. 4 Elution of americium and contaminating elements using 0.1% ammonium citrate, pH 8.0.

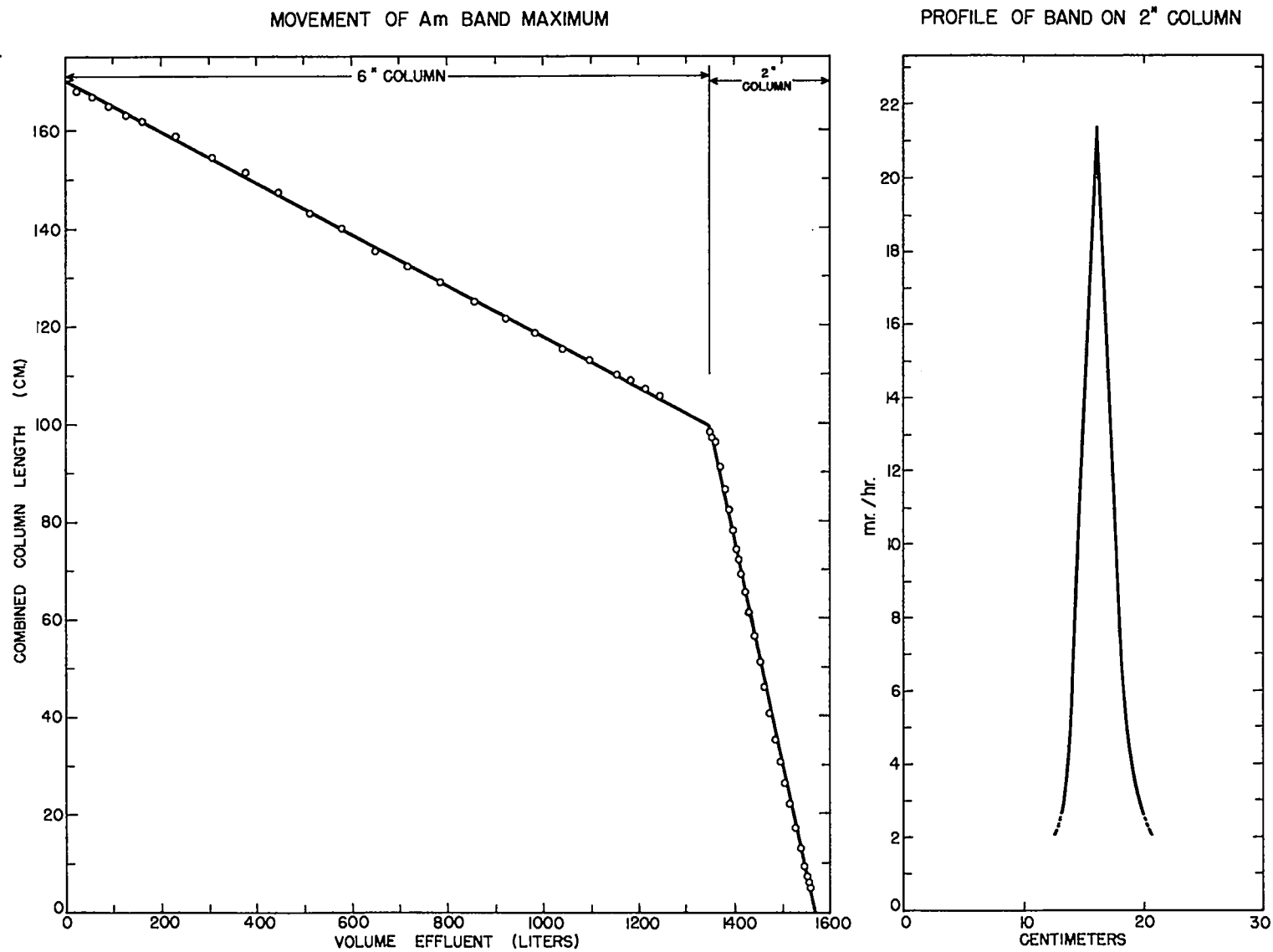


Fig. 5 Citrate elution of americium using Dowex-50 resin with particle size of 60 to 100 mesh and 0.1% ammonium citrate, pH 8.0, as the eluant.

interposed between those of americium and lanthanum, complete separation from lanthanum was obtained.

These results demonstrate that even at very high initial flow rates (9 cm./min.), the elution of americium proceeds in a normal fashion, and that reduction of the flow rate very shortly before the americium appears in the effluent is sufficient to sharpen the band and permit elution of the americium in a small volume.

4.2 Ammonium Thiocyanate-Anion Exchanger Process

A large and rapidly growing number of processes that utilize anion exchangers for the separation of the metallic elements have been developed. In the presence of sufficiently powerful complexing agents, even an element with as little tendency to form complexes as sodium can be induced to form species absorbable on anion exchangers.¹⁸ Further, simply through variations in concentration, an impressive variety of separations may be achieved using hydrochloric acid, for example, as complexing agent.⁴

Even in concentrated hydrochloric acid, neither the rare earths nor americium are appreciably absorbed by anion exchangers. Saturated lithium chloride, as noted in the first part of this section, will cause the selective absorption of americium, though its application is restricted because of the hazard of neutron emission to small amounts of Am^{241} . Use of substances as eluants having a somewhat greater tendency

18. F. Nelson, J. Am. Chem. Soc. 77, 813 (1955).

to complex americium than that of chloride ion is thus indicated. For separation of macro amounts on anion exchanger columns, the necessity of moderately high solubility imposes an important restriction upon the choice of reagents. (We have, for example, avoided use of citrate on this basis.)

Batch equilibration experiments have indicated, though by no means conclusively, that americium is not strongly absorbed by strong base anion exchangers in the presence of sulfuric acid, ammonium acetate, or ammonium iodide. On the other hand, americium is strongly absorbed by thiocyanate-form anion exchanger in the presence of ammonium thiocyanate. Since this phase of our work was undertaken, we have learned that absorption of americium by thiocyanate resin was earlier noted by Diamond¹⁹ and has recently been applied to the separation of tracer amounts of americium by Barnes and Sackett.²⁰

We have treated the americium concentrates from the citrate-cation exchanger process described in Section 4.1 by a process involving the selective extraction of americium into thiocyanate-form anion exchanger from 4.9f ammonium thiocyanate. Essentially complete separation from rare earths was obtained, and, with suitable modifications, the process appears applicable to the concentration of americium from a wide variety of crudes.

19. R. M. Diamond, K. Street, Jr., and G. T. Seaborg, UCRL-1434 (1951).

20. J. W. Barnes and W. M. Sackett, private communication.

4.2.1 Materials

A strong base anion exchanger (Bio-Rad AG 1 X 10, 100 to 200 mesh) was water washed with repeated decantation to remove fines, converted to the thiocyanate form by treatment with a 20-fold stoichiometric excess of 2f ammonium thiocyanate, and stored under water.* The cation exchanger previously used (see Section 4.1.2) was treated with ammonium thiocyanate, or, more efficiently, with ammonium fluoride and then ammonium thiocyanate until the effluent no longer showed the red color of iron thiocyanate. It was then washed thoroughly with water and used in the ammonium form. Analytical reagent grade chemicals were employed throughout.

4.2.2 Distribution Experiments

The distribution of americium and lanthanum between aqueous ammonium thiocyanate solutions and cation or anion exchangers was measured by a batchwise equilibration technique. Known amounts of americium and lanthanum tracer were added to about 1 ml. of resin and 2.5 ml. of ammonium thiocyanate solution and equilibrated overnight at room temperature ($25 \pm 2^\circ\text{C}$). Final concentrations in the aqueous phase were determined by radiochemical assay. Evaporation of the ammonium thiocyanate deposits from the sample plates by careful heating in an induction heater was found in separate experiments to cause less than 2% loss in

* We now use 0.01f H_2SO_4 to regenerate the anion columns with high efficiency; subsequent treatment with 5f NH_4SCN reconverts the column to SCN^- form very easily.

total activity. Quantities of resin were measured as milliliters of settled bed volume.

4.2.3 Feed Composition and Prior Treatment

Forty-three liters of stock containing 2.43 grams of americium, about 5 to 6 times as much cerium, and equal amounts of lanthanum, calcium, and iron were obtained from americium-rich fractions of the effluent from the citrate columns. Since a dark, americium-free precipitate had formed in these fractions and more slowly formed after filtration, the combined fractions were filtered and then passed through a column containing chloride-form anion exchanger, which proved sufficient to remove the unknown precipitate-forming components. One-tenth of this treated stock was used for a pilot run, during which sufficient data were collected to determine the elution curves of the rare earths and americium. Subsequent purification of the remaining stock gave equally satisfactory overall results.

4.2.4 Apparatus

The apparatus consisted essentially of a 25 cm. long column of ammonium-form cation exchanger containing 5.8 ml. of resin per liter of stock used, and a 40 cm. long column of thiocyanate-form anion exchanger containing 35 ml. of resin per liter of stock used. The resin beds were supported by glass frits, and the glass columns were wrapped with sheet lead to absorb the gamma radiation from the americium. The apparatus was contained in a glove box.

4.2.5 Procedure

The process used involved six steps:

1. Absorption of the americium and impurities in cation exchanger.
2. Water wash of the cation exchanger to remove unwanted anions.
3. Elution of the americium and impurities from the cation exchanger with 4.9f ammonium thiocyanate.
4. Absorption of americium and some impurities in anion exchanger from the concentrated effluent of the previous step.
5. Elution with 4.9f ammonium thiocyanate to remove the weakly absorbed rare earths.
6. Stripping of the americium from the column with water or 1f HCl.

The linear flow rate through the cation exchanger column was maintained at 10 to 15 $\text{cm}^3/\text{cm}^2\text{-min.}$ (steps 1 and 2) and the rate through the anion exchanger column at 1 $\text{cm}^3/\text{cm}^2\text{-min.}$ The effluent from the cation exchanger of step 3 was fed directly through the anion exchanger column. The process was completed without interruption to avoid radiation-induced bubble formation in the columns and decomposition of thiocyanate. Stripping of the americium was begun when the americium concentration in the effluent reached about 3 mg./liter.

4.2.6 Results and Discussion

Results of the distribution experiments are shown in Fig. 6. Although the scatter of the experimental points is rather large, a striking difference between the absorption by anion exchangers of lanthanum and americium is evident. This difference seems even more striking in view of the rather similar behavior of these two elements in regard to their absorption by cation exchangers in the presence of ammonium thiocyanate.

Figure 7 presents data obtained during the pilot run. The combined rare earth concentrations were determined by comparison of volumes of oxalate precipitates with appropriate standards. About 99% of the americium was obtained with rare earth contamination (principally as ytterbium) reduced, as estimated from spectrographic analysis, to less than 1.5%. Some iron, nickel, aluminum, and manganese were stripped from the column along with the americium. The americium was recovered by precipitation of the hydroxide with ammonia; the only non-rare earth impurity detected in this final product was iron.

Even the heavier rare earths (i.e., ytterbium) were found to reach a concentration maximum in the effluent well before the start of the americium stripping operation. Further, the order of elution of the rare earths present in detectable amounts (La, Ce, Pr, Nd, Yb) was that of increasing atomic number, with yttrium falling between neodymium and ytterbium.

The americium on the anion exchanger column (as followed with a

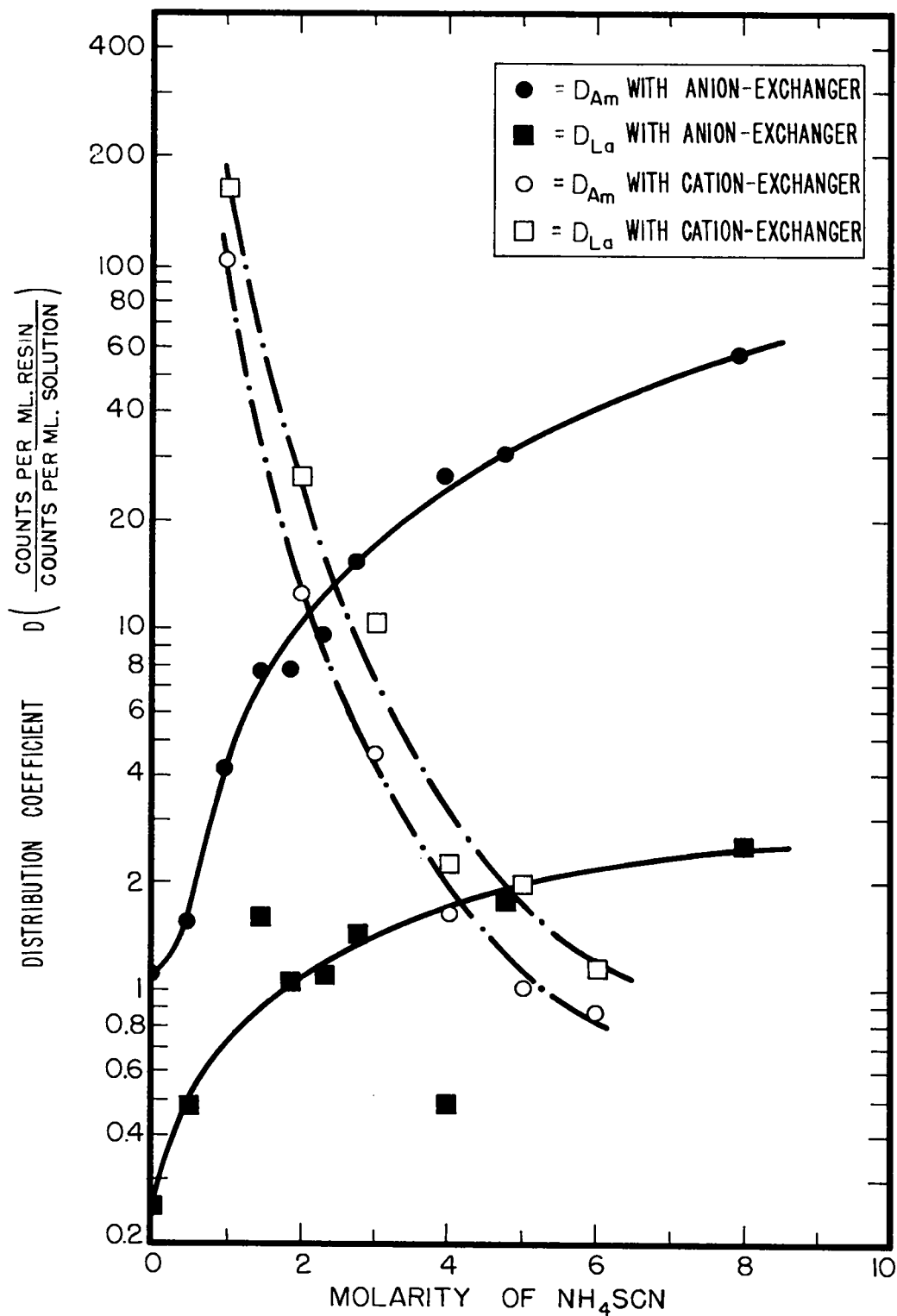


Fig. 6 Ion-exchange absorption of La(III) and Am(III) from aqueous ammonium thiocyanate.

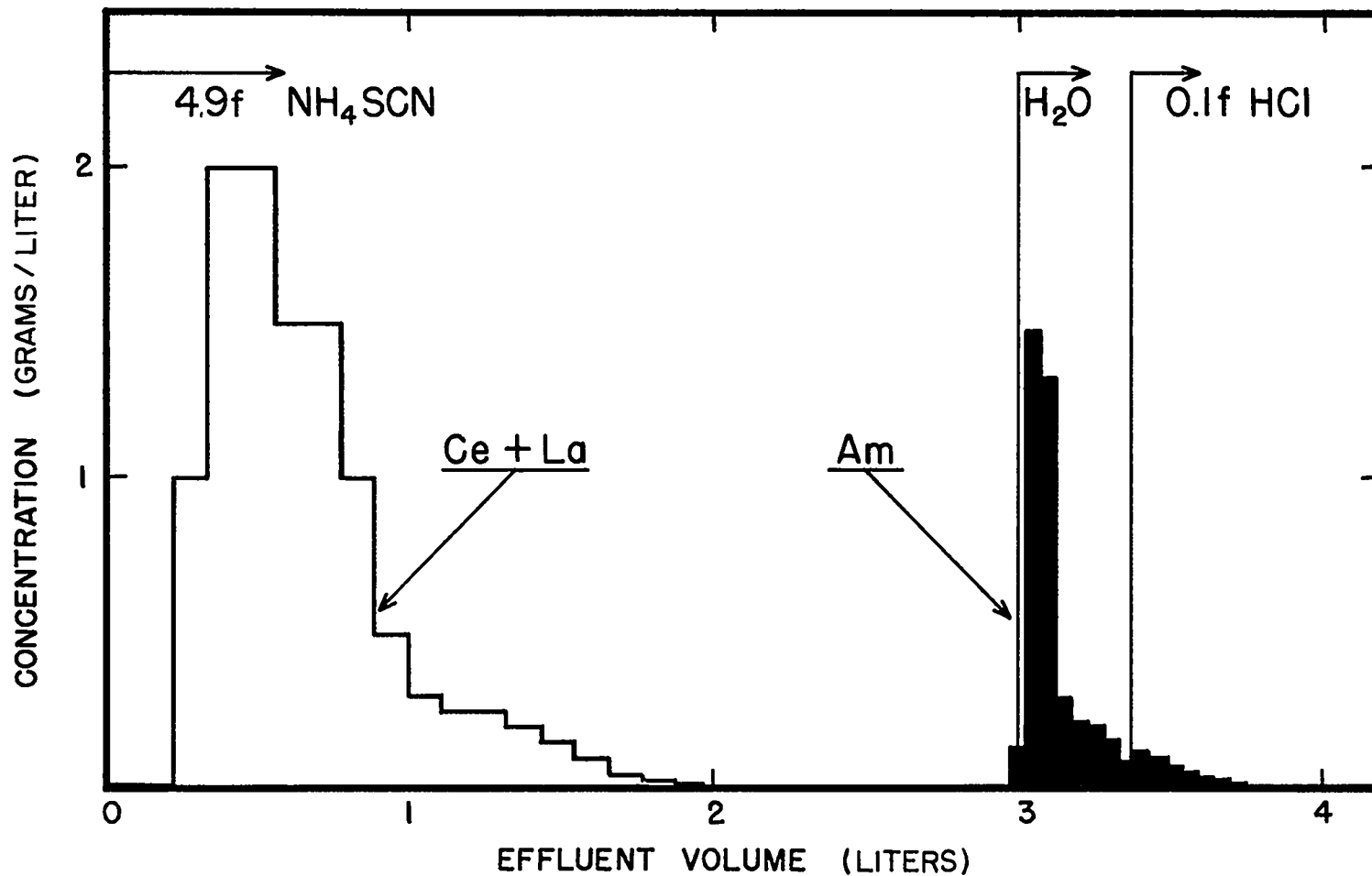


Fig. 7 Separation of Am(III) from Ce(III) + La(III) with thiocyanate anion exchanger. (38 x 2.15 cm. column, Bio Rad AG-1X10, SCN⁻ form)

gamma survey meter) gradually spread out during the elution with ammonium thiocyanate and was distributed at the start of the stripping operation in a symmetrical fashion all along the length of the column. The rate of movement of the americium band maximum was 7.3 cm./liter 4.9f NH_4SCN , which corresponds to a volume distribution coefficient, D , of 38. If, for comparison with a simple theory, we assume that this column followed the plate model of Mayer and Tompkins,¹⁷ then for volume distribution coefficients $D \gg 1$

$$t = P^{1/2}(V/DV_R - 1) \quad (1)$$

where t is the number of σ units (standard deviations) corresponding to the fraction eluted between V and DV_R , V is the volume of effluent that has passed through the column, V_R is the bed volume of the resin, and P is the number of theoretical plates. Since 0.74% of the americium was eluted by the first 2970 ml. of 4.9f ammonium thiocyanate, we estimate from Eq. 1 a height equivalent to a theoretical plate (HETP) of about 1.3 cm. This high value indicates that with a different choice of operating conditions, e.g., lower loading or lower flow rates, even less overlap of the rare earth and americium peaks is obtainable. Equation 1 as used here provides a very convenient check on the efficiency of ion exchanger separations operated under the conditions of elution analysis.

The concentration step involving absorption of the americium and impurities in cation exchanger was introduced for two purposes: (1) to eliminate the possibility of interference with the separation from the

presence of anions other than thiocyanate and thiocyanate complexes of metals, and (2) to reduce the volume of anion exchanger needed to compensate for the elution which, of course, proceeds during the absorption of the americium. If, for example, the initial stock had been made 5f in ammonium thiocyanate directly, an amount of anion exchanger considerably larger than the 1.5 liters actually used would have been required merely to prevent the appearance of americium in the effluent before all of the stock had been passed through the column.

The process described in this section appears outstanding for the separation of americium from rare earths, and, presumably, from other elements which show little absorption by anion exchangers in the presence of ammonium thiocyanate. In this connection, it is worth noting that we have found calcium to be essentially non-absorbed in this system; in particular, using the column technique described by Kraus and co-workers,⁴ we have found the volume distribution coefficient, D, for calcium to be 0.8 in both 3f and 6f ammonium thiocyanate.

We have recently completed processing by the procedure outlined in Section 4.2.5 an additional 200 liters of impure stock containing 1.7 grams of americium and about 260 grams of rare earths. Results obtained in these and earlier runs are summarized in Table II.

TABLE II DATA FROM AMMONIUM THIOCYANATE - ANION EXCHANGER PROCESS

Initial Am (grams)	Initial rare earth (grams)	Am loss (grams)	Final rare earth impurity (gms./gm. Am)	Volume anion exchanger (liters)
0.24	1.3	0.004	<0.015	0.15
2.19	12	0.002	<0.015	1.4
0.20	35	0.002	0.42	1.4
0.28	100	0.001	21.0	1.4
0.50	130	0.003	0.19	2.3
0.69	9	0.003	<0.01	2.3

With rare earth to americium ratios of about 300/1, about 20 ml. of anion exchanger appears to be required for each gram of rare earth in order to achieve essentially complete separation. Only 94% of the rare earth was removed in the fourth run shown in Table II during which 15.6 ml. of anion exchanger was used per gram of rare earth, but 99.3% was removed in the fifth run with 17.7 ml. of exchanger per gram of rare earth. These ratios correspond to roughly 5 milliequivalents of anion exchanger for each millimole of rare earth.