NAS-NS 3010

National Academy of Sciences

National Research Council

NUCLEAR SCIENCE SERIES

The Radiochemistry of Barium, Calcium, and Strontium

U.S. Atomic Energy Commission

COMMITTEE ON NUCLEAR SCIENCE

L. F. CURTISS, *Chairman*
National Bureau of Standards

ROBLEY D. EVANS, *Vice Chairman*
Massachusetts Institute of Technology

J. A. DeJUREN, *Secretary*
Westinghouse Electric Corporation

H. J. CURTIS
Brookhaven National Laboratory

SAMUEL EPSTEIN
California Institute of Technology

HERBERT GOLDSTEIN
Nuclear Development Corporation of America

H. J. GOMBERG
University of Michigan

E. D. KLEMA
Northwestern University

ROBERT L. PLATZMAN
Argonne National Laboratory

G. G. MANOV
Tracerlab, Inc.

W. WAYNE MEINKE
University of Michigan

A. H. SNELL
Oak Ridge National Laboratory

E. A. UEHLING
University of Washington

D. M. VAN PATTER
Bartol Research Foundation

LIAISON MEMBERS

PAUL C. AEBERSOLD
Atomic Energy Commission

J. HOWARD McMILLEN
National Science Foundation

W. D. URRY
U. S. Air Force

WILLIAM E. WRIGHT
Office of Naval Research

SUBCOMMITTEE ON RADIOCHEMISTRY

W. WAYNE MEINKE, *Chairman*
University of Michigan

NATHAN BALLOU
Navy Radiological Defense Laboratory

GREGORY R. CHOPPIN
Florida State University

GEORGE A. COWAN
Los Alamos Scientific Laboratory

ARTHUR W. FAIRHALL
University of Washington

HARMON FINSTON
Brookhaven National Laboratory

EARL HYDE
University of California (Berkeley)

HAROLD KIRBY
Mound Laboratory

GEORGE LEDDICOTTE
Oak Ridge National Laboratory

ELLIS P. STEINBERG
Argonne National Laboratory

PETER C. STEVENSON
University of California (Livermore)

LEO YAFFE
McGill University

The Radiochemistry of Barium, Calcium, and Strontium

By D. N. SUNDERMAN
and
C. W. TOWNLEY

Battelle Memorial Institute
Columbus, Ohio

January 1960

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

Printed in USA. Price $1.25. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, the problems of stockpiling uncontaminated materials, the availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman

Subcommittee on Radiochemistry

CONTENTS

INTRODUCTION

This volume which deals with the radiochemistry of barium, calcium, and strontium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques; and finally, a collection of radiochemical procedures for the elements as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrent. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of barium, calcium, and strontium which might be included in a revised version of the monograph.

I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF BARIUM, CALCIUM, AND STRONTIUM

Pp. 259-269 in Vol. I and pp. 244-254 in Vol. II of "Analytical Chemistry", F. P. Treadwell, tr. and rev. by William T. Hall, John Wiley and Sons, Inc., New York, ninth edition, 1937.

Chapter 40, pp. 611-631 in "Applied Inorganic Analysis", W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, Wiley, New York, second edition, 1953.

Pp. 398-413 in "Prescott and Johnson's Qualitative Chemical Analysis", R. K. McAlpine and B. A. Soule, Van Nostrand, New York, 1933.

Chapter 19, pp. 845-867 in "Inorganic Chemistry", T. Moeller, John Wiley and Sons, Inc., New York, 1952.

Pp. 117-136, 205-217, and 899-902 in Vol. I of "Scott's Standard Methods of Chemical Analysis", N. H. Furman, Van Nostrand, New York, 1939.

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF BARIUM, CALCIUM, AND STRONTIUM

"Evaluation of Radiochemical Separation Procedures", Duane N. Sunderman and W. Wayne Meinke, Analytical Chemistry 29, 1578, November 1957.

"The Development and Evaluation of Radiochemical Separation Procedures for Barium, Calcium, Strontium, Silver, and Indium", Duane N. Sunderman, AECU-3159, February 1956.

III. TABLE OF ISOTOPES OF BARIUM, CALCIUM, AND STRONTIUM

Isotope	Half Life	Primary Radiations		Method of Preparation
		Type of Decay	Gamma Rays	
Ca^{38}	0.66 sec.	β^+	3.5 Mev	
Ca^{39}	1.0 sec.	β^+ 6.1 Mev	(none)	Ca^{40} + gamma rays
Ca^{40}	Stable - 96.97%			
Ca^{41}	1.1×10^5 yr.	EC (100%)	(none)	Ca^{40} + neutrons
Ca^{42}	Stable - 0.64%			
Ca^{43}	Stable - 0.145%			

III. TABLE (CONTINUED)

Isotope	Half Life	Primary Radiations: Type of Decay	Primary Radiations: Gamma Rays	Method of Preparation
Ca^{44}	Stable - 2.06%			
Ca^{45}	164 days	β^- 0.254 (100%)	(none)	Ca^{44} + neutrons
Ca^{46}	Stable - 0.0033%			
Ca^{47}	4.7 days	β^- 1.94 (17%) 0.66 (83%)	1.29 (71%) 0.81 (5%) 0.50 (5%)	Ca^{46} + neutrons
Ca^{48}	Stable - 0.185%			
Ca^{49}	8.8 min.	β^- 2.1 (89%) ~ 1.0 (11%)	3.07 (89%) 4.04 (10%) 4.7 (0.8%)	Ca^{48} + neutrons
Sr^{81}	29 min.	β^+		Rb^{85} (p, 5n)
Sr^{82}	25.5 days	EC		Rb^{85} (p, 4n)
Sr^{83}	34 hrs.	β^+ 1.15 EC	0.040 0.074 0.101 0.151 0.165	Daughter of Y^{83}
Sr^{84}	Stable - 0.56%			
Sr^{85m}	70 min.	IT (86%) EC (14%)	0.225 (85%) 0.150 (14%)	Sr^{84} + neutrons
Sr^{85}	64 days	EC (100%)	0.513 (100%)	Sr^{84} + neutrons
Sr^{86}	Stable - 9.86 %			
Sr^{87m}	2.9 hrs.	IT (100%)	0.388	Sr^{86} + neutrons
Sr^{87}	Stable - 7.02%			
Sr^{88}	Stable - 82.56%			
Sr^{89m}	~ 10 days	IT		
Sr^{89}	51 days	β^- 1.462 (99%)	0.913 (from Y^{89m}) 0.01%	Sr^{88} + neutrons, fission product
Sr^{90}	28 yrs.	β^- 0.545 (100%)	(none)	Fission product
Sr^{91}	9.7 hrs.	β^- 1.09 (33%) 1.36 (28%) 2.67 (28%)	0.551 (42%) ← (from Y^{91m}) 0.645 (11%) 0.748 (19%) 1.025 (22%)	Fission product
Sr^{92}	2.6 hrs.	β^- 0.55 (90%) 1.5 (10%)	1.37 (92%) 0.44 (4%) 0.23 (4%)	Fission product
Sr^{93}	8.2 min.	β^-		Fission product
Sr^{94}	1.3 min.	β^-		Fission product
Sr^{95}	~ 0.7 min.	β^-		Fission product
Sr^{97}	Short	β^-		Fission product

III. TABLE (CONTINUED)

Isotope	Half Life	Primary Radiations: Type of Decay	Primary Radiations: Gamma Rays	Method of Preparation
Ba^{126}	97 min.	EC	0.23 (75%) 0.70 (25%)	
Ba^{127}	12 min.	β^+		
Ba^{128}	2.4 days	EC	0.270	Cs^{133} (p, 6n)
Ba^{129}	2.45 hrs.	β^+ 1.6		Cs^{133} (p, 5n)
Ba^{130}	Stable - 0.13%			
Ba^{131}	11.5 days	EC (100%)	0.496 (42%) 0.122 (23%) 0.214 (17%) 0.372 (12%)	Ba^{130} + neutrons
Ba^{132}	Stable - 0.19%			
Ba^{133m}	38.9 hrs.	IT (100%)	0.276	Ba^{132} + neutrons
Ba^{133}	7.2 yrs.	EC (100%)	0.357 (69%) 0.300 (31%) 0.082 (22%)	Ba^{132} + neutrons
Ba^{134}	Stable - 2.60%			
Ba^{135m}	28.7 hrs.	IT (100%)	0.268	Ba^{134} + neutrons
Ba^{135}	Stable - 6.7%			
Ba^{136}	Stable - 8.1%			
Ba^{137m}	2.6 min.	IT (100%)	0.662	Ba^{136} + neutrons, daughter of Cs^{137}
Ba^{137}	Stable - 11.9%			
Ba^{138}	Stable - 70.4%			
Ba^{139}	84 min.	β^- 2.23 (66%) 2.38 (15%) 0.82 (19%)	0.163	Ba^{138} + neutrons, fission product
Ba^{140}	12.80 days	β^- 1.0 (75%) ~0.4 (25%)	0.030 0.436 0.132 0.537 0.162 0.304	Fission product
Ba^{141}	18 min.	β^- 2.8		Fission product
Ba^{142}	6 min.	β^-		Fission product
Ba^{143}	< 0.5 min.	β^-		Fission product
Ba^{144}	Short	β^-		Fission product

For more complete information of the radiations of the isotopes of calcium, strontium, and barium and for references to the original literature, see "Table of Isotopes", D. Strominger, J. M. Hollander, and G. T. Seaborg, Reviews of Modern Physics, 30, No. 2, Part II, April 1958.

IV. REVIEW OF THOSE FEATURES OF BARIUM, CALCIUM, AND STRONTIUM CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS

1. Metallic Barium, Calcium, and Strontium

Barium, calcium, and strontium are strong reducing agents and are prepared either by electrolytic or thermal means in the absence of moisture. Methods used for this purpose include the electrolysis of the fused chlorides, heating the oxides with aluminum in a vacuum furnace, and electrolysis of an aqueous solution with a mercury cathode with subsequent heating of the mercury amalgram in hydrogen to drive off the mercury.

Barium, calcium, and strontium are very reactive and are readily oxidized in air to the plus two oxidation state. The hydroxides are formed in cold water with an evolution of hydrogen. The metals react vigorously with acids to form the plus two charged cations and evolve hydrogen. The reaction with nitric acid is very rapid, with the formation of nitric oxide. The reaction with dilute sulphuric acid is slow because of the formation of insoluble sulphates.

2. Soluble Salts of Barium, Calcium, and Strontium

The soluble salts of barium, calcium, and strontium include the acetates, chlorides, bromides, iodides, nitrates, nitrites, permanganates, sulfides, chlorates, bromates, and perchlorates. Calcium chromate is soluble. The hydroxides of barium, calcium, and strontium are slightly soluble and may be precipitated only from concentrated solutions. The solubilities range from 1.2 g/liter for $Ca(OH)_2$ to 30 g/liter for $Ba(OH)_2$.

3. Insoluble Salts of Barium, Calcium, and Strontium-Precipitation and Coprecipitation Characteristics of Barium, Calcium, and Strontium

The common insoluble salts of barium, calcium, and strontium are listed in Table 1. A number of these precipitates are suitable for radiochemical separation procedures. The general references listed in Parts I and II describe the insoluble compounds of barium, calcium, and strontium and their use in analyses. The precipitates used most frequently

in radiochemical and analytical procedures are the chromates, nitrates, oxalates, sulfates, and barium chloride.

Chromate. The chromate precipitation is used in the classical separation of the alkaline earths. Barium chromate is precipitated from a hot solution buffered to a pH of 4 to 8. Ammonia is then added to the solution, and the strontium chromate is precipitated. In radiochemical work a pH of 4 is recommended[1] for the barium precipitation to minimize the strontium and calcium contamination of the barium precipitate.

Nitrate. The Willard and Goodspeed nitric acid method[2] has been frequently used for the separation of barium and strontium from fission products (see Section VII). Fuming nitric acid is added to the solution to yield 60 to 80 per cent HNO_3. The barium and strontium nitrates precipitate under these conditions, but calcium nitrate does not. With 70 to 80 per cent HNO_3 100 per cent yields of barium and strontium have been obtained, but calcium contaminated the precipitates[1]. The calcium contamination was reduced by using 60 per cent HNO_3.

The precipitation of strontium nitrate has been employed as a method of separating Sr^{90} from its Y^{90} daughter[3]. Inactive strontium was added as a carrier, and strontium nitrate was precipitated from a solution of 80 per cent nitric acid, leaving the Y^{90} in solution.

TABLE 1. INSOLUBLE COMPOUNDS OF BARIUM, STRONTIUM, AND CALCIUM

Reagent	Precipitate	Solubility in Water	Solubility in Other Reagents
F^-	BaF_2	slightly soluble (0.17 g/100 cc)	soluble in acids and in NH_4Cl
	SrF_2	insoluble	soluble in hot HCl
	CaF_2	insoluble	slightly soluble in acids, soluble in solution of NH_4^+ salts
$CO_3^=$	$BaCO_3$	insoluble	soluble in acids & in NH_4Cl
	$SrCO_3$	insoluble	soluble in acids
	$CaCO_3$	insoluble	soluble in acids & in NH_4Cl
$C_2O_4^=$	BaC_2O_4	insoluble	soluble in acids & in NH_4Cl

TABLE 1. (CONTINUED)

Reagent	Precipitate	Solubility in Water	Solubility in Other Reagents
	$SrC_2O_4 \cdot H_2O$	insoluble	soluble in HCl and HNO_3
	$CaC_2O_4 \cdot H_2O$	very insoluble	soluble in acids
$SO_4^=$	$BaSO_4$	very insoluble	slightly soluble in H_2SO_4
	$SrSO_4$	insoluble	insoluble in alcohol slightly soluble in acids
	$CaSO_4$	slightly soluble	insoluble in alcohol soluble in HCl
$CrO_4^=$ or $Cr_2O_7^=$	$BaCrO_4$	very insoluble	soluble in mineral acids
	$SrCrO_4$	slightly soluble (0.11 g/100 cc)	soluble in acids
c. HCl and ether	$BaCl_2 \cdot 2H_2O$	soluble	insoluble in c. HCl-ether reagent
60-80% HNO_3	$Ba(NO_3)_2$	soluble	insoluble in boiling amyl alcohol insoluble in 60-80% HNO_3
	$Sr(NO_3)_2$	soluble	insoluble in boiling amyl alcohol insoluble in 60-80% HNO_3
$HPO_4^=$	$BaHPO_4$	insoluble	soluble in acids
	$SrHPO_4$	insoluble	soluble in acids
	$CaHPO_4 \cdot 2H_2O$	insoluble	soluble in acids
$PO_4^=$	$Ba_3(PO_4)_2$	insoluble	soluble in acids
	$Sr_3(PO_4)_2$	insoluble	soluble in acids
	$Ca_3(PO_4)_2$	insoluble	soluble in acids
$SO_3^=$	$BaSO_3$	insoluble	soluble in HCl
	$SrSO_3$	insoluble	soluble in HCl
	$CaSO_3 \cdot 2H_2O$	insoluble	soluble in HCl, HNO_3, and H_2SO_3
IO_3^-	$Ba(IO_3)_2 \cdot H_2O$	insoluble	soluble in HCl and HNO_3
	$Sr(IO_3)_2$	slightly soluble	soluble in boiling water
H_2SiF_6	$BaSiF_6$	slightly soluble	insoluble in alcohol
alkaline $MoO_4^=$	$BaMoO_4$	insoluble	slightly soluble in acids
	$SrMoO_4$	insoluble	soluble in acids
	$CaMoO_4$	insoluble	soluble in acids

Chloride. The insolubility of barium chloride in strong hydrochloric acid solution is a basis for a method of separating barium from calcium, strontium, and other elements. This method has been used in radiochemical work (see Section VII). The precipitation is performed either by adding an ether-hydrochloric acid solution to the aqueous radioisotope solution or by bubbling dry hydrogen chloride gas into an aqueous solution or a mixture of ether and water. The barium chloride precipitate is readily soluble in water, thus facilitating further separations.

Oxalate. The oxalates of all three alkaline earths are insoluble; so the oxalate precipitation does not constitute a good method of decontaminating one alkaline earth from another. The precipitation of the oxalate from a basic solution with ammonium oxalate is generally used as a convenient way to reduce an alkaline earth to a weighable and reproducible form suitable for radioassay.

Sulfate. The precipitation of barium sulfate is not generally used in a separation procedure because of difficulty in performing further operations on this highly insoluble substance. It is more useful as a final step in a procedure to secure a form which can be readily dried, weighed, and mounted for counting. Barium is quantitatively precipitated as the sulfate by slowly adding dilute sulfuric acid to a hot barium solution and digesting the precipitate[4]. For the precipitation of strontium (or calcium) sulfate, a reagent such as alcohol is required to lower the solubility, and coagulation must be accelerated by heat[5].

Yields of Precipitation Reactions. The yi[illegible] strontium, and barium in the chromate, nitrate, chloride

TABLE 2. SUMMARY OF YIELD DATA OF PRECIPITATION REACTIONS FOR BARIUM, STRONTIUM, AND CALCIUM[6]

Precipitating Solution	Condition	Per Cent Carried			
		Barium	Strontium	Ca on Ba	Ca on Sr
Ammonium Dichromate	pH 4	70 ± 3.4	1.6 ± 0.3	0.8 ± 0.08	
	pH 5	73 ± 4.0	8 ± 0.2	1.1 ± 0.08	
	pH 6	86 ± 1.3	22 ± 2.0	1.7 ± 0.22	
Nitric Acid	80%	100 ± 5.3	100 ± 1.7	27 ± 2.2	51 ± 3.2
	70%	100 ± 3.6	98 ± 1.4	2.4 ± 0.3	11 ± 2.3
	60%	86 ± 3.3	81 ± 4.2	0.9 ± 0.05	2.6 ± 1.0
Hydrochloric Acid	A. 3 ml H_2O	82 ± 1.1	2.8 ± 0.9	0.6 ± 0.4	
	B. 1.5 ml H_2O	92 ± 2.2	11 ± 0.7	0.8 ± 0.08	
	C. Dry HCl	99 ± 0.4	7.3 ± 1.6	1.0 ± 0.1	
	D. Ether-dry HCl	93 ± 2.4	6.0 ± 3	1.5 ± 0.1	
Ammonium Oxalate	95°	59 on SrC_2O_4 15 on CaC_2O_4	99		100
Sulfuric Acid	Excess Sulfate	100	57 on Ba Very slight alone	10	3.6

All values are average of quadruplicate runs. Errors are "standard deviations". The yield data applies only to the experimental conditions described in the text.

sodium acetate-ac · acid buffer of the desired pH (4,5, or 6) were added.

The pre- -formed with 2 ml of ammonium dichromate

-ume of solution was 15 ml.

mixture. The HCl-ether reagent consisted of 4 parts of ACS reagent grade hydrochloric acid and 1 part of ACS reagent grade anhydrous ether. In procedure C, a 10 ml initial solution was cooled in an ice bath and dry hydrogen chloride was bubbled in until the solution was saturated. In procedure D, an initial solution containing 8 ml of water and 3 ml of ether was cooled in an ice bath and the dry HCl was bubbled in.

In the oxalate precipitations the initial solution was diluted to 8 ml with water and an excess of concentrated ammonium hydroxide was added. One ml of the hydroxide was usually satisfactory. The solution was heated to boiling and 2 ml of saturated ammonium oxalate solution added with stirring. Again the solution was heated to boiling and allowed to stand for 5 minutes with occasional stirring.

The sulfate precipitation was performed by diluting the initial solution to 10 ml with 1 M nitric acid and adding 1 ml of 2M sulfuric acid. Strontium sulfate was found to be more completely precipitated in the presence of barium or calcium than in their absence.

Contamination of Alkaline Earth Precipitates by Other Activities. The contamination of alkaline earth precipitates by other activities was determined by adding 10 mg of carrier and a tracer of the contaminating ion (e.g., Co, Ru, Sb, etc.) to a carrier solution containing 10 mg each of the alkaline earths and carrying out the precipitation by the procedures discussed in the preceding section. A summary of the results is given in Table 3. The yield and decontamination data presented in this table and in Table 2 have been used to develop the optimum alkaline earth procedures given in Section VII (see Procedures 1, 2, and 3).

Ferric Hydroxide as a Carrier for Barium and Strontium. Carrier-free barium and strontium will coprecipitate with iron precipitated as the hydrated oxide. This is an effective method for removing trace amounts of barium or strontium from solution. Strontium-85 activity produced by a cyclotron bombardment of a rubidium target has been separated from the large quantity of rubidium by coprecipitation with iron[8]. About 75 per cent of

TABLE 3. CONTAMINATION OF ALKALINE EARTH PRECIPITATES BY OTHER ACTIVITIES[7]

Element	Precipitating Solution, per cent carried						
	Chromate pH_4	80% HNO_3	60% HNO_3	HCl	Oxalate on SrC_2O_4	Oxalate on CaC_2O_4	Sulfate
Antimony	55	47	30	28	44	46	28
Barium	70	100	86	82	59	15	100
Calcium	0.8	51 on Sr 27 on Ba	2.6 on Sr 0.9 on Ba	0.6	--	100	10
Cerium	6	3.2	2.5	0.9	98	95	7.1
Cesium	3.5	1	2	1	0.8	1.6	2.9
Chromium	1.2	1.8	1.0	0.7	89	96	0.5
Cobalt	1.1	3	3.5	1	52	21	0.5
Iodine	2.0	1.2	0.8	0.9	2.3	5.0	1.5
Iridium	27	4.2	0.9	5.4	47	68	11
Ruthenium	5	1.5	2.4	2	23	38	0.6
Selenium	5.7	1.4	1.3	0.9	21	23	1.2
Silver	89	1.9	1.5	0.8	1.2	2	14
Strontium	1.6	100	81	2.8	99	--	57
Tantalum	10	1	0.7	0.5	49	24	0.6
Tin	99.5	1	1.2	0.8	73	95	0.5
Zirconium	6.3	2.6	3.3	2	93	88	20

NO_3^- ions present in all solutions

Cl^- ions present in all solutions except with I, Ag, and Zr

F^- ions present only in Ta solution and possibly Zr

The data above applies only to the experimental conditions described in the text.

the strontium is precipitated with the ferric hydroxide, leaving the rubidium in solution. The iron is removed from the strontium by ether-extraction.

The optimum conditions for coprecipitation of barium with ferric hydroxide have been investigated[9], and the amount of barium carried has been found to increase with the amount of iron precipitated, the time of settling, and the pH of the supernate. At a pH of 8, approximately 90 per cent of the barium is carried. Similar studies with strontium have shown that approximately 50 per cent of the strontium coprecipitates with the ferric hydroxide at a pH of 8[10]. Calcium has been found to not coprecipitate with ferric hydroxide[11].

Lead Sulfate as a Carrier for Barium and Strontium. The coprecipitation of barium and strontium on $PbSO_4$ can be used to separate carrier-free quantities of these elements from fission products[12]. The $PbSO_4$ is precipitated with $Pb(NO_3)_2$ and sulfuric acid. About 90 to 95 per cent of the barium and 80 per cent of the strontium are coprecipitated. Small amounts of other elements such as cerium, uranium, and thorium are also precipitated. Most of the lead can be removed by converting the sulfate to carbonate, dissolving it in hot HCl, and precipitating the chloride. The lead not removed by this procedure can be precipitated as the sulfide, or it might be removed by selective elution from an EDTA-loaded Dowex-1 ion exchange resin[13].

Lead chromate can be used as a carrier for barium to separate trace quantities of barium from tracer strontium, and lead nitrate can be used as a carrier for both barium and strontium[14].

4. Chelate Complexes of Barium, Calcium, and Strontium

Chelate complexes of barium, calcium, and strontium have not been applied to radiochemical procedures to any great extent. It is worthwhile, however, to consider some of the complexes formed in order to understand what effect various chelating agents may have on a solution of alkaline earth ions.

A summary of some of the chelating agents forming complexes with the alkaline earths is given in Table 4. The formation constants of the 1:1

TABLE 4. BARIUM, CALCIUM, AND STRONTIUM COMPLEXES OF SOME COMPLEXING AGENTS

Chelating Agent	Alkaline Earth	Log K	Ionic Strength	Reference
EDTA	Ba	7.76	0.1	a
	Ca	10.59	0.1	a
	Sr	8.63	0.1	a
Oxalic acid	Ba	2.31	0	b
	Ca	3.00	0	b
	Sr	2.54	0	b
Malonic acid	Ba	1.23	0.2	c
		1.71	0.04	d
	Ca	1.46	0.2	c
		2.49	0.04	d
	Sr	1.25	0.2	c
Succinic acid	Ba	0.97	0.15	e
	Ca	1.16	0.15	e
	Sr	0.75	0.16	f
Maleic acid	Ca	1.2	0.16	f
	Sr	1.1	0.16	f
Citraconic acid	Ca	1.3	0.16	f
	Sr	1.3	0.16	f
Citric acid	Ba	2.3	0.16	g
	Ca	3.4	0.16	f
	Sr	2.7	0.16	g
Tartaric acid	Ba	1.62	0.2	c
	Ca	1.80	0.2	c
	Sr	1.65	0.2	c
Trimetaphosphoric acid	Ba	3.35	0	h
	Ca	3.45	0	h
O-phthalic acid	Ba	0.92	0.15	e
Ammoniatriacetic acid	Ba	6.41	0	i

TABLE 4. (CONT'D)

Chelating Agent	Alkaline Earth	Log K	Ionic Strength	Reference
Ammoniatriacetic acid	Ca	6.41	0.1	j
		8.18	0	i
	Sr	4.98	0.1	j
		6.73	0	i
Lactic acid	Ba	0.55	0.2	c
	Ca	1.07	0.2	c
	Sr	0.70	0.2	c
Malic acid	Ba	1.30	0.2	c
	Ca	1.80	0.2	c
	Sr	1.45	0.2	c
Methylamine-N, N,-diacetic acid	Ba	2.59	0.1	j
	Ca	3.75	0.1	j
	Sr	2.85	0.1	j
δ -Quinolinol	Sr	2.39	0.1	k
		0.84 (log K_2)*	0.1	k

* Formation constant for SrA_2.

a. G. Schwarzenbach and H. Ackerman, Helv. Chim. Acta 31, 1029 (1948).

b. R. W. Money and C. W. Davies, Trans. Faraday Soc. 28, 609 (1932).

c. R. K. Cannan and A. Kibrick, J. Am. Chem. Soc. 60, 2314 (1938).

d. D. I. Stock and C. W. Davies, J. Chem. Soc. 1949, 1371.

e. N. R. Joseph, J. Biol. Chem. 164, 529 (1946).

f. A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, Inc., New York (1952).

g. J. Schubert and J. Richter, J. Am. Chem. Soc. 70, 4259 (1948).

h. H. W. Jones, C. B. Monk, and C. W. Davies, J. Chem. Soc. 1949, 2693.

i. G. Schwarzenbach, E. Kampitisch, and R. Steiner, Helv. Chim. Acta 28, 828 (1945).

j. G. Schwarzenbach, H. Ackerman, and P. Ruckstuhl, Helv. Chim, Acta 32, 1175 (1949).

k. D. Dyrssen, Svensk Kem. Tidskr 67, 311 (1955).

chelates are also given, and they show that the stability of the complexes formed with a particular chelating agent decreases with increasing atomic weight. Calcium forms the most stable complexes and barium, the least stable.

The ethylene diamine tetra-acetic acid (EDTA) complex of calcium has been used in an analytical procedure[15]. The calcium is titrated with EDTA, using "arsenazo" as an indicator. The indicator changes from violet to orange at the end point. The formation of the barium EDTA complex may be used to dissolve barium sulfate[16]. This procedure can be employed in the course of a separation to assist in decontamination of a barium sulfate precipitate. The precipitate is dissolved in a hot ammoniacal solution of EDTA and reprecipitated by dilution and acidification.

Sodium rhodizonate forms chelate complexes with barium and strontium that are used as spot tests for these ions[17]. Insoluble chelate complexes of barium, calcium, and strontium are formed with picrolonic acid[18]. These chelates are soluble in acetic acid. Complexing agents such as EDTA, citric acid, and lactic acid are used in ion exchange procedures for the alkaline earths.

5. Extraction of the Thenoyl Trifluoroacetone (TTA) Complexes of Barium, Calcium, and Strontium Into Organic Solvents. A thenoyl trifluoroacetone extraction has been used for the purification of carrier-free Ca^{45} produced in the neutron bombardment of scandium[19]. The scandium is removed by solvent extraction at pH5 into a 0.5M solution of TTA in benzene, and the calcium is extracted by a 0.5M solution of TTA in benzene at pH 8.2. The calcium is removed from the benzene phase by back-extraction with water or dilute acid. The equilibrium constant for the calcium extraction at 25 C is:

$$K_{Ca} = \frac{(CaT_2)_B (H^+)^2_A}{(Ca^{+2})_A (HT)^2_B} = 1 \times 10^{-12}$$

where B and A represent the benzene and aqueous phases, respectively[20]. More than 99 per cent of the calcium is extracted at pH 8.2.

Strontium has been extracted at a pH greater than 10 into a 0.02 M solution of TTA in benzene[21]. The equilibrium constant for this extraction is 7.5×10^{-15}. A TTA extraction at pH 5 has been used to separate Y^{90} from Sr^{90}. [22, 23, 24] Yttrium extracts into a benzene solution of TTA at this pH, but strontium does not. Kiba and Mizukami[25] report the extraction of strontium at pH 8 into a 0.05 M solution of TTA in hexane.

No information has been located on the extraction of a TTA complex of barium into an organic solvent, but considering the pH values required to extract calcium and strontium into a benzene solution of TTA, a pH of greater than 10 or 11 would probably be required for the extraction of barium into this solvent.

6. Extraction of Barium, Calcium, and Strontium Into Organic Solvents. Applications of solvent extraction to the radiochemical analysis of barium, calcium, and strontium are not extensive. Morrison and Freiser[26] have reviewed extraction procedures, and some of the solvents they mention for the alkaline earths are discussed below. Few procedures are specific for barium, calcium, and strontium, and the applications have mainly been to the separation of the alkaline earths from one another.

Alcohol and Ether - A 1:1 mixture of absolute alcohol and absolute ether has been used to extract anhydrous calcium nitrate from strontium and barium[27]. A solution of the alkaline earths is evaporated to dryness in the presence of nitric acid, and the calcium nitrate is extracted from the dry mass by washing with the alcohol-ether mixture. The solubility of the calcium nitrate in the alcohol-ether mixture is 0.37 grams of $Ca(NO_3)_2$ per ml.

Butyl Cellosolve - Anhydrous calcium nitrate can be separated from strontium and barium in the same manner as discussed above with alcohol and ether, using the monobutyl ether of ethylene glycol (butyl cellosolve)[28]. The hydrated nitrates and the butyl cellosolve are rendered anhydrous by boiling the nitrates in the reagent. The solubility of anhydrous calcium nitrate in butyl cellosolve is 0.243 g/ml. The solubilities of the barium

and strontium nitrates in the solvent are not more than 2.3×10^{-6} and 1.1×10^{-5} g/ml, respectively.

Acetone - The anhydrous calcium nitrate can also be extracted into acetone to the extent of 0.212 g/ml[29].

8-Quinolinol in Chloroform - Strontium can be extracted into a 1M solution of 8-quinolinol in chloroform[30]. An aqueous solution of less than 0.1 mg of strontium is brought to a pH of 11.3 with sodium hydroxide and diluted to 15 ml. This is shaken with the organic solvent, and approximately 96 per cent of the strontium will be extracted.

A 3 per cent 8-quinolinol solution in chloroform can be used to extract calcium from a solution at a pH of 13 containing butyl cellosolve and up to 80 micrograms of calcium[31].

Di (2-ethyl hexyl) Orthophosphoric Acid in Toluene - A 1.5 M solution of di (2-ethyl hexyl) orthophosphoric acid (HDEHP) in toluene has been used to separate Y^{90} from Sr^{90}, and La^{140} from Ba^{140}.[32] The Y^{90} is extracted by this reagent from a 0.1 M HCl solution leaving most of the strontium in the aqueous phase. The distribution ratio (K), i.e., the ratio of the concentration of a specific nuclide in the organic phase to the concentration of that nuclide in the organic phase to the concentration of that nuclide in the aqueous phase, for strontium in this system is 1.6×10^{-2} and that for yttrium is greater than 10^{4}.

La^{140} is separated from Ba^{140} by extracting the lanthanum from a 0.05 M HCl solution. The K value for the barium is 3×10^{-2}, and that for lanthanum is 50. A detailed study of the extraction of strontium and barium by HDEHP in toluene has not been made, but the distribution ratios are known to be approximately inversely proportional to the second power of the aqueous acid concentration and directly proportional to the second power of the HDEHP concentration[32].

7. Ion Exchange Behavior of Barium, Calcium, and Strontium. Time considerations have thus far prevented the general applicability of ion exchange procedures to rapid radiochemical separations of the

alkaline earths. Good separations have been obtained, but most procedures require six hours or more. Ion exchange is very good, however, for trace quantities of barium, calcium, and strontium; and this method has been applied to the separation of alkaline earths from fission products, from products of neutron irradiations, and from each other.

Cation Exchange. A cation exchange resin such as Dowex-50 will adsorb ions of the same valence in the order of their increasing hydrated ionic radii, the smaller hydrated ions being adsorbed first. Bonner and Smith[33] list a selectively scale for divalent ions or Dowex-50, and from this scale one can determine that the sequence of adsorption of the alkaline earths will be Ba^{++} first, then Sr^{++}, and then Ca^{++}. When the alkaline earths are eluted from a resin with a complexing agent, the order of elution depends upon the relative stabilities of the metal complexes formed. The alkaline earth forming the most stable complex will be eluted first, and normally this will be calcium.

Carrier-free strontium and barium have been separated from fission products on a column of Amberlite IR-1 (40-60 mesh)[34]. Zirconium and niobium were removed first with 0.5 per cent oxalic acid, and yttrium, cerium, and the rare earths were eluted next with 5 per cent citric acid adjusted to a pH of 3 with NH_4OH. The strontium and barium were removed with an eluant of 5 per cent citric acid at a pH of 5. The strontium came off the column first.

Tompkins[35] separated radioactive strontium, barium, and radium on a 1 cm^2 x 15 cm column of colloidal agglomerates of Dowex-50. The initial solution contained 20 mg of strontium, 20 mg of barium, and 20 μg of radium. The elution was carried out with 0.5 M ammonium citrate at a pH of 7.8 and with a flow rate of 0.3 ml per minute. All of the strontium was in the first 4 ml of eluate, all of the barium was in the next 4 ml, and the radium was in the last 8 to 10 ml. W. H. Power, et al., separated barium and radium on a Dowex-50 column by adding the barium and radium to the column in a solution of 0.2 N nitric or hydrochloric acid and eluting with 0.32 M

ammonium citrate at pH 5.6[36]. The barium was eluted first. Barium to radium ratios as high as 4440 to 1 were separated with one elution.

Strontium-90 has been separated from its Y^{90} daughter by ion exchange with Dowex-50[37,38]. The Sr^{90}-Y^{90} solution is added to the column after the resin has been converted to the ammonium form with ammonium citrate at pH 6. The yttrium is eluted with a 5 per cent solution of ammonium citrate at pH 3.8. The strontium is eluted with ammonium citrate at pH 6.0. Barium-140 has been separated from its La^{140} daughter in the same manner[39]. The La^{140} is eluted from a Dowex-50 column with citric acid at pH 3.8, and the Ba^{140} is eluted with the same reagent at pH 6.0.

An ion exchange separation with Dowex-50 has been employed in the radiochemical analysis of strontium and barium in urine[40]. The EDTA chelates of the alkaline earths in urine at a pH of 5.5 are passed through the column. Calcium and magnesium are eluted with a solution of citric acid and EDTA at pH 5, and sodium is eluted with 0.5 N hydrochloric acid. The strontium and barium are then removed from the column with 6 N nitric acid.

Milton and Grummitt[41] studied the cation-exchange separation of the alkaline earths with a 1.1 x 8 cm. Dowex-50 column at elevated temperatures and applied this to the analysis of Sr^{90} in milk ash samples. They eluted magnesium, calcium, strontium, barium, and radium in that order with 1.5 M ammonium lactate at pH 7 and at 78 degrees Centigrade. They also obtained good separations with 1.5 M and 4 M hydrochloric acid eluants and with an eluant of 5 per cent ammonium citrate at pH 5. Temperatures of 60 degrees and 78 degrees Centigrade were used for the hydrochloric acid and ammonium citrate elutions, respectively.

Strontium and calcium have been separated on a Zeokarb 225 column in the sodium form[42]. The strontium and calcium in an EDTA solution at pH 5.25 are added to the column. The strontium is retained on the resin and

the calcium-EDTA complex passes through. The strontium is then eluted with 3 N hydrochloric acid.

Calcium has been separated by ion exchange from tracer scandium and the radioactive impurities produced in it by neutron irradiation[43]. The calcium is adsorbed on a 4.5 cm column containing 0.25 g of 50 micron particle size Zeokarb 225 and eluted with hydrochloric acid.

The alkaline earths have been quantitatively separated from each other in millimole quantities on a column of Dowex-50 (120 mesh)[44]. The column size was 2.5 cm^2 x 19 cm, and the eluant was 1.20 M ammonium lactate at a flow rate of 1.4 ml per minute. The first 74 ml contained all of the calcium, the next 58 ml contained all of the strontium, and the barium was in the last 325 ml. The separation required 6 hours.

Anion Exchange. A few procedures utilizing anion exchange columns have been reported for the alkaline earths. Strontium-90 has been separated from Y^{90} on a Dowex-1 column pretreated with hydroxide[45]. The strontium is eluted from the column with water, and the yttrium remains on the column as $Y(OH)_3$. The yttrium may be eluted with 1 M hydrochloric acid. Another strontium and yttrium separation has been reported, using a nitrate loaded Dowex-1 column containing some 8-hydroxyquinoline -5- sulfonic acid (HCS)[46]. The strontium is eluted from the column first with a solution 0.1 molar in $NaNO_3$ and 0.0005 molar in HCS at a pH of 5.5.

Barium-140 has been separated from La^{140} on an hydroxide charged Dowex-1 column[47]. A 0.01 N hydrochloric acid solution of the barium and lanthanum is passed through the column, and the effluent contains radiochemically pure Ba^{140}. Any barium remaining on the column may be eluted with water. The La^{140} stays on the column and may be eluted with dilute nitric acid.

The alkaline earths have been separated from each other on a citrate resin pretreated with 0.05 M ammonium citrate at pH 7.5[48]. A chloride solution of the alkaline earths was added to the column, and the

elution was performed with 0.05 M ammonium citrate at pH 7.5. The barium was eluted first, followed by the strontium and then the calcium.

James and Welch[49] report the adsorption of trace amounts of strontium on an Amberlite IRA-400 resin by the formation of an insoluble salt. Trace amounts of strontium were adsorbed on the resin in the oxalate form (the solubility of strontium oxalate is 0.05 g/l). The strontium was readily eluted with dilute acid. With a chromate resin form only about 80 per cent of the strontium was adsorbed, and with an hydroxide resin form the strontium was not adsorbed. Strontium chromate has a solubility of 1.5 g/l, and strontium hydroxide, 17.4 g/l. The limit of solubility for the application of this technique appears to be approximately 1.5 g/l.

The fact that strontium is not adsorbed on an Amberlite IRA-400 column in the hydroxide form has been employed to separate strontium and cesium from fission products[50]. All of the fission products present in their solutions except strontium and cesium are removed from solution by this column (assuming barium is absent).

V. DISSOLUTION OF MATERIAL CONTAINING BARIUM, CALCIUM, AND STRONTIUM

The problem of dissolving a sample for the subsequent radiochemical analysis of the alkaline earths is in most cases a simple one. Water can be used to dissolve such compounds as the acetates, bromides, chlorides, chlorates, perchlorates, cyanides, ferricyanides, iodides, nitrates, nitrites, and permanganates. Hydrochloric or nitric acid dissolves the fluorides, carbonates, oxalates, chromates, phosphates, sulfates (except barium), and oxides.

Barium sulfate can be dissolved by treatment with hot, concentrated sulfuric acid, but dilution with water causes reprecipitation of the sulfate. To obtain a solution of barium ions from barium sulfate, it is best to convert the sulfate to barium carbonate by fusion with sodium carbonate[51]. The sulfate is mixed with four to six times as much anhydrous sodium carbonate and fused in a platinum crucible. The residue is cooled, boiled in a little water, filtered, and washed with hot sodium carbonate solution to remove

the sulfate ions. The barium carbonate residue is then dissolved in dilute hydrochloric or nitric acid.

Frequently barium-, calcium-, or strontium-containing materials such as limestone, cement, soil, bones, and biological materials must be brought into solution. Hot hydrochloric acid can be used to dissolve limestone and cement. An insoluble residue of silica will remain, and this can be filtered or centrifuged.

In removing alkaline earths from soil it may not be necessary to bring the soil into solution. Strontium, for example, has been leached from soil with acid[52]. Twenty-five milliliters of 1M nitric acid is added to ten grams of soil and stirred to suspend the soil. This is heated and stirred for three to four minutes and centrifuged. Kahn[53] reports that 86.2 $\pm$ 1.1 per cent of the strontium is removed per leach and 99.5 per cent is removed in three leaches. To separate the strontium from calcium dissolved by the acid, add strontium carrier and precipitate the alkaline earth carbonates from basic solution; redissolve the carbonates in nitric acid and precipitate strontium nitrate with fuming nitric acid, leaving the calcium in solution.

An ammonium acetate leach can also be employed to extract calcium and strontium from soil[54]. The soil is crushed and suspended overnight in a normal solution of ammonium acetate at pH 7. The suspension is filtered, and the filtrate is evaporated to dryness and ashed at 600 degrees Centigrade. The ashed residue is dissolved in hydrochloric acid, and iron and aluminum are removed by a hydroxide precipitation. Calcium and strontium are then precipitated as the oxalate.

In some cases the leaching procedure may not work and the soil must be dissolved by an alkali fusion[55]. The soil is ground to a powder in a mortar and pestle and added to a fusion mixture of 2:1:1 by weight of potassium hydroxide, nitrate, and carbonate. The fusion mixture should be five to ten times the weight of the soil sample. The fusion mixture is heated for two hours at 550 degrees Centigrade, while swirling the contents

at fifteen minute intervals. The mixture is then cooled and leached with 10 ml of water. The alkaline earths remain in the melt. Ten ml of 6N nitric acid is added and the mixture is heated. This is taken to dryness twice with addition of conc. nitric acid to dehydrate the silica. The melt is redissolved in nitric or hydrochloric acid, and the silica is centrifuged.

Biological samples such as plant material or dairy products are first ashed by heating at 600 C for several hours[54]. Milk samples are first evaporated to dryness and then ashed. The milk ash goes readily into solution in hot, concentrated hydrochloric acid, but in the case of the plant ash it is necessary to perform two extractions with aqua regia[54]. In some cases one may prefer to wet ash biological material by treatment with nitric acid followed by an equal volume mixture of nitric and perchloric acids[56].

Human and animal bone samples are first ashed for about 4 hours at 900 C and then dissolved in hot, concentrated hydrochloric acid[54].

VI. RADIOASSAY TECHNIQUES FOR BARIUM, CALCIUM, AND STRONTIUM

In the radioassay of solutions or precipitates containing radioisotopes of barium, calcium, or strontium particular attention must be paid to the decay schemes and radiations of these isotopes. Such factors as half life, type of radiation, and energy of radiation must be considered. Nuclear characteristics of the isotopes of the alkaline earths can be found in the literature[57] and are summarized in Section III.

Calcium-45 is the radioisotope commonly used as a tracer in calcium analysis. This isotope emits beta particles with a maximum energy of 0.254 Mev, and it emits no gamma radiation. A thin-window Geiger or proportional counter is useful for radioassay of Ca^{45}. In neutron activations of calcium Ca^{41}, Ca^{47}, and Ca^{49} may be produced in addition to Ca^{45}. Long-lived Ca^{41} emits no radiation other than 0.003 Mev X-rays which are difficult to measure. These low energy X-rays may be counted in a proportional counter with a thin window. The 8.8 minute Ca^{49} will not be

encountered unless work is begun very soon after irradiation, in which case it is best determined by counting the 1.0 and 2.1 Mev beta particles with a Geiger or proportional counter. The 4.7 day Ca^{47} emits 0.66 and 1.94 Mev beta particles in addition to gamma rays at 0.50, 0.81, and 1.29 Mev. The beta particles can be detected with a Geiger or proportional counter, and the gamma radiation can be determined with a scintillation detector. Decay corrections must be made in counting Ca^{49}, and they should be made for Ca^{47} if the counting extends over a period of a few hours.

If Ca^{45}, Ca^{47}, and Ca^{49} are present in an activated sample, they will all contribute to the beta count and a decay curve must be determined and resolved to obtain the quantity of each isotope. If only 164 day Ca^{45} is to be counted, the chemical separation of calcium should be carried out after the decay of the short-lived isotopes.

Strontium-89 and strontium-90 are commonly used as tracers for strontium analysis and are often determined in fission product and fall-out studies. Both are beta-emitters and can be determined with a Geiger or proportional counter. Sr^{89} is always determined by beta-counting the strontium precipitate. Sr^{90} decays to 61 hour Y^{90} which is also a beta-emitter. When activities from daughter products interfere in counting, three methods of measurement are possible. In one, a time lapse of about 10 half lives is allowed between the strontium separation and the counting to permit the mixture to reach radioactive equilibrium, when the ratio of parent-to-daughter activity is constant. In the second method, the Y^{90} is removed by precipitating it as the hydroxide[58], extracting it from an acetate buffered solution at pH 5 into a 5 per cent solution of TTA in benzene[59], or selectively eluting the yttrium from an ion exchange column[60,61]. The Sr^{90} is then separated and radioassayed before the Y^{90} again becomes measurable.

The third method, which is most commonly used, also involves a separation of the Sr^{90} and Y^{90}. After the complete chemical procedure is performed to separate the strontium from the fission product or fall-out

sample, the strontium is stored for a period of time to permit ingrowth of Y^{90}. The Y^{90} is then milked from the strontium by one of the methods described above and beta-assayed. The Sr^{90} disintegration rate, I_{Sr90}, of the original sample is calculated by means of the equation[60,124]:

$$I_{Sr90} = \frac{I_{Y90}}{Y_{Sr} \cdot Y_Y (1 - e^{-t/93})}$$

where Y_{Sr} and Y_Y are the chemical yields for the strontium separation and the yttrium milking. The factor $1/(1-e^{-t/93})$ is the correction factor for Y^{90} growth when the ingrowth time is t hours. I_{Y90} is the disintegration rate of the Y^{90} milked from the strontium. The Y^{90} counting rate must be corrected for decay occurring during the time between the yttrium milking and the counting of the Y^{90}.

In a neutron-activated strontium sample Sr^{85m}, Sr^{85}, Sr^{87m}, and Sr^{89} will be observed. Sr^{89m} may be present, but very little is known about this isomer of Sr^{89}. Sr^{89} is the only beta emitter in this group. The others emit only gamma rays and can be measured with a scintillation counter. Again the short-lived activities can be permitted to decay, and only the 51 day Sr^{89} and 64 day Sr^{85} need be measured. The gamma rays from the latter isotope can be easily distinguished with a scintillation spectrometer.

In a fission product mixture all of the radioactive isotopes of strontium with mass numbers above 88 may be present. Sr^{89} and Sr^{90} may be measured as discussed above. Sr^{91} and Sr^{92} emit both beta and gamma radiation and can be counted either with a Geiger or proportional counter or a scintillation counter. They have short half lives, however, so decay corrections must be made. Sr^{93}, Sr^{94}, Sr^{95}, and Sr^{97} are all beta emitters but they have very short half lives and may not be observed. All of the short-lived isotopes can be permitted to decay, and only the Sr^{89} and Sr^{90} need be counted.

Barium-140 is used as a tracer in barium analysis. This isotope emits beta particles with upper energy limits of 1.0 Mev and

about 0.4 Mev and several gamma rays. Thus, it can be measured either with a Geiger or proportional counter or with a scintillation detector. Ba^{140} with a half life of 12.80 days decays to 40 hour La^{140} which also emits both beta particles and gamma rays. At least 134 hours[62] may be allowed to elapse between the chemical separation and the radioassay to permit radioactive equilibrium to be established, or the Ba^{140} can be separated from the La^{140} and radioassayed before the La^{140} again becomes measurable. The separation of Ba^{140} and La^{140} can be performed by precipitation of $BaCl_2 \cdot 2H_2O$[62], by selectively eluting the La^{140} from an ion exchange column[63], or by extracting the La^{140} from a 0.05 M HCl solution into a 1.5 M solution of di(2-ethyl hexyl) orthophosphoric acid in toluene[64].

In a neutron activation Ba^{131}, Ba^{133m}, Ba^{133}, Ba^{135m}, Ba^{137m}, and Ba^{139} may be produced. Ba^{131} with a half life of 11.5 days, 38.9 hour Ba^{133m}, 7.2 year Ba^{133}, 28.7 hour Ba^{135m}, and 2.6 minute Ba^{137m} emit only gamma rays and can be measured with a scintillation detector, with appropriate decay corrections for the short half lives. The only beta emitter in this group is 84 minute Ba^{139}, which also emits a 0.163 Mev gamma ray.

In a fission product mixture short-lived Ba^{141}, Ba^{142}, Ba^{143}, and Ba^{144} may be found in addition to Ba^{137m}, Ba^{139}, and Ba^{140}. These higher-mass isotopes are all beta emitters. If a fission product mixture is allowed to decay for a few hours before chemical separation, only Ba^{140} will remain; and it can be permitted to come to equilibrium with its La^{140} daughter or it can be counted before the La^{140} becomes measurable.

INDEX OF PROCEDURES

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR BARIUM, CALCIUM, AND STRONTIUM

PROCEDURE 1

Radiochemical Determination of Barium

1. Introduction

A radiochemical procedure for barium has been developed from the yield and decontamination data presented in Tables 2 and 3 in Section IV. The procedure involves a separation of barium from strontium, calcium, and other contaminants by precipitation of $BaCl_2 \cdot 2H_2O$ with an HCl-ether reagent. This gives an 82 per cent yield for barium and results in a 50- to 100-fold decrease in contaminants for each cycle. The barium chloride precipitate is readily soluble in water, thus facilitating the recycling of the barium. The method is fast and efficient, and it requires no precautions other than those normally used in handling ether. The results are generally better than those of nitrate precipitations, because of the lower viscosity of the supernate, which allows more complete removal by suction tube. The barium is converted to a form suitable for counting and yield determinations by a final precipitation as the sulfate.

2. Equipment

Centrifuge

Centrifuge cones, borosilicate glass, graduated, with cone point, 15 ml.

Stirring rods

Pipets, 1 ml.

Glass suction tube connected to a vacuum flask - and through a trap to a water aspirator.

Planchets, 1 inch diameter flat stainless steel

3. Reagents

HCl-ether reagent: 4 volumes of ACS reagent grade hydrochloric acid to 1 volume of ACS reagent grade anhydrous ether (Mallinckrodt).

Nitric acid, 1M

Sulfuric acid, 10 ml of concentrated acid, ACS reagent grade, per 100 ml of water (about 1.8M).

4. Carriers (Depending Upon Suspected Contaminants)

Antimony: $SbCl_3$, 10 mg/ml Sb^{+3} in 3M HCl.

Barium: $Ba(NO_3)_2$, 10 mg/ml Ba^{+2} in water.

Calcium: $Ca(NO_3)_2 \cdot 4H_2O$, 10 mg/ml Ca^{+2} in water.

Cerium: $Ce(NO_3)_3 \cdot 6H_2O$, 10 mg/ml Ce^{+3} in dilute HNO_3.

Cesium: CsCl, 10 mg/ml Cs^{+} in water.

Chromium: $Cr(NO_3)_3 \cdot 9H_2O$, 10 mg/ml Cr^{+3} in dilute HNO_3.

Cobalt: $Co(NO_3)_2 \cdot 6H_2O$, 10 mg/ml Co^{+2} in water.

Iodine: NaI, 10 mg/ml I^{-} in water.

Iridium: $IrCl_4$, 10 mg/ml Ir^{+4} in 0.1M HCl.

Ruthenium: $RuCl_3$, 10 mg/ml Ru^{+3} in 0.1M HCl.

Selenium: H_2SeO_3, 10 mg/ml Se^{+4} in 1.2M HCl.

Silver: $AgNO_3$, 10 mg/ml Ag^{+} in water.

Strontium: $Sr(NO_3)_2$, 10 mg/ml Sr^{+2} in water.

Tantalum: K_2TaF_7, 10 mg/ml Ta^{+5} - add K_2TaF_7 to 1 ml. of water containing one drop of conc. HCl and 1 drop of 1 to 1 HF and heat to dissolve. Make up fresh immediately before use because of instability.

Tin: $SnCl_2 \cdot 2H_2O$, 10 mg/ml Sn^{+2} in 5% HCl

Zirconium: $ZrO(NO_3)_2 \cdot 2H_2O$, 10 mg/ml Zr^{+4} in 0.5M HNO_3 and 0.1M HF.

5. Procedure

An outline of the procedure is given in Table 1 along with the yields and decontamination factors. A more complete description of each step is given below.

Step 1. Add 10 mg of carrier of the contaminating ion and 10 mg of barium carrier to the solution of the sample in a 15 ml centrifuge cone. Total volume should be 3 ml. Composit carrier solutions can be prepared to reduce volume requirements.

TABLE 1. RADIOCHEMICAL DETERMINATION OF BARIUM

Ba and Sr, Ca, Ag, Ce, Co, Cr, Cs, I, Ir, Ru, Se, Sb, Sn, Ta, or Zr

1.	Add carriers	Decontamination factors:
2.	Precipitate with 4:1 HCl-ether	1-10 Sb
3.	Digest and centrifuge	10-100 Ir, Sr, Ru, Zr
4.	Remove supernate	100-1000 Ag, Ca, Ce, Co, Cr, Cs, I, Se, Sn, Ta
	$BaCl_2 \cdot 2H_2O$	Yield 82%
5.	Dissolve precipitate, add carriers	Decontamination factors:
6.	Reprecipitate with HCl-ether reagent	10-100 Sb
7.	Digest and centrifuge	10^2-10^3 Ir, Sr
8.	Remove supernate	10^3-10^4 Ru, Zr
		10^4-10^5 Ag, Ca, Ce, Co, Cr, Cs, I, Se, Sn, Ta
	$BaCl_2 \cdot 2H_2O$	Yield 67%
9.	Dissolve precipitate, add carriers	Decontamination factors:
10.	Reprecipitate with HCl-ether reagent	10-100 Sb
11.	Digest and centrifuge	10^3-10^4 Ir
12.	Remove supernate	10^4-10^5 Sr
		10^5-10^7 Ag, Ca, Ce, Co, Cr, Cs, I, Ru, Se, Sn, Ta, Zr
	$BaCl_2 \cdot 2H_2O$	Yield 55%
13.	Dissolve precipitate, add carriers	Decontamination factors: 10^2-10^3 Sb
14.	Precipitate with 10% H_2SO_4	10^4-10^5 Ir, Sr
15.	Digest and centrifuge	10^6-10^8 Ag, Ca, Ce, Cs, Ru, Zr
16.	Remove Supernate	10^8 -10^9Co, Cr, I, Se, Sn, Ta
	$BaSO_4$	Yield 55%
17.	Transfer precipitate to plate and dry	
18.	Weigh precipitate for yield	
19.	Mount and count	

PROCEDURE 1 (Cont'd.)

Step 2. Precipitate $BaCl_2 \cdot 2H_2O$ from the 3 ml aqueous volume by addition of 10 ml of the HCl-ether reagent with thorough stirring.

Step 3. Digest for 5 minutes at room temperature with occasional stirring. Centrifuge for 5 minutes at top speed.

Step 4. Remove the supernate with the suction tube.

Step 5. Dissolve the precipitate in water and add a carrier for the contaminating ion. Bring the volume to 3 ml.

Steps 6, 7, and 8. Repeat Steps 2, 3, and 4.

Step 9. Repeat Step 5.

Steps 10, 11, and 12. Repeat Steps 2, 3, and 4.

Step 13. Repeat Step 5.

Step 14. Make volume to 10 ml with 1M HNO_3 and precipitate $BaSO_4$ with addition of 1 ml of 10% H_2SO_4 with thorough stirring.

Step 15. Digest for 5 minutes at room temperature and centrifuge at top speed for 5 minutes.

Step 16. Remove the supernate with suction tube.

Step 17. Slurry the precipitate onto a planchet and dry.

Step 18. Weigh the precipitate to determine the yield.

Step 19. Mount in a counting chamber and count.

6. Discussion

If a ratio of HCl-ether reagent volume to solution volume of 10:1.5 is used, the barium yield can be increased to 92 per cent per cycle, but the contamination by strontium is increased by a factor of 4. Calcium is not a significant interference in either case.

A precipitate of AgCl forms upon addition of the HCl-ether reagent when silver is present, but it readily dissolves in excess reagent.

PROCEDURE 2

Radiochemical Determination of Calcium

1. Introduction

A radiochemical procedure for calcium has been developed from the yield and decontamination data presented in Tables 2 and 3 in Section IV. The procedure involves a nitrate precipitation of calcium with strontium and barium to separate the alkaline earths from contaminating activities, a sulfate precipitation to remove the barium and strontium, and a final precipitation of calcium oxalate. The calcium yield in each nitrate precipitation cycle is 78 per cent, and 10 per cent is lost in the sulfate separation of barium and strontium.

2. Equipment

Centrifuge

Centrifuge cones, borosilicate glass, graduated, with cone point, 15 ml.

Stirring rods

Pipets, 1 ml

Glass suction tube connected to a vacuum flask - and through a trap to a water aspirator.

Water bath, composed of 400 ml beaker containing 300 ml of water supported on a small hot plate.

Planchets, 1 inch diameter flat stainless steel.

3. Reagents

Fuming nitric acid, ACS reagent grade, 90 to 95 per cent HNO_3.

Nitric acid, 1M.

Sulfuric acid, 10 ml of concentrated acid, ACS reagent grade, per 100 ml of water (about 1.8M).

Ammonium hydroxide, concentrated.

Ammonium oxalate, saturated solution in water.

4. Carriers

See Procedure 1. The carriers used in this procedure are the same as those used in the radiochemical determination of barium.

PROCEDURE 2 (Cont'd.)

5. Procedure

An outline of the procedure, with yields and decontamination factors, is given in Table 1. A more complete discussion of each step is given below.

Step 1. Add 10 mg of carrier for strontium, barium, calcium, and the contaminating ions to the solution of the sample in a centrifuge cone.

Step 2. Add sufficient fuming nitric acid precipitant and water to secure 80% HNO_3, and stir thoroughly.

Step 3. Digest for 5 minutes at room temperature with occasional stirring, and centrifuge at top speed for 5 minutes.

Step 4. Remove the supernate by decantation to waste storage for HNO_3. Explosions are likely to occur if this solution is mixed with other wastes that may contain organic compounds.

Step 5. Dissolve the precipitate in water and add 10 mg of carrier for each contaminating ion.

Steps 6, 7, and 8. Repeat Steps 2, 3, and 4.

Step 9. Repeat Step 5.

Steps 10, 11, and 12. Repeat Steps 2, 3, and 4.

Step 13. Dissolve the precipitate in water.

Step 14. Make volume to 10 ml with 1M HNO_3, and precipitate $BaSO_4$ and $SrSO_4$ with addition of 1 ml of 10% H_2SO_4 with thorough stirring.

Step 15. Repeat Step 3.

Step 16. Decant the supernate into another centrifuge cone and discard the precipitate.

Step 17. Add 10 mg of carrier for strontium and barium.

Steps 18, 19, and 20. Repeat Steps 14, 15, and 16.

Step 21. Repeat Step 17.

Steps 22, 23, and 24. Repeat Steps 14, 15, and 16.

Step 25. Dilute the solution to 8 ml with water and add sufficient

TABLE 1. RADIOCHEMICAL DETERMINATION OF CALCIUM

Ca and Sr, Ba, Ag, Ce, Co, Cr, Cs, I, Ir, Ru, Se, Sb, Sn, Ta, or Zr	
1. Add carriers	Decontamination factors:
2. Precipitate with 80% HNO_3	1-10 Sb
3. Digest and centrifuge	10-100 Ce, Cr, Co, I, Ir, Ru, Se, Ag, Zr, Cs, Sn, Ta
4. Remove supernate	
Ca^{++} on $Ba(NO_3)_2$ and $Sr(NO_3)_2$	Yield-Ca 78%, Ba and Sr 100%
5. Dissolve precipitate and add carriers	Decontamination factors:
6. Precipitate with 80% HNO_3	1-10 Sb
7. Digest and centrifuge	10^2-10^3 Ce, Ir
8. Remove supernate	10^3-10^4 Cs, Cr, Co, I, Ru, Se, Ag, Sn, Ta, Zr
Ca^{++} on $Ba(NO_3)_2$ and $Sr(NO_3)_2$	Yield-Ca 61%, Ba and Sr 100%
9. Dissolve precipitate and add carriers	Decontamination factors:
10. Precipitate with 80% HNO_3	1-10 Sb
11. Digest and centrifuge	10^4-10^5 Ce, Co, Ir, Zr
12. Remove supernate	10^5-10^6 Cs, Cr, I, Ru, Se, Ag, Sn, Ta
Ca^{++} on $Ba(NO_3)_2$ and $Sr(NO_3)_2$	Yield-Ca 48%, Ba and Sr 100%
13. Dissolve precipitate	Decontamination factors 1-10 Sr
14. Precipitate with 10% H_2SO_4	10-100 Sb, Ba
15. Digest and centrifuge	10^4-10^5 Ce, Co, Ir, Zr
16. Discard precipitate	10^5-10^7 Cs, Cr, I, Ru, Se, Ag, Sn, Ta

TABLE 1. (CONTINUED)

	Ca^{++} Yield-43%
17. Add Sr and Ba carriers	Decontamination factors: 1-10 Sr
18. Precipitate with 10% H_2SO_4	$10-10^2$ Sb 10^3-10^4 Ba
19. Digest and centrifuge	10^4-10^5 Ce, Co, Ir, Zr
20. Discard precipitate	10^5-10^7 Cs, Cr, I, Ru, Se, Ag, Sn, Ta
	Ca^{++} Yield-39%
21. Add Sr and Ba carriers	Decontamination factors:
22. Precipitate with 10% H_2SO_4	10-100 Sr, Sb
23. Digest and centrifuge	10^4-10^5 Ce, Co, Ir
24. Discard precipitate	10^5-10^7 Ba, Cs, Cr, I, Ru, Se, Ag, Sn, Ta, Zr
	Ca^{++} Yield-35%
25. Add excess NH_4OH and heat to boiling	Decontamination factors: 10-100 Sr, Sb
26. Precipitate with $(NH_4)_2C_2O_4$	10^4-10^5 Ce, Ir
27. Heat to boiling, digest, and centrifuge	10^5-10^6 Co, Cr, Ru, Zr
28. Remove supernate	10^6-10^8 Ba, Cs, I, Se, Ag, Sn, Ta
	CaC_2O_4 Yield-35%
29. Transfer precipitate to plate and dry	
30. Weigh precipitate for yield	
31. Mount and count	

concentrated NH_4OH to neutralize the acid and give an excess. One ml is usually satisfactory. Heat to boiling.

Step 26. Add 2 ml of a solution of saturated ammonium oxalate and stir thoroughly to precipitate CaC_2O_4.

Step 27. Heat again to boiling and allow to stand for 5 minutes without applying heat, while stirring occasionally. Centrifuge at top speed for 5 minutes.

Step 28. Remove the supernate with the suction tube.

Step 29. Slurry the precipitate onto a planchet and dry.

Step 30. Weigh the precipitate to determine the yield.

Step 31. Mount in a counting chamber and count.

6. Discussion

The precipitation of the barium and strontium nitrates must be done in 80% nitric acid. If the concentration of the nitric acid were lower, the coprecipitation of the calcium would be much reduced. In 70% nitric acid only 13.4 per cent of the calcium is carried, and in 60% nitric acid only 3.5 per cent of the calcium is coprecipitated with the barium and strontium.

Care must be exercised in handling the fuming nitric acid. The work should be done in a well ventilated hood, and the operator should wear rubber gloves and a face shield to avoid severe acid burns.

PROCEDURE 3

Radiochemical Determination of Strontium

1. Introduction

A radiochemical procedure for strontium has been developed from the yield and decontamination data presented in Tables 2 and 3 in Section IV. The procedure involves a nitrate precipitation of strontium and barium, a chloride precipitation to remove the barium, and a final precipitation of strontium oxalate. The nitrate precipitation is done in 60 per cent nitric acid to minimize the calcium contamination. The yield of strontium nitrate is 81 per cent. About 3 per cent of the strontium is precipitated with the $BaCl_2 \cdot 2H_2O$.

2. Equipment

Centrifuge

Centrifuge cones, borosilicate glass, graduated, with cone point, 15 ml.

Stirring rods

Pipets, 1 ml

Glass suction tube connected to a vacuum flask - and through a trap to a water aspirator.

Water bath, composed of 400 ml beaker containing 300 ml of water supported on a small hot plate.

Planchets, 1 inch diameter flat stainless steel.

3. Reagents

Fuming nitric acid, ACS reagent grade, 90 to 95% HNO_3.

HCl-ether reagent: 4 volumes of ACS reagent grade hydrochloric acid to 1 volume of ACS reagent grade anhydrous ether (Mallinckrodt).

Ammonium hydroxide, concentrated.

Ammonium oxalate, saturated solution in water.

4. Carriers

See Procedure 1. The carriers used in this procedure are the same as those used in the radiochemical determination of barium.

5. Procedure

An outline of the procedure, with yields and decontamination factors, is given in Table 1. A more complete discussion of each step is given below.

Step 1. Add 10 mg of carrier for strontium, barium, and the contaminating ions to the solution of the sample in a centrifuge cone.

Step 2. Add sufficient fuming nitric acid precipitant and water to secure 60% HNO_3, and stir thoroughly.

Step 3. Digest for 5 minutes at room temperature with occasional stirring, and centrifuge at top speed for 5 minutes.

Step 4. Remove the supernate by decantation to waste storage for HNO_3. Explosions are likely to occur if this solution is mixed with other wastes that may contain organic compounds.

Step 5. Dissolve the precipitate in water and add 10 mg of carrier for each contaminating ion.

PROCEDURE 3 (Cont'd.)

Steps 6, 7, and 8. Repeat Steps 2, 3, and 4.

Step 9. Dissolve the precipitate in 3 ml of water.

Step 10. Precipitate $BaCl_2 \cdot 2H_2O$ from the 3 ml aqueous volume by addition of 10 ml of the HCl-ether reagent with thorough stirring.

Step 11. Repeat Step 3.

TABLE 1. RADIOCHEMICAL DETERMINATION OF STRONTIUM

Sr and Ba, Ca, Ag, Ce, Co, Cr, Cs, I, Ir, Ru, Se, Sb, Sn, Ta, or Zr	
1. Add carriers	Decontamination factors:
2. Precipitate with 60% HNO_3	1-10 Sb
3. Digest and centrifuge	10-100 Ca, Ce, Cs, Co, Ru, Se, Ag, Sn, Zr
4. Remove supernate	100-1000 Cr, I, Ir, Ta
$Ba(NO_3)_2$ and $Sr(NO_3)_2$	Yield-Sr 81%, Ba 86%
5. Dissolve precipitate and add carriers	Decontamination factors: 10-100 Sb
6. Precipitate with 60% HNO_3	10^2-10^3 Ca, Co, Zr
7. Digest and centrifuge	10^3-10^4 Ce, Cs, Cr, Ru, Se, Ag, Sn
8. Remove supernate	10^4-10^5 I, Ir, Ta
$Ba(NO_3)_2$ and $Sr(NO_3)_2$	Yield-Sr 66%, Ba 74%
9. Dissolve precipitate	Decontamination factors: 1-10 Ba
10. Precipitate $BaCl_2 \cdot 2H_2O$ with HCl-ether	10-100 Sb 10^2-10^3 Ca, Co, Zr
11. Digest and centrifuge	10^3-10^4 Ce, Cs, Cr, Ru, Se, Ag, Sn
12. Discard precipitate	10^4-10^5 I, Ir, Ta
Sr^{++}	Yield-64%
13. Add barium carrier to precipitate $BaCl_2 \cdot 2H_2O$	Decontamination factors: 10-100 Ba, Sb 10^2-10^3 Ca, Co, Zr
14. Digest and centrifuge	10^3-10^4 Ce, Cs, Cr, Ru, Se, Ag, Sn
15. Discard precipitate	10^4-10^5 I, Ir, Ta

TABLE 1. (CONTINUED)

	Sr^{++} Yield-62%
16. Evaporate and redissolve	Decontamination factors:
17. Add excess NH_4OH and heat to boiling	10-100 Ba 10^2-10^3 Ca, Sb, Zr
18. Precipitate with $(NH_4)_2C_2O_4$	10^3-10^4 Co, Ce, Cr, Ru, Sn
19. Heat to boiling, digest, and centrifuge	10^4-10^5 Se, Ir, Ta
20. Remove supernate	10^5-10^7 Cs, I, Ag
	SrC_2O_4 Yield-61%
21. Transfer precipitate to plate and dry	
22. Weigh precipitate for yield	
23. Mount and count.	

Step 12. Decant the supernate into another centrifuge cone and discard the precipitate.

Step 13. Add 10 mg of Ba carrier. $BaCl_2 \cdot 2H_2O$ will precipitate.

Steps 14 and 15. Repeat Steps 11 and 12.

Step 16. Evaporate the HCl-ether supernate and redissolve the residue in 8 ml of water.

Step 17. Add sufficient NH_4OH to make the solution basic, and heat to boiling.

Step 18. Add 2 ml of a solution of saturated ammonium oxalate and stir thoroughly to precipitate SrC_2O_4.

Step 19. Heat again to boiling and allow to stand for 5 minutes without applying heat, while stirring occasionally. Centrifuge at top speed for 5 minutes.

Step 20. Remove the supernate with the suction tube.

Step 21. Slurry the precipitate onto a planchet and dry.

Step 22. Weigh the precipitate to determine the yield.

Step 23. Mount in a counting chamber and count.

PROCEDURE 3 (Cont'd.)

6. Discussion

The precipitation of the strontium and barium nitrates is done in 60% nitric acid to minimize the calcium contamination. At this acid concentration only 3.5 per cent of the calcium is coprecipitated with the strontium and barium, but at a concentration of 70 per cent, 13.4 per cent of the calcium is carried. If the acid concentration gets as high as 80 per cent, 78 per cent of the calcium is carried.

Care must be exercised in handling the fuming nitric acid. The work should be done in a well ventilated hood, and the operator should wear rubber gloves and a face shield to avoid severe acid burns. Good ventilation should also be provided for the ether, and it should not be brought close to open flames.

PROCEDURE 4

BARIUM

Source - C. O. Minkkinen in "Collected Radiochemical Procedures", Los Alamos report LA-1721. Jan. 1958.

The procedure for the separation and determination of barium is a modification by C. O. Minkkinen of one described by L. E. Glendenin, CC-971 (September 15, 1943).

1. Introduction

Barium may be separated from fission-product material by the specific precipitation in the cold as $BaCl_2 \cdot H_2O$ by means of a concentrated hydrochloric acid-ethyl ether mixture. The procedure for the determination of barium as outlined below consists in the isolation of $BaCl_2 \cdot H_2O$, followed by conversion to the chromate. Three precipitations of the chloride are carried out, the first and second being followed by ferric hydroxide scavenging steps. The final precipitation of barium as the chromate is preceded by a lanthanum hydroxide scavenging step to remove lanthanum and other fission products which form insoluble hydroxides and which were not removed by the iron scavenger.

The chemical yield of barium chromate is 65 to 75%. A single analysis requires about 2 hours.

2. Reagents

Ba carrier: 10 mg Ba/ml $Ba(NO_3)_2$ solution--standardized

Fe carrier: 10 mg Fe/ml (added as aqueous $FeCl_3 \cdot 6H_2O$)

La carrier: 10 mg La/ml (added as aqueous $La(NO_3)_3 \cdot 6H_2O$)

HCl-ethyl ether mixture: 5 parts (by volume) conc. HCl to 1 part ethyl ether

NH_4OH: 6M

NH_4OH: 1M

HCl: 6M

$HC_2H_3O_2$: 6M

$NH_4C_2H_3O_2$: 3M

Na_2CrO_4: 1.5M

Phenolphthalein indicator solution

Ethanol: 95%.

3. Equipment

Drying oven

Centrifuge

Hot plate

Fisher burner

Block for holding centrifuge tubes

Forceps

Mounting plates

15-ml sintered glass crucible (fine porosity)

Ground-off Hirsch funnels: Coors 000A (one per sample)

Filter chimneys (one per sample)

Filter flask (one per sample)

250-ml beakers (one for each standardization)

Pipets: 2- and 5-ml

Wash bottle

40-ml conical centrifuge tubes: Pyrex 8320 (four per sample)

No. 50 Whatman filter paper: 7/8" diameter

Stirring rods

Ice bath.

4. Preparation and Standardization of Carrier

Dissolve 19.0 gm of $Ba(NO_3)_2$ in H_2O and dilute to 1 liter.

Pipet 5.0 ml of carrier solution into a 250-ml beaker and dilute to approximately 100 ml. Add 5 ml of 6M $HC_2H_3O_2$ and 10 ml of 3M $NH_4C_2H_3O_2$. Place on hot plate and bring to a boil. Add 5 ml of 1.5M Na_2CrO_4 dropwise with stirring, boil for 1 min with stirring, cool to room temperature, and filter the $BaCrO_4$ on a fine sintered glass crucible which has been washed with water andethanol, dried at 110° for 15 min, and weighed. Wash the precipitate three times with 5-ml portions of H_2O and three times with 5-ml portions of ethanol. Dry at 110°, cool, and weigh.

Four standardizations of the carrier solution are performed. The spread in results is about 0.5%.

5. Procedure

Step 1. To the sample in a 40-ml centrifuge tube, add 2 ml of standardized Ba carrier (combined volume not to exceed 5 ml). Place tube in ice bath and add 30 ml of cold HCl-ether reagent (Note 1). Stir for 1 min or until a precipitate of $BaCl_2 \cdot H_2O$ is formed. Centrifuge and discard the supernate. Washingprecipitate twice with 5 ml of HCl-ether mixture, centrifuging after each eashing and discarding the supernate.

Step 2. Dissolve precipitate in 4 ml of H_2O. Add 1 drop of phenolphthalein solution and 6 drops of Fe carrier. Neutralize with 6M NH_4OH and add 12 drops in excess. Centrifuge and pour the supernate into a clean centrifuge tube.

PROCEDURE 4 (Cont'd.)

Step 3. Add 30 ml of HCl-ether mixture to the supernate and proceed as in Steps 1 and 2.

Step 4. Repeat precipitation of $BaCl_2 \cdot H_2O$ with HCl-ether reagent. Wash precipitate twice with 5-ml portions of HCl-ether reagent, dissolve precipitate in 10 ml of H_2O, and add 1 drop of phenolphthalein solution and 10 drops of La carrier. Neutralize with 6M NH_4OH and add 10 drops in excess. Centrifuge and pour the supernate into centrifuge tube. Wash precipitate twice with 5-ml portions of 1M NH_4OH, adding the washings to the supernate from scavenger precipitation.

Step 5. Neutralize supernate with 6M HCl, and then add 2.5 ml of 6M $HC_2H_3O_2$ and 10 ml of 3M $NH_4C_2H_3O_2$. Heat to boiling and add dropwise 2 ml of 1.5M Na_2CrO_4. Boil for 1 min with constant stirring. Cool and filter the $BaCrO_4$ on a previously washed, dried, and weighed filter paper, using a filter chimney and ground-off Hirsch funnel. Wash the precipitate three times with 5-ml portions of H_2O and three times with 5-ml portions of ethanol. Dry at 110°, cool, weigh, and mount (Note 2).

Notes

1. For maximum yield of $BaCl_2 \cdot H_2O$ the solution must be cooled to about 5°.

2. The $BaCrO_4$ precipitates are set aside for 134 hours before counting. This permits Ba^{140} and the La^{140} daughter activities to come to equilibrium.

PROCEDURE 5

BARIUM

Solution - L. J. Beaufait, Jr., and H. R. Lukens, Jr., page 77 in "Handbook of Radiochemical Analysis Volume II Radiochemical Procedures", U. S. Atomic Energy Commission report NP-5057 (Del.), March 5, 1952.

1. To the solution containing the barium activity in a volume of 5 to 8 ml (in a 40-ml heavy-wall centrifuge cone), add barium carrier, stir thoroughly and let stand for ten minutes. Add 20 ml of yellow fuming HNO_3 to precipitate $Ba(NO_3)_2$ (Note a). The solution is stirred while cooling in an ice bath for five minutes. Centrifuge, decant, and discard the supernate.

2. Dissolve the precipitate completely in 2 ml of water (Note b). Re-precipitate $Ba(NO_3)_2$ by adding 10 ml of fuming HNO_3 and cooling in an ice bath for 20 minutes with occasional stirring. Centrifuge the solution, decant, and discard the supernate. Dissolve the precipitate in 7 ml of water.

3. Add 5 mg of Fe^{+++} carrier and precipitate $Fe(OH)_3$ by the addition of 2 ml of 6N NH_4OH while stirring (Note c). Centrifuge and transfer the supernate with a pipette to a clean 40-ml centrifuge cone. Wash the precipitate by slurrying in 7 ml of a 1N NH_4NO_3 solution containing 2 drops of NH_4OH. Centrifuge and remove the wash supernate with a transfer pipette. Combine this wash supernate with the supernate above and save. Discard the $Fe(OH)_3$ scavenge precipitate.

4. Neutralize the combined supernates by the dropwise addition of 6N HNO_3, testing the acidity with pH paper. Add 1 ml of 6M HAc and 2 ml of 6M NH_4Ac. Heat the solution nearly to boiling and add 1 ml of 1.5M Na_2CrO_4, dropwise with stirring. Continue stirring the solution for one minute, then centrifuge. Discard the supernate. Wash the yellow $BaCrO_4$ with 10 ml of hot water. Centrifuge and discard the supernate. The remaining steps in the procedure, including the final counting, must

be finished within two hours to prevent error due to La^{140} daughter contamination in the Ba precipitate.

5. Dissolve the $BaCrO_4$ in 2 ml of 6N HCl (Note d). Add 15 ml of HCl-ether reagent, and stir for two minutes to coagulate the $BaCl_2$ and let stand for five minutes in an ice bath. Centrifuge the solution, decant, then discard the supernate.

6. Dissolve the precipitate in a few drops of water (Note b), and re-precipitate the $BaCl_2 \cdot H_2O$ by the addition of 15 ml of HCl-ether reagent and stir the solution for two minutes. Allow the solution to cool in an ice bath for five minutes. Centrifuge, decant, and discard the supernate.

7. Have ready a Whatman No. 42 paper disc which has been previously prepared by washing it with three 3-ml portions of water and three 3-ml portions of ethanol. Dry in an oven at 90-100° for 15 minutes, cool in a desiccator for ten minutes, and weigh. Repeat this procedure until constant weight ($\pm$ 0.1 mg) has been obtained.

8. Dissolve the $BaCl_2$ in 10 ml of water. Heat the solution nearly to boiling and add 5 drops of 1.5M H_2SO_4. Continue heating for three minutes to coagulate the precipitate, then filter onto the prepared filter paper. Wash and dry the precipitate according to the filter paper treatment in step 7. Weigh as $BaSO_4$, mount, and count immediately (Note e).

NOTES

a. At least 3 volumes of fuming nitric acid should be added to insure quantitative precipitation of $Ba(NO_3)_2$.

b. It may be necessary to add several additional drops of water to effect complete solution.

c. The addition of several drops of 1% aerosol solution sometimes prevents excess creepage.

d. A precipitate of white $BaCl_2$ may appear but will dissolve with the addition of 0.5 ml of water.

e. The counting error due to growth of the La^{140} daughter will become

appreciable (approximately 3%) after two hours from the $BaCrO_4$ precipitation. A curve, "$Barium^{140}$-$Lanthanum^{140}$ Growth", is provided in Vol. I, Section two in case the two hour time limit cannot be met.

PROCEDURE 6

BARIUM

Source - R. L. Folger in report AECD-2738
edited by W. W. Meinke, August 1949.

Target material: Approximately 3 g U metal

Time for separation: Approximately 1-1/2 hr.

Type of bombardment: 184" high energy particles

Equipment required: Centrifuge, cones (50 ml-2 ml), ice bath.

Yield: 50-75%

Degree of purification: Approximately 10^3 from other elements - sufficient for mass spectrograph or ion exchange column.

Advantages: Gives good yield of Ra-Ba with only approximately 75 μg carrier.

Procedure:

(1) Dissolve target in small amount conc. HNO_3 (heat if necessary). Add 100 μg Ba (as $Ba(NO_3)_2$ carrier solution) and 20 mg Sr^{+2} carrier (as nitrate).

(2) Add fuming HNO_3 to make up approximately 25 ml and chill in ice bath for 10 minutes. Centrifuge out $Sr(NO_3)_2$ (Carries Ba and Ra).

(3) Dissolve in H_2O, transfer to 15 ml conc and buffer with HAc + NH_4Ac (1 ml 6 N HAc and 2 ml 6 N NH_4Ac or pH 5-6). Add approximately 5 mg Pb and precipitate $PbCrO_4$ by addition of 1.5 M Na_2CrO_4 to hot solution. Wash with hot HAc and NH_4Ac buffer (1 ml to 2 ml as above) containing 1 drop 1.5 M Na_2CrO_4.

(4) Dissolve precipitate in hot 2 N HCl, pass in H_2S to reduce $Cr_2O_7^{=}$ to Cr^{+3} and dilute to 0.2 N, precipitate PbS scavenge with few mg CuS.

(5) Boil out H_2S, make basic with NH_3 and precipitate $SrCO_3$ by adding 2 mg Sr and a few drops 2 M Na_2CO_3.

(6) Dissolve $SrCO_3$ in 1 drop 6 N HCl, boil out CO_2, buffer with 1/2 ml 6 N HAc and 1 ml 6 N NH_4Ac (pH 5-6). Transfer to 5 ml cone, adding not more than 1 ml H_2O. Heat to near boiling, add minimum Pb^{+2} to precipitate $PbCrO_4$ with 1 drop 1.5 M Na_2CrO_4. Centrifuge.

(7) Dissolve $PbCrO_4$ in 1 drop conc. HCl. Transfer to 2 ml cone with 1 ml HCl-ether reagent. Chill 10 min in ice bath and centrifuge out $BaCl_2 \cdot 2H_2O$. Wash with 1/2 ml HCl-ether reagent.

(8) Dissolve in 1 drop H_2O and add 1 drop 0.5 N H_2SO_4. Centrifuge out $BaSO_4$ for mass spectrograph.

(8a) Dissolve in 1 drop H_2O and add 1 drop 0.5 N NaOH plus 1 drop 2 M Na_2CO_3. Centrifuge $BaCO_3$ and dissolve in 0.1 N HCl for equilibration with resin for column run.

Remarks: If the target solution is obtained in large volume, buffer with NH_4Ac until uranium precipitates out. Centrifuge and precipitate $PbCrO_4$ from supernatant (20 mg or more may be required). Remove Pb by dissolving the chromate in 1-2 N HCl, passing in H_2S, diluting to 0.2 N and precipitation PbS. After H_2S has been boiled out, the solution may be made basic and $SrCO_3$ precipitated to reduce the volume. Follow with $Sr(NO_3)_2$, $PbCrO_4$ and $BaCl_2 \cdot 2H_2O$ precipitations.

For mass spectrograph work, steps 5 and 6 may be replaced by:

(5-6a) Boil out H_2S. Buffer to pH 5-6 and precipitate min. $PbCrO_4$ by addition of Pb^{+2} and 1.5 M Na_2CrO_4. Centrifuge. Wash with 2 drops 6 M NH_4Ac.

To remove excess alkali salts add:

(9) Fume $BaSO_4$ to dryness to remove any NH_4Cl. Take up in 1 drop 0.5 N H_2SO_4. Centrifuge and rewash with 1 drop 0.5 N H_2SO_4.

For resin column separation of Sr, Ba, and Ra see E. R. Tompkins AECD-1998. Elute from resin with citrate at pH 7.5-8.0.

PROCEDURE 7

BARIUM

Source - D. Z. Lippmann and R. H. Goeckermann in report AECD-2738 edited by W. W. Meinke, August 1949.

Target material: Au foil, about 1 g

Time for separation: 1 hr. for barium.

Type of bombardment: Full energy protons, helium ions, or deuterons

Equipment required: Ice bath and hot water bath.

Yield: Ba 25%

Degree of purification: Good - about 10^5 from Au and spallation products and at least 10^3 from fission products.

Advantages: Sr, Ba, and Mo can all be separated from the same target material.

Procedure: Dissolve target in hot solution containing 10 mg each of Sr, Ba, and Mo, 5 ml of 12 M HCl and 5 ml of fuming HNO_3. Cool solution in ice bath and slowly add about 30 ml fuming HNO_3. $Sr(NO_3)_2$ and $Ba(NO_3)_2$ precipitate. Centrifuge.

Dissolve precipitate in 5 ml H_2O, add 5 mg Fe^{III}, warm in hot water bath, and precipitate $Fe(OH)_3$ with 6 M NH_4OH. Centrifuge. If desired add more Fe^{III} and centrifuge out $Fe(OH)_3$ again. Neutralize supernatant with a few drops of 6 M HC_2H_3O, heat to boiling, and add 2 ml of 1.5 M Na_2CrO_4 dropwise. Digest $BaCrO_4$ precipitate in hot water bath and centrifuge.

PROCEDURE 7 (Cont'd.)

Wash $BaCrO_4$ precipitate with 10 ml of hot H_2O and centrifuge. Dissolve $BaCrO_4$ in 1 ml of 6 M HCl with heating, add 10 mg Sr carrier, 2 ml 6 M $NH_4C_2H_3O_2$, 1 ml of 6 M $HC_2H_3O_2$, heat to boiling, add 2 ml 1.5 M Na_2CrO_4 dropwise, digest in hot water bath, and centrifuge. Dissolve $BaCrO^4$ in 1 ml 6 M HCl with heating, add 15 ml HCl-ether reagent (5 volumes of 12 M HCl plus 1 volume of ether), cool in ice bath until $BaCl_2$ precipitates, and centrifuge. Dissolve $BaCl_2$ in 5 ml H_2O, add 5 mg Fe^{III}, warm, precipitate $Fe(OH)_3$ with 6 M NH_4OH, and centrifuge. Neutralize supernatant with 6 M HNO_3, add 2 ml 6 M $NH_4C_2H_3O_2$, 1 ml 6 M $HC_2H_3O_2$, heat to boiling, add 2 ml 1.5 M Na_2CrO_4 dropwise, digest in hot water bath, filter, wash three times with 5 ml H_2O and three times with 5 ml alcohol, dry 15 minutes at 110 C. Weigh as $BaCrO_4$.

Remarks:

All additions of fuming or concentrated HNO_3 should be made cautiously; they tend to react violently after a short induction period.

PROCEDURE 8

BARIUM

Source - R. W. Fink in report AECD-2738
edited by W. W. Meinke, August 1949.

Target material: CsCl

Time for separation: 90 min.

Type of bombardment: 85 Mev Protons for 1 hour

Equipment required: Standard

Yield: Sufficient for mass spectrograph work.

Degree of purification: Cesium is persistent, but may be removed in successive recyclings. Pure enough for mass spectrograph work.

Advantages:

Carrier free Ba for mass spectrograph.

Procedure:

(1) Target CsCl is dissolved in 2 cc 0.1-N HAc, 1 cc NH_4Ac saturated added, and 10 mg Pb carrier added. K_2CrO_4 solution is then added until complete precipitation. This precipitate is then washed with 1% NH_4Ac until free from Cesium. If necessary, the precipitate may be dissolved in 0.1 - N HCl and reprecipitated to free it from Cs.

(2) The Cs-free $PbCrO_4$ precipitate is then dissolved in 1 cc 0.1-N HCl and excess H_2S is bubbled in to precipitate black PbS and reduce the CrO_4 to $CrCl_3$ (green).

(3) The solution from (2) containing radiobarium, is made alkaline, after boiling to expel H_2S and radioargons, and some $Fe(Cl)_3$ added to help precipitate $Cr(OH)_3$.

(4) The final, colorless solution has carrier-free barium. It is converted to the sulfate for mass spectrometer work.

Remarks:

The cesium, being the target material, is very persistent, and several precipitations in step (1) may be needed to free the barium of it.

PROCEDURE 9

BARIUM

Source - R. H. Goeckermann in report AECD-2738 edited by W. W. Meinke, August 1949.

Target material: Approximately 1 g Bi metal

Time for separation: 1-2 hrs.

Type of bombardment: 184" all particles

Equipment required: Centrifuge, tubes, ice, vacuum dessicator.

Yield: Approximately 80%

Degree of purification: Decontamination factor approximately 10^4 from fission and spallation products. Ba decontaminated approximately 10^4 from Sr.

Advantages: Good yield of Ba and Sr, separation from all other elements except Ba, very good separation of Sr and Ba from each other.

Procedure:

(1) To aliquot of HNO_3 solution of target, add 10 mg Sr and Ba, 30 ml fuming HNO_3, digest cold 1-2 min.

(2) Dissolve precipitate in 2 ml H_2O and reprecipitate with 15 ml fuming HNO_3.

(3) Dissolve precipitate in 5-10 ml H_2O, add 5 mg Fe^{+3}, and precipitate $Fe(OH)_3$ with tank NH_3 ($CO_3^=$ free!) Repeat $Fe(OH)_3$ scavenge.

(4) Neutralize supernatant with 6 N HNO_3, add 1 ml 6 M HAc and 2 ml 6 M NH_4Ac. Heat to boiling and add 1 ml 1.5 M Na_2CrO_4 dropwise with stirring. Digest one min. (Save the supernatant for Sr fraction).

(5) Ba - Wash $BaCrO_4$ precipitate with 10 ml hot H_2O. Dissolve in 1 ml 6 N HCl, add few mg Sr, and reprecipitate $BaCrO_4$. Redissolve, add 15 ml ether-HCl reagent (5 parts conc. HCl to 1 part di-ethyl ether), digest cold 2 min, wash with 5 ml absolute EtOH containing a few drops of HCl.

Dissolve $BaCl_2$ in 1 ml H_2O, make just basic with NH_3 and scavenge with $Fe(OH)_3$ (5 mg). Add 15 ml ether-HCl and reprecipitate $BaCl_2$. Repeat if necessary. Filter last $BaCl_2$ precipitate, wash three times with 5 ml ether, dry in vacuum dessicator - 2 min. evacuate release, 5 min. evacuate. Weigh as $BaCl_2 \cdot 2H_2O$ (17.8 mg per 10 mg Ba).

Remarks: Procedure adapted for use when Sr activity much greater than Ba, Ra follows the Ba well, can be separated from it by use of a resin column.

PROCEDURE 10

BARIUM

Source - H. Hicks, R. L. Folger, and R. H. Goeckermann in report AECD-2738, edited by W. W. Meinke, August 1949.

Target material: U or Th or Bi

Time for separation: 30-45 min.

Type of bombardment: Fission

Equipment required: ice bath

Yield: Approximately 100%

Degree of purification: excellent

Advantages: Fast and easy

Procedure:

(1) Take aliquot of HNO_3 or HCl solution of target and add Ba carrier. If necessary evaporate to less than 1 cc. With tube in ice bath, add 10 cc ether -- HCl reagent (ether-HCl reagent - 400 cc conc. HCl + 80 cc diethyl-ether). Stir and digest 2 or 3 minutes to bring down silky appearing $BaCl_2 \cdot 2H_2O$.

(2) Centrifuge, dissolve in 0.5 cc H_2O, repeat (1).

(3) Centrifuge, dissolve in 0.5 cc H_2O, dilute to 7-8 cc, make to pH $>$ 10 with carbonate free ammonia and scavenge twice with $Fe(OH)_3$.

(4) Precipitate $BaCO_3$ by adding 3 drops saturated Na_2CO_3, and digest 5 min. in hot water bath.

(5) Dissolve $BaCO_3$ in 1 cc 6 N HCl, repeat (1) and (2).

(6) Centrifuge, wash with 5 cc absolute alcohol, then 3 portions of 5 cc other, weigh as $BaCl_2 \cdot 2H_2O$.

Remarks: (2) can be modified by adding double volume of ether saturated with HCl gas to $BaCl_2 \cdot 2H_2O$ dissolved in H_2O and continuing to introduce HCl gas until the precipitate appears and the aqueous and organic layers become miscible.

PROCEDURE 11

BARIUM

Source - A. S. Newton in report AECD-2738, edited by W. W. Meinke, August 1949.

Target material: Thorium metal (.1-1 gm)

Time for separation: 1 hr.

Type of bombardment: 60" alphas

Equipment required: Standard

Yield: Approximately 60% on Ba

Degree of purification: 10^6 other Fission Products approximately 10^3 from Strontium.

Advantages: Ba and Sr can be taken out in same procedure.

Procedure: The Th metal is dissolved in conc. HCl plus a few drops of ,2 M $(NH_4)_2SiF_6$ to clear up the black residue. The HCl is diluted to 2 N and an aliquot taken.

(1) Add 20 mg each Ba and Sr carrier and 30 ml fuming nitric acid. Cool 1-2 minutes with stirring and centrifuge. (If $SO_4^=$ present add H_2SO_4 to precipitate $BaSO_4$. Wash with 10 ml H_2O. Metathesize with 50% K_2CO_3 by boiling 5 min. Centrifuge, wash with water, Dissolve precipitate in 1 N HNO_3. Discard residue. Then make fuming nitric acid precipitation.)

(2) Dissolve precipitate in 2 ml H_2O. Reprecipitate with 15 ml fuming HNO_3.

(3) Dissolve precipitate in 5 to 10 ml H_2O. Add 5 mg Fe^{+++}, precipitate $Fe(OH)_3$ by adding 2 ml carbonate free 6 M NH_4OH or pass in NH_3 gas to precipitate $Fe(OH)_3$. Centrifuge.

(4) Neutralize supernate with 6 N HNO_3. Add 1 ml 6 M HAc, 2 ml 6 M NH_4Ac. Heat solution to nearly boiling. Add 1 ml of 1.5 M Na_2CrO_4 dropwise with stirring. Let stand 1 min. Centrifuge, Reserve supernate for Sr.

(5) Wash precipitate of $BaCrO_4$ with 10 ml hot H_2O. Dissolve in 1-2 ml 6 M HCl add 15 ml HCl-Et_2O reagent, stir 1-2 min. Centrifuge.

(6) Dissolve precipitate in 1 ml H_2O. Reprecipitate $BaCl_2$ with 15 ml HCl-Et_2O reagent. Centrifuge. Transfer precipitate to weighed filter paper with 4% HCl in EtOH. Wash 3 x 5 ml EtO_2. Dry by evacuation 2 min, release, evacuate, 5 min. Weigh as $BaCl_2 \cdot H_2O$.

Remarks: This procedure has been described previously. (Phys. Rev. 75 17 (1949).

PROCEDURE 12

BARIUM

Source - A. S. Newton in report AECD-2738, edited by W. W. Meinke, August 1949.

Target material: Thorium metal (.1-1 gm) Time for separation: 45 min.

Type of bombardment: 60" alphas Equipment required: Standard

Yield: 90%

Degree of purification: $> 10^6$ from all activities present

Procedure: The Th metal is dissolved in conc HCl plus a few drops of .2 M $(NH_4)_2 SiF_6$ solution to clear up the black residue. The HCl is diluted to 2 N and an aliquot taken.

(1) 1-5 ml sample in 50 ml centrifuge tube. Add 20 mg Ba^{++} carrier. If total volume is $>$ 5 ml, boil down to 5 ml or less. To cold solution add 30-35 ml HCl-ether reagent. Stir 1-2 min while

cooling in ice bath. Centrifuge. Wash precipitate with 5 ml HCl-Et_2O. Centrifuge.

(2) Dissolve precipitate in 1 ml H_2O, add 15 ml HCl - Et_2O to precipitate barium. Centrifuge and wash with HCl - ether solution.

(3) Repeat (2).

(4) If scavenging is necessary dissolve in 4 ml H_2O, add 1-2 mg Fe^{+++} and fresh (carbonate free) NH_4OH till an excess is present. Centrifuge and discard precipitate. To solution add 5 ml HCl-Et_2O, cool and centrifuge.

(5) Dissolve precipitate in H_2O. Dilute to 10 ml, add 6 drops HCl + 10 mg Ag, digest, centrifuge off AgCl. Repeat,

(6) Add 1-2 mg Fe^{+++}, then NH_4OH. Make 2 hydroxide precipitations of $Fe(OH)_3$.

(7) Add Na_2CO_3, precipitate $BaCO_3$. Dissolve in 1 ml conc HCl, precipitate $BaCl_2$ by adding HCl - Et_2O reagent.

(8) Transfer precipitate to weighed filter with 3-5 ml portions of absolute EtOH containing 4% HCl. Filter with suction. Wash three times with 5 ml Et_2O. Dry by evacuation. 2 min. evacuation, release, 5 min. evacuation. Weigh as $BaCl_2 \cdot H_2O$.

Remarks: This method has been described previously. (Phys. Rev. 75 17 (1949)).

Preparation of carrier solution: Dissolve 19.0 gms $Ba(NO_3)_2$ in water and dilute to 1 liter.

Standardization as $BaCl_2 \cdot H_2O$: Take 5 ml carrier, add 50 ml ether-HCl mixture. Cool in ice bath for 10 minutes. Stir, filter onto a sintered glass crucible. Use 3 - 5 ml portions of absolute EtOH containing 3-5 drops conc HCl to transfer and wash the precipitate. Wash with three 5 ml portions of Et_2O. Evacuate and weigh as $BaCl_2 \cdot H_2O$.

PROCEDURE 13

BARIUM

Source - L. E. Glendenin, Paper 288 in "Radiochemical Studies: The Fission Products", edited by C. D. Coryell and N. Sugarman, McGraw-Hill Book Co., Inc., New York, 1951. It is based on report CN-1312, dated May 15, 1945.

1. INTRODUCTION

The specific precipitation of $BaCl_2$ by conc. HCl is the classical method for the isolation of barium from fission-product mixtures.[65] The method[66] previously employed on the Project consisted in three precipitations of barium as $BaCl_2 \cdot H_2O$, a $La(OH)_3$ scavenging precipitate, and a final precipitation

of barium as $BaCrO_4$. A mixture of HCl and ether has also been used to precipitate $BaCl_2$, since the precipitation by this reagent is more complete than the precipitation by HCl alone.[67,68] The solubility is less than 1 part in 120,000.

In the search for a method applicable to all types of fission-product solutions, a more rapid method of analysis has been developed which consists simply in a triple precipitation of $BaCl_2 \cdot H_2O$ by a HCl-ether mixture (5 parts of conc. HCl to 1 part of ethyl ether) and weighing as such after alcohol-ether washing and vacuum desiccation. The improved procedure is given below. Further testing of the procedure for special applications has been done by Nelson, Boldridge, and Hume.[69]

2. PREPARATION AND STANDARDIZATION OF CARRIER

Dissolve 19.0 g of $Ba(NO_3)_2$ in H_2O and dilute to 1 liter.

Standardization as $BaCl_2 \cdot H_2O$: Pipet 5 ml of carrier solution into a beaker and add 50 ml of HCl-ether mixture (5 parts of conc. HCl to 1 part of ethyl ether). Cool in an ice bath for about 10 min with occasional stirring. Filter quantitatively on a weighed sintered-glass crucible with suction, transferring and washing with three 5-ml portions of absolute ethanol containing 4 per cent conc. HCl. Wash three times with 5 ml of ether, rinsing down the inside of the crucible with each washing. Wipe the outside of the crucible carefully with Kleenex or a lintless cloth, and place in a vacuum desiccator. Evacuate for 2 min., release the suction, and evacuate again for 5 min. Weigh as $BaCl_2 \cdot H_2O$ and repeat the desiccation until the weight is constant to 0.2 mg.

3. PROCEDURE

Step 1. Take 1 to 5 ml of a sample of fission material (Note 1) in a 50-ml centrifuge tube and add 2 ml of standardized barium carrier. If the total volume exceeds 5 ml, boil down to 5 ml or less. Add 30 to 35 ml of HCl-ether reagent to the cool solution, and stir for 1 to 2 min while cooling under running tap water. Centrifuge, decant completely, wash with

5 ml of HCl-ether mixture, centrifuge, and again decant completely.

Step 2. Dissolve the precipitate in 1 ml of H_2O and reprecipitate with 15 ml of HCl-ether mixture. Centrifuge and decant.

Step 3. Repeat the precipitation, centrifuge, and decant thoroughly. Note the time.

Step 4. Transfer the precipitate to a weighed filter-paper disk (Note 2) in a small Hirsch funnel with three 5-ml portions of 4 per cent HCl in ethanol (Note 3). Filter with suction. Wash three times with 5-ml portions of ether and suck dry. Transfer the paper with the precipitate to a small watch glass, and place in a vacuum desiccator. Evacuate for 2 min, release the suction, and then evacuate again for 5 min. Weigh the precipitate as $BaCl_2 \cdot H_2O$ and mount for counting (Note 4). For samples of higher purity than those obtained in this procedure, a $Fe(OH)_3$ scavenging precipitation can be performed (Note 5).

Notes. 1. The solution taken for analysis should be free of acid-insoluble residue, since any solid material present will be weighed with the $BaCl_2 \cdot H_2O$. The sample should be filtered or put into solution if it is not perfectly clear, provided it does not contain SO_4^{--}. For samples containing SO_4^{--} proceed as follows: Add 2 ml of standardized barium carrier (ignoring any precipitate formed), dilute to 10 ml, and add 2 ml of 6N H_2SO_4. Heat and stir for 1 to 2 min, centrifuge, and wash with 10 ml of H_2O. Convert the $BaSO_4$ to $BaCO_3$ by boiling with 10 ml of 50 per cent K_2CO_3 for 5 min, centrifuge, and wash with 10 ml of H_2O. Dissolve the precipitate of $BaCO_3$ in a little 6M HCl, centrifuge or filter out any precipitate present, and proceed with the boiling in step 1.

2. The filter-paper disk must be washed with ethanol and ether and must be dried under the same conditions as in the procedure before the weighing.

3. Barium chloride is appreciably soluble in absolute ethanol. The presence of the HCl represses the solubility and allows a quantitative recovery.

4. The β -activity measurement of the barium sample should be taken as soon as possible after the last precipitation; this is considered zero time for the lanthanum daughter growth. The growth of La^{140} activity is nearly linear with time at the beginning, and the observed β activity of the Ba^{140} can be corrected to zero La^{140} growth by the relation $A_o = A_t/(1 + 0.0151t)$, where A_o is the original activity and A_t is the activity after t hr. This expression is valid for about the first 10 or 12 hr of growth.

Alternatively the sample cam be set aside to allow the 40h La^{140} daughter to grow and its γ radiation to be measured. The maximum La^{140} activity is attained at 134 hr after separation, and the measurement should be made at this time. A discussion of the growth of β activity in Ba^{140} as affected by absorption is given elsewhere.[70]

5. The rapid procedure provides a decontamination factor of about 10^3 from other fission activities. In special cases where greater purity may be desired, the following procedure should be used: Dissolve the $BaCl_2 \cdot H_2O$ from step 1 in 5 ml of H_2O, and add 1 to 2 mg of Fe^{+3} carrier. Heat nearly to boiling and add 1 ml of 6M NH_4OH (CO_2-free). Centrifuge, and discard the precipitate of $Fe(OH)_3$. Reprecipitate the $BaCl_2 \cdot H_2O$ from the supernatant solution with 34 ml of HCl-ether mixture, centrifuge, and proceed with step 3.

The addition of the $Fe(OH)_3$ scavenging step increases decontamination considerably and requires little extra time.

4. DISCUSSION

In standardization of the carrier the presence of a small amount of HCl (3 to 5 per cent) in the ethanol wash was found necessary to prevent the loss of barium in this step. There is no loss in the HCl-ether precipitation or in the ether wash. All the filtrates and washings in the standardization procedure gave negative tests for barium on the addition of H_2SO_4, whereas the presence of as little as 0.5 mg of barium gave a distinct precipitate.

The composition of the $BaCl_2$ precipitate was determined by standardizing a barium carrier solution that had also been standardized as $BaCrO_4$. For 5 ml

of solution, 93.2 mg of $BaCrO_4$ was obtained; this is equivalent to 50.6 mg of barium or 83.2 mg of $BaCl_2 \cdot H_2O$. Standardization of the carrier solution in triplicate by the method described here gave $BaCl_2$ precipitates with an average weight of 83.2 mg and with a mean deviation of 0.8 per cent.

PROCEDURE 14

CALCIUM

Source - W. H. Burgus in "Collected Radiochemical Procedures", Los Alamos report LA-1721. Jan. 1958.

This procedure is an adaption by W. H. Burgus of one previously reported by E. P. Steinberg in Radiochemical Studies: The Fission Products, Book 1, McGraw-Hill, New York, 1951, p. 482.

1. Introduction

Calcium is first separated from most of the fission products by appropriate ferric hydroxide, acid sulfide, and ammonium sulfide scavenging steps. This is followed by separation of calcium, strontium, and barium as oxalates. The oxalates are then dissolved, and strontium and barium are removed quantitatively by precipitation of their nitrates from fuming nitric acid. The 40h La^{140}, which has grown in from 12.5d Ba^{140} during the interval between the ferric hydroxide scavenging step and the last separation of barium and strontium from calcium, is separated by means of lanthanum hydroxide scavenger. Calcium is finally precipitated as calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$, and counted in this form. The chemical yield approximates 30%, and the time for a single analysis is about 1-3/4 hours.

2. Reagents

Ca carrier: 10 mg Ca/ml (added as $Ca(NO_3)_2 \cdot 4H_2O$ in very dilute HNO_3) --standardized

Fe carrier: 10 mg Fe/ml (added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl)

Pd carrier: 10 mg Pd/ml (added as $PdCl_2 \cdot 2H_2O$ in very dilute HCl)

Cu carrier: 10 mg Cu/ml (added as $CuCl_2 \cdot 2H_2O$ in H_2O)

Ni carrier: 10 mg Ni/ml (added as $Ni(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3)

Co carrier: 10 mg Co/ml (added as $Co(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3)

Sr carrier: 10 mg Sr/ml (added as $Sr(NO_3)_2 \cdot 4H_2O$ in very dilute HNO_3)

Ba carrier: 10 mg Ba/ml (added as $Ba(NO_3)_2$ in H_2O)

La carrier: 10 mg La/ml (added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O)

HCl: 6M

HNO_3: conc.

HNO_3: white fuming

NH_4OH: conc.

$(NH_4)_2CO_3$: saturated aqueous solution

$(NH_4)_2C_2O_4$: 4% aqueous solution

$NaBrO_3$: 1M

H_2S: gas

Ethanol: 95%

3. Equipment

Drying oven

Centrifuge

Fisher burner

Block for holding centrifuge tubes

Forceps

Mounting plates

Tongs for holding Erlenmeyer flasks

Ground-off Hirsch funnels: Coors 000A (one per sample)

Filter chimney (one per sample)

Filter flask (one per sample)

Pipets: 2-ml

Wash bottle

125-ml Erlenmeyer flasks (three per sample)

2", 60° short stem glass funnels (two per sample)

40-ml conical centrifuge tubes: Pyrex 8320 (11 per sample)

100-ml beakers (one per standardization)

15-ml sintered glass Gooch crucibles: fine porosity (one per standardization)

Filter flasks and holders for Gooch crucibles (one each per standardization)

No. 40 Whatman filter paper (9 cm)

No. 42 Whatman filter paper (tared for mounting): 7/8" diameter

Stirring rods

Ice bath.

4. Preparation and Standardization of Carrier

Dissolve 59.0 gm of $Ca(NO_3)_2 \cdot 4H_2O$ in H_2O, add 1 ml of HNO_3, and dilute to 1 liter with H_2O.

Pipet a 2-ml aliquot of the above carrier solution into a 100-ml beaker, dilute to 50 ml, heat to boiling, and precipitate $CaC_2O_4 \cdot H_2O$ by the addition of a slight excess of 4% $(NH_4)_2C_2O_4$ solution. Filter onto a tared sintered glass Gooch crucible (fine porosity). Wash three times with 10-ml portions of hot H_2O and once with ethanol. Suck dry for several minutes. Dry to constant weight in oven at no more than 100°.

Four standardizations are performed. The results should agree within 0.5%.

5. Procedure

Step 1. To the sample in a 40-ml centrifuge tube, add sufficient H_2O to bring the volume to 15 to 20 ml, then add 2 ml of standard Ca carrier. If U is present, heat the solution to boiling and by the dropwise addition of conc. NH_4OH precipitate ammonium diuranate. Centrifuge and discard the precipitate, transferring the supernate to a 40-ml centrifuge tube. If no appreciable quantity of U is present, proceed immediately to Step 2.

Step 2. Acidify the solution with conc. HNO_3, add 6 drops of Fe carrier, heat to boiling, and by the dropwise addition of conc. NH_4OH precipitate $Fe(OH)_3$. Centrifuge and discard the precipitate, transferring the supernate to a 40-ml centrifuge tube.

Step 3. Repeat Step 2.

Step 4. Repeat Step 2 again.

Step 5. Make the supernate, after the $Fe(OH)_3$ scavenging operation, 0.1M in HCl, and add 4 drops of Pd and 8 drops of Cu carriers. Heat to boiling and pass in H_2S for 4 to 5 min. Filter the acid sulfide scavenging precipitate on a No. 40 Whatman paper and discard it, catching the filtrate in a 40-ml centrifuge tube.

Step 6. Add 4 drops each of Ni and Co carriers to the filtrate and heat to boiling. Add conc. NH_4OH until the solution is basic to litmus, then add an additional 0.5 ml of NH_4OH. Pass in H_2S for 3 min and filter the ammonium sulfide scavenge on a No. 40 Whatman paper, catching the filtrate in a 40-ml centrifuge tube. Discard the precipitate.

Step 7. Add 3 ml of 4% $(NH_4)_2C_2O_4$ solution to the filtrate from above. Centrifuge and discard the supernate. Wash the precipitate with 30 ml of H_2O.

Step 8. Dissolve the precipitate in 5 ml of H_2O and 1 ml of conc. HNO_3. Add 1 ml each of Ba and Sr scavengers. Precipitate $Ba(NO_3)_2$ and $Sr(NO_3)_2$ by the addition of 30 ml of white fuming HNO_3. Cool in an ice bath for several minutes. Centrifuge and discard the precipitate, transferring the supernate to a 125-ml Erlenmeyer flask.

Step 9. Boil down the Ca-containing supernate to a volume of 1 to 2 ml. Add 5 ml of H_2O, 1 ml each of Ba and Sr carriers, and 30 ml of fuming HNO_3 to precipitate $Ba(NO_3)_2$ and $Ca(NO_3)_2$. Cool and transfer the mixture to a 40-ml centrifuge tube. Centrifuge, transfer the supernate to a 125-ml Erlenmeyer flask, and discard the precipitate.

Step 10. Repeat Step 9.

Step 11. Boil down the supernate to 2 to 3 ml and add 30 ml of H_2O. Transfer to a 40-ml centrifuge tube and make ammoniacal with conc. NH_4OH. Add 2 ml of 4% $(NH_4)_2C_2O_4$ solution to insure complete precipitation of $CaC_2O_4 \cdot H_2O$. Centrifuge and discard the supernate.

PROCEDURE 14 (Cont'd.)

Step 12. Dissolve the $CaC_2O_4 \cdot H_2O$ in 2 ml of conc. HNO_3 and 2 ml of 1M $NaBrO_3$ (Note 1). Boil down to about 1 ml. Add 30 ml of H_2O, make strongly ammoniacal, and add 4 ml of saturated $(NH_4)_2CO_3$ solution. Centrifuge the $CaCO_3$ and discard the supernate.

Step 13. Dissolve the $CaCO_3$ in 1 to 2 ml of Conc. HNO_3. Dilute to 30 ml, and add 1 ml of La carrier. Precipitate $La(OH)_3$ by the addition of conc. NH_4OH. Centrifuge, transfer the supernate to a 40-ml centrifuge tube, and discard the precipitate.

Step 14. Heat the supernate to boiling anf precipitate $CaC_2O_4 \cdot H_2O$ by the dropwise addition of 3 ml of 4% $(NH_4)_2C_2O_4$. Filter the $CaC_2O_4 \cdot H_2O$ on a tared Whatman No. 42 circle, using a ground-off Hirsch funnel and a chimney. Wash three times with 10-ml portions of hot H_2O, and then with ethanol. Suck dry. Dry in oven at 100° for 5 min. Weigh, mount, and count (Note 2).

Notes

1. $NaBrO_3$ is used to destroy oxalate and thus avoid precipitation of lanthanum oxalate when the La carrier is added (Step 13).

2. No special precautions need be taken in counting. If short-lived isotopes are present, the decay curve must be resolved. If 150d Ca^{45} is to be counted, the chemistry employed for separation of Ca is carried out after the decay of the short-lived isotopes.

PROCEDURE 15

CALCIUM

Source - D. Stewart and S. Softky in report AECD-2738, edited by W. W. Meinke, August 1949.

Target material: Copper (up to 10 g)

Type of bombardment: Neutrons 184"

Time for separation: 4 hrs.

Equipment required:
200 ml stainless steel beaker
Pt stirrer electrode
D. C. source
200 ml centrifuge cone

Yield: 60 - 80%

Degree of purification: 10^6 from Cu

Procedure:

(1) Dissolve Cu in minimum dilute HNO_3 in a stainless steel beaker, add 10 mg Ca carrier as nitrate and 2-3 drops of conc. H_2SO_4. Dilute to 100-150 ml.

(2) Electrodeposit copper at 2-3 volts using the beaker as the cathode and a rotating platinum anode. Keep the stainless steel beaker in an ice bath during the electrolysis.

(3) When solution is water-white remove the anode and transfer the solution quickly to a 200 ml centrifuge cone. Neutralize with NH_4OH and make just acid with HNO_3. Warm in a hot water bath.

(4) Add 20 g crystalline ammonium oxalate and stir solution for 30 minutes, keeping it warm. Transfer to an ice bath and continue stirring for another 30 minutes.

(5) Let settle, and finally centrifuge. Pipet off the supernatant. Wash CaC_2O_4 with hot water containing a little $(NH_4)_2C_2O_4$ until wash solution is colorless.

PROCEDURE 16

CALCIUM

Source - R. E. Batzel in report AECD-2738, edited by W. W. Meinke, August 1949.

Target material: copper

Time for separation - 45 min.

Type of bombardment: All 60" and 184"

Equipment required: standard

Yield: 95%

Degree of purification: 10^3

Advantages: Pure fraction with good yield.

Procedure:

(1) Dissolve the copper in the minimum amount of concentrated HNO_3. Add few mg carriers (Zn and below) including Ca and make the solution ammonical with carbonate free NH_4OH.

(2) Precipitate the sulfides with H_2S. Add holdback carriers and scavenge with another sulfide precipitation. Repeat.

(3) Boil to remove the H_2S and make acid with oxalic acid . Add 5 ml of 4% $(NH_4)_2C_2O_4$ and allow precipitate to settle for 10 minutes in a steam bath.

(4) Wash the precipitate with water containing oxalic acid and ammonium oxalate.

(5) Dissolve the precipitate in 6N HNO_3 and add a crystal of $KClO_3$ to remove oxalate ions.

(6) Make ammonical and scavenge 2 times with $Fe(OH)_3$.

(7) Make acid with oxalic acid and add 3 cc of 4% $(NH_4)_2C_2O_4$. Allow to settle for 10 minutes on a steam bath.

(8) Centrifuge, wash, filter, and dry at 100 C. The precipitate is weighed as $CaC_2O_4 \cdot H_2O$.

Remarks:

(1) See Scott's Standard Methods of Chemical Analysis, Page 210-211, Vol. I, Fifth Edition, 1939.

PROCEDURE 17

CALCIUM

Source - R. H. Goeckermann in report AECD-2738, edited by W. W. Meinke, August 1949.

Target material: Approximately 1 g Bi metal

Time for separation: Few hrs.

Type of bombardment: 184" bombardment all particles

Equipment required: Centrifuge

Yield: Approximately 20%

Degree of purification: 30 c/m of Ca separated from approximately a millicurie of fission and spallation products.

Advantages: Separates Ca from all other elements.

Procedure:

(1) To aliquot of HNO_3 solution of Bi, add 20 mg Ca and 10 mg each of Ru, Cb, Fe, & La. Make 0.5 N in HCl & precipitate with H_2S.

(2) Add 10 mg Ru and Bi to supernatant and repeat H_2S precipitation.

(3) Boil out H_2S and precipitate with NH_3.

(4) Add 10 mg Fe and Y to supernatant and repeat NH_3 precipitation.

(5) Boil down to approximately 5 ml, add 10 mg Ba and Sr, and precipitate with cold fuming HNO_3.

(6) Add more Sr and Ba to supernatant and repeat precipitation three times.

(7) Add Sr alone and repeat two times more.

(8) Boil down to approximately 5 ml, add 5 ml saturated $(NH_4)_2C_2O_4$, and make basic with NH_3.

(9) Dissolve CaC_2O_4 precipitate in HNO_3, destroy $C_2O_4^=$ with $KClO_3$, and make basic with NH_3. Add Fe, La, and Y , centrifuge.

(10) Add more Fe, La, and Y to supernatant and repeat precipitation, centrifuge.

(11) Repeat step (5).

(12) Boil supernatant down to approximately 5 ml, make basic with NH_3, heat, add 5 ml saturated $(NH_4)_2C_2O_4$ slowly. Stir 2 min, filter, wash three times with 5 ml H_2O, three times with 5 ml 95% $EtOH$, three times with 5 ml ether. Dry in vacuum **desiccator** -- 2 min. evacuation, release, 5 min. evacuation. Weigh as CaC_2O_4 (32 mg per 10 mg Ca).

PROCEDURE 18

CALCIUM

Source - Abraham Broido in U. S. Atomic Energy Commission Report AECD-2616, July, 1947.

APPLICATION OF THENOYL TRIFLUORACETONE (TTA) EXTRACTION TO THE PREPARATION OF Ca^{45}

This report presents the development of a satisfactory method for the preparation of carrier-free Ca^{45} from bombarded scandium based on the use of the chelating agent TTA. The following general flow sheet was used to prepare several samples of "carrier-free" Ca^{45} from scandium.

Irradiated Sc_2O_3: (1) — Dissolve in HCl and evaporate off excess acid. Add H_2O to 0.5 mg Sc/ml and transfer to Stang Precipitator, while drawing air upward through a sintered glass disc. Add equal volume of 0.5M TTA in benzene and stir 10 minutes. Break vacuum, and allow aqueous phase to flow out by gravity.

(2) Benzene phase: Contains Sc and more extractable cations (Note 1)

(3) Aqueous phase: Contains Ca^{45} and all salts not extractable at pH 1.5. Add NaOH to final pH 5 and extract with 0.5 M TTA in benzene.

(4) Benzene phase: Contains Sc and all cations extractable between pH 1 and pH 5.

(5) Aqueous phase: Contains Ca^{45}, anions, alkali metals. Add 0.5 M TTA in benzene; add NaOH to neutralize 90% of TTA; final pH = 8.2.

(6) Benzene phase: Ca^{45} (Note 2). Add water (Note 4)

(7) Aqueous phase: Anions, alkali metals, etc. (Discard) (Note 3)

(8) Benzene phase: (Discard) (Note 3)

(9) Aqueous phase: (Ca^{45} prep) (Note 5)

Notes:

(1) As a check on possible calcium loss here, calcium carrier was added and the extraction repeated. The quantitatively recovered calcium carrier contained no Ca^{45} activity.

(2) Up to this point the benzene phases may be washed with water. Washing with water here will extract the Ca^{45}, so, if washing is necessary a solution of the Na salt of TTA at pH 8 should be used.

(3) If more quantitative recovery of the Ca^{45} is desired, fraction 8 may be alternately shaken with fractions 7 and 9 until the desired recovery is attained.

(4) If there are no radiochemical impurities in fraction 5, dilute acid may be used here.

(5) The final solution may be extracted with benzene to remove last traces of TTA.

PROCEDURE 19

STRONTIUM-90

Source - B. P. Bayhurst in "Collected Radiochemical Procedures", Los Alamos report LA-1721. Jan. 1958.

1. Introduction

In the determination of strontium-90 the element is first separated as the nitrate. This is an excellent decontamination step, the major impurity being barium. The latter is removed by a series of barium chromate precipitations. The strontium is then converted to the carbonate, the chemical yield at this stage being about 75%. Yttrium-90 is permitted to grow into equilibrium with the strontium-90 and the former is separated from the strontium by precipitation as hydroxide. Finally, yttrium is precipitated as oxalate and ignited to oxide, in which form it is counted. The chemical yield of yttrium is about 85%, based on the quantity of strontium carbonate obtained.

2. Reagents

Sr carrier: 10 mg Sr/ml [added as $Sr(NO_3)_2$ in dilute HNO_3]

Fe carrier: 10 mg Fe/ml (added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl)

Y carrier: 10 mg Y/ml (for preparation and standardization see yttrium procedure)

Ba carrier: 10 mg Ba/ml [added as $Ba(NO_3)_2$ in H_2O]

HCl: 1M

HCl: conc.

HNO_3: fuming

HNO_3: conc.

$HC_2H_3O_2$: glacial

NH_4OH: conc.

Na_2CO_3: saturated aqueous solution

Na_2CrO_4: 10% aqueous solution

$(NH_4)_2C_2O_4$: saturated aqueous solution

$KClO_3$: solid

Ethanol: 95%

3. Equipment

Bunsen burner

Steam bath

Drying oven

Muffle furnace

Centrifuge

Block for holding centrifuge tubes

Mounting plates

Forceps

Pipets: assorted sizes

Wash bottle

Ice bath

Ground-off Hirsch funnels: Coors 000A (three per sample)

Filter chimneys (three per sample)

Filter flasks

Porcelain crucibles: Coors 000 (one per sample)

2", 60° funnels

No. 42 Whatman filter paper: 11 cm

No. 42 Whatman filter circles: 7/8" diameter - weighed

40-ml conical centrifuge tubes: Pyrex 8320 (eight per sample; one per standardization)

Stirring rods

Sintered glass crucible: 15-ml, fine porosity (one per standardization)

4. Preparation and Standardization of Carrier

Dissolve 241.5 g of $Sr(NO_3)_2$ in H_2O, add 10 ml of conc. HNO_3, and dilute to 1 liter with H_2O.

Into a 40-ml centrifuge tube, pipet 5.0 ml of the carrier solution and add 15 ml of saturated Na_2CO_3 solution. Stir and allow to stand for at least 15 min. Filter the $SrCO_3$ precipitate through a weighed 15-ml (fine porosity) sintered glass crucible. Wash the precipitate with 10 ml of water and then with 5 ml of 95% ethanol. Dry in oven at 110°.

Four standardizations are carried out, with results agreeing within about 0.5%.

5. Procedure

Step 1. Pipet 2.0 ml of standard Sr carrier into a 40-ml conical centrifuge tube. Add an aliquot of sample and adjust the volume to about 5 ml with H_2O. Add 30 ml of cold (Note 1) fuming HNO_3 and permit the mixture to stand in an ice bath for approximately 10 min. Centrifuge and discard the supernate.

Step 2. Dissolve the $Sr(NO_3)_2$ precipitate in 10 ml of H_2O and add 5 drops of Fe carrier. Make the solution basic by the dropwise addition of conc. NH_4OH and then add 10 drops in excess. Stir, centrifuge, and decant the supernate into a precipitate.

Step 3. Add 2 ml of glacial $HC_2H_3O_2$ to bring the pH of the solution to 3.5 to 4.0. Then add 2 ml of Ba carrier and 2 ml of 10% Na_2CrO_4 solution and digest for 10 to 15 min on a steam bath with occasional stirring. Centrifuge, decant the supernate into a clean 40-ml centrifuge tube, and discard the precipitate.

Step 4. Add 5 ml of saturated $(NH_4)_2C_2O_4$ and digest on a steam bath for 5 to 10 min. Centrifuge and discard the supernate. Wash the precip-

itate by adding 2 ml of saturated $(NH_4)_2C_2O_4$ and 20 ml of H_2O and stirring. Centrifuge and discard the wash.

Step 5. Add 2 ml of conc. HNO_3, 5 ml of H_2O, stir, and then add 30 ml of fuming HNO_3. Allow to stand in ice bath for approximately 10 min. Centrifuge and discard the supernate.

Step 6. Repeat Steps 2, 3, and 4.

Step 7. To the precipitate of SrC_2O_4 add 2 ml of conc. HNO_3 and about 200 mg of $KClO_3$. Carefully bring the solution to a boil and then boil vigorously for about 2 min.

Step 8. Adjust the volume to about 15 ml with H_2O and add 5 drops of Fe carrier. Make the solution basic by the dropwise addition of conc. NH_4OH and then add 10 drops in excess. Stir, centrifuge, and decant the supernate into a clean 40-ml centrifuge tube, discarding the precipitate.

Step 9. Repeat Step 3, except filter the $BaCrO_4$ precipitate through a 2", 60° funnel on No. 42 Whatman filter paper. Collect the filtrate in a clean 40-ml centrifuge tube.

Step 10. To the filtrate add conc. NH_4OH until the solution is just basic. Then add 5 ml of saturated Na_2CO_3 solution to precipitate $SrCO_3$. Centrifuge and discard the supernate. Wash the precipitate with a mixture of 10 ml of H_2O and 2 ml of saturated Na_2CO_3. Centrifuge and discard the wash. Slurry the precipitate and filter onto a weighed No. 42 Whatman filter circle, 7/8" diameter, contained in a ground-off Hirsch funnel-filter chimney setup. Wash the precipitate with 5 ml of H_2O and 5 ml of 95% ethanol, dry in an oven at 110°, and weigh (Note 2). Transfer the precipitate into a clean 40-ml centrifuge tube and permit Y^{90} to grow into equilibrium with the Sr^{90}. (This requires about 18 days. Note 3.)

Step 11. After equilibrium has been attained, wash down the sides of the tube with 10 to 15 ml of 1M HCl. Add 2 ml of standard Y carrier and stir. Slide the filter circle up the side of the tube with the stirring rod and, while holding the paper, wash with 1M HCl and remove it.

Step 12. Add conc. NH_4OH dropwise until $Y(OH)_3$ precipitates and then add 5 ml in excess. Centrifuge and save the supernate until the results of analysis for Y have been checked. Record the time (Note 4).

Step 13. Dissolve the $Y(OH)_3$ in a minimum of conc. HCl and add 15 ml of H_2O. Add 20 mg of Sr holdback carrier and precipitate $Y(OH)_3$ with excess conc. NH_4OH. Centrifuge and discard the supernate.

Step 14. Repeat Step 13.

Step 15. Wash the precipitate with H_2O, dissolve in a minimum of conc. HCl, and add 15 ml of H_2O. Again precipitate $Y(OH)_3$ with conc. NH_4OH (this time in the absence of Sr carrier).

Step 16. Wash the precipitate and dissolve as in Step 15.

Step 17. Add 5 ml of saturated $(NH_4)_2C_2O_4$ solution (and a small amount of HCl if necessary) to precipitate $Y_2(C_2O_4)_3$. Digest on a steam bath for 5 to 10 min.

Step 18. Filter the $Y_2(C_2O_4)_3$ precipitate onto a weighed No. 42 Whatman filter circle, 7/8" diameter, contained in a ground-off Hirsch funnel-filter chimney setup. Wash the precipitate with H_2O and place in a porcelain crucible (Coors 000). Ignite at 900° for 30 min. Grind the Y_2O_3 into a powder with a stirring rod and add a few drops of ethanol. Continue grinding until the precipitate is smooth and transfer with 95% ethanol onto a weighed No. 42 Whatman filter circle, 7/8" diameter. Wash down the sides of the filter chimney with ethanol, dry the precipitate in an oven at 110°, cool, weigh, and mount.

Notes

1. By use of refrigerated fuming HNO_3, the time required for cooling in an ice bath is reduced.

2. The $SrCO_3$ formed in this step may be mounted and counted for Sr^{89}.

3. The 18-day waiting period may be shortened provided a growth correction is made for the time interval between the centrifugation operations in Step 8 and Step 12.

PROCEDURE 19 (Cont'd.)

4. The time at which Y^{90} is separated from Sr^{90} is recorded, as t_o and all Y counts are corrected to this time.

PROCEDURE 20

STRONTIUM

Source - L. J. Beaufait, Jr., and H. R. Lukens, Jr., page 122 in "Handbook of Radiochemical Analysis Volume II Radiochemical Procedures," U. S. Atomic Energy Commission report NP-5057 (Del.), March 5, 1952.

1. To the solution containing the strontium activity in a volume of 5 to 8 ml (in a 40-ml heavy-wall centrifuge cone), add Sr carrier add 20 mg of Ba carrier, stir thoroughly, and let stand for ten minutes. Add 20 ml of yellow fuming HNO_3 to precipitate $Ba(NO_3)_2$ and $Sr(NO_3)_2$ (Note a). Cool the solution in an ice bath for 30 minutes with occasional stirring. Centrifuge at low speed for five minutes, decant, and discard the supernate.
2. Dissolve the total precipitate with a minimum volume of water (about 2-3 ml) and repeat precipitation of the nitrates with fuming HNO_3 (Note a). Centrifuge as above, decant and discard the supernate. Dissolve the precipitate in 7 ml of water.
3. Add 5 mg of Fe^{+++} carrier and precipitate $Fe(OH)_3$ by the addition of 2 ml of 6N NH_4OH while stirring (Note b). Centrifuge and transfer the supernate to a clean 40-ml centrifuge cone. Wash the precipitate by slurrying with 7 ml of 5% NH_4NO_3 containing 2 drops of NH_4OH. Centrifuge, remove the wash solution, and combine with the supernate above. Discard the $Fe(OH)_3$ scavenge precipitate.
4. Neutralize the combined supernates by the dropwise addition of 6N HNO_3, testing the acidity with pH paper. Add 1 ml of 6M HAc and 2 ml of 6M NH_4Ac. Heat the solution nearly to boiling and add 1 ml of 1.5M Na_2CrO_4 dropwise with stirring. Continue stirring the solution for one minute, then centrifuge. Decant the supernate into a clean 40-ml centrifuge cone. Discard the $BaCrO_4$ precipitate.

5. Examine the supernate, and if it is not perfectly clear, centrifuge and discard any residue. Add 2 ml of NH_4OH, heat nearly to boiling, and add 5 ml of a saturated ammonium oxalate solution slowly with stirring. Continue stirring for two minutes. Centrifuge, decant and discard the supernate.
6. Dissolve the SrC_2O_4 precipitate with 4 ml of 6N HNO_3. Add 15 ml of fuming HNO_3, stir well and cool in an ice bath for 20 minutes with occasional stirring. Centrifuge, decant and discard the supernate.
7. Dissolve the $Sr(NO_3)_2$ precipitate in 10 ml of water, neutralize the solution with NH_4OH, heat nearly to boiling and add 2 ml of 1M Na_2CO_3 solution slowly with stirring. Heat gently for several minutes and allow to cool in an ice bath for 10 minutes.
8. Have ready a Whatman No. 42 filter disc which has been previously prepared by washing it with three 5-ml portions of H_2O and three 5-ml portions of ethanol. Dry in an oven at 90-100 C for 10 minutes, cool in a desiccator for 10 minutes and weigh. Repeat this procedure until a constant weight ($\pm$ 0.1 mg) has been obtained.
9. Filter the $SrCO_3$ onto the prepared filter paper. Wash, dry, and weigh the precipitate according to the filter paper treatment in step 8. Weigh as $SrCO_3$, mount, and count.

NOTES

a. At least three volumes of fuming HNO_3 should be added to insure the quantitative precipitation of the nitrates.

b. The addition of several drops of a 1% aerosol solution will help prevent creepage.

PROCEDURE 21

STRONTIUM

Source - S. Castner in report AECD-2738,
edited by W. W. Meinke, August 1949.

Target material: RbCl(~ 30 mg) finely divided

Time for separation: 35 min without column; 1-1/2 hr with column

Type of bombardment: 184" deuterons and protons

Equipment required: 1 ml cones, pipettes, etc.

Yield: ~ 90%

Degree of purification: Excellent - ~ 5% Rb contamination without column. .2% or less Rb contamination with column.

Advantages: Quick, may be modified to give carrier free Sr.

Procedure:

(1) Dissolve target in 500 λ of $Na_2C_2O_4$ (3 gms/100 ml). Heat in boiling water for 1 min. Stir.

(2) Add Sr carrier, stir and cool in ice bath centrifuge, withdraw the supernatant. (5~ gms of Sr^{++} produce visible ppt) see remarks #1.

(3) Wash the precipitate with $Na_2C_2O_4$ (500 λ), stirring up and then centrifuging and discarding the wash solution.

(4) Repeat wash 3 times.

(5) Wash with H_2O (500 λ) twice (see remarks) #2.

(6) Dissolve the precipitate in 100 λ 11.0M-$HClO_4$. Heat. Add 5~ gms Rb^+, stir, cool in ice bath and centrifuge. This gives the Sr practically carrier free in ~ 100 λ of solution.

Remarks:

(1) and (2) While 5~ gms of Sr^{++} produce a visible precipitate as stated when washed with 1 ml of H_2O, 25% of the precipitate will dissolve.

(3) If carrier free Sr^{++} is desired, 10~ gms of Ba^{++} carrier may be added instead in step (2). The precipitate is not washed but is dissolved in 0.1 N HCl and placed on a 2 mm diameter ion exchange column, 2" long. The Sr^{++} comes off well after the Rb^+. (Flow rate of ~ 1 drop/2.5 min.)

$SrCO_3$ carries Rb with it in large quantities.

PROCEDURE 22

STRONTIUM

Source - R. H. Goeckermann in report AECD-2738, edited by W. W. Meinke, August 1949.

Target material: approximately 1 g Bi metal

Time for separation: 1-2 hrs.

Type of bombardment: 184" all particles

Equipment required: Centrifuge, tubes, ice, vacuum dessicator

Yield: approximately 80%

Degree of purification: Decontamination factor approximately 10^4 from fission and spallation products. S_r decontaminated $>$ 100 from Ba.

Advantages: Good yield of Ba and Sr, separation from all other elements except Ra, very good separation of Sr and Ba from each other.

Procedure:

(1) To aliquot of HNO_3 solution of target, add 10 mg Sr and Ba, 30 ml fuming HNO_3, digest cold 1-2 min.

(2) Dissolve precipitate in 2 ml H_2O and reprecipitate with 15 ml fuming HNO_3.

(3) Dissolve precipitate in 5-10 ml H_2O, add 5 mg Fe^{+3}, and precipitate $Fe(OH)_3$ with tank NH_3 ($CO_3^=$ free!) Repeat $Fe(OH)_3$ scavenge.

(4) Neutralize supernatant with 6 N HNO_3, add 1 ml 6 M HAc and 2 ml 6 M NH_4Ac. Heat to boiling and add 1 ml 1.5 M Na_2CrO_4 dropwise with stirring. Digest one min. (Save the supernatant for Sr fraction).

(5) Sr - Precipitate 5 mg $BaCrO_4$ scavenge from supernatant saved from Ba separation. Add 2 ml conc. NH_4OH, heat, add 5 ml saturated $(NH_4)_2$ Ox slowly. Stir 2 min, filter, wash three times with 5 ml H_2O, three times with 5 ml EtOH, three times with 5 ml ether, dry like $BaCl_2$. Weigh as $SrC_2O_4 \cdot H_2O$ (22.1 mg per 10 mg Sr).

Remarks: Procedure adapted for use when Sr activity much greater than Ba. Ra follows the Ba well, can be separated from it by use of a resin column.

PROCEDURE 23

STRONTIUM

Source - A. S. Newton in report AECD-2738
edited by W. W. Meinke, August 1949.

Target material: Thorium metal (.1-1 gm) Time for separation: 1 hr.

Type of bombardment: 60" alphas Equipment required: Standard

Yield: 75% on Sr

Degree of purification: 10^6 from other Fission Products, approximately 10^3 from barium

Advantages: Ba and Sr can be taken out in same procedure.

Procedure: The Th metal is dissolved in conc HCl plus a few drops of .2 M $(NH_4)_2SiF_6$ to clear up the black residue. The HCl is diluted to 2 N and an aliquot taken.

(1) Add 20 mg each Ba and Sr carrier and 30 ml fuming nitric acid. Cool 1-2 minutes with stirring and centrifuge. (If SO_4 present add H_2SO_4 to precipitate $BaSO_4$. Wash with 10 ml H_2O. Metathesize with 50% K_2CO_3 by boiling 5 min. Centrifuge, wash with water. Dissolve precipitate in 1 N HNO_3. Discard residue. Then make fuming nitric acid precipitation.)

(2) Dissolve precipitate in 2 ml H_2O. Reprecipitate with 15 ml fuming HNO_3.

(3) Dissolve precipitate in 5 to 10 ml H_2O. Add 5 mg Fe^{+++}, precipitate $Fe(OH)_3$ by adding 2 ml carbonate free 6 M NH_4OH or pass in NH_3 gas to precipitate $Fe(OH)_3$. Centrifuge.

(4) Neutralize supernate with 6 N HNO_3. Add 1 ml 6 M HAc, 2 ml 6 M NH_4Ac. Heat solution to nearly boiling. Add 1 ml of 1.5 M Na_2CrO_4 dropwise with stirring. Let stand 1 min. Centrifuge. Reserve supernate for Sr.

(5) To clear supernate add 2 ml conc NH_4OH. Heat nearly to boiling. Add 5 ml saturated ammonium oxalate slowly with stirring. Stir 1-2 min., filter with suction into a weighed filter paper. Wash three times with 5 ml dil hot NH_4OH, three times with 5 ml 95% EtOH, three times with 5 ml Et_2O. Dry by vacuum 2 min, release, 5 min. Weigh as $SrC_2O_4 \cdot H_2O$.

Remarks: This procedure has been described previously (Phys. Rev. 75 17 (1949)).

Preparation of carrier solution: Dissolve 24.1 gms of $Sr(NO_3)_2$ in water and dilute to 1 liter.

Standardization: Take 5 ml carrier add 30 ml H_2O. Add 5 ml saturated oxalic acid and heat nearly to boiling. Add 2 ml conc NH_4OH dropwise with stirring. Let stand 10 minutes, cool in tap water. Filter into a sintered glass crucible. Wash 3 times with hot water containing a slight amount of NH_4OH, three times with 95% EtOH and three times with 5 ml portions Et_2O. Evacuate in vac desiccator for 2 min., release vac and evacuate five minutes longer, and weigh as $SrC_2O_4 \cdot H_2O$. Repeat evacuations until weight constant to 0.2 mg.

PROCEDURE 24

STRONTIUM

Source - D. Z. Lippmann and R. H. Goeckermann in report AECD-2738 edited by W. W. Meinke, August 1949.

Target material: Au foil, about 1 g Time for separation: 1 hr. for Sr

Type of bombardment: Full energy protons, helium ions, or deuterons Equipment required: Ice bath and hot water bath

Yield: Sr 50%

Degree of purification: Good - about 10^5 from Au and spallation products and at least 10^3 from fission products.

Advantages: Sr, Ba, and Mo can all be separated from the same target material.

Procedure:

Dissolve target in hot solution containing 10 mg each of Sr, Ba, and Mo, 5 ml of 12 M HCl and 5 ml of fuming HNO_3. Cool solution in ice bath, and slowly add about 30 ml fuming HNO_3. $Sr(NO_3)_2$ and $Ba(NO_3)_2$ precipitate. Centrifuge.

Dissolve precipitate in 5 ml H_2O, add 5 mg Fe^{III}, warm in hot water bath, and precipitate $Fe(OH)_3$ with 6 M NH_4OH. Centrifuge. If desired add more Fe^{III} and centrifuge out $Fe(OH)_3$ again. Neutralize supernatant with a few drops of 6 M $HC_2H_3O_2$, heat to boiling, and add 2 ml of 1.5 M Na_2CrO_4 dropwise. Digest $BaCrO_4$ precipitate in hot water bath and centrifuge.

Heat supernatant from first $BaCrO_4$ precipitation to boiling, add 1 ml of Ba carrier dropwise, digest in hot water bath, and centrifuge. To supernatant add 2 ml of 15 M NH_4OH (color of solution should just change from orange to yellow), heat to boiling, add 5 ml saturated $(NH_4)_2C_2O_4$ dropwise, digest in hot water bath, cool, filter, wash three times with 5 ml H_2O, three times with 5 ml alcohol, and three times with 5 ml other. Dry in a vacuum desiccator by pumping 2 minutes, letting in air, and then pumping for 5 more minutes. Weigh as $SrC_2O_4 \cdot H_2O$.

Remarks:

All additions of fuming or concentrated HNO_3 should be made cautiously: they tend to react violently after a short induction period.

PROCEDURE 25

STRONTIUM

Source - R. L. Folger and H. Hicks in report AECD-2738 edited by W. W. Meinke, August 1949.

Target material: Appr.4 g U metal Time for separation: 1-2 hrs.

Type of bombardment: 184" all high energy particles Equipment required: Centrifuge, tubes, ice, vacuum desiccator

Yield: Appr. 80%

Degree of purification: Decontamination factor $\sim 10^4$ from fission and spallation products. Sr decontaminated $>$ 100 from Ba.

Advantages: Good yield of Ba and Sr, separation from all other elements except Ra, very good separation of Sr and Ba from each other, and Sr from Ra (which follows Ba).

Procedure:

(1) To aliquot of HNO_3 solution of target containing 10 mg each Sr and Ba, and reduced in volume to approximately 1.5 ml, add 12-13 ml fuming HNO_3, digest cold 5 min.

(2) Dissolve precipitate in 1 ml H_2O and reprecipitate with approximately 13 ml fuming HNO_3.

(3) Dissolve precipitate in 5 ml H_2O, add 2 mg Fe^{+3}, and precipitate $Fe(OH)_3$ with tank NH_3 ($CO_3^=$ free!) Repeat $Fe(OH)_3$ scavenge (1 mg Fe^{+3}).

(4) Neutralize supernatant with conc. HNO_3 to methyl orange end point, add 1 ml 6 M HAc and 2 ml 6 M NH_4Ac. Heat to boiling and add 1 ml of 1.5 M Na_2CrO_4 dropwise with stirring. Digest one min. (Save the supernatant for Sr fraction).

(5) Precipitate 5 mg $BaCrO_4$ scavenge from supernatant saved from Ba separation. Add 2 ml conc. NH_4OH, heat, and precipitate $SrCO_3$ by adding saturated Na_2CO_3. Digest 2 min, centrifuge and dissolve in 6 N HCl (minimum). Boil out CO_2.

(6) Make basic with NH_3 and add saturated $Na_2C_2O_4$. Stir 2 min (hot), cool, filter, wash three times with 5 ml H_2O, three times with 5 ml EtOH, three times with 5 ml ether, dry like $BaCl_2$. Weigh as $SrC_2O_4 \cdot H_2O$ (22.1 mg per 10 mg Sr).

Remarks: Procedure adapted for use when Sr activity much greater than Ba. Ra follows the Ba well, can be separated from it by use of a resin column. See AECD 1998 (Edward R. Tompkins)

In step (4) add 1 drop Me-orange to the solution before neutralization starts.

PROCEDURE 26

STRONTIUM

Source - P. C. Tompkins, A. Broido, G. W. Parker, E. R. Tompkins, W. E. Cohn, W. Kisieleski, and R. D. Finkle, Paper 240 in "Radiochemical Studies: The Fission Products", edited by C. D. Coryell and N. Sugarman, McGraw-Hill Book Co., Inc., New York, 1951.

PROCEDURE FOR SEPARATING STRONTIUM FROM PILE-URANIUM SOLUTION

(1) Pile Uranium Dissolved in Conc. HNO_3. Dilute solution to 0.5N HNO_3; add 1.5 g of $PbCl_2$ per liter of solution; add 70 ml of 9M H_2SO_4 per liter of solution (use continuous stirring for 1 hr); allow $PbSO_4$ to settle; decant supernatant solution. → (1a) Solution. Discard.

↓

(2) Precipitate. $PbSO_4$. Wash with H_2O, discard washings; add 50 ml of sat. Na_2CO_3, stir, and decant solution. → (2a) Solution. Discard.

↓

(3) Precipitate. $PbCO_3$. Wash with H_2O discard washings; add 50 ml of 3M HCl, evaporate to low volume, cool, and centrifuge. → (3a) Precipitate. $PbCl_2$. Discard.

↓

(4) Solution. Boil with HNO_3; add 1 mg each of Ce, La, and Y; add 50 ml of H_2O and 50 ml of fuming HNO_3, and centrifuge. → (4a) Solution, Evaporate to low volume.

↓

(5) Precipitate. $Pb(NO_3)_2$, Ba, and Sr activities. Reprecipitate three times; and add 5 ml of 1N HCl; heat, cool, and centrifuge. → (5a) Precipitate. $PbCl_2$. Discard.

↓

(6) Solution. Evaporate to 1 ml, add 4.5 ml of conc. HCl, 1 ml of ether, and 10 mg of Ba in two portions; centrifuge. → (6a) Precipitate. $BaCl_2 \cdot H_2O$. Dissolve in H_2O.

↓

(7) Solution. Evaporate to small volume. Add 0.3N HCl, heat to 80 C, saturate with H_2S; filter.

(8) Solution. Sr activity. Evaporate to dryness*; add dil. HCl.

(7a) Precipitate. PbS. Discard.

(9) Solution. Sr activity.

(8a) Insoluble residue.

(6b) Solution. Add conc. HCl; centrifuge.

(6a) Insoluble residue.

(6c) Solution. Sr activity. Combine with Solution 9.

(6b') Precipitate. $BaCl_2$ with Ba activity. Dissolve in H_2O.

*Found 3 mg of residue here.

PROCEDURE 27

STRONTIUM

Source - R. Overstreet, L. Jacobson, K. Scott, and J. G. Hamilton, Paper 24l in "Radiochemical Studies: The Fission Products", edited by C. D. Coryell and N. Sugarman, McGraw-Hill Book Co., Inc., New York, 1951.

1. PROCEDURE

A sample of RbCl was bombarded on a copper target with 300 μ a-hr of deuterons at the 60-in. Berkeley cyclotron. Five days later the target was treated with 0.1N HCl. The resulting solution was filtered and made up to 0.3N with HCl. The copper was precipitated with H_2S and filtered off. Fifty milligrams of zinc as $ZnCl_2$ was added to the filtrate. The solution was made alkaline with NH_4OH, and the zinc was precipitated with H_2S. The filtrate from the ZnS precipitation was acidified and concentrated to about 25 ml. Fifty milligrams of iron carrier as $FeCl_3$ was added. Equal volumes of ammonium carbonate reagent [9N $(NH_4)_2CO_3$ in 6N NH_4OH] and ethyl alcohol were added, and the resulting solution was brought to boiling. The $Fe(OH)_3$ precipitate was filtered off and washed with 3N NH_4OH. About 75 per cent of the activity was retained in the precipitate. The $Fe(OH)_3$ precipitate was dissolved in 1N HCl, and 50 mg of RbCl was added. The iron was reprecipitated with an equal volume of the $(NH_4)_2CO_3$ reagent, and the $Fe(OH)_3$ was centrifuged down. The precipitate was dissolved in 1N HCl and reprecipitated three more times with the $(NH_4)_2CO_3$ reagent. In each case the supernatant solution was found to be inactive. The precipitate was finally dissolved in 6N HCl, and the solution was extracted with several portions of ether to remove the iron. The iron-free solution was evaporated to dryness, and the residue was heated gently to remove NH_4Cl. The residue was taken up in dil. HCl.

2. TESTS

To a small fraction of the final strontium tracer solution, 10 mg each of zinc, yttrium, rubidium, and strontium carriers was added. The zinc and yttrium were precipitated in alkaline solution with H_2S. The strontium was precipitated from the filtrate with $(NH_4)_2CO_3$ reagent and ethyl alcohol.

PROCEDURE 27 (Cont'd.)

The activities of the zinc and yttrium fraction, the strontium fraction, and the rubidium fraction were determined with an electroscope. Of the total activity, 98.5 per cent was associated with the strontium fraction.

The absorption curves determined for the strontium prepared without carrier and for the radiostrontium precipitated and purified with strontium carrier were found to be identical.

PROCEDURE 28

STRONTIUM

Source - J. C. Dalton and G. A. Welch in Anal. Chim. Acta 15, 317 (1956).

THE RAPID SEPARATION AND DETERMINATION OF RADIOSTRONTIUM AND RADIOCAESIUM IN FISSION PRODUCT MIXTURES

A technique has been described[71] for precipitating cations and removing them from solution without the use of filtration or centrifugation, by passing the solutions through anion exchange resin beds saturated with the precipitating anion. The precipitate forms around the resin beads as an adhering film, and the eluate from the column is clear. More recently the technique has been applied with success to the precipitation of radioactive tracers in the carrier-free state.[72] Employing a column in the hydroxide form the authors have removed all the activity from an aged fission product solution with the exception of that due to radiostrontium and radiocaesium. Any anionic activity was removed by normal ion exchange processes, while all the other long-lived cationic activity was precipitated on the hydroxide column. Separation of the strontium and caesium in the eluate was then carried out prior to the precipitation of each element in a form suitable for counting after gravimetric determination of chemical yield. By this means the determinations of these two elements were accomplished more rapidly and with better precision than by existing procedures.[73] Under conditions of routine use, 8 determinations of each radioelement were made simultaneously in under 2 days per operator and the

precisions obtained (3σ for about 30 results) were 10% for strontium and 8% for caesium.

EXPERIMENTAL

Aliquots of fission product solution (at least several months old and therefore containing very little Ba^{140} (12.8d) with added known amounts of caesium and strontium carriers were passed down columns of Amberlite IRA-400 (OH) and eluted with several column volumes of water. The eluates were heated almost to boiling and saturated ammonium oxalate was then added to precipitate the strontium. The precipitates were centrifuged off, washed several times with water, dried, weighed and counted. After correcting to 100% chemical yield, the results showed a good accuracy and precision.

The supernatant solutions from the oxalate precipitations were made about 5M in hydrochloric acid and an 0.1M solution of silicotungstic acid was added to precipitate the caesium. This again was centrifuged off, washed, dried, weighed and counted. Many of the sources became discoloured on drying, and this discoloration was associated with poor agreement among the results from the individual sources. It appeared that the caesium silicotungstate was unsuitable as a method of gravimetric determination. Several other reagents were considered (e.g. see reference[74]), but eventually it was decided to employ perchloric acid.[75] The solution had to be free from any ammonium ion during this precipitation of caesium, because ammonium perchlorate also precipitates under the conditions used. Therefore, either the ammonium oxalate used in the precipitation of strontium had to be volatilized, or else the caesium and strontium had to be separated without the use of ammonium oxalate. The removal of ammonium oxalate by volatilization was avoided as it would prove time consuming, and a rapid separation was being sought. Using a column of anion exchange resin in the oxalate form, the strontium could be removed from the caesium without the introduction of any cation which would interfere in the subsequent precipitation of caesium as perchlorate. However, the strontium carrier immediately precipitated as a pad on top of the resin, and this slowed down the column flow-rate to such an extent that it made its use in a routine method impracticable.

A much simpler and more rapid separation was effected by the addition of carbon dioxide (in the solid state for convenience) to the eluate from the hydroxide column. Thus the strontium was removed quantitatively without the addition of any interfering cation. The caesium could then be precipitated as perchlorate, while the strontium carbonate was dissolved in acid and the strontium reprecipitated as oxalate.

Analysis of the strontium sources by β-absorption measurements showed the activity to be entirely due to Sr^{89}, Sr^{90} and Y^{90}. The last-named isotope begins to grow in from its Sr^{90} parent after chemical separation has occurred. Only negligible traces of γ-activity were observed in the sources. γ-spectrometric analysis of the caesium sources showed them to be more than 99% Cs^{137}/Ba^{137m} with a trace of Cs^{134}.

Reagents

Strontium carrier solution (9.5 g $SrCl_2 \cdot 6H_2O$ in 100 ml water).
Caesium carrier solution (2.75 g CsCl in 100 ml water).
(The strontium and caesium contents of the respective solutions should be determined accurately by normal gravimetric procedures).
Carbon dioxide (solid or from Kipp's Apparatus).

Procedure

The columns should be 40-50 cm long, 1.2-1.4 cm internal diameter and should contain 8-10 g Amberlite IRA-400 (OH) resin. Before use, wash the columns with about 50 ml of 4M nitric acid to remove any retained activity from previous experiments. Remove the excess of acid with water, then pour through the columns a strong sodium hydroxide solution prepared from carbon-dioxide-free distilled water. Fit an absorption tube containing soda-lime in the top of each column. Remove the excess of sodium hydroxide by washing.

Pipette an aliquot of the solution for analysis, which should contain negligible amounts of Ba^{140} into a small beaker and add 2.0 ml of both caesium and strontium carrier solutions. The aliquot should be chosen to contain quantities of activity suitable for counting. The strontium-89 activity should be between 3×10^3 and 1.5×10^6 disintegrations per minute and the caesium-137 activity 2×10^4 to 6×10^5 dpm. In addition, the aliquot should not contain more than four milliequivalents of anion other than hydroxyl, otherwise the effectiveness of the column may be impaired owing to replacement of the hydroxyl ions by other non-precipitating anions.

Transfer the solution and washings into the column and allow the liquid to flow through slowly at a rate of 0.5-1 ml per minute. Collect the eluate in a 150 ml beaker, and when the liquid level in the column has almost reached the level of the resin, add distilled water. Continue the elution until about 40 ml has been collected, then precipitate the strontium with carbon dioxide. (If solid carbon dioxide is being used add 1-2 g.) Centrifuge off the precipitate and dissolve it in a little dilute hydrochloric acid and dilute to about 20 ml with water. Retain the supernate from the precipitation for the determination of caesium.

Boil the strontium solution to expel any carbon dioxide, cool, add 2 ml of 18M ammonium hydroxide and heat again almost to boiling. Slowly add 5 ml of saturated ammonium oxalate solution, and allow the beaker and its contents to cool. Centrifuge off the precipitate, wash it several times with water and then transfer it as a slurry with acetone to a weighed stainless steel or glass counting tray. Dry the precipitate carefully, weigh it and count the source without delay.

Standard G.M. counting equipment with a total absorber thickness of 130-140 mg/cm^2 should be used. Thus the 0.6 MeV β -activity of Sr^{90} is absorbed and only the 1.5 MeV β -emission of Sr^{89} is counted. However, Y^{90} the daughter element of Sr^{90} commences to grow in with a half-life of 61 hours immediately after elution from the column, and the energy of its β -radiation is 2.2 MeV. The time interval between the column separation and the counting should therefore be noted. Recount the sample several days later, using the same equipment, and note the time of counting. Correct the counts for counting efficiency, background, back-scatter and self-absorption as necessary. Calculate the fraction of the total Y^{90} which has grown in during the interval between the first and second countings, and hence find the Sr^{90} activity. The amount of Y^{90} activity present during the first counting is therefore known, and by difference calculate the Sr^{89} activity.

Fume down the supernate containing the caesium with 6 ml of 9M perchloric acid. After fuming has continued for 10 minutes, cool the mixture in a 50 ml centrifuge tube in an ice-bath. Add 15 ml of absolute alcohol and allow to stand for 10 minutes, stirring occasionally. Centrifuge off the precipitate, wash it several times with absolute alcohol and transfer it as a slurry with acetone to a weighed stainless steel or glass counting tray. Dry under a radiant heater, weigh and count the source.

Standard γ -scintillation counting equipment fitted with a 2 g/cm^2 absorber of lead and aluminium (to prevent formation of **Bremsstrahlung**) should be used. The γ -rays are actually emitted by Ba^{137m}, the meta-stable daughter, which has a half-life of 2.6 minutes and therefore quickly reaches equilibrium. Corrections are made for counting efficiency (including the absorber) and also for the fact that only 82.5% of the total Cs^{137} disintegrations produce γ -rays from Ba^{137m}, the rest being lost either by direct decay to stable Ba^{137}, or else by interval conversion of the γ -rays.**76**

PROCEDURE 29

STRONTIUM

Source - E. A. Martell in "The Chicago Sunshine Method", U. S. Atomic Energy Commission Report AECU-3262, page 47, May, 1956.

Ion Exchange Procedure for Sr^{90} in Water Samples

(Nuclear Science and Engineering Corporation Method)

Summary

The Sr^{90} in water samples may be concentrated by passing the water through an ion exchange column. The Y^{90} may be milked from the Sr^{90} on the column or the Sr^{90} may be stripped from the column for further purification.

Treatment of Resin

The resin used was Dowex-50, 100-200 mesh. The resin was air-dried and then washed with 6M HCl (Note 1) and water. The particles which floated in the solution after 15 minutes were decanted off. A 25 mm O.D. glass tube was filled with resin to a height greater than 10 cm by slurrying the resin in water, pouring it into the column, and allowing the resin to settle onto a glass wool plug without flow of water. After the desired height of resin was reached, the resin bed was suspended in water and allowed to settle. The column was washed with about 200 ml of water, until the pH of the effluent was the same as that of the influent, then with 400 ml of ammonium citrate, pH = 6.0, to convert the column to the ammonium form. After washing with 400 ml of water, it was ready for use.

Passage of Water Through Resin Bed

The water sample was filtered and passed through the column at a

rate of about 1 liter per hour. The solution was discarded after the volume had been measured.

Purification of Sr^{90}

To strip the Sr^{90}-Y^{90} off the column, 400 ml of ammonium citrate (prepared by adjusting the pH of a 5% solution of citric acid to 6.0 with NH_4OH, and then adding 5 ml of formaldehyde per liter as preservative) were passed through the column at a flow rate of about 1 liter per hour.

Strontium carrier was added and the solution heated. Thirty ml saturated $H_2C_2O_4$ were added and the SrC_2O_4 digested for at least 2 hours, (frequently overnight) to enable precipitation to be complete. The solution was decanted through a filter and the precipitate slurried into a centrifuge tube. This was centrifuged and the precipitate on the filter paper washed through a hole punctured in the paper into the tube, which was centrifuged again.

After the precipitate had been centrifuged down, it was dissolved in HNO_3 with heating. The tube was cooled in an ice bath and about 30 ml of fuming HNO_3 added. After sitting for a few minutes in the ice bath, the $Sr(NO_3)_2$ was centrifuged off and washed with 15 ml fuming HNO_3 (Note 2).

The precipitate was dissolved in 20 ml H_2O and 10 drops Fe carrier (10 mg Fe/ml) were added, if necessary. The solution was heated nearly to boiling, made basic with NH_4OH from a freshly opened bottle and the $Fe(OH)_3$ centrifuged off (Note 3). The time of $Fe(OH)_3$ separation was recorded as zero time for Y^{90} growth.

The solution was neutralized with 6N HNO_3 and 2 ml 6M NH_4OAc and 1 ml 6M HOAc added. Fifteen drops of Ba carrier (50 mg Ba/ml) were added, the solution heated nearly to boiling, and 1 ml 1.5N K_2CrO_4 added dropwise with stirring. The $BaCrO_4$ was allowed to digest for a few minutes and then decanted through a #42 Whatman filter paper into a 150 ml beaker. Two ml NH_4OH were added and the solution heated. Five ml of $(NH_4)_2CO_3$ were added and the $SrCO_3$ digested for a short time. This was filtered on a weighed

fritted glass filter, dried at 110° for 15 minutes, cooled, and weighed. The $SrCO_3$ was then dissolved in 2 ml 6M HCl and washed into a glass vial to be stored for Y^{90} growth and milking.

Separation of Sr^{90}-Y^{90}

The Y^{90} was milked from the Sr^{90} on the column by passing through the column 50 ml citric acid (pH = 2.0) and 350 ml citric acid (pH = 3.8), combining the washes in a beaker (Note 4). Yttrium carrier was added, the solution heated, and 30 ml saturated $H_2C_2O_4$ added. The solution was allowed to cool and then filtered. If there were not calcium present, this precipitate was ignited and the Y_2O_3 weighed and mounted for counting. If calcium were present, the YPO_4 separation would have to be done after ignition.

Notes:

1. The HCl removes traces of impurities which are present in quantities sufficient to impart a color to the initial washes.

2. If calcium is present, the concentration of the fuming HNO_3 should be not over 75%.

3. It is necessary to use fresh NH_4OH to prevent the precipitation of $SrCO_3$ by CO_2 picked up from the atmosphere.

4. The citric acid, pH - 2.0, is passed through the column to reduce the pH rapidly so as not to elute the Sr^{90}.

PROCEDURE 30

STRONTIUM

Source - W. B. Silker in U. S. Atomic Energy Commission, Report HW-55117, May 20, 1958.

Three types of samples were analyzed for strontium-90: soil, vegetation, and animal bones. A cursory investigation of soil from the arid region of the Hanford Reservation indicated that about 75 per cent of the radiostrontium was held in the top one-half inch of soil. This surface layer was subsequently sampled for the present study. Vegetation samples were limited, with a few exceptions, to grasses of different varieties. No attempt was made to differentiate the variety or age of the vegetation sample. Bones of animals, primarily rabbit femurs, were collected at various locations throughout the Hanford Reservation. Rabbits should be extremely good indicators of localized contamination, as their forage range is limited to approximately one square mile[77], and as vegetarians they will tend to furnish an integrated sample of the diet in their immediate environment.

SAMPLE PRETREATMENT

Samples were pretreated by methods which were similar to those employed by the Chicago Sunshine Group.[78] Detailed procedures are appended. The available calcium and strontium was leached from soil samples by the ammonium acetate method.[78] Vegetation samples were reduced by wet ashing with nitric acid. The residual material was baked on a hot plate and then muffled at 600 C for two to four hours. Sample solution was accomplished by digestion in dilute nitric acid. The residual material from the first few samples was fused with sodium carbonate, dissolved, and upon analysis was found to contain no strontium-90. This residue was subsequently discarded. Animal bones were placed directly into a muffle furnace and ashed for two to four hours at 600 C and then dissolved in nitric acid.

CALCIUM ANALYSIS

Whenever possible, the calcium concentration was determined by precipitation of the alkaline earths as oxalates, which were oven-dried at 120 C and weighed. The oxalates were then muffled to the oxide at 800 C and reweighed. When the oxide to oxalate ratio corresponded very nearly to the molecular weights of calcium oxide and calcium oxalate monohydrate, the calcium was taken as 0.715 times the oxide weight. When this ratio was not obtained an aliquot of the acid solution of the oxide was taken for calcium analysis. This method for calcium analysis involved the precipitation of the oxalate from slightly acid solution. The oxalate was dissolved in dilute sulfuric acid and titrated with potassium permanganate.

STRONTIUM SEPARATION

The presence of rare earth fission products which follow yttrium necessitated chemical separation of strontium, which was then reserved to allow buildup of yttrium-90. Strontium was separated by a modification of the method of Glendenin[79] which employed initial barium and strontium isolation by precipitation as nitrates with fuming nitric acid. Calcium decontamination was made by washing the nitrate precipitate with anhydrous acetone. After an iron hydroxide scavenge, barium was precipitated as the chromate, and strontium was separated as strontium carbonate. The carbonate was weighed for yield determination and reserved for buildup of yttrium-90.

YTTRIUM EXTRACTION

The need for the highest possible sensitivity for yttrium-90 measurement made a carrier separation undesirable because carrier would decrease the effective counting efficiency of the emitted beta particles. Solvent extraction of yttrium-90 from the dissolved strontium salt offered a technique for the carrier-free isolation of yttrium-90, thus eliminating the counting error introduced by self absorption of the yttrium-90 beta particles. Yttrium was extracted from acetate-buffered solutions with thenoyltrifluoro-

acetone in benzene according to the procedure described by Perkins.[80] The decay of yttrium-90 from all samples was followed for several half-lives, and with only three exceptions the yttrium-90 was free from contamination.

Preparation of Bone Samples

1. Place a sample of bone, not exceeding thirty grams, in a tared Vycor evaporating dish.
2. Muffle the sample at 600 C for two hours, or until all of the organic material is destroyed.
3. Cool and reweigh the dish and sample, and record the weight of ash.
4. Dissolve the bone ash in 4 N nitric acid, and dilute with water to volume in a suitable volumetric flask.
5. Reserve an aliquot of the sample for calcium determination, and proceed with the strontium determination with the remainder.

Preparation of Vegetation Samples

1. Place the vegetation sample in a drying oven at 110 C for forty-eight hours.
2. Pass the sample through a Wiley mill.
3. Weigh a 100 g sample and place it in a 2000 ml beaker.
4. Add sufficient 8 N nitric acid to cover the sample, and evaporate to dryness on a hot plate at low heat. Raise the temperature of the hot plate to high heat, and bake the sample.
5. Transfer the sample to a tared 400 ml Vycor evaporating dish and muffle at 400 C for two hours, or until the organic matter is destroyed.
6. Reweigh the dish plus sample, and record the ashed weight.
7. Digest the ash with 200 ml 3 N nitric acid by boiling on a hot plate for five minutes.
8. Cool, centrifuge, and decant the supernatant liquid into a liter beaker.
9. Repeat steps 7-8 and discard the residue.

Extraction of Exchangeable Calcium and Strontium in Soils

1. Crush the air-dry sample and pass the sample through a 2 mm sieve.

2. Place 500 g of the prepared sample in a four liter beaker and add sufficient neutral normal ammonium acetate to cover.
3. Stir well and let stand overnight.
4. Filter the sample through two thicknesses of coarse filter paper, and leach the sample with ammonium acetate until a total of two liters of leachate is obtained.
5. Transfer the leachate to a four liter beaker and evaporate to dryness.
6. Bake the residue until dehydration of the salt is complete.
7. Loosen as much of the dry residue as possible with a spatula and transfer to an evaporating dish.
8. Place the evaporating dish in a muffle at about 150 C, heat to 600 C, and hold this temperature for about one hour.
9. To the small amount of residue remaining in the beaker, add 200 ml of water, and 10 ml of 30% hydrogen peroxide.
10. Cover and boil for 15-20 minutes.
11. Combine the ashed residue and peroxide treated residue.
12. Add small portions of hydrochloric acid with stirring until all of the carbonates are decomposed; add 10-15 ml in excess.
13. Heat the solution to about 90 C and add 1:1 ammonium hydroxide with stirring until a faint odor of ammonia persists.
14. Boil for 2-3 minutes to coagulate the precipitate and filter through coarse filter paper.
15. Wash the filter with 200 ml of a hot 2% ammonium chloride solution.
16. To the combined filtrate and wash, add 20 drops of methyl red indicator and acidify with hydrochloric acid; add 10-15 ml in excess.
17. Heat to 90 C and add 25 grams of oxalic acid.
18. Continue heating for 2-3 minutes and slowly add 1:1 ammonium hydroxide until the solution turns a light yellow.
19. Digest at 90-95 C for 1-2 hours.

20. Collect the oxalate precipitate in a Gooch crucible.
21. Determine calcium and strontium in the oxalate precipitate.

Strontium Separation

1. Place the acid extract in a beaker of suitable size, and add 40 mg of strontium carrier and 10 mg of barium carrier.
2. Neutralize the sample with 12 N sodium hydroxide.
3. Heat to boiling.
4. Add 40 ml of saturated sodium carbonate with stirring.
5. Allow the sample to cool for thirty minutes.
6. Centrifuge.
7. Discard the supernatant liquid.
8. Dissolve the carbonate precipitate in a minimum of concentrated nitric acid.
9. Add fuming nitric acid until precipitation starts.
10. Cool for one minute with running tap water and centrifuge.
11. Suspend the well drained precipitate in 20 ml of anhydrous acetone. Cool for one minute with running tap water and centrifuge.
12. Dissolve the precipitate in 6 ml of water and add 18 ml of fuming nitric acid. Cool for one or two minutes with running tap water. Centrifuge and discard the supernatant liquid.
13. Dissolve the precipitate in 10 ml of water, add 2-3 mg of iron carrier and precipitate iron hydroxide by addition of 6 N ammonium hydroxide.
14. Centrifuge and decant the supernatant liquid into a clean centrifuge tube.
15. Neutralize the solution to the phenolphthalein end point with 6 N nitric acid, add 1 ml of 6 N acetic acid and 2 ml of 6 N ammonium acetate. Heat the solution nearly to boiling and add 1 ml of 1.5 N sodium chromate drop by drop with stirring. Continue stirring for about one minute and centrifuge.
16. Decant the supernatant liquid into a clean centrifuge tube, and add 5 ml

of saturated sodium carbonate with stirring. Centrifuge and discard the supernatant liquid.

17. Wash the precipitate twice with water and once with ethanol.
18. Transfer the precipitate to a tared one inch counting dish with ethanol.
19. Dry under an infra-red heat lamp, weigh and reserve for build-up of yttrium-90.

Yttrium-90 Extraction Procedure

1. To a 60 ml separatory funnel, add 10 ml of TTA solution (10 g thenoyltrifluoroacetone in 100 ml of benzene). 5 ml of 0.5 N nitric acid, and shake mechanically for five minutes. Discard the aqueous phase.
2. Dissolve the strontium precipitate in 5 ml of 0.5 N nitric acid and transfer the solution to the separatory funnel.
3. Add 10 ml of buffer solution (0.5 M Sodium acetate, 0.1 M acetic acid) and extract for 10 minutes. Discard the aqueous phase.
4. Extract five minutes each with two 10 ml portions of 0.1 M sodium acetate-0.1 M acetic acid.
5. Back extract the yttrium-90 into 10 ml of 0.1 N nitric acid.
6. Evaporate the aqueous phase to dryness on a one inch stainless steel counting dish and measure the yttrium-90 disintegration rate.

PROCEDURE 31

STRONTIUM

Source - A. S. Goldin, R. J. Velten, and G. W. Frishkorn in Anal. Chem. 31, 1490 (1959).

The radioactive isotopes strontium-89 and strontium-90 are determined in a wide variety of environmental samples. Strontium-90 is determined by beta-counting the daughter activity, yttrium-90, after extraction into 2-thenoyltrifluoroacetone reagent. Total radioactive strontium is determined by beta-counting a strontium carbonate precipitate. The method includes procedures for treating different types of material

and removing common interferences.

The basic procedures for the determination of radiostrontium were developed for use in samples of fresh water. Other samples require pre-treatment to convert them to a form which will fit into this scheme of analysis. These procedures differ from ordinarily used procedures in several ways. A large amount of strontium carrier (1 or 2 mmoles) is used, so that solubility and transfer losses will amount to a smaller percentage of total strontium. Second no attempt is made to obtain a pure, weighable strontium precipitate for chemical yield determination - chemical yield when required is determined by flame spectroscopy. Third, no carrier yttrium is used. This eliminates the possibility of radioactivity in the yttrium salt and also permits counting from a weightless yttrium extract, eliminating the troublesome correction for self-absorption.

Determination of Strontium-90 in Fresh Water. The sample containing 4 ml of 1 N carrier strontium is made strongly alkaline and brought to boiling, and sodium carbonate is added to precipitate strontium carbonate. The collected precipitate is dissolved in hydrochloric acid, neutralized with ammonia to a methyl orange end point, and buffered at pH 5. Barium is added, followed by potassium chromate to precipitate barium chromate, which is discarded. Strontium is reprecipitated as carbonate and again brought into solution with hydrochloric acid. Ferric iron is added and precipitated with ammonia and the precipitate is discarded. Zirconium and rare earth (usually cerium or lanthanum) carriers are added and the warm solution is acidified and then made basic with ammonia. The precipitated rare earth and zirconium hydroxides are discarded and the strontium is again concentrated by precipitation with sodium carbonate.

The strontium carbonate, thus obtained is stored overnight or longer for ingrowth of the yttrium daughter of the strontium-90. The length of this ingrowth period depends on the strontium-90 content expected; it is shorter for samples of high activity. At the lowest levels an ingrowth period

of 2 weeks is allowed, during which the yttrium-90 reaches 97% of its final equilibrium value. For an ingrowth period of only 18 hours, on the other hand, the yttrium-90 reaches about 18% of the equilibrium value.

After ingrowth of yttrium, the strontium carbonate precipitate is dissolved with hydrochloric acid, neutralized to methyl orange with ammonia, and buffered at pH 5. The yttrium is extracted into 2-thenoyltrifluoroacetone solution. After the organic phase is washed with water buffered at pH 5, the yttrium-90 is stripped by extraction with 1 N hydrochloric acid. The hydrochloric acid extract is evaporated on copper planchets, heated thoroughly to destroy residual organic matter, and counted, correcting for decay of the yttrium-90 between its extraction and the counting time.

In this procedure the decontamination factor for contaminating isotopes is about 10^4. Typical results for a number of common fission products chosen as representative are given in Table 1.

TABLE 1. YIELD OF CONTAMINATING ISOTOPES

Isotope	Amount Added, C.P.M.	Amount Recovered C.P.M.	Amount Recovered %
Sr^{89}	51,000	19	0.04
Cs^{137}	178,000	18	0.01
Ce^{144}	584,000	39	0.007
$ZrNb^{95}$	585,000	51	0.009

Chemical yields for strontium range from 70 to 100%, with a mean of approximately 85%. Recovery of yttrium in the solvent extraction is greater than 95%.

Total Radiostrontium in Fresh Water. The strontium is collected by precipitating 2 ml of 1 N carrier strontium as carbonate and treated with concentrated (70%) nitric acid to remove calcium and magnesium impurities. Thirty milliliters of concentrated nitric acid are used in this treatment. The mixture is digested in a warm water bath with occasional stirring for about 10 minutes and cooled in an ice bath for

5 minutes, after which the precipitated strontium nitrate is separated and collected by centrifugation. (In soft waters where the additional weight of the carbonate precipitate would be of no concern, this nitric acid treatment may be omitted, leaving the calcium in the final carbonate precipitate.) The strontium nitrate (or carbonate) is redissolved and purified by barium chromate precipitation and iron and zirconium-rare earth hydroxide scavenging as above. The purified strontium is precipitated finally as strontium carbonate, transferred to counting dishes, and counted directly to obtain total radiostrontium content. Strontium-89 is calculated by difference between the total radiostrontium value and the strontium-90 activity.

Average chemical yield is 85%. Because strontium-89 is determined by difference, the error is dependent on the error of the strontium-90 determination and on the relative amounts of strontium-90 and strontium-89.

Strontium-90 and Total Radiostrontium in Salt and Brackish Waters. The determination of radiostrontium in salt and brackish waters is complicated by the mass of precipitate obtained. In salt water this is largely due to the magnesium which is present in sea water to the extent of 1.27 grams per kilogram. If the pH is adjusted to minimize the precipitation of magnesium carbonate, the precipitation of strontium carbonate is not quantitative, the loss amounting to about 10% when 1 mmole of carrier strontium is used. Accordingly, the carbonate precipitation was carried out from strongly alkaline solution, a preliminary separation of magnesium being made to facilitate this operation.

The heated sample containing strontium carrier is treated with ammonia and alcoholic 8-quinolinol to precipitate magnesium. This precipitate is filtered off, washed thoroughly, and discarded, the washings being added to the filtrate. Sodium hydroxide and sodium carbonate are added to the heated filtrate to precipitate strontium, calcium, and other salts. The

washed precipitate is collected and thoroughly dried, after which it is treated with concentrated nitric acid to remove calcium from the precipitated strontium nitrate. A second nitric acid treatment is usually required for adequate removal of calcium. The strontium is purified by the standard barium chromate and hydroxide precipitations, after which strontium carbonate is precipitated for determination of total radiostrontium. After total radiostrontium activity has been counted, the strontium carbonate precipitate is stored for yttrium ingrowth and the yttrium is extracted and back-extracted as described above.

Loss of strontium in the magnesium precipitate is only about 2% and precipitation from the sodium hydroxide-sodium carbonate solution is quantitative. Over-all chemical recovery is about 85%, most of the loss being in the nitric acid treatments.

Determination of Radiostrontium in Soils and Sludges. The sample is converted to ash in a muffle furnace and an aliquot of 1 to 50 grams is taken for analysis. After addition of strontium and barium carriers and drying, the ash is mixed with 5 times its weight of sodium hydroxide and fused in a nickel crucible. Sodium carbonate is added to the melt and the mixture is heated again. The fusion mixture is taken up in hot water to complete disintegration of the solid, and centrifuged; the supernatant is discarded. The residual solid is dissolved in hydrochloric acid and the strontium precipitated as carbonate by addition of ammonia and sodium carbonate. Strontium is purified by nitric acid treatment, barium chromate precipitation, and hydroxide scavengings before counting for total radiostrontium content or separation of yttrium-90. In these samples, nitric acid treatment usually is necessary, even if only strontium-90 is to be determined.

If only leachable radiostrontium is desired, the original sample is extracted several times with hot 6 M nitric acid. After addition of carrier, the acid is neutralized and the strontium precipitated with

carbonate, which is then treated in the same way as the carbonate obtained after fusion.

Radiostrontium in Biological Materials. The sample is converted to ash, usually in a muffle furnace. For some samples, however, wet ashing with nitric acid followed by an equal-volume mixture of nitric and perchloric acids may be preferred. A suitable aliquot is taken, dissolved in hydrochloric acid, and evaporated to near dryness. The chlorides are converted to nitrates by evaporation with nitric acid and strontium nitrate is precipitated from concentrated nitric acid. After a second precipitation from nitric acid, the precipitate is dissolved in water and made alkaline with ammonia to test for completeness of phosphate removal. Any precipitate (indicative of unremoved phosphate) is digested with sodium carbonate to convert the phosphate to carbonate. This is dissolved in acid, warmed to drive off carbon dioxide, and again made alkaline with ammonium hydroxide. If a precipitate forms, it is discarded. Sodium carbonate is added to the combined strontium-containing supernatants to precipitate the strontium as carbonate. This precipitate is collected and purified by barium chromate precipitation and hydroxide scavenging. In all cases with biological samples, treatment with nitric acid is necessary to prevent phosphate interference.

PROCEDURE 32

STRONTIUM AND BARIUM

Source - "Determination of Strontium and Barium Activities in Fission", L. E. Glendenin, Paper 236 in "Radiochemical Studies: The Fission Products", edited by C. D. Coryell and N. Sugarman, McGraw-Hill Book Co., Inc., New York, 1951. It is based on report CN-1312, dated May 15, 1945.

1. INTRODUCTION

The precipitation of $Sr(NO_3)_2$ and $Ba(NO_3)_2$ by fuming HNO_3 is a classical method for the separation of strontium and barium from fission-product mixtures.[81] Although the method is fairly specific for strontium and barium, it has been known for some time that contaminating activities may be present even after several reprecipitations.[82-84] In order to remove this contamination, a $Fe(OH)_3$ scavenging precipitation is made after a single reprecipitation of the strontium and barium nitrates. The barium is then separated from strontium as the chromate in a buffered $HC_2H_3O_2$ solution (of pH 5), in which strontium is soluble, and converted to $BaCl_2 \cdot H_2O$ for added purification from strontium and for weighing.[85] The strontium is isolated from the acetic acid-chromate solution as $SrC_2O_4 \cdot H_2O$ and is weighed as such after an alcohol-ether washing and vacuum desiccation. The precipitation of the $SrC_2O_4 \cdot H_2O$ is made in an ammoniacal solution[86] to prevent the reduction of the chromate to Cr(III) by oxalic acid and the subsequent coprecipitation of Cr(III) with the $SrC_2O_4 \cdot H_2O$.

The procedure previously employed[83] was somewhat longer, involving added reprecipitations of the alkaline-earth nitrates and an added $BaCrO_4$ separation from the strontium fraction. These unnecessary operations have been deleted from the procedure. The simplified method is given below.

2. PREPARATION AND STANDARDIZATION OF CARRIER

Strontium Carrier. Dissolve 24.1 g of $Sr(NO_3)_2$ in water and dilute to 1 liter. Pipet 5 ml of carrier solution into a beaker and add about 30 ml of H_2O. Add 5 ml of saturated oxalic acid and heat nearly to boiling. Add 2 ml of conc. NH_4OH drop by drop with constant stirring.

Allow to stand for about 10 min in cool tap water with occasional

stirring. Filter quantitatively on a weighed sintered-glass crucible with suction. Wash three times with 5 ml of hot H_2O containing a few drops of NH_4OH, three times with 95 per cent ethanol, and three times with 5 ml of ether, rinsing down the inside of the crucible with each washing. Wipe the outside of the crucible with Kleenex or a lintless cloth and place in a vacuum desiccator. Evacuate for 2 min. Weigh as $SrC_2O_4 \cdot H_2O$ and repeat the desiccation until the weight is constant to 0.2 mg.

3. PROCEDURE

Step 1. To 1 to 5 ml of neutron-irradiated uranyl nitrate in a 50-ml centrifuge tube add 2 ml each of barium and strontium carrier and then 30 ml of fuming HNO_3. Cool (under running tap water), stirring for 1 to 2 min, and centrifuge.

Step 2. Dissolve the precipitate in about 2 ml of H_2O (Note 1), re-precipitate with 15 ml of fuming HNO_3, and centrifuge.

Step 3. Dissolve the precipitate in 5 to 10 ml of H_2O, add 5 mg of iron carrier, and precipitate $Fe(OH)_3$ with about 2 ml of 6M NH_4OH. Centrifuge and discard the $Fe(OH)_3$.

Step 4. Neutralize the supernatant solution with 6M HNO_3 and add 1 ml of 6M $HC_2H_3O_2$ and 2 ml of 6M $NH_4C_2H_3O_2$. Heat the solution nearly to boiling and add 1 ml of 1.5M Na_2CrO_4 drop by drop with stirring. Continue stirring for about 1 min and centrifuge (Note 2). Reserve the supernatant solution for strontium determination.

Step 5. Determination of Barium^{85} (Note 3). Wash the precipitate with 10 ml of hot H_2O and dissolve in 1 to 2 ml of 6M HCl (Note 4). Add 15 ml of HCl-ether reagent, chill, and stir for 1 to 2 min. Centrifuge and decant completely.

Step 6. Dissolve the precipitate in 1 ml of H_2O. Reprecipitate with 15 ml of HCl-ether mixture. Centrifuge and decant. Note the time.

Step 7. Transfer the precipitate to a weighed filter-paper disk (Note 5) on a small Hirsch funnel with three 5-ml portions of absolute

ethanol containing 3 to 5 drops of conc. HCl (Note 6). Filter with suction. Wash three times with 5-ml portions of ether and such dry. Transfer the paper with the precipitate to a small watch glass and place in a vacuum desiccator. Evacuate for 2 min, release the suction, and evacuate again for 5 min. Finally, weigh the precipitate as $BaCl_2 \cdot H_2O$ and mount for counting.

Step 8. Determination of Strontium. Add 2 ml of conc. NH_4OH to the clear supernatant solution from step 4, heat nearly to boiling, and add 5 ml of sat. $(NH_4)_2C_2O_4$ slowly with stirring. Stir for 1 to 2 min and filter with suction on a weighed paper (Note 5) in a small Hirsch funnel. Wash three times with 5 ml of H_2O, three times with 5 ml of 95 per cent ethanol, and three times with 5 ml of ether. Transfer the paper containing the $SrC_2O_4 \cdot H_2O$ to a small watch glass and place in a vacuum desiccator. Evacuate for 2 min, release the suction, and evacuate again for 5 min. Weigh the precipitate as $SrC_2O_4 \cdot H_2O$ and mount.

Notes.

1. Heating may be required in order to effect complete solution.

2. A few drops of Aerosol solution facilitates clean centrifugation. If any particles of $BaCrO_4$ remain, the supernatant solution should be filtered.

3. If only strontium is to be determined, the precipitate may be discarded and the supernatant solution may be treated at once as in step 8.

4. A small residue (probably $BaCl_2$) may be formed, but it can be ignored.

5. The filter-paper disk is washed with ethanol and ether and dried in a vacuum desiccator under the conditions of the procedure before the weighing.

6. Barium chloride is appreciably soluble in absolute ethanol. The presence of the HCl represses the solubility and increases recovery.

PROCEDURE 32 (Cont'd.)

4. DISCUSSION

In the standardization of the strontium carrier, the $SrC_2O_4 \cdot H_2O$ is precipitated by the method of the neutralization of an oxalic acid solution with NH_4OH rather than by the addition of $(NH_4)_2C_2O_4$ to an ammoniacal solution, as is required in the analytical procedure. The precipitation is not performed by the latter method because it was observed in several instances that a precipitate of $SrCO_3$ was formed in the hot ammoniacal solution (apparently by the absorption of CO_2 from the atmosphere) before the addition of $(NH_4)_2C_2O_4$. The presence of $SrCO_3$ could lead to erratic results in the weighing; therefore, this method was discarded in favor of the method described above. The formation of $SrCO_3$ in the analytical procedure has not been observed.

PROCEDURE 33

STRONTIUM AND BARIUM

Source - "Preparation of Carrier-Free Strontium and Barium Tracers by Use of Lead Nitrate and Lead Chromate Precipitations", L. E. Glendenin, Paper 238 in "Radiochemical Studies: The Fission Products", edited by C. D. Coryell and N. Sugarman, McGraw-Hill Book Co., Inc., New York, 1951. It is based on report CC-1050 dated November 8, 1943.

1. INTRODUCTION

The precipitation of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ by fuming HNO_3 is a classical method of separating barium and strontium from fission material.[87,88] Since lead nitrate is also highly insoluble under these conditions,[89] the carrying of radioactive barium and strontium on $Pb(NO_3)_2$ precipitated in this manner was tested. The method proved to be highly efficient for the separation of carrier-free barium and strontium from the other fission products. On this same basis the carrying of barium on $PbCrO_4$ precipitated in a buffered $HC_2H_3O_2$ solution, in which strontium is soluble, was studied, and the results showed that such a procedure separates barium tracer from strontium tracer very efficiently.

The $PbCrO_4$, carrying the active barium is dissolved, the CrO_4^{--} is reduced by $NaNO_2$, the Pb^{++} and the Cr^{+3} are precipitated with NH_4OH and the barium tracer is left in solution with Na^+, NH_4^+, and NO_3^-. The mother liquor from the $PbCrO_4$ precipitation is freed of CrO_4^{--} by the addition of excess Pb^{++}, and the excess is removed with H_2S. The strontium is left in solution with the Na^+ and NO_3^- ions.

2. PROCEDURE

Step 1. Add 20 mg of lead carrier to the fission-product material and evaporate the solution to about 2 ml (Note 1). Add 15 to 20 ml of fuming HNO_3, cool, and stir occasionally for 3 to 5 min. Centrifuge, and discard the supernatant solution.

Step 2. Dissolve the precipitate of $Pb(NO_3)_2$ in 1 ml of H_2O and reprecipitate with 10 to 15 ml of fuming HNO_3. Centrifuge as before, and discard the supernatant solution.

Step 3. Dissolve the $Pb(NO_3)_2$ in about 10 ml of H_2O, add 10 mg of lanthanum carrier, heat the solution nearly to boiling, and add 5 N NH_4OH (CO_2-free) in slight excess with stirring to precipitate $La(OH)_3$ and $Pb(OH)_2$. Centrifuge, and discard the precipitate.

Step 4. Neutralize the supernatant solution with 6N HNO_3 and add 1 ml of 6N $HC_2H_3O_2$ and 4 ml of 3N $NH_4C_2H_3O_2$. Add 10 mg of lead carrier, heat nearly to boiling, and add 1 ml of 3N Na_2CrO_4 drop by drop with stirring. Heat and stir for 2 min. Centrifuge, heat the supernatant solution, and add 10 mg of lead carrier drop by drop with stirring. Centrifuge, and combine the $PbCrO_4$ precipitate with the first precipitate (Note 2). The supernatant solution is reserved for strontium separation in step 10.

Step 5. Dissolve the combined $PbCrO_4$ precipitates by heating with 2 to 3 ml of 6N HNO_3. Add 5 mg of strontium carrier and 10 ml of H_2O. Heat nearly to boiling and neutralize with 6N NH_4OH. Add 1 ml of 6N $HC_2H_3O_2$ and 4 ml of 3N $NH_4C_2H_3O_2$. Heat the solution, add 10 mg of lead carrier, and precipitate by adding 1 ml of 3N Na_2CrO_4 drop by drop with

stirring (Note 3). Centrifuge, and discard the supernatant solution.

Step 6. Dissolve the $PbCrO_4$ in 2 to 3 ml of 6N HNO_3 and dilute to about 10 ml. Heat nearly to boiling, add 1 ml of 1M $NaNO_2$ drop by drop, and add 6N NH_4OH (CO_2-free) in slight excess to precipitate $Cr(OH)_3$ and $Pb(OH)_2$. Centrifuge, and reserve the supernatant solution for barium separation. Redissolve the precipitate in 1 ml of 6N HNO_3, dilute to 10 ml, and reprecipitate with 6N NH_4OH. Centrifuge, and combine the supernatant solution with the supernatant solution from the first precipitation (Note 4).

Step 7. Neutralize the combined supernatant solutions with 6N $HC_2H_3O_2$ and add 20 mg of lead carrier, 2 ml of 6N $HC_2H_3O_2$, and 8 ml of 3N $NH_4C_2H_3O_2$. Heat nearly to boiling and add 2 ml of 3N Na_2CrO_4 drop by drop with stirring. Centrifuge, and discard the supernatant solution (Note 5.)

Step 8. Proceed as in step 6.

Step 9. Boil the combined solution containing the radioactive barium to expel NH_3, and dilute to the desired volume (Note 6).

Step 10. Heat the solution from step 4 and add 1 ml of 6N HNO_3. Add drop by drop with stirring a solution of 0.5 g of $Pb(NO_3)_2$ dissolved in a few milliliters of H_2O. Heat and stir for 2 min (Note 7). Centrifuge, wash with 10 ml of hot H_2O, and discard the precipitate of $PbCrO_4$. Heat the supernatant solution nearly to boiling and saturate with H_2S. Centrifuge, and discard the PbS precipitate.

Step 11. Evaporate the supernatant solution containing the radioactive strontium nearly to dryness. Add a few milliliters of conc. HNO_3, again evaporate nearly to dryness, and make up to the desired volume (Note 8).

Notes. 1. The fission-product material is the aqueous phase of ether-extracted uranyl nitrate. With suitable modifications, other starting materials can be used.

2. The second precipitation of $PbCrO_4$ is made to improve the recovery of barium.

3. The precipitation of $PbCrO_4$ in the presence of strontium holdback

carrier removes coprecipitated strontium. The additional lead is precipitated to recover barium more completely.

4. Chromic hydroxide and lead hydroxide are reprecipitated to recover any barium that may have been coprecipitated.

5. Lead chromate (carrying barium) is again precipitated in a buffered solution to ensure the removal of strontium.

6. The barium tracer solution will contain Na^+, NH_4^+, and NO_3^- ions.

7. Lead is added to remove all the CrO_4^{--} from solution. The amount of lead added is slightly more than the amount required.

8. The treatment with HNO_3 removes $NH_4C_2H_3O_2$. The strontium tracer solution will contain Na^+, H^+, and NO_3^- ions.

3. DISCUSSION

The method was tested for separation by starting with aliquots of a 60-day-old fission-product concentrate prepared by an exhaustive ether extraction of uranyl nitrate. The barium fraction from 1 ml isolated in the first $PbCrO_4$ operation and reprecipitated once with $PbCrO_4$ in the presence of strontium holdback carrier had an activity of 20,000 counts per minute (c/m), or a 35 per cent yield of the value of 58,200 c/m determined by a conventional assay of the original concentrate.[88] The activity of the strontium fraction was 370,000 c/m, or a yield of 67 per cent of the value of 548,000 c/m in the original concentrate.

A standard analysis[88] of the barium fraction for strontium activity showed the presence of 1,000 c/m of strontium. The performance of the second $PbCrO_4$ precipitation provided for in the procedure would undoubtedly lower this contamination considerably. An analysis of the strontium fraction for barium activity showed the presence of only 220 c/m of barium. Other fission species are probably removed to negligible values by the $Pb(NO_3)_2$ recrystallization, followed by the $Pb(OH)_2$-$La(OH)_3$ precipitation, as shown by extensive studies on alkaline-earth preparations by the closely analogous $(Ba,Sr)(NO_3)_2$ method described elsewhere.[88]

PROCEDURE 33 (Cont'd.)

It may be mentioned that an attempt to carry $BaCl_2$ on NaCl precipitated from uranyl nitrate with conc. HCl was unsuccessful. This result was confirmed by Hamilton.[90]

PROCEDURE 34

STRONTIUM AND BARIUM

Source - Lawrence B. Farabee in Oak Ridge National Laboratory Report ORNL-1932, September, 1955.

PROCEDURE FOR THE RADIOCHEMICAL ANALYSIS OF STRONTIUM AND BARIUM IN HUMAN URINE

ABSTRACT

An analytical procedure for the determination of radioactive strontium and barium in large volumes of urine is described. The method is based on the preferential chelation of calcium over strontium using versene. This difference is greatest at a pH of 4.5 to 6.0. When a versenate chelate of the alkaline earths in a urine specimen, at a pH of 5.5, is passed over a cation exchange column all of the strontium and barium is adsorbed, whereas almost all of the calcium and about 1/2 of the magnesium passes into the effluent as the chelate. The extraneous calcium and magnesium can be removed from the resin with a solution of citric acid and versene at a pH of 5.0. The sodium is removed with 0.5 N HCl, while the radioactive strontium and barium is eluted with 6 N HNO_3.

EXPERIMENTAL

PART I. THE ALKALINE PHOSPHATE PRECIPITATION

A short approach to a urinalysis procedure would utilize the urine direct without preliminary concentration by precipitation. However, certain difficulties arise in using urine direct with ion exchange resins in a separation procedure. The high concentration of dissolved salts, as well as the variability in individual specimens, and the presence of organic matter

in urine makes a preliminary precipitation an important adjunct in this procedure. Quantitative recovery of barium and strontium can be achieved by a basic phosphate precipitate from urine. Since these elements do not form complexes with the organic materials present in urine, the precipitation can be carried out directly, thereby avoiding the laborious process of ashing the urine sample. This precipitate also serves two major purposes: (1) The separation of the above elements from sodium and potassium and (2) the separation from organic matter which is present in the urine sample.

Procedure

1. Add concentrated hydrochloric acid (HCl) to a 1500 ml urine sample to make the urine 0.1 N in HCl and yield a clean solution.
2. Heat the sample on a hot plate to a temperature of 85° to 90° C.
3. Add 6 ml of 6M phosphoric acid to provide an excess of phosphate to insure complete precipitation of all calcium and magnesium.
4. Use an electric motor stirrer to provide vigorous stirring for the subsequent precipitation.
5. Add slowly 6 M sodium hydroxide until a basic phosphate precipitate is visible. Continue the addition until the solution is basic to a pH of 8 to 10. Universal pH paper can be used to determine the pH in this case.
6. The precipitate is allowed to settle for 2 hours or longer.
7. The supernatant liquid is decanted by suction to the lowest possible level such that the precipitate is not disturbed. Discard the supernatant solution.
8. The remaining slurry is poured into a centrifuge cup. The precipitate is centrifuged at 1500 rpm for 5 minutes. The supernatant liquid is decanted by suction and discarded.

PART II. PREPARATION OF THE COLUMN

(a) Description of column system

Beds of 50-100 mesh Dowex-50 x 12 resin are prepared in a Pyrex glass column 18.5 cm long and 1.8 cm inside diameter. The bottom is fitted with a one-way stopcock in a one-hole rubber stopper. Glass wool over the rubber stopper holds the resin bed. A 6 inch Pyrex funnel fitted to the top of the glass column with a rubber tubing serves as a reservoir for the feed and wash solutions.

(b) Preparation of the resin

New Dowex-50 resin is conditioned by several washings, alternately with 5 per cent NaCl and 5 per cent HCl. During the conditioning process a considerable quantity of "fines" are removed. This is accomplished by stirring the resin sample in a large beaker filled with the conditioning solution. Most of the resin is allowed to settle, whereupon the liquid containing the "fines" is decanted. The resin is then converted to a sodium cycle with 5% NaCl. About 250 gms. of the resin is put into a Pyrex glass tube 4 ft. long and 2.5 cm. diameter. Six liters of 5% NaCl is then passed over the resin at a maximum flow rate (4.7 ml/min/cm^2). The resin is then emptied into a large beaker and washed free of NaCl with distilled water. The resin which has been used in urinalysis, can be re-used by converting to the sodium cycle as described above.

For practical reasons, it is expedient to keep the amount of resin used to a minimum in order to reduce the volume of elutriant solutions and thereby reduce the time required to perform a single analysis. Experimentally it was found that 16.3 gms. of the above resin (air dried), or about 25 ml by volume (wet form) was sufficient for an individual analysis.

PART III. OPERATION OF COLUMN

(a) Preparation of feed solution

The alkaline earth phosphate precipitate can be dissolved in 10 to 20 ml concentrated nitric acid. The resulting solution contains calcium, magnesium, phosphates, plus an indeterminate amount of sodium, potassium, ammonia ions, and organic material adsorbed on the gelatinous precipitate. The organic material can be destroyed by wet ashing in the presence of nitric acid and hydrogen peroxide. The inorganic residue is dissolved in 2 to 3 ml of concentrated hydrochloric acid plus about 20 ml distilled water. The solution is then diluted to about 800 ml with distilled water.

This urinalysis procedure was designed primarily to analyze urine supernatant from a previous plutonium analysis in which 600 mg of extra calcium had been added. The total calcium under these conditions was about 800 mg while the magnesium was about 100 to 200 mg. When adsorbed on a cation exchanger of the size used in this procedure, such large quantities of alkaline earths would utilize most of the exchange capacity of the resin, thereby making the operation vulnerable to losses of strontium and barium. In order to circumvent the above difficulty, it was necessary to devise some way in which the amount of alkaline earths that were adsorbed on the resin could be held to a minimum. The greater complexing efficiency for calcium over strontium was used to develop a method whereby a large per cent of the calcium and some of the magnesium, being chelated with versene, would pass through the resin column while while strontium and barium are adsorbed. The alkaline earths of the feed solutions are first chelated with versene at pH 10.5. At this pH a dye indicator can be used to determine the end point of chelation of the alkaline earths. The pH of the solution is then reduced to 5.5 and put over the resin column. In 22 experimental runs using samples with added calcium as well as samples without, 94 to 97 per cent of the calcium passed through the column as a complex, while 36 to

63 per cent of the magnesium also passed into the effluent. Losses of Sr^{89} tracer averaged from 0.11 to 0.19 per cent.

Procedure

1. The precipitate from Step 1, 8 is dissolved in about 15 ml concentrated nitric acid.

2. This solution is poured into the two liter beaker in which the original phosphate precipitation was carried out.

3. The organic matter is destroyed by heating the solution, and by alternately adding conc. HNO_3 and 30% hydrogen peroxide.

4. This is repeated until a white residue remains. The residue is then taken to dryness.

5. Remove the beaker from the hot plate and wash down the walls with about 20 ml distilled water. Add 2 to 3 ml concentrated hydrochloric acid and heat until the inorganic material is dissolved. The volume is diluted to 800 ml with distilled water and the pH of the solution is checked in subsequent operations.

6. Add 1 N sodium hydroxide until the pH is about 9.0.

7. Add 2 ml Eriochrome Black T*.

8. Add a solution of 7.5%† technical grade versene until the indicator changes from wine red to blue at pH 10.5. This point indicates complete chelation of all calcium and magnesium.

9. Reduce the pH to 5.5 with concentrated hydrochloric acid. The final adjustment can be made with 1 N HCl.

10. Pass this solution over the resin column at a flow rate of not greater than 8 $ml/min/cm^2$.

11. Wash down the walls of the funnel with about 50 ml distilled water.

12. Discard the effluents.

---

* Mix 0.5 gms. Eriochrome Black T and 4.5 gms. hydroxylamine hydrochloride. Dissolve in 100 ml of alcohol and filter.

† Dissolve 75 gms. tetrasodium ethylenediamine tetraacetic acid (technical grade) in about 800 ml distilled water. Filter and dilute to one liter.

(b) Elution of Adsorbed Calcium and Magnesium from the Resin Column

The efficiency of versene to chelate the alkaline earths is reduced when the pH is lowered to 8.0 to 5.5. Since the feed solution is put over the column at a pH of 5.5, there will be some exchange of the cations between the feed solution and the resin because of this reduction. This indeterminate amount of calcium and magnesium that is adsorbed on the resin must be removed without loss of strontium and barium. The citrate complex would remove the alkaline earths in the following order: Mg > Ca > Sr > Ba. Versene would be expected to remove calcium from the resin before the other alkaline earths. A combination of versene and citric acid at pH 5.0 is a better elutriant than citric acid alone. This is due to the greater affinity for calcium by versene. There is no loss of Sr^{89} even at twice the volume of elutriant necessary to remove all of the calcium and magnesium.

Procedure

1. Pass 800 ml of a solution of one per cent citric acid and 0.75% versene over the resin column at a flow rate of 4 ± 0.8 ml/min/cm^2 (10.93 gms. citric acid monohydrate, 100 ml of 7.5% versene, dilute to one liter and adjust the pH to 5.0 with 6 M NaOH).
2. Discard the effluent wastes.

(c) Removal of sodium from the resin column

Since the Dowex-50 resin had been put on the sodium cycle in preparation for urinalysis, this sodium must be removed in order that the final eluate of the strontium and barium can be evaporated and prepared for counting without further chemical purification. Dilute acids will elute the monovalent sodium with no significant loss of Sr^{89}. In 22 experimental urinalyses, losses of Sr^{89} averaged 0.22 per cent when 0.5 N HCl was used to remove the sodium from the resin.

Procedure

1. Pass 800 ml of 0.5 N hydrochloric acid over the resin column at a flow rate of 4 ± 0.8 ml per minute per cm^2.
2. Discard the effluent wash.

D. ELUTION OF STRONTIUM AND BARIUM

The strontium and barium can be eluted from the resin column with 200 ml 6 N nitric acid. This volume removes about 99.6 per cent of the strontium and barium.

Procedure

1. Pass 200 ml 6 N HNO_3 over the resin at a flow rate of 2 $ml/min/cm^2$.
2. Catch the eluate in a 400 ml beaker.

PART IV. PREPARATION OF THE SAMPLE FOR COUNTING

The eluate is evaporated on a hot plate to almost dryness at a temperature just below the boiling point. The residue is transferred to a counting dish*. The inorganic residue, which is mostly sodium and inert strontium and barium, will have a density of less than 1 mg/cm^2, therefore self-absorption of the radiations by the sample should be nil.

Since the rare earth daughter products of Sr^{90} and Ba^{140} are chelated by the versene-citric acid wash, these radioactive products will be removed from the column by this wash. Therefore, the time of separation of these daughter products can be established for subsequent identification of the isotope by growth and/or decay measurements.

Procedure

1. Evaporate the nitric acid eluate to almost dryness on a hot plate.
2. Wash the contents into a 50 ml beaker with distilled water. Clean the walls of the larger beaker with nitric acid and water. (This transfer to the

* This counting dish is made from a circular piece of type 304 stainless steel 1-3/4 inch diameter and 0.005 in. thick. A cup, one inch diameter and 0.125 inch depth, is die pressed for holding the sample.

small beaker facilitates the final transfer to a counting dish.)

3. Evaporate the liquid in the small beaker to dryness.

4. Dissolve the residue in about 1/2 ml 1 N HNO_3. Transfer this liquid to a counting dish using a pipette. Wash the walls of the beaker with another 1/2 ml of acid, and add this to the dish.

5. Dry under an infra-red lamp.

The radioactivity of the sample can be counted in a conventional end window Geiger-Mueller counter.

RESULTS

More detailed studies of the various steps indicated that the average total losses in the column operation were less than one per cent. About 10^6 c/m of Sr^{89} was used to study the losses. Similar studies with Ba^{140} likewise gave losses of about one per cent.

This procedure was also tested for total recovery of Sr^{89} tracer at levels of about 75 c/m. This test was made on urine samples from individuals who had not been exposed to fission product contamination. To 18 of the samples was added the extra 600 mg calcium; the other 4 had no extra calcium. No difference was noted in the per cent of recovery. In the 22 experimental runs, the recovery averaged 93.7% $\pm$ 2.5 per cent (standard deviation) of Sr^{89} tracer. The average counting error was about 2.7 c/m at a 90% confidence level. In determining the per cent recovery, a volume of Sr^{89} tracer equal to that put in the urine samples was evaporated in the center of a counting dish and used as a "standard". The "standards" and urinalysis samples were counted at about the same time to avoid errors due to decay of Sr^{89}. Since some of the residue in a urinalysis sample is displaced farther from the center than the "standards", a reduction in efficiency of counting can be expected due to this lateral displacement. The final per cent recovery took into consideration both chemical losses and decreased counting efficiency.

PROCEDURE 34 (Cont'd.)

SEPARATION FROM K^{40}

In order to determine the presence of radioactive strontium and barium at very low levels, a urinalysis procedure must provide good separation from K^{40}, a beta emitter that is present in urine. Urine specimens from 17 persons who had not been exposed to fission product contamination, were checked by this procedure. Average radioactivity due to K^{40} was 0.7 c/m at about 25% geometry. The maximum was 1.7 c/m.

SUMMARY

In the radiochemical analysis of strontium and barium in large volumes of urine, an alkaline earth phosphate precipitation is used to concentrate the strontium and barium. The separation of large amounts of calcium and magnesium from tracer amounts of strontium and barium is done on one ion exchange column by the use of versene and citric acid as complexing agents. Over-all losses of Sr^{89} on the column are about one per cent. Urine samples containing from 150 to 800 mg calcium gave equally good recovery. Since no "carriers" are added, this method may be useful for analyzing bone or urine for non-radioactive strontium and barium. This procedure is simple in operation, has a minimum number of steps, and provides excellent recovery of radioactive strontium and barium in human urine.

PROCEDURE 35

STRONTIUM

Source - E. A. Martell in "The Chicago Sunshine Method", U. S. Atomic Energy Commission Report AECU-3262, Page 44, May, 1956.

Strontium Separation Procedure for 5 Grams of Bone Ash

(Method of Dr. John Harley, Health and Safety Laboratory, New York Operations Office, U. S. Atomic Energy Commission)

1. Ash in nickel crucible at 900 C.

2. Grind in mortar to a fine powder.

3. Weigh out 5 grams into a 250 ml centrifuge bottle.

4. Add 44 ml of water and then slowly add 154 ml of 90% nitric acid to bring concentration to 75%.

5. Add 20 mg of strontium carrier as $Sr(NO_3)_2$ in a 2 ml solution.

6. Stir rapidly for 30 minutes (mechanically).

7. Centrifuge for 10 minutes at 2000 r.p.m.

8. Decant and repeat steps 4, 5, and 7 at half the original volume.

9. Decant as much as possible and transfer to 100 ml beaker with H_2O.

10. Evaporate to dryness to expel all the nitric acid.

11. Pick up with 50 ml H_2O; complete solution should result.

12. Heat this solution to boiling. Adjust pH to approximately 7 with NaOH. Add 10 ml of 10% Na_2CO_3, digest with heating until precipitation of $SrCO_3$ is complete.

13. Filter through Tracerlab section filter apparatus and wash with 0.5% Na_2CO_3. Draw air through the filter for a few minutes to dry out the precipitate. (The Na_2CO_3 is dried to constant weight in an oven at 110 C for yield determination, dissolved in HCl, and reserved for Y growth and subsequent milking.)

Notes:

1. The recovery of strontium by this procedure can be maintained at about 95%. The direct solubility of strontium nitrate in the 75% nitric acid is about 13 mg of strontium per liter. This is very markedly reduced by the presence of calcium nitrate. For this reason, the calcium nitrate is maintained at, at least 50% of saturation in the first separation. The solubility of calcium nitrate is equivalent to 23.5 grams of CaO per liter of 75% nitric acid.

2. Other types of samples are given a preliminary chemical treatment to bring them to the form calcium oxide plus strontium oxide. The nitrate separation is then carried out as for bone except that the amount of 75% nitric acid is regulated to take solubility considerations into account.

PROCEDURE 36

STRONTIUM

Source - E. A. Martell in "The Chicago Sunshine Method", U. S. Atomic Energy Commission Report AECU-3262, Page 49, May, 1956.

Strontium Separation from 40 Liters of Seawater

1. Filter original sample of 40 liters of seawater to remove suspended organic and inorganic material. Since the suspended material is discarded, the filter may be changed frequently to speed filtration.

2. To filtrated seawater add $SrCl_2$ standard solution containing about 3.5 grams of strontium. Add 400 grams NH_4Cl as a buffer to hold magnesium in solution. Add ~ 700 grams Na_2CO_3 to precipitate calcium and strontium and allow mixture to settle overnight. Discard bulk of supernate by decantation and filter remainder through Whatman #42 paper in large Buchner funnel.

3. Dissolve carbonates in 6 N HCl and dilute to a volume of 3 liters. Heat nearly to boiling and add solid $(NH_4)_2SO_4$ to first cloudiness. Add an additional 6 grams of solid $(NH_4)_2SO_4$, digest for 30 minutes on hot plate (on low), filter and wash with distilled water.

4. Transfer $SrSO_4$ precipitate to a clean beaker and add at least 50% excess of $(NH_4)_2CO_3$ solution. Digest for 20 minutes on low hot plate. Filter and wash $SrCO_3$ precipitate.

5. Dissolve $SrCO_3$ precipitate in minimum acid and proceed with strontium separation, carrying out at least two barium chromate scavenging precipitations before final determination of strontium as carbonate.

[Note added in proof]

During the routine use of this method for strontium analysis a very small variable positive bias was encountered. Following a discussion with FUDGE AND JENKINS of A.E.R.E. Harwell, special attention was directed to the behaviour of cerium.

A high activity run was carried out and following precipitation of strontium carbonate the strontium was precipitated from fuming nitric acid. A small amount of 141 cerium was identified remaining in solution on analysis by β-absorption curve. It is believed that formation of a radiocolloid is the cause of the solution of a small variable proportion of the cerium in the sample. The addition of 10 mg of cerium carrier (as cerous nitrate) before column treatment has been proved to prevent elution of the radiocerium, and the bias was removed from the method.

REFERENCES

1. D. N. Sunderman and W. W. Meinke, reference cited in General Reference Section II.
2. H. H. Willard and E. W. Goodspeed, Ind. Eng. Chem., Anal. Ed., 8, 414 (1936).
3. M. L. Salutsky and H. W. Kirby, Anal. Chem. 27, 567 (1955).
4. N. H. Furman, "Scott's Standard Methods of Chemical Analysis", Van Nostrand, New York, 1939.
5. P. J. Elving and R. E. VanAtta, Anal. Chem. 22, 1375 (1950).
6. D. N. Sunderman and W. Wayne Meinke, Anal. Chem. 29, 1578 (1957).
7. D. N. Sunderman and W. W. Meinke, Anal. Chem. 29, 1578 (1957).
8. R. Overstreet, L. Jacobson, K. Scott, and J. G. Hamilton, Procedure 26 in Section VII.
9. M. Kurbatov, F. Yu, and J. Kurbatov, J. Chem. Phys. 16, 87 (1948).
10. J. Kurbatov, J. Kulp, and E. Mack, J. Am. Chem. Soc. 67, 1923 (1945).
11. J. Khym, P. Tompkins, and W. Cohn, MDDC-1214 (1947).
12. P. C. Tompkins, L. Wish, and J. X. Khym, Paper 239 in "Radiochemical Studies: The Fission Products", edited by C. Coryell, and N. Sugarman, McGraw-Hill, New York, 1951.
13. T. Schonfield, M. Weld, and M. Brund, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy (1958), Paper No. 1439.
14. L. E. Glendenin, Procedure 28 in Section VII.
15. J. S. Fritz, R. T. Oliver, and D. J. Pietrzyk, Anal. Chem. 30, 1111 (1958).
16. R. Pribil and D. Marcova, Chem. Listy 45, 542 (1951).
17. F. Feigl and H. A. Suter, Ind. Eng. Chem. Anal. ed. 14, 840 (1942).
18. J. F. Flagg, "Organic Reagents Used in Gravimetric and Volumetric Analysis", Interscience Publishers, Inc., New York, 1948, p. 217.
19. A. Broido, in Procedure 18 in Section VII.
20. A Broido, U. S. Atomic Energy Commission Report AECD-2616, July, 1947.
21. R. A. Bolomey and L. Wish, J. Am. Chem. Society 72, 4483 (1950).
22. A. S. Goldin, U. S. Atomic Energy Commission Report TID-7517 (Part 1b), p. 323 (1956).
23. W. B. Silker, Hanford Atomic Products Operation Report HW-55117, May, 1958.
24. A. S. Goldin, R. J. Velten and G. W. Frishkorn, Anal. Chem. 31, 1490 (1959).
25. T. Kiba and S. Mizukami, Bull. Chem. Soc. Japan 31, 1007 (1958).
26. G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley and Sons, Inc., New York, 1957.
27. W. F. Hillebrand, et al., Reference cited in Section I.
28. H. H. Barber, Ind. Eng. Chem., Anal. Ed. 13, 572 (1941).
29. N. M. Tillu and N. S. Telang, J. Indian Chem. Soc. 19, 231 (1942).
30. D. Dyrssen, Svensk Kem. Tidskr. 67, 311 (1955).

31. G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley and Sons, Inc., New York, 1957.
32. D. F. Peppard, G. W. Mason, and S. W. Moline, J. Inorg. Nuclear Chem. 5, 141 (1957).
33. O. Bonner and L. Smith, J. Phys. Chem. 61, 326 (1957).
34. E. R. Tompkins, J. X. Khym, and W. E. Cohn, J. Am. Chem. Soc. 69, 2769 (1947).
35. E. R. Tompkins, J. Am. Chem. Soc. 70, 3520 (1948).
36. W. H. Power, H. W. Kirby, W. C. McCluggage, G. D. Nelson, and J. H. Payne, Jr., Anal. Chem. 31, 1077 (1959).
37. E. A. Martell, Procedure 29 in Section VII.
38. C. W. Stanley and P. Kruger, Nucleonics 14, No. 11, 114 (1956).
39. P. Kruger and C. D. Coryell, J. Chem. Educ. 32, 280 (1955).
40. L. B. Farabee, Arch. Ind. Health 17, 200 (1958).
41. G. W. Milton and W. E. Grummitt, Can. J. Chem. 35, 541 (1957).
42. P. S. Davis, Nature 183, 674 (1959).
43. M. J. Cabell, AERE-C/M, Dec. 29, 1954.
44. M. Lerner and W. Rieman III, Anal. Chem. 26, 610 (1954).
45. H. L. Finston and J. Miskel, Ann. Rev. Nuclear Sci. 5, 274 (1955).
46. T. Schonfield, M. Wald, and M. Brund, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva (1958), Paper No. 1439.
47. R. W. Perkins, Anal. Chem. 29, 152 (1957).
48. F. Nelson and K. Krause, J. Am. Chem. Soc. 77, 801 (1955).
49. R. H. James and G. A. Welch, Nature 177, 183 (1956).
50. J. C. Dalton and G. A. Welch, Anal. Chim. Acta. 15, 317 (1956).
51. F. P. Treadwell and W. T. Hall, reference cited in General Reference Section I.
52. B. Kahn, Oak Ridge National Laboratory Report ORNL-1951, October 14, 1955.
53. B. Kahn, Anal. Chem. 28, 216 (1956).
54. E. A. Martell, U. S. Atomic Energy Commission Report AECU-3262, May, 1956.
55. W. F. Merritt, Can. J. Chem. 36, 425 (1958).
56. A. S. Goldin, R. J. Velten, and G. W. Frishkorn, Anal. Chem. 31, 1490 (1959).
57. D. Strominger, J. M. Hollander, and G. T. Seaborg, Revs. Modern Phys. 30, 585 (1958).
58. B. P. Bayhurst, in Procedure 18 in Section VII.
59. A. S. Goldin, U. S. Atomic Energy Commission Report, TID-7517 (Part 1b), P. 323 (1956).
60. E. A. Martell, U. S. Atomic Energy Commission Report AECU-3262, May 1956.
61. E. A. Bryant, J. E. Sattizahn, and B. Warren, Anal. Chem. 31, 334 (1959).
62. L. E. Glendenin in Procedure 13 in Section VII.
63. L. B. Farabee, Oak Ridge National Laboratory Report, ORNL-1932, P. 12 (1955).
64. D. F. Peppard, G. W. Mason, and S. W. Moline, J. Inorg. Nuclear Chem. 5, 141 (1957).
65. O. Hahn and F. Strassmann, Naturwissenschaften, 27: 11 (1939).
66. L. E. Glendenin, Report CC-971, Sept. 15, 1943.
67. A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, p. 158, D. Van Nostrand Company, Inc., New York, 1940.
68. W. Rubinson, Report CC-1142, Dec. 13, 1943.
69. C. M. Nelson, W. F. Boldridge, and D. N. Hume, Report CN-2570, February 1945.
70. B. Finkle and N. Sugarman, Paper 166 in "Radiochemical Studies: The Fission Products", edited by C. D. Coryell and N. Sugarman, McGraw-Hill, New York, 1951.
71. E. Glueckauf and P. J. P. Roberts, A.E.R.E., C/R 1443.

72. R. H. James and G. A. Welch, Nature, 177 (1956) 183.
73. L. E. Glendenin, Radiochemical Studies: The Fission Products, Nat. Nucl. En. Series, IV, 9, VI, McGraw-Hill Book Co., Inc., New York 1951, Paper 236, pp. 1460-64 and Paper 283, pp. 1642-45.
74. R. B. Hahn and B. O. Backer, Report A.E.C.U.-2903, April 1955.
75. A. A. Noyes and W. C. Bray, A System of Quantitative Analysis for the Rare Elements, MacMillan Co., New York, 1927.
76. J. M. Hollander, I. Perlman and G. T. Seaborg, Rev. Mod. Phys. 25 (1953) 469.
77. Hanson, W. C., Private Communication.
78. Martell, E. A., Chicago Sunshine Method: Absolute Assay of Strontium-90 in Biological Materials, Soils, Waters, and Air Filters, AECU-3262, May 1956.
79. Glendenin, L. E., Paper 236 (Coryell and Sugarman, Radiochemical Studies: The Fission Products, McGraw-Hill Book Co., Inc., New York, 1951) National Nuclear Energy Series, Plutonium Project Record, Vol. 9, Div. IV.
80. Perkins, R. W., To be published.
81. C. Lieber, Naturwissenschaften, 27: 421 (1939).
82. W. H. Sullivan, Report CC-765, June 30, 1943.
83. L. E. Glendenin, Report CC-971, September 15, 1943.
84. D. N. Hume, Clinton Laboratories Weekly Report, January 21, 1944.
85. L. E. Glendenin, Paper 288 in "Radiochemical Studies: The Fission Products", edited by C. D. Coryell and N. Sugarman, McGraw-Hill, New York, 1951.
86. E. H. Swift, "A System of Chemical Analysis", p. 376, Prentice-Hall, Inc., New York, 1938.
87. C. Lieber, Naturwissenschaften, 27: 421 (1939).
88. L. E. Glendenin, Paper 236 in "Radiochemical Studies: The Fission Products", edited by C. D. Coryell and N. Sugarman, McGraw-Hill, New York, 1951.
89. A Seidell, "Solubilities of Inorganic and Metal Organic Compounds", 3d ed., D. Van Nostrand Company, Inc., New York, 1940.
90. J. G. Hamilton, Report CH-957, Sept. 25, 1943.

AEC Technical Information Service Extension
Oak Ridge, Tennessee