

THE UNIVERSITY OF MICHIGAN
INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

RADIOCHEMICAL SEPARATIONS:

I. Barium, Strontium, and Calcium

Duane N. Sunderman
W. Wayne Meinke

September, 1955

IP-133

ACKNOWLEDGEMENT

We would like to express our appreciation to the authors for permission to give this prepaper limited distribution under the Industry Program of the College of Engineering.

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Duane N. Sunderman and W. Wayne Meinke

Department of Chemistry, University of Michigan
Ann Arbor, Michigan

ABSTRACT

A program of critical evaluation of radiochemical separation procedures has been instituted. Procedures for individual elements reported in the literature are collected and subdivided into individual separation steps. Those steps which are found unique and possessing general applicability are studied experimentally to determine optimum conditions (of both yield and contamination) for separation. These procedures are then further evaluated under optimum conditions to determine the effects on the separation of a number of diverse but representative elements and materials.

The alkaline earth elements, barium, strontium, and calcium were the first elements studied in this manner. Several common precipitations were studied to determine the conditions for optimum radiochemical separation within this group. It was found that conditions of operation must vary widely from commonly accepted analytical methods due to the demands of such factors as non-equilibrium operation, necessity for rapid precipitation, character of the precipitate, and manipulatory techniques. Nitrate, chromate and chloride precipitations were studied to give quantitative information concerning the contributions of these factors. Yield data are given for calcium, strontium and barium in the above separations under conditions varied to show the effects of excess or deficiency of reagents, quantitative or nonquantitative

precipitation and methods of adding precipitating reagents. Decontamination factors were determined with tracers of 16 typical elements. An optimum procedure is given for the systematic separation of these three ions in tracer solutions.

INTRODUCTION

Radiochemical separation procedures are composed of those chemical separation steps which, when applied to radioactive mixtures, yield a chemical species of sufficient purity to be uniquely counted or detected by the use of existing equipment and present-day techniques. These procedures may include extraction, precipitation, ion exchange, electrolysis or volatilization steps. Separation may be required from a large variety of diverse elements, as in the case of fission product analysis, or from neighboring elements in the periodic table, as in procedures following bombardment by low energy (a few Mev) nuclear particles. In many cases interfering activities must be reduced by a factor of 10^4 to 10^6 or more but the yield of the desired activity does not have to be quantitative. Often the nuclear characteristics of the isotope desired are such that the separation must be completed rapidly.

The general inorganic-analytical literature (26, 51, 53), while quite detailed in many cases, is not directly applicable to radiochemical work where nonequilibrium conditions are the rule rather than the exception. A program of critical evaluation of radiochemical separation procedures has thus been instituted at the University of Michigan. In this program, certain groups of elements are being studied, procedures previously reported in the literature are being evaluated, and the most promising separation steps are being explored in detail to determine optimum conditions for high decontamination and yield.

LITERATURE REPORTS

The first elements that have been explored are the alkaline earths: barium, strontium and calcium. Since barium and strontium are high yield fission products, considerable work has already been done on their radiochemical separations. By comparison, few radiochemical separation procedures are reported in the literature for calcium.

Typical procedures for the separation of these elements are suggested by standard analytical references (26, 51, 53). These references have been supplemented by the experimental work of Willard and Goodspeed (68) who used nitric acid for the quantitative separation of barium and strontium from calcium.

To determine the separation procedures favored in recent work a complete survey was made of the nuclear chemical literature. Compilations of radiochemical procedures (5, 18, 33, 35, 36, 44) were consulted for separations involving these three elements. A number of references were located in the German literature (37), and additions to these detailed procedures were made from references for the isotopes of barium, strontium and calcium listed both in "Table of Isotopes" by Hollander, Perlman and Seaborg (28) and in "Nuclear Data" compiled by the National Bureau of Standards (67). References to all of these procedures are included in the Bibliography.

The literature search indicated that the separations of primary interest for these three elements were the precipitations with nitric acid (1, 3, 4, 6, 7, 11, 15, 19, 21, 24, 26, 27, 39, 42, 44, 45, 59, 60, 62, 65), ammonium dichromate (1, 7, 10, 11, 16, 19, 21, 24, 25, 27, 34, 39, 40, 42, 45, 61, 65), and hydrochloric acid (7, 8, 9, 10, 11, 12, 15, 16, 19, 23, 34, 35, 39, 44, 55, 61). Sulfate (23, 25, 47, 48, 58) and oxalate (1, 4, 11, 17, 20, 27, 29, 35, 38, 45, 46, 54, 65, 66) precipitations were also included in this study since they are widely used as a final step for the preparation of material for measurement.

Applications of solvent extraction or chelation (57) to these separations were not promising, and although good separations have been made by ion exchange (41, 63), time considerations prevent their general applicability to this work at the present time. Certain other minor methods involving precipitation of carbonate or 8-hydroxyquinolate (2, 13, 30, 43, 49, 50, 56, 64) were also found. Scavenging steps, involving precipitation of hydrous oxides of iron (III) or lanthanum (III), while often found in the procedures (1, 7, 10, 11, 13, 17, 19, 20, 21, 23, 27, 29, 35, 42, 45, 46, 54, 60, 61, 65, 66), will not be considered here.

EXPERIMENTAL PROGRAM

Precipitation separations are conducted under conditions which are standard in laboratories engaged in fission-product and bombardment work (18, 33, 35, 36, 44). In all cases, commercially available equipment is used. The carriers are added to a clean 15 ml centrifuge cone, radioactive tracers of these carrier elements are added, and the necessary steps taken to secure exchange. (In all the decontamination and yield studies on the alkaline earths 10 mg of carrier was present with the tracer.) Reagents are added to adjust conditions for precipitation, the precipitant is added, and the solution is stirred manually and digested for five minutes. The tubes are then centrifuged for five minutes at top speed, and the supernate is removed by use of a glass tube connected to a vacuum flask and through a trap to a water aspirator (a "slurp" tube). The precipitate is slurried onto a stainless steel plate to be dried and mounted, and then counted with a Geiger-Miller tube or transferred to a glass culture tube to be counted in the scintillation well counter.

In radiochemical separations, it is important to know the behavior of elements quite dissimilar from the desired constituent under the conditions of the separation. The spectrum of dissimilar elements present in a mixture

may be quite broad and in some cases may include as many as 50 different species. In order to have sufficient information at hand to choose a separation for a given decontamination requirement, a number of representative elements were chosen to indicate the behavior of their respective groups. The elements used in these decontamination studies are shown graphically in Fig. 1.

APPARATUS AND REAGENTS

Apparatus

International Clinical Centrifuge.

Centrifuge cones, 15 ml, borosilicate glass.

Planchets, 1 in.-diameter stainless steel, No. E-24, Tracerlab, Boston, Mass.

Geiger tube, halogen quenched, 1.4 mg/cm² window, Model D-34, Nuclear Instrument and Chemical Corporation, Chicago, Ill.

Scaler, Nuclear Instrument and Chemical Corporation, Model 163, scale of 12⁸ (used with Geiger tube).

Scintillation well counter, Nuclear Instrument and Chemical Corporation, Model DS-3 with 2-in. additional lead shield.

Scaler, Nuclear Instrument and Chemical Corporation, Model 162, scale of 12⁸, used with well counter, modified to count with preset time and preset count and to reset automatically.

Lead housing for Geiger tube, Technical Associates, Glendale, California, No. AL 14A.

pH Meter, Beckmann Instruments, Pasadena, California, Model H.

Reagents

Ammonium dichromate solution (B and A reagent No. 1274), 100 g/l in water.

Buffer solutions, sodium acetate (B and A reagent No. 2191) and acetic acid (B and A reagent No. 1019) (22).

Fuming nitric acid 90-95% HNO₃ (B and A reagent No. 1121), analyzed by the pycnometer specific gravity method.

Hydrochloric acid: ether reagent, 4 volumes HCl (B and A reagent No. 1090) to 1 volume ether (Mallinckrodt reagent No. 0848).

Sulfuric acid solution (B and A reagent No. 1080) H_2SO_4 , 10% by volume in water.

Ammonium oxalate reagent (B and A reagent No. 1307), saturated solution in water.

Hydrochloric acid, dry gas (Matheson, 99.0%).

Carriers

Antimony: SbCl_3 , MW 228.13, (B and A reagent No. 1369), 10 mg/ml Sb(III) in dilute HCl.

Barium: $\text{Ba}(\text{NO}_3)_2$, MW 261.38 (B and A reagent No. 1420), 10 mg/ml Ba(II) in water.

Calcium: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, MW 236.16 (Mallinckrodt reagent No. 4236), 10 mg/ml Ca(II) in water.

Cerium: $\text{Ce}(\text{NO}_3)_3$, MW 434.25 (B and A reagent No. 1560), 10 mg/ml Ce(III) in dilute HNO_3 .

Cesium: CsCl , MW 168.37 (Fotte Mineral Co.), 10 mg/ml Cs(I) in water.

Chromium: $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, MW 400.18 (B and A reagent, No. 1578), 10 mg/ml Cr(III) in dilute HNO_3 .

Cobalt: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, MW 291.05 (B and A reagent, No. 1597), 10 mg/ml Co(II) in dilute HNO_3 .

Iodine: NaI , MW 149.92 (Mallinckrodt reagent No. 1139), 10 mg/ml I(-I) in water.

Iridium: IrCl_4 , MW 334.94 (American Platinum Co., Ir metal) 10 mg/ml Ir(IV) in dilute HCl.

Ruthenium: RuCl_3 , MW 208.07 (Fisher reagent No. R-322), 10 mg/ml Ru(III) in dilute HCl.

Selenium: H_2SeO_3 , MW 128.98 (Fisher reagent No. A-286) 10 mg/ml Se(IV) in dilute HCl.

Silver: $\text{Ag}(\text{NO}_3)$ MW 169.89 (Merck reagent No. 2169), 10 mg/ml Ag(I) in water.

Strontium: $\text{Sr}(\text{NO}_3)_2$, MW 211.65 (Merck reagent, No. 748.94), 10 mg/ml Sr(II) in water.

Tantalum: K_2TaF_7 , MW 392.08 (Fisher reagent, No. T-17), 10 mg/ml Ta(V) in 0.5 M HCl and 0.5 M HF, made up immediately before use.

Tin: $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, MW 225.65 (Merck reagent No. 7488), 10 mg/ml Sn(II) in 5% HCl.

Zirconium: $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, MW 267.26 (Fisher reagent No. Z-82) 10 mg/ml Zr(IV) in 0.5 M HNO_3 and 0.1 M HF.

Tracers

Table I outlines the characteristics of the tracer solutions used for the yield and decontamination determinations. Daughter activities are listed with the parent. The valence states given in the table are either those listed in the Isotopes Division Catalog (32) or are those most stable for the conditions under which they were received. To minimize losses from hydrolysis or adsorption, dilutions of the tracers were made with solutions similar to those in which they were received. Small losses from hydrolysis or adsorption are not generally noticeable, because the materials are standardized at each use and small changes are ignored, but considerable loss did occur in silver by absorption on the walls of the soft glass bottles.

Carrier-tracer exchange required individual attention for each element. Multiple valence elements and those readily complexed were given special attention.

Cr⁵¹

From results of a study of the chromium(III)-chromium(VI) exchange, it was found that a negligible amount of the chromium tracer existed in the hexavalent form. Trivalent carrier was used throughout.

Ir¹⁹²

Iridium tracer was obtained in a chloride complexed form, and the carrier was also kept in this form prior to mixing.

Ru¹⁰⁶

The ruthenium obtained from Oak Ridge National Laboratory was found totally in the reduced trivalent form, and no special treatment was necessary for exchange.

Sb¹²⁴

The tracer antimony was used as received, trivalent antimony carrier added, the mixture oxidized to the pentavalent form with bromine and then reduced with hydrazine. A comparison of the solution obtained in this manner with that obtained

by thorough mixing showed only minor differences in the contamination studies of the alkaline earth separations. Separations specifically requiring either the tri- or pentavalent antimony were not studied.

Sn¹¹³

To assure exchange, the tin carrier was added as the divalent ion and oxidized to the tetravalent ion with hypochlorite in the presence of the tracer.

Ta¹⁸²

Tantalum tracer is present as the potassium tantalate in KOH solutions. The carrier, potassium heptafluotantalate, was added to the solution of the tracer, hydrochloric acid was added, and the solution was warmed to complete solution of the heptafluotantalate. Exchange was presumed complete since the procedure involved heating in the presence of the complexing fluoride ion. This presumption was further supported by the fact that all the tantalum activity in contamination studies was found to accompany the macro amount of tantalum.

Zr⁹⁵

In all cases, zirconium tracer was separated from its niobium daughter by precipitation of barium fluozirconate, and the zirconium was separated from the barium by two precipitations of zirconium hydroxide (36). Complete exchange between carrier and tracer zirconium took place during the treatment with HF and precipitation of the fluozirconate.

Special attention must be paid to the decay schemes and radiations of the tracers as well as to their chemical characteristics if the decontamination results are to be reproducible. Table II summarizes these nuclear characteristics (8). The scintillation well counter is suitable for measuring most tracers having gamma rays or high energy beta rays, but a thin window G-M counter is required for tracers emitting weak beta rays.

Where activities from daughter products would interfere with the counting of the parent, two methods were possible. In one, a suitable time (ten half

lives) could be allowed to elapse after the separation prior to counting. This time elapse would allow the mixture to reach equilibrium, i.e., where the parent-to-daughter activity ratio would be constant. In the second method, the daughter activity would be removed by suitable precipitation steps and the parent activity would be measured before the daughter activity would again become appreciable.

The first method was used in all experiments with the Ce-Pr, Ru-Rh and Sn-In pairs and in some experiments with the Ba-La and Sr-Y couples. Other samples of barium, strontium and all those of zirconium were counted by use of the second method. Growth and decay curves for the mixtures used in this work are presented in Figs. 2-8. From these curves, an evaluation can be made of the errors in the measurement introduced by daughter activities. Thus, it can be seen that following separation of the daughter, Zr remained sufficiently pure for counting purposes for several days, while barium and strontium had to be counted within two to four hours.

EXPERIMENTAL PROCEDURES

Six different precipitation procedures applicable to one or more of the alkaline earths were explored in detail to determine whether the procedures could completely carry macro amounts of these elements. Additional experiments were run to determine the contamination of the precipitates by other typical trace elements.

Chromate Separation

The classical method for the separation of barium from strontium is that of the precipitation of the chromate with ammonium dichromate from an acetate buffered solution (26). When there are few interfering elements that are not easily hydrolyzed, the precipitation can be made under more alkaline conditions in the region of Ph 7-8. The precipitant is added slowly to a relatively large volume of hot solution and the solution digested for one or two hours

after precipitation is complete. In recently reported work (31) a pH of five has been used successfully.

In this work precipitations were made from solutions maintained at a pH of four, five, and six (22). The conditions are not those in which equilibrium is established since precipitation is rapid, the experiment is conducted at room temperature, and only a five-minute digestion time is allowed; however, quantitative yields are not required. To determine interferences, a complete separation of barium carrier from strontium carrier was made in duplicate for each contaminant under optimum conditions (pH 4). Ten mg of carrier plus the tracer for the contaminating element were used in these determinations.

The itemized procedure is as follows:

1. Add ten mg barium carrier and barium tracer to 15 ml glass centrifuge cone. Mix thoroughly to effect exchange.
2. Add ten mg amounts of carrier and tracer of contaminating element to be studied, e.g., Sr, Ca, or Co, Ru, etc, and take steps necessary to secure exchange. In cases where the yield of barium is not to be determined, the barium carrier (without tracer) is added last.
3. Add ten ml of acetic acid-sodium acetate buffer solution of the desired pH. Stir thoroughly.
4. Add two ml $(\text{NH}_4)\text{Cr}_2\text{O}_7$ solution with stirring. Digest with occasional stirring at room temperature for five minutes.
5. Centrifuge at top speed for five minutes.
6. Remove supernate with slurp tube.
7. For geiger counting, transfer the precipitate by pipet to a stainless-steel planchet; then dry, mount and count. For scintillation counting, transfer to a glass culture tube, stopper and count in well counter. Yields obtained with this procedure are shown in Table III. Table IV shows the results of the contamination experiments at pH 4. For comparison, the barium, strontium and calcium yield data are included in this table.

Nitric Acid Separation

The insolubility of barium and strontium nitrate in strong nitric acid has been known for many years, but, in 1936, Willard and Goodspeed (68) made a thorough study of its analytical applications. Its applicability as a method for separation of barium and strontium from fission products was recognized early in the atomic energy program, and this method occurs quite frequently in the manuals of the National Laboratories (18, 33, 35, 44).

Three different concentrations of nitric acid (87%, 70% and 60%) were used to determine the effect of nitrate concentrations on the separation from calcium. The following procedure was used.

1. Add ten mg carrier and sufficient tracer of the contaminating ion (e.g., Ca or Co, Ru, etc.) to a clean 15 ml centrifuge cone and take steps necessary to secure exchange.
2. Add carrier solution containing ten mg each of barium and strontium. (Also add barium or strontium tracer when determining their yield.)
3. Add sufficient fuming HNO_3 and water to secure the desired concentration of HNO_3 (total volume 10-15 ml). Stir thoroughly.
4. Digest for five minutes at room temperature with occasional stirring.
5. Centrifuge for five minutes at top speed.
6. 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.
7. Prepare the precipitate for counting.

The results of the above procedure for barium, strontium and calcium are given in Table III.

To account for the different uses to which this procedure might be put, decontamination studies were conducted with the representative elements of Table I using both the 80% and the 60% HNO_3 conditions. Ten mg of carriers were used for all contaminants. The results are given in Table IV.

Hydrochloric Acid Separations

Another method for the separation of barium from strontium, calcium and other elements is based on the insolubility of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in strong HCl solutions. Many variations of this method have been used in atomic energy work (7, 12, 44). Two of the techniques most often applied are: (a) the use of an ether: HCl solution of about 7.5 to 8.5 M HCl as precipitant, keeping the aqueous volume of the radioisotope mixture very low prior to its addition, and (b) the use of dry HCl gas bubbled into either an aqueous solution or a mixture of ether and water. The first technique involves the use of a fairly stable reagent which can be kept for several days without discoloration. The latter technique requires the use of dry HCl, a very nasty reagent, and an ice bath is necessary to remove the heat of solution of HCl. Two modifications of each of these two techniques were evaluated: (1) 1.5 ml of aqueous solution containing tracers and carriers to which ten ml of the 4:1 HCl:ether reagent was added, (2) three ml of aqueous solution containing tracers and carriers to which ten ml of the HCl:ether solution was added, (3) ten ml of aqueous solution containing tracers and carriers into which dry HCl gas is bubbled until the solution is saturated, and (4) eight ml of aqueous solution containing tracers and carriers to which three ml ether is added and into which dry HCl gas is bubbled until the solution is saturated.

The concentration of chloride was determined by titrating the HCl with standard NaOH to the phenolphthalein end point. In the 1.5 ml H_2O case using HCl:ether reagent, a concentration of 8.5 M was found compared to 7.5 M in the 3 ml H_2O case. In the case of dry HCl, a 12 M solution resulted, and in the case of dry HCl and ether, a molarity of 7.3 was found. The following procedures were used.

A. HCl - Ether Solution

1. Add ten mg of carrier and sufficient tracer of the contaminating ion (e.g., Sr, Ca or Co, Ru, etc.) to a clean 15 ml centrifuge cone and take necessary steps to secure exchange.
2. Add ten mg of barium carrier and make up to either 1-1/2 ml or 3 ml with water. (Also add barium tracer when determining barium yield.)
3. Add ten ml of HCl:ether solution containing four volumes of concentrated HCl and one volume of ether. Stir thoroughly.
4. Digest for five minutes at room temperature with occasional stirring.
5. Centrifuge for five minutes at top speed.
6. Remove the supernate by slurping and prepare the precipitate for counting.

B. Dry HCl Gas

1. Add carriers and tracers as in A above.
2. Make up volume either to ten ml with water for procedure using plain dry HCl or to eight ml and add three ml ether for the combination.
3. Immerse in ice bath.
4. Bubble dry HCl gas through the solution to saturation. This requires about one minute. (Note: When no ether is present, large bubbles of HCl come to the surface at saturation, but in the presence of ether, the saturated solution forms one phase from the aqueous and organic phases initially present.)
5. Digest the solution at room temperature for five minutes with occasional stirring.
6. Centrifuge at top speed for five minutes.
7. Remove the supernate by slurp tube and prepare the precipitate for counting.

The yield data obtained for these procedures are shown in Table III. The effect of the various contaminating elements (Table IV) was determined using the optimum conditions for low Sr and Ca contamination (3 ml H₂O).

Oxalate Separations

Precipitation of strontium and calcium as the oxalates is discussed thoroughly in standard works (26, 53), and it is a convenient way of quantitatively reducing these elements to a weighable and reproducible form, suitable for counting. Precipitation is complete only when the solution is heated and an excess of ammonia is present. The following procedure was used:

1. Add ten mg of carrier and sufficient tracer of the contaminating ion, e.g., Ba or Co, Ru, etc., to a clean 15 ml centrifuge cone and take necessary steps to secure exchange.
2. Add ten mg carrier of either strontium or calcium and stir thoroughly. Also add strontium and calcium tracers when determining their yield.
3. Dilute the solution to eight ml with water.
4. Add sufficient concentrated NH₄OH to obtain an excess. One ml is usually satisfactory.
5. Heat to boiling and add two ml of a saturated solution of (NH₄)₂C₂O₄, and stir thoroughly.
6. Heat again to boiling and allow to stand for five minutes without applied heat, while stirring occasionally.
7. Centrifuge at top speed for five minutes.
8. Remove the supernate by slurp tube and prepare precipitate for counting.

The results obtained by use of this procedure are shown in Table III, while the decontamination values for representative elements, when present at the point of separation, are presented in Table IV.

Sulfate Separation

The precipitation of BaSO_4 has been used generally for the separation of barium from simple solutions in a form suitable for weighing and counting. It is not a general decontamination step because of the difficulty in performing further operations on this highly insoluble substance. It is most useful, however, as a final step to secure a form which may readily be dried, weighed, and mounted for counting.

The conditions for quantitative determination involve the slow addition of dilute sulfuric acid to the hot barium solution followed by a lengthy digestion period (53). In more recent work, the sulfate ion is liberated by the thermal decomposition of dimethyl sulfate thus accomplishing homogeneous precipitation (14).

The following procedure was used in this work:

1. Add ten mg carrier and sufficient tracer of the contaminating ion e.g., Sr, Ca or Co, Ru, etc., to a clean 15 ml centrifuge cone and take necessary steps to secure exchange.
2. Add ten mg of barium carrier. Also add barium tracer when determining barium yield.
3. Dilute to ten ml with one M HNO_3 and stir thoroughly.
4. Add one ml 10% H_2SO_4 , stir thoroughly and digest at room temperature for five minutes with occasional stirring.
5. Centrifuge at top speed for five minutes.
6. Remove the supernate by slurp tube and prepare the precipitate for counting.

The results obtained with this procedure for the alkaline earths are shown in Table III, and the decontamination results obtained with the carrier, and tracers of the contaminants are shown in Table IV.

DISCUSSION OF RESULTS

Under the conditions prevalent in radiochemical separation procedures for activity derived from bombardment or fission, equilibrium conditions are seldom, if ever, obtained. As a result, the conditions chosen for a given separation are compromises based on standard analytical methods, modified to give the maximum separation from the undesirable elements even at the cost of a lower yield of the desired constituent. The time required to perform the separation may also be a determining factor in its choice.

Chromate

The yields reported in Table III indicate the type of procedure required to secure a good separation of barium from strontium and calcium. As the pH of this precipitation is raised from four to six the yield of barium rises from 70 to 86%, but the contamination due to strontium is raised from 1.6 to 22%. The calcium contamination is also increased from 0.8 to 1.7%, but the change is of little consequence due to the lack of reproducibility of the results. Thus, the optimum conditions chosen for the separation of barium from strontium are those at pH 4 in the acetic acid-sodium acetate buffered solution.

Most of the elements such as Ce, Ir, Zr, Sb, Se, Ru, Sn, and Ta that interfere with this precipitation are easily hydrolyzed. Some separation can be obtained from Ce, Zr, Ru, and Ta, however, due to the slow precipitation of their hydrous oxides under the conditions of separation. In the case of silver, the insolubility of the chromate accounts for the large interference. Antimony gives a large contamination, due not only to hydrous oxide formation but also to the precipitation of basic salts in the weakly acid solution.

Visual observation of conditions during and following precipitation indicate that Sb, Sn and Ta form precipitates upon addition of the buffer. In

the case of tin this is undoubtedly the hydrous oxide and antimony probably forms an oxy-chloride or nitrate. Latimer (40) mentions the insolubility of oxy-fluorides of tantalum, and this is probably the mechanism of its contamination.

A high degree of separation from diverse elements is not required for this method since its applicability is primarily in the separation of barium from strontium. A higher degree of separation from elements easily hydrolyzed is best obtained by strong acid precipitations of members of the alkaline earth groups using reagents such as 80% HNO_3 , concentrated HCl , or dilute H_2SO_4 .

Nitrate

The yield of barium and strontium is lowered as the concentration of HNO_3 is reduced from 80% to 60% and a better separation from calcium is obtained as this concentration is lowered. If high yields are desired and calcium is not present, 80% HNO_3 should be used. If calcium is present, however, it would probably be worth the loss in yield to use 60% HNO_3 and secure more complete separation from the calcium. A coprecipitation with barium and strontium will carry a sizeable portion of calcium, if it is desired. Calcium nitrate is soluble, however when present alone in any of these three concentrations of HNO_3 (68).

Of the other elements studied, only antimony is a major interference. Visually, the antimony solution was cloudy at the end of centrifugation, indicating the presence of a slowly forming solid phase, probably the antimony acid. Two distinct layers of precipitate were visible at the tip of the centrifuge cone, substantiating this premise.

Hydrochloric Acid

Use of the more complicated and hazardous procedures involving dry HCl gas are not warranted by the results of these experiments given in Table III. In fact, observations indicate that precipitation in the three ml acid is slower than that on addition of dry HCl , thereby giving better decontamination as is shown in the case of strontium. Calcium is not a significant

interference under any of the conditions used. The best separation of barium from strontium was obtained with ten ml HCl:ether reagent and three ml of aqueous solution containing the tracers and carriers. While the yield was 10% lower than by the procedure involving 1.5 ml of aqueous solution, in most cases this is not restrictive.

Upon addition of the ether reagent there is formed a precipitate of silver chloride which is readily soluble in excess reagent. While antimony is again the most prominent interference, the mechanism is not obvious. If antimony is not present, however, this method is fast and efficient, and it requires no precautions other than those normally required when handling ether. The results are generally better than those of nitrate precipitations, due to a lower viscosity of the supernate which allows more complete removal by vacuum. The precipitate of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ is easily soluble in water, facilitating further separations.

Oxalate

For this precipitation, the yields of strontium and calcium are sufficiently high to make the oxalate step applicable to any overall alkaline earth separation procedure. It is not designed as a decontamination from barium, but barium is not completely carried by this procedure, and a separation may be made with careful control of conditions. This was pointed out by Hillebrand et al (26). The similarity between the crystalline forms of barium and strontium is undoubtedly the cause for the higher contamination by barium of the strontium precipitate even though the calcium oxalate is more flocculent

Hydrous oxides, on the other hand, are carried to a larger extent on the more bulky calcium oxalate. For example, in the cases of Ce, Zr, Sb, and Sn, the addition of the ammonia causes immediate precipitation, and coagulation is accelerated by boiling. Iridium and ruthenium are complexed by the addition of ammonia, but the complex is destroyed by boiling and the oxide is precipitated.

The case of these two elements shows most clearly the flocculent character of the calcium oxalate since precipitation of the oxide occurs concurrently with that of the oxalate. For tantalum and cobalt, the coagulation of the oxide precipitate was visibly more rapid with strontium than with calcium. Selenium begins to precipitate upon heating the ammoniacal solution prior to addition of oxalate.

Sulfate

This method is completely unsatisfactory for the precipitation of strontium sulfate since some agent is required to lower its solubility and accelerate its coagulation. This is usually accomplished by the addition of alcohol and by heating the solution (14). As the results indicate, barium is completely precipitated under these conditions, while about half of the strontium and only 10% of the calcium is carried on the barium sulfate. Strontium sulfate is more completely precipitated in the presence of barium or calcium under these conditions than when these ions are not present.

It if is necessary to work with a barium sulfate precipitate in the course of a separation, it may be dissolved by heating in an ammoniacal solution of versene (52). Upon dilution the barium sulfate again precipitates but some decontamination is accomplished. For example, in one case, 7.1% of the cerium present was carried on the initial barium sulfate precipitate. After dissolution of this precipitate, warming with versene, and reprecipitating by dilution and acidification, this contamination was lowered to about 1% of the original amount present. Acidification with concentrated acids will cause precipitation of the hydrogen versenate which lowers the decontamination.

The precipitate of barium sulfate is highly compact, resulting in the small contamination of 0.5-0.6% for certain elements. Those ions carried to a larger extent are carried by other than purely mechanical means. For example, Ag_2SO_4 is sparingly soluble in these solutions as are the oxy-sulfates of ions such as Zr(IV) and Sb(III). Also precipitation of a barium salt of the

sulfate complexes of zirconium may contribute to its contamination by analogy with the insolubility of the barium salt of the hexa-fluoride of zirconium. This may also cause the high cerium contamination. An insoluble barium chloro-iridate may be induced to precipitate accompanying the barium sulfate, a possible reason for its 5.4% contamination of the $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ precipitation.

SUMMARY: OPTIMUM PROCEDURES

It is possible from the results of Table III and IV and the discussion of the previous section to synthesize optimum procedures for each of the three alkaline earth elements, barium, strontium and calcium.

Barium

The primary separation of barium and strontium from other elements would appear to be a precipitation of barium and strontium nitrates with 60% HNO_3 . This will give one 80% yield for barium and strontium and result in at least a 50-100 fold decrease in contaminants for each cycle. Separation of barium from strontium may be accomplished by either chromate precipitation at $\text{pH} = 4$ or by chloride precipitation in 7.5 M HCl with ether present for a comparable separation. The amount of strontium in the precipitate is a factor of 50 below that present in the solution in each case. By use of the chromate method, a precipitate is obtained which is readily usable for counting, although the pH of precipitation may cause contamination by other elements. The chloride separation is performed in strong acid solution and decontamination is better for other elements. The yield of barium is around 80%. Final precipitation as the sulfate is the usual method for preparation of counting plates. Yields may also be obtained in this manner with fair accuracy. A sample procedure based on these separations is shown in Table V.

Strontium

Strontium may best be separated from other elements by first separating barium and strontium together as nitrates. Barium is then separated by chloride precipitation in 12 M HCl in as small a volume as is practical. Over 90% of the strontium should remain in the supernate. This precipitation may be repeated to secure a better separation, the amount of barium being reduced by a factor of 100 by each cycle. The HCl supernate solution containing the strontium is then evaporated or neutralized and the strontium separated as oxalate in basic solution. Scavenging steps may also be of value in these separations and are being investigated.

Calcium

Calcium may also be separated as the nitrate with strontium and barium in 80% HNO₃. The yield is about 70% per cycle. Barium and strontium are then removed by repeated sulfate precipitations in acid solutions. This sulfate separation will remove over 99% of the barium and 60% of the strontium while removing only 5-10% of the calcium per cycle. The supernate is then neutralized and the calcium separated as the oxalate.

SUMMARY

The yield and decontamination data presented in Tables III and IV can be used with a minimum of further development as a basis for specific procedures for separations of the alkaline earths to fit a particular problem. It is important to remember, however, that these rapid separations are made under non-equilibrium conditions and are reproducible only if the conditions of the separation are closely duplicated. Changing the order of addition of reagents, amounts of carriers, concentration of reagents, solution volumes or the size of equipment, may change significantly both the yields and decontaminations.

ACKNOWLEDGEMENTS

This program was supported in part by the Atomic Energy Commission.

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FIGURE AND TABLE CAPTIONS

Fig. 1. Periodic Table of the Elements.

Figs. 2-8. Growth and Decay of Tracer Mixtures.

2. Ba¹⁴⁰, La¹⁴⁰.

3. Ce¹⁴⁴, Pr¹⁴⁴.

4. Ru¹⁰⁶, Rh¹⁰⁶.

5. Sn¹¹³, In^{113m}.

6. Sr⁹⁰, Y⁹⁰.

7. Zr⁹⁵, Nb⁹⁵, covering 15 days.

8. Zr⁹⁵, Nb⁹⁵, covering 320 days.

Curves: A. Total activity of an initially pure parent fraction.

B. Activity due to parent.

C. Decay of freshly isolated daughter fraction.

D. Daughter activity growing in freshly purified parent fraction.

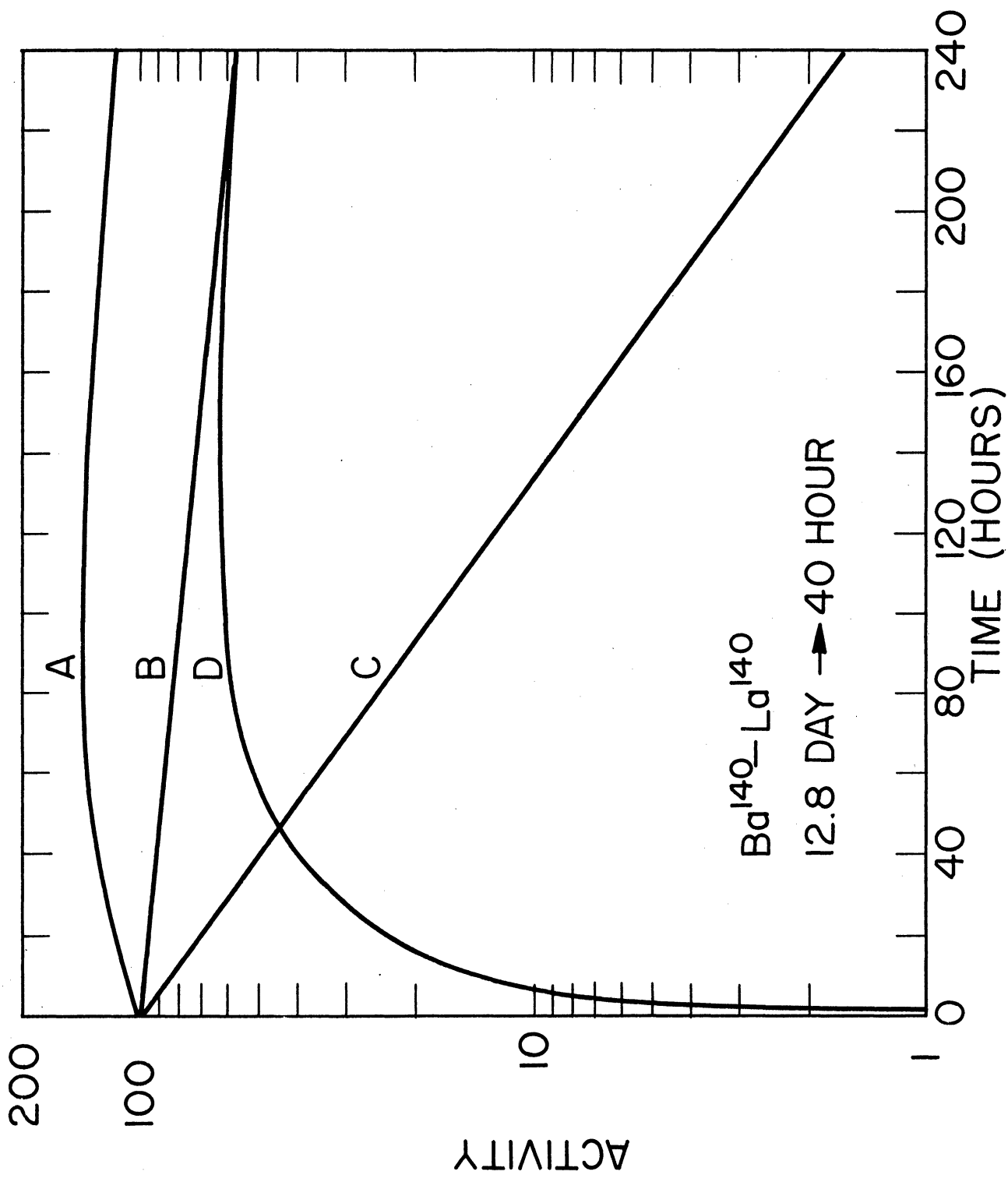
Table I. Chemical Characteristics of Tracer Solutions.

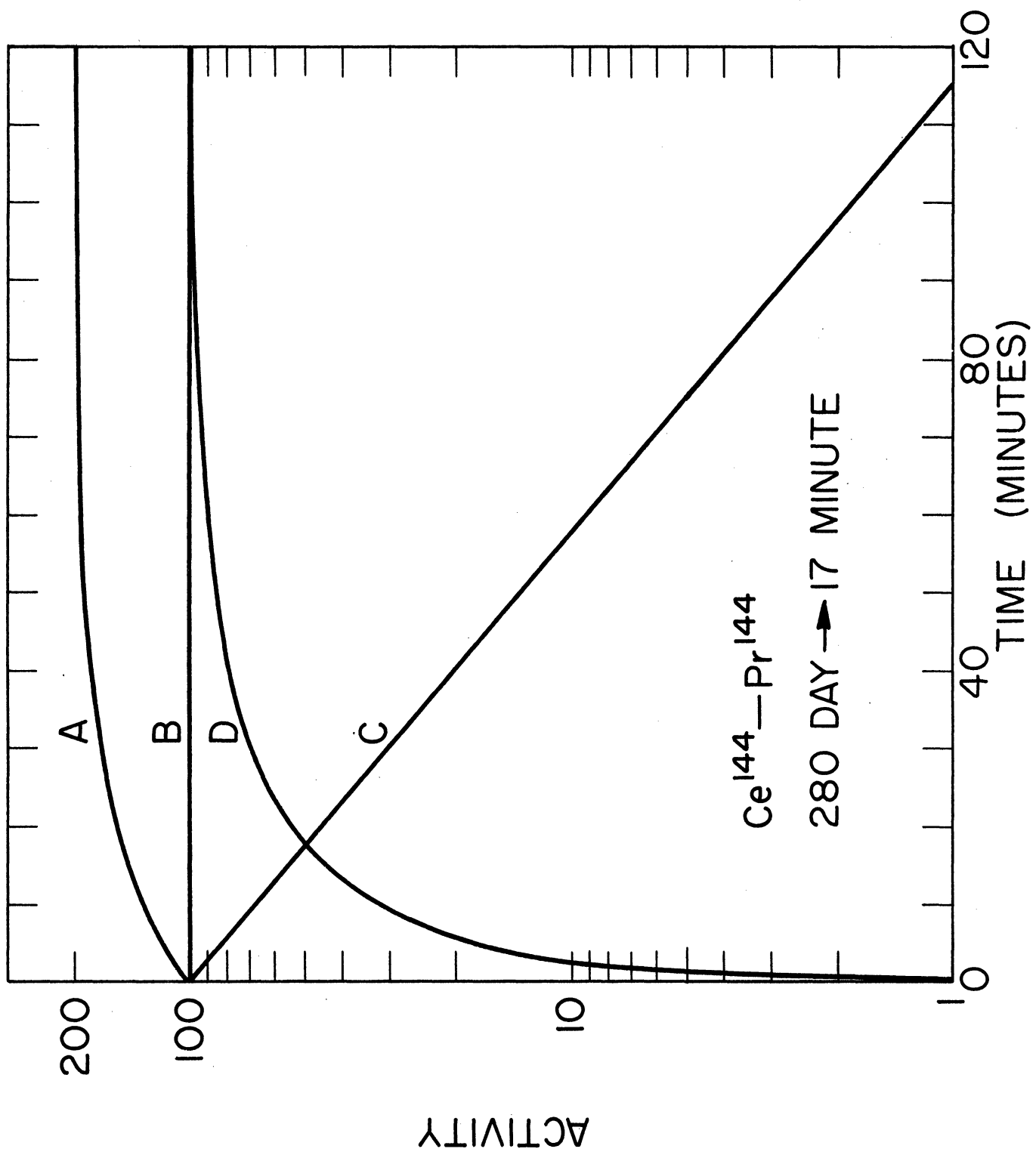
Table II. Nuclear Characteristics of Tracers.

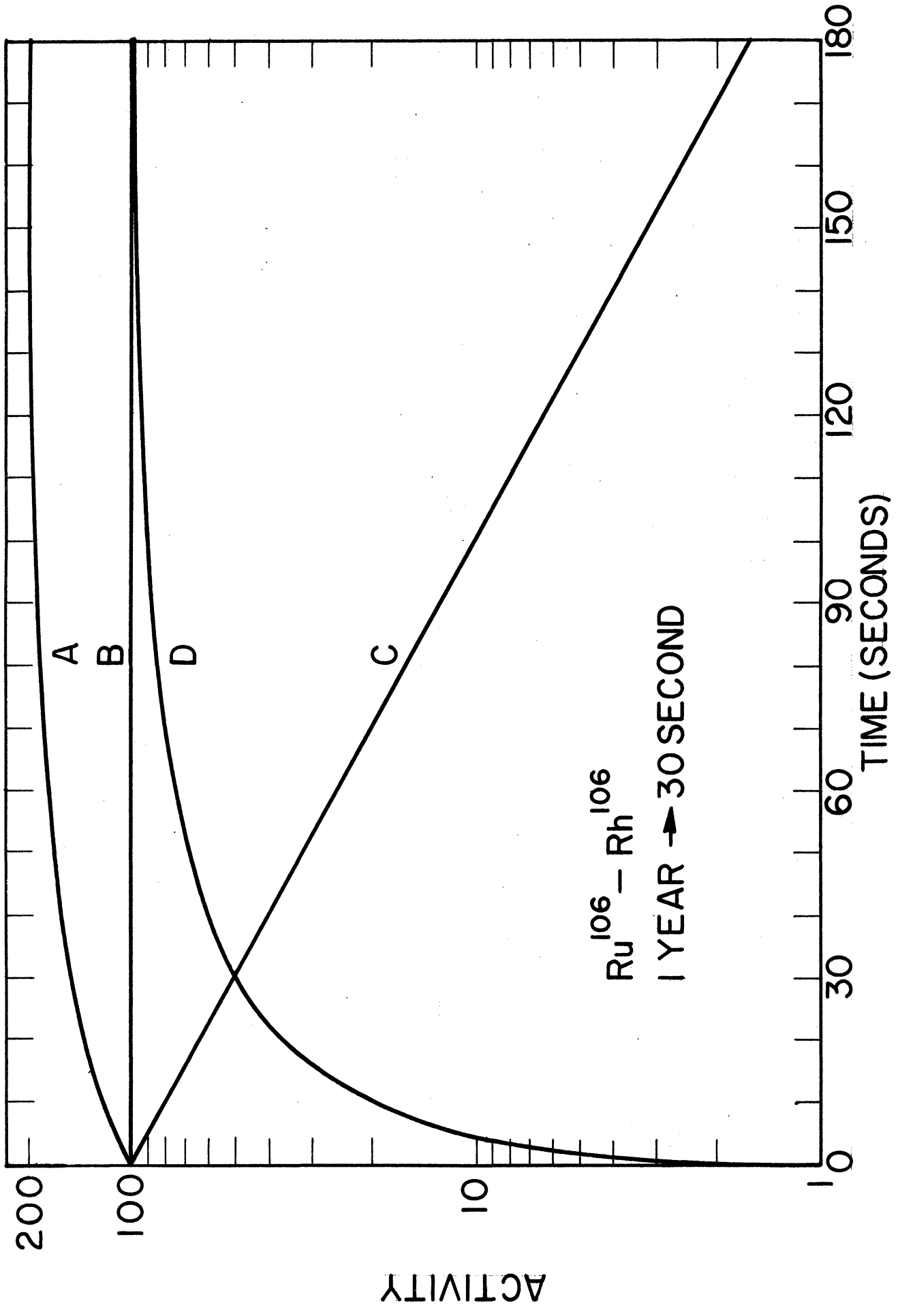
Table III. Summary of Yield Data of Precipitation Reactions for Barium, Strontium, and Calcium.

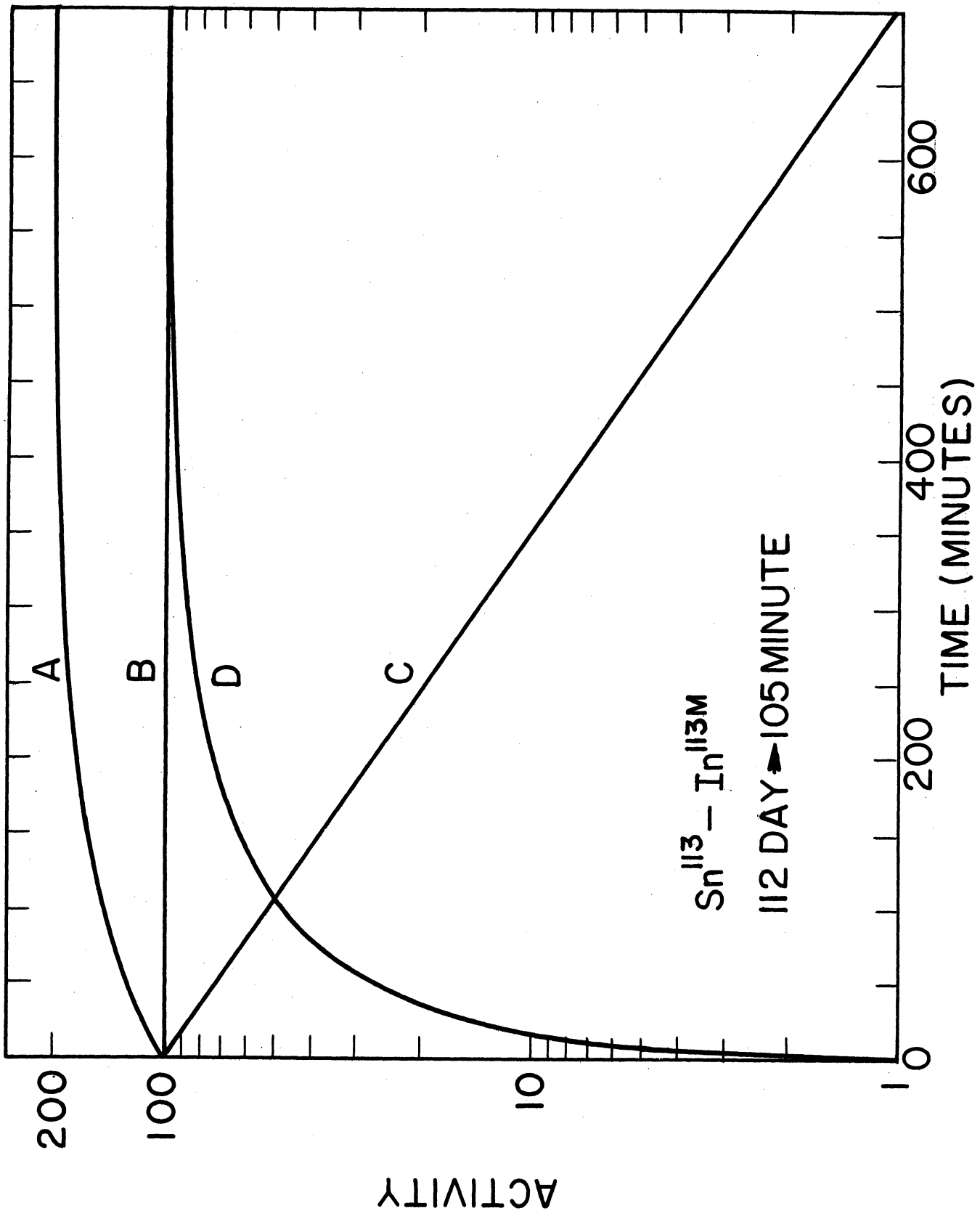
Table IV. Contamination of Alkaline Earth Precipitates by Other Activities.

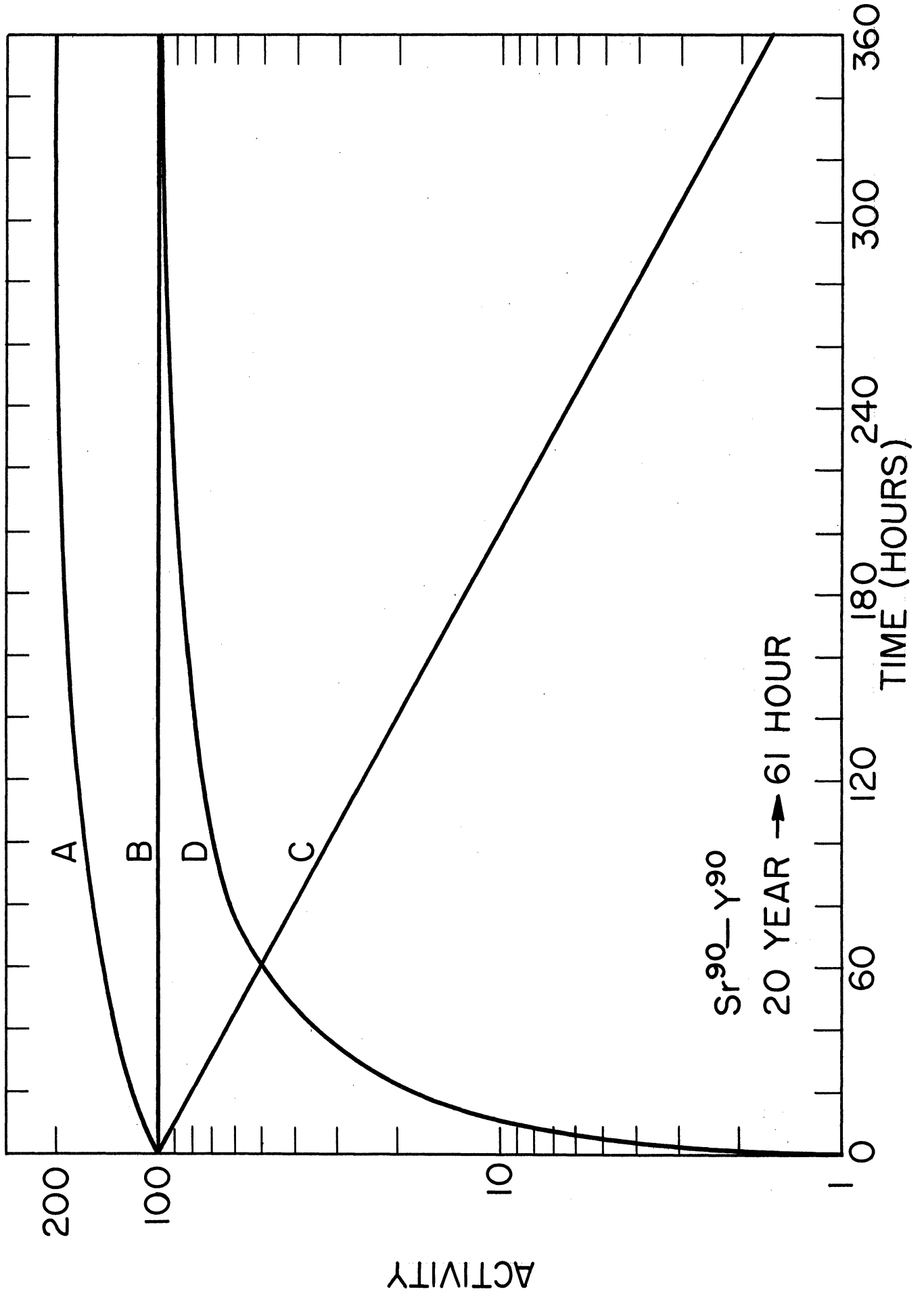
Table V. Sample Procedure for the Separation of Barium from other Activities.

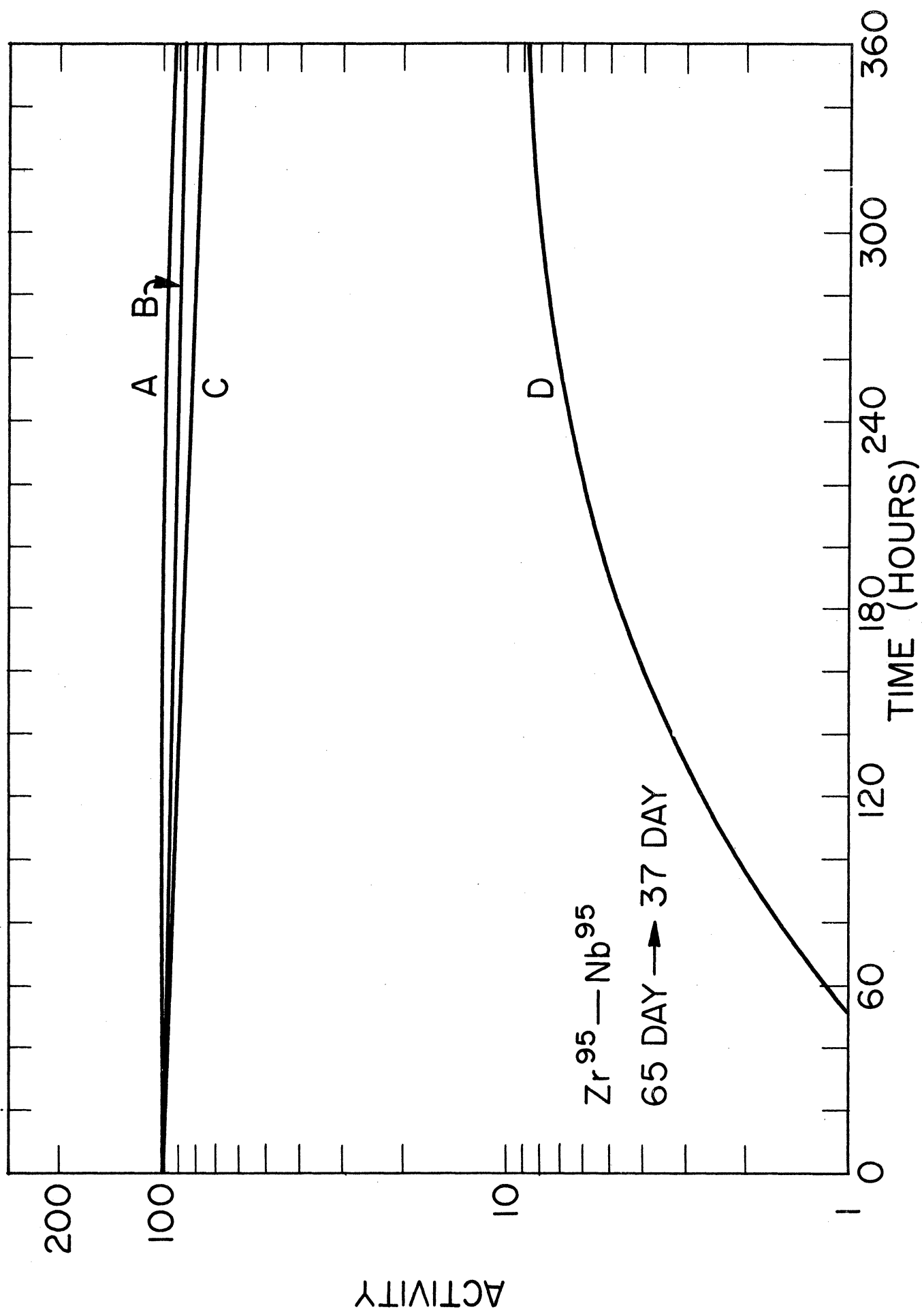












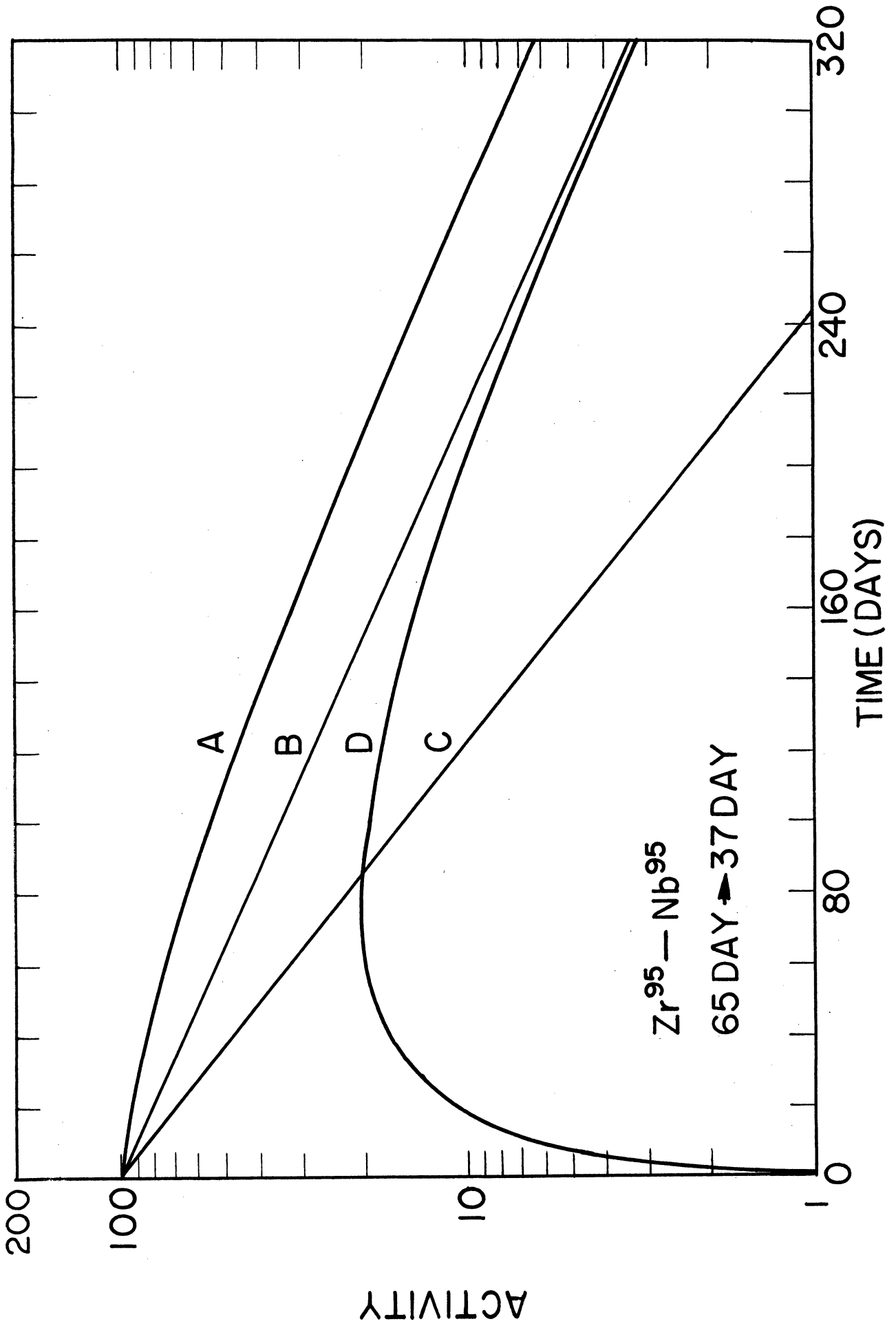


TABLE I

CHEMICAL CHARACTERISTICS OF TRACER SOLUTIONS

Isotope	Received from ORNL* as:	Diluted with	Loss from Hydrol or Absorption	For Carrier-Tracer Exchange
1. Ag-110	AgNO ₃ in HNO ₃ soln.	3M HNO ₃	large loss by abs. on glass from dil. acid soln. of tr. Highly acid soln. of tr. in borosilicate glass, no loss	thorough mixing
2. Ba-140 La-140	BaCl ₂ in 0.8 M HCl soln.	0.1M HCl	none	thorough mixing
3. Ca-45	CaCl ₂ in HCl soln.	0.1M HCl	none	thorough mixing
4. Ce-144 Pr-144	CeCl ₃ in HCl soln.	3M HCl	none	thorough mixing
5. Co-60	CoCl ₂ in HCl soln.	1M HCl	none	thorough mixing
6. Cr-51	CrCl ₃ in HCl soln.	1M HCl	none	thorough mixing with Cr(III)
7. Cs-134	CsCl in HCl soln.	0.1M HCl	none	thorough mixing
8. I-131	NaI in NaOH, NaHSO ₃ soln.	0.1M NaOH	none	thorough mixing
9. Ir-192	IrCl ₆ in HCl soln.	0.1M HCl	none	thorough mixing, carrier also in HCl before mixing
10. Ru-106 Rh-106	RuCl ₃ in HCl soln.	dil. HCl	none	thorough mixing of tracer plus Ru(III) in HCl

TABLE I (cont.)

Isotope	Received from ORNL* as:	Diluted with	Loss from Hydrol. or Absorption	For Carrier-Tracer Exchange
11. Se-75	SeCl ₄ in HCl soln.	1M HCl	none	thorough mixing
12. Sb-124	SbCl ₃ in 3.3M HCl soln.	3M HCl	none	Sb(III) plus tracer, oxid. to Sb(V) with Br ₂ : red. to Sb(III) with hydrazine
13. Sn-113 In-113	SnCl ₂ in HCl soln.	5% HCl	none	SnCl ₂ in 5% HCl plus tracer oxid. in excess NaClO.
14. Sr-89	SrCl ₂ in HCl soln.	dil. HCl	none	thorough mixing
15. Sr-90 Y-90	SrCl ₂ in HCl soln.	none	none	thorough mixing
16. Ta-182	KTaO ₃ in KOH	KOH soln.	after standing, the original ORNL soln. showed tan ppt. containing the Ta-182	dissolution of carrier in HCl and Hf with warming in presence of tracer
17. Zr-95 Nb-95	complex in oxalic acid	dil. oxalic acid	none	addition of Hf and separation as BeZrF ₆

*All radioisotopes used in this work were obtained from the Isotopes Control Department of the Oak Ridge National Laboratories.

TABLE II

NUCLEAR CHARACTERISTICS OF TRACERS (B)

Isotope	Half Life	Primary Radiations		Daughter	Spec. Act. Orig. Soln.	Counting
		β	γ			
1. Ag-110	270 days	0.087 (58%) 0.530 (35%) 2.12 (3%) 2.86 (3%)		Cd-110 (stable)	55.5 mc/gm	scint. well
2. Ba-140	12.80 days	1.022 (60%) 0.480 (30%)	0.162 0.304 0.537	La-140 (40.0 hr)	C.F.	GM- 1.4 mg/cm ² counter
La-140	40.0 hr	1.32 (70%) 1.64 (20%) 2.26 (10%)	0.49 (22%) 0.82 (16%) 1.62 (56%)	Ce-140 (stable)		
3. Ca-45	152 days	0.254 (100%)	(none)	Sc-45 (stable)	27.65 mc/gm	GM- 1.4 mg/cm ² window
4. Ce-144	275 days	0.3 (70%) 0.17 (30%)		Pr-144	C.F.	scint. well
Pr-144	17 min	2.97 (98%)		Nd-144 (stable)		
5. Co-60	5.27 yr	0.306 (100%)	1.33 (100%) 1.17	Ni-60 (stable)		scint. well
6. Cr-51	27.8 days	EC - 92% EC - 8%	0.32 (8%)	V-51 (stable)	831 mc/gm	scint. well
7. Cs-134	2.3 yr	0.079 (21%) 0.253 (6%) 0.640 (54%) 0.676 (19%)	0.601 (100%) 0.794 0.570 (30%) 1.35 (3%) others weak	Ba-134		scint. well

TABLE II (cont.)

Isotope	Half Life	Primary Radiations		Daughter	Spec. Act. Orig. Soln.	Counting
		β	γ			
8. I-131	8.0 days	0.595 0.315	0.363 0.638 0.283 0.080	Xe-131 (stable)	C.F.	scint. well
9. Ir-192	74.37 days	0.67	0.137 0.208 0.296 0.308 0.317 to 0.615	Pt-192 (stable)	4517 mc/gm	scint. well
10. Ru-106	1 yr	0.0392 (100%)		Rh-106	C.F.	scint. well
Rh-106	30 sec	3.53 3.1 2.44	0.513 (68%) 0.624 (11%) (12%)	Pd-106 (stable)		
11. Se-75	127 days		0.10 0.12 0.14 0.26 0.40	As-75 (stable)	49.5 mc/gm	scint. well
12. Sb-124	60 days	2.29 1.69 0.95 0.68 0.50	(21%) (7%) (7%) (26%) (39%)	Te-124 (stable)	1142 mc/gm	scint. well
13. Sn-113 In-113m	112 days 105 min		EC-0.393 (100%) 2.04 (6%)	In-113m In-113 (stable)	15.79 mc/gm	scint. well

TABLE II (cont.)

Isotope	Half Life	Primary Radiations		Daughter	Spec. Act. Orig. Soln.	Counting
		β	γ			
14. Sr-89	54 day	1.50		Y-89 (stable)	C.F.	scint. well
15. Sr-90	19.9 yr	0.61 (100%)		Y-90	C.F.	GM Tube 1.4 mg/cm ² scint. well
Y-90	61 hr	2.18 (100%)		Zr-90 (stable)		
16. Ta-182	111 days	0.53	1.2	W-182 (stable)	409 mc/gm	scint. well
		1.1	1.1			
			0.05-1.0			
17. Zr-95	65 days	0.371 (99%)	0.721 (99%)	Nb-95	C.F.	scint. well
Nb-95	35 days	0.16 (100%)	0.745 (100%)	Mo-95 (stable)		

TABLE III

SUMMARY OF YIELD DATA OF PRECIPITATION REACTIONS FOR BARIUM, STRONTIUM AND CALCIUM*

Precipitating Solution	Condition	Percent Carried			
		Barium	Strontium	Calcium on Barium	Calcium on Strontium
Ammonium	pH 4	70 ± 3.4	1.6 ± 0.3	0.8 ± 0.08	
Dichromate	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	3 ml H ₂ O	82 ± 1.1	2.8 ± 0.9	0.6 ± 0.4	
	1.5 ml H ₂ O	92 ± 2.2	11 ± 0.7	0.8 ± 0.08	
	dry HCl	99 ± 0.4	7.3 ± 1.6	1.0 ± 0.1	
	Ether:dry HCl	93 ± 2.4	6.0 ± 3	1.5 ± 0.1	
Ammonium Oxalate	95%	59 on SrC ₂ O ₄			100
		15 on CaC ₂ O ₄	< 90		
Sulfuric Acid	xs Sulfate	100	57 on Barium very slight alone	10	3.6

*All values are average of quadruplicate runs. Errors are "standard deviations".

TABLE IV

CONTAMINATION OF ALKALINE EARTH PRECIPITATES BY OTHER ACTIVITIES*

Element	pH 4 Chromate	Precipitating Solution, Percent Carried				Sulfate in Precipitating Solution	Ions Always Present in Precipitating Solution	
		80% Nitric Acid	60% Nitric Acid	Nitric Hydrochloric Acid	Oxalate on SrC ₂ O ₄ on CaC ₂ O ₄			
Antimony	55	47	30	28	44	46	28	NO ₃ ⁻ , Cl ⁻
Barium	70	100	86	82	59	15	100	NO ₃ ⁻ , Cl ⁻
Calcium	0.8	51 on Sr 27 on Ba	2.6 on Sr 0.9 on Ba	0.6	--	100	10	NO ₃ ⁻ , Cl ⁻
Cerium	6	3.2	2.5	0.9	98	95	7.1	NO ₃ ⁻ , Cl ⁻
Cesium	3.5	1	2	1.0	0.8	1.6	2.9	NO ₃ ⁻ , Cl ⁻
Chromium	1.2	1.8	1.0	0.7	89	96	0.5	NO ₃ ⁻ , Cl ⁻
Cobalt	1.1	3	3.5	1	52	21	0.5	NO ₃ ⁻ , Cl ⁻
Iodine	20	1.2	0.8	0.9	2.3	5.0	1.5	NO ₃ ⁻
Iridium	27	4.2	0.9	5.4	47	68	11	NO ₃ ⁻ , Cl ⁻
Ruthenium	5	1.5	2.4	2	23	38	0.6	NO ₃ ⁻ , Cl ⁻
Selenium	5.7	1.4	1.3	0.9	21	23	1.2	NO ₃ ⁻ , Cl ⁻
Silver	89	1.9	1.5	0.8	1.2	2	14	NO ₃ ⁻
Strontium	1.6	100	81	2.8	790	--	57	NO ₃ ⁻ , Cl ⁻
Tantalum	10	1	0.7	0.5	49	24	0.5	NO ₃ ⁻ , Cl ⁻ , F ⁻
Tin	99.5	1	1.2	0.8	73	95	0.5	NO ₃ ⁻ , Cl ⁻
Zirconium	6.3	2.6	3.3	2	93	88	20	NO ₃ ⁻ , (F ⁻)?

*Values are average of duplicates on barium precipitates except where noted.

TABLE V

