THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

THE DEVELOPMENT AND EVALUATION OF RADIOCHEMICAL SEPARATIONS PROCEDURES FOR BARIUM, CALCIUM, STRONTIUM, SILVER AND INDIUM

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ABSTRACT

The objective of this research was to conduct a program of development and critical evaluation of radiochemical separation procedures. 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 decontamination) for separation. These steps 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, calcium and strontium were the first elements studied in this manner. It was found that the conditions for nitrate, chromate and chloride precipitations must vary widely from commonly accepted analytical methods due to the demands of such factors as nonequilibrium operation, necessity for rapid precipitation, character of the precipitate and manipulatory techniques. Yield data are given for barium, calcium and strontium 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 a large number of typical elements (Ag, Ba, Ca, Ce, Co, Cr, Cs, I, Ir, Ru, Sb, Se, Sn, Sr, Ta, Zr). An optimum procedure is given for the systematic separation of these three ions in tracer solutions.

The precipitation of the hydrous oxides of iron (III) and lanthanum (III) for scavenging purposes has been studied and their action and efficiency have been evaluated. Representative tracers have been used to determine the portion of each specie which would be carried either in the presence or absence of macro amounts of the contaminating activity. It was found that higher decontamination may be accomplished by scavenging in the presence of carrier amounts of the contaminating species. Lanthanum precipitation is more specific with respect to the activities carried, while the more bulky iron hydroxide may give higher decontamination factors for certain elements.

The principle of isotopic exchange has been adapted to a novel separation and determination of radioactive silver in a mixture of radioactive species, and a quantitative procedure has been developed. The separation of radioactive silver by isotopic exchange with a silver

chloride surface was found to be quantitative in fifteen minutes or less, even in the presence of high concentrations of many inorganic salts and organic solvents. The method is highly specific for silver, with decontamination factors between 10^3 and 10^7 for eighteen representative radioactive species. The technique was also applied to the separation of silver from fission product mixtures and bombardment samples and found satisfactory in both cases.

The standard procedures for the separation of radioactive silver, by chloride precipitation and electrodeposition, as well as a new method, that of precipitation with benzotriazole from ammoniacal versene solution, were evaluated. The precipitation reactions produce decontamination factors from 40 to 200 for many elements, those made in acid solution being more specific than those in basic solutions. The electrodeposition of silver affords decontamination factors from 100 to 500 for many elements. A sample procedure is given which illustrates the high decontamination of which these methods are capable.

The separation of indium by sulfide precipitation, by solvent extraction of the bromide with diethyl ether, and by anion exchange in hydrochloric acid solution has been evaluated. A comparison of the efficiency of separation from the representative radioactive tracers

showed that the sulfide precipitation lacked specificity as a decontamination step. The use of solvent extraction was found to give decontamination factors of 10^4 for dissimilar elements when conditions were well standarized. The technique of ion exchange loses much of its specificity when the flow rate is high as is required when time is an important factor. When operating far from equilibrium with a short column, however, decontamination factors of about 10^3 were possible for many elements with a procedure that requires one hour.

INTRODUCTION

The uses of radioactive isotopes have multiplied greatly in the last five years. This multiplication has accompanied and been aided by the availability of people trained to handle radioactive materials and who are familiar with the unusual characteristics of trace quantities of these elements. This knowledge includes not only the chemistry of familiar elements but also that of many elements of only recent use, some of which exist only as outgrowths of the atomic energy program.

Because of the secret nature of atomic weapons work, much of the early application of radioactive isotopes was by the national laboratories. A great deal of this work is reported in the compilation of Coryell and Sugarman.(16) One of the applications described in this work is the characterization of the fission products, a program which required the effort of many trained scientists during the period of World War II. Also presented are methods for the separation of these radioactive materials for analytical purposes.

Many of the early radiochemical separation processes were based on the precipitation technique (16). However, the post-war period saw the development of newer techniques which more closely satisfied the requirements of radiochemical work. Recent applications are described in the paper by Flanary and Culler given before the Geneva Conference on the Peaceful Uses of Atomic Energy (32). The combination of solvent extraction and ion exchange for the separation of uranium and plutonium from the fission products, and for the further separation of uranium from plutonium is described in detail. Isotopic tracers have been used extensively by the national laboratories for the development of these methods. Radiochemical separation procedures are also used by analysts for quality control of large scale processes. Methods for disposal of the large volumes of waste solutions accompanying these processes were also evaluated by the use of separated radioactive tracers.

Industrial application was foreseen for process development and analysis due to the widespread use of these materials in the atomic energy program. Following the war period a large number of separated radioactive materials of both fission product and neutron irradiation

origin were made available to private industrial and research organizations. The catalog of the Isotopes Division of Oak Ridge National Laboratory (62) describes these materials and also their cost and handling procedures.

With these radioactive materials available at low cost, immediate industrial use was made in many fields. Isotopes were found valuable for automotive wear studies. Figure 1 illustrates the use of radioactive Fe-59 for friction and lubrication research. When radioactive material of this type was included in internal combustion engines and fuels, the determination of wear and deposit formation was made a much less lengthy process. Much research is being conducted to develop thickness gauges using radiation, and applications have already been found in the cigarette and plastic film industries. Putman describes many examples of the use of radiation for such gauges (117). As the cost is reduced and the functions better known, radioactive sources may find application in chemical and petroleum processing and in sterilization of food and drugs. General utilization of this type is described in the paper by Aebersold (1).

Independent and academic research organizations have applied radioactive materials to many medical, physical and chemical research problems as well as those of the natural sciences. There are the examples of the use of

iodine, gold and phosphorous in medical diagnostics and treatment. This is illustrated by Figure 2 which portrays the function of radioactive I-131 for the treatment of thyroid disorders. Physical research has been quite extensive toward the determination of the characteristics of nuclei and radiation as well as to the production and study of individual radioactive species. Radioactive carbon isotopes and more recently hydrogen isotopes are playing a strong role in the study of reaction rates and mechanisms for the organic chemist.

Many elements have been used for the evaluation of analytical procedures. An extensive review of the uses of radioisotopes for measurement applications, with an emphasis upon analysis, has been prepared by Meinke (94). The period covered by this review extends from 1953 through 1955 and will serve as a starting point for searches for material from earlier periods as well, as a result of the extensive review of the papers presented at the Geneva Conference on the Peaceful Uses of Atomic Energy. The use of Ca-45 for botanical studies of plant nutrition is illustrated in Figure 3. Similar techniques are of use for the study of insecticides, fertilizers and trace elements in agricultural research.

Many tracers cannot be formed by direct neutron irradiation of the inactive form of the element. Some

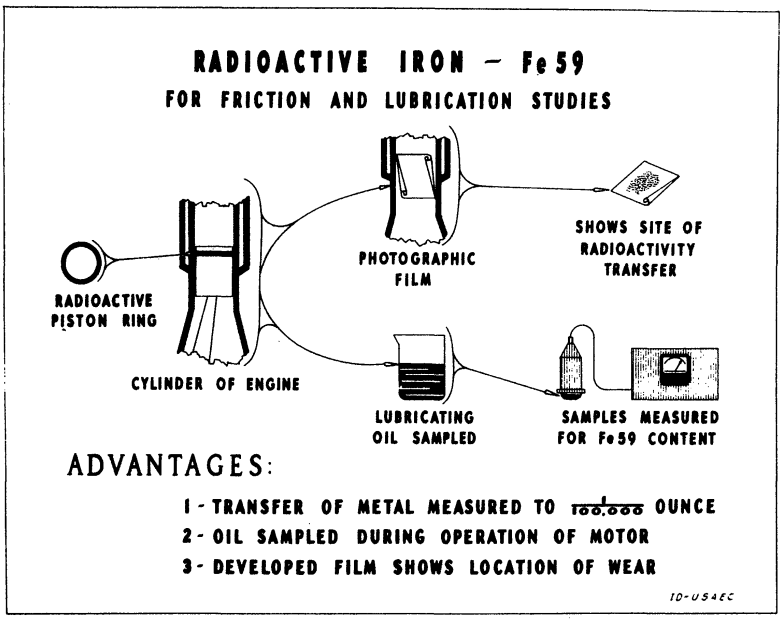


FIGURE 1. Industrial Application of Radioactive Tracers.

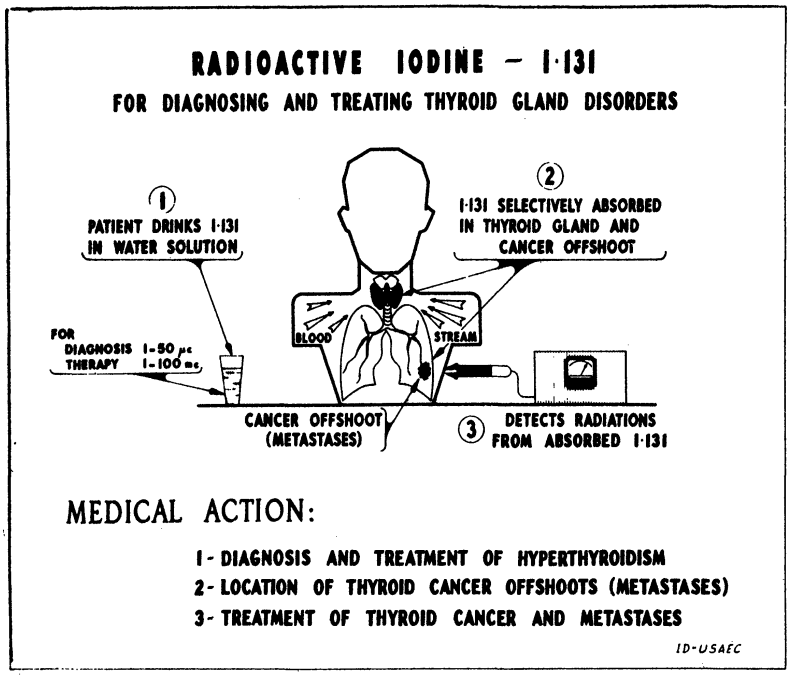


FIGURE 2. Medical Application of Radioactive Tracers.

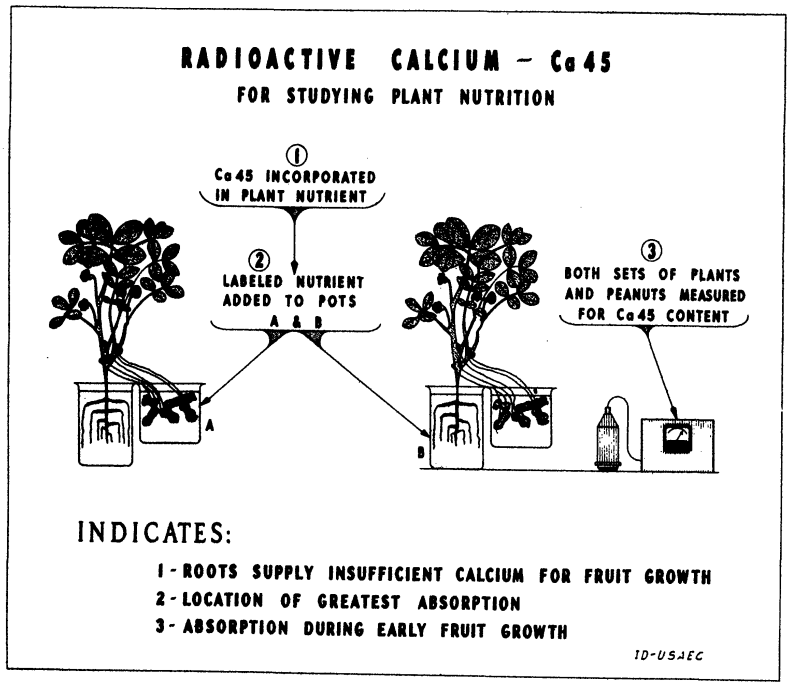


FIGURE 3. Botanical Application of Radioactive Tracers.

are obtained as fission products while others are formed in low yields by irradiation of the inactive forms of other elements. In most cases it is necessary to purify them before use; the extent of purification being dependent upon the mode of production. What might be considered insignificant amounts of impurities in standard analytical work can become major in radiochemical applications. This is the result of the high radioactivity which may be associated with very minute amounts. In these cases extensive purification procedures must be developed for quantities of material which may be in the range of thousands of atoms. Standard analytical methods fall short of providing this decontamination unless they are very carefully adapted to radiochemical needs.

Radiochemical separation procedures are composed of those chemical separation steps which, when applied to radioactive mixtures, yield 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 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 need not be quantitative. Often the nuclear characteristics of the isotope desired are such that the separation must be completed rapidly.

The methods for the separation of the radioactive species for the above mentioned uses have been developed concurrently with their application. Since the background of the user may vary widely from field to field, the development of these procedures for separation have widely varying origin. Many were developed under 'crash' programs during World War II by very capable inorganic and analytical chemists at the national laboratories. In most cases these were developed for one particular application and for separations from a well defined group of fission products. Many procedures were developed by those engaged in physical research for the separation of nuclides produced by bombardment, and the applications were again quite specific. This has resulted in a confusion in the literature. Many procedures are available but there is little information concerning their general applicability. Many older methods could well be modified to take advantage of the new techniques of solvent extraction, ion exchange and isotopic

exchange. The methods which apply to an individual element should be collected so that information concerning the efficiency and applicability could be compared with other methods.

There is also a need for more generalized research and evaluation so that a new development program is not required when a slightly different need arises. New techniques should be evaluated with an eye toward increasing their efficiency and applicability. Procedures should be evaluated under the conditions prevalent in radiochemical work to insure that the step from research to application is as short as possible. New techniques which fit the individual needs of the radiochemist must be evaluated in a manner which gives them general applicability. The needs within the field of the application of radioactive isotopes are sufficiently great to allow the analyst the luxury of procedures particularly adapted to his needs rather than those which are 'hand-me-downs' from analytical or preparative inorganic chemistry. The presence of hundreds of technically trained persons engaged in such work warrants an evaluation program which answers these needs.

CHAPTER I

EXPERIMENTAL

PROGRAM

The evaluation program described here was undertaken in order to fill the need for a group of well characterized separation procedures for the use of the radiochemist and others who require radioactive materials of high purity. Methods for the separation of barium, calcium, strontium, silver and indium were considered first, and the results of the study will be reported in detail.

Preliminary work indicated that a method consisting of the following five steps would yield the greatest amount of pertinent information in the shortest period of time. First, a literature survey is made to find the applicable separation procedures for each element; second, these procedures are divided into individual steps for evaluation; third, these steps are studied to determine optimum conditions for separation from similar elements; fourth, these optimum conditions are studied with a large number of representative contaminating species; and fifth, the most applicable separation steps are molded into a separation procedure

which most closely fits the needs of the analyst for yield and decontamination. The function of each of these steps is more easily understood if they are examined individually.

1. A complete literature survey is made for each element to determine the methods of analysis which have proven of value in standard analytical work as well as methods for the separation of the element for radiochemical purposes. This survey summarizes the applicable techniques, gives conditions under which they were used, the methods for carrying out the separation, and the efficiency of the separation step where available. In most cases this information is incomplete. Many references to this type of work are found in journals of physics such as the Physical Review and the Zeitschrift für Physik in which separation procedures may be described with no volumes, reagents, apparatus or times specified. "Barium was separated as the nitrate" may mean quite different things to different investigators although they may report the operation with no more description than the statement itself. Such a survey of the literature for an individual element also gives the analyst hints to new methods or improvements in existing methods and these may prove of lasting importance. The radiochemical procedure compilations of Coryell (16), Kleinberg (69, 70) and Meinke (96)

are of general applicability. The first two pertain primarily to fission products while the third describes procedures for almost the entire periodic table.

2. The procedures gleaned from the literature were found to consist of a series of steps, each providing a portion of the decontamination required by the experimenter and each contributing to a lower yield of the desired constituent. In order to determine the general applicability of the steps it was found desirable to evaluate each step individually. For example, a typical procedure for the separation of barium-140 from fission product solutions consists of five distinct separation steps: a) the precipitation of barium and strontium as nitrates, b) the precipitation of ferric hydroxide to remove rare earth activities, c) the precipitation of barium chromate to separate it from strontium, d) the precipitation of ferric hydroxide again as a scavenging agent and finally, e) the reprecipitation of barium chromate as a separation from strontium and to reduce the barium to a form readily dried and counted. An evaluation of the entire procedure would give information concerning a gross decontamination which would be much larger than that required in many cases. Also there is the possibility that one or more of these steps do not contribute appreciably to the general

decontamination, or that one step is sufficiently better than another to be substituted for it. It was for these reasons that the procedures were broken into individual separation steps for evaluation.

3. It was then determined experimentally which conditions would best separate the desired constituent from the elements which could be expected to interfere most seriously with its separation. Information was sought in the general analytical literature as well as that particularly applicable to radiochemical separations. The variables of a particular separation were determined, and then the conditions adjusted to determine those which were optimum for the separation step. For example, this resulted in varying the nitric acid concentration for the precipitation of barium and strontium, and in varying the method of introduction of the reagents and rapidity of precipitation for the hydrochloric acid separation of barium from strontium. In another case the pH was found to be the controlling factor.

4. When the optimum conditions had been defined they were evaluated for general applicability by use of a large number of different radioactive tracers. These tracers were chosen to cover a wide variety of periodic groups and to represent a large number of different chemical characteristics.

Figure 4 shows in bold face the broad spectrum of chemical species represented by this group of tracer activities. The yield of the desired constituent was also determined and the standard deviation of these yields was calculated.

5. After a number of separation steps have been studied in this manner it is possible to compare the results of yield and decontamination determinations. It is then possible to construct a procedure from the individual steps which closely satisfies the requirements for decontamination from other active species, and which also furnishes a sufficiently high yield of the desired constituent for counting purposes. It is also possible, following the evaluation of several types of separations, for example ion exchange, solvent extraction and precipitation, to predict which is most likely to fit the needs for decontamination and yield prior to a development program to determine conditions for an individual separation.

There are a number of advantages to an evaluation program of this type. The literature survey will be useful in the future for development of separation procedures. The evaluation of the separation steps individually makes the data of general applicability. The information should apply to those applications requiring very high decontamination factors as well as those where speed is the major requirement and the decontamination a secondary consideration.

FIGURE 4.

THE PERIODIC TABLE OF THE ELEMENTS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	RARE EARTHS	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	RARE EARTHS															

LANTHANIDE RARE EARTHS	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

ACTINIDE RARE EARTHS	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	E	Fm	Mv

Further development is facilitated by a knowledge of the nature of the variables in the individual processes and some information concerning their relative importance. Finally, quantitative information is made available concerning specific interferences. Much qualitative or intuitive information was available but any application required further development work. These data will remove the need for such development in many cases.

Disadvantages of the program defined above also exist. By being of general applicability it loses what might be gained from being aimed at specific conditions. Higher efficiency is possible for many separation steps if their conditions are studied with a specific purpose in mind. The use of the methods produced in this work requires the reproduction of the conditions used here. In non-equilibrium work and where time is important, the conditions of addition of reagents, time of manipulation, and technique of the operator, all become part of the analytical method. These must be reproduced or closely approximated if the data are to be of value. Every effort was made to use conditions which could be easily reproduced and to specify clearly those which are most critical. This effort toward standardization was found justified by the increased reproducibility of results which gave greater statistical significance to the work. Methods were

preferred which depended least upon the training of the operator and this effect was further minimized by careful study of the individual manipulations and the standardization of conditions.

TECHNIQUES

At this point a short description of each technique will be given and a comparison made between standard analytical applications and those of the radiochemist, each to suit his own particular needs. More complete discussions of individual applications are to be found in the chapters in which the techniques were first studied; for example Chapter II for precipitation, Chapter IV for isotopic exchange, Chapter V for electrodeposition and Chapter VI for solvent extraction and ion exchange. See the Table of Contents for more specific references.

Precipitation:

By far the most frequently used technique for the separation or purification of a chemical specie in analysis is that of precipitation. It may be defined as the formation in solution of a non-supported solid phase containing all or a portion of the desired constituent. This solid phase is then separated from the bulk of the solution by filtration or centrifugation.

It may then be washed, dried and either weighed, titrated, counted or assayed in some other manner to determine the quantity of the desired constituent which it contains. Much general information concerning the applicability of this technique may be found in the works of Lundell and Hoffman (89), Willard and Furman (153), Hillebrand (52) and in other standard analytical texts. More specific information concerning the characteristics of traces of material in precipitation separations may be found in the work reported by Garrison and Hamilton (38) and many unique applications are reported there. Some of the equipment required for separations by precipitation is shown in Figure 5.

A precipitate may be entirely inorganic or it may consist of an organic salt of the desired constituent. Organic precipitants have found increasing applications as the nature of specific reactive groups is more thoroughly understood. Formation of the precipitate may be induced by chemical reduction of the desired constituent to the elemental form. Electrolytic reduction will be discussed separately.

Scavenging is a form of precipitation which is not generally applicable to standard chemical analysis. It involves the formation of a bulky precipitate of an inactive specie which carries large quantities of the

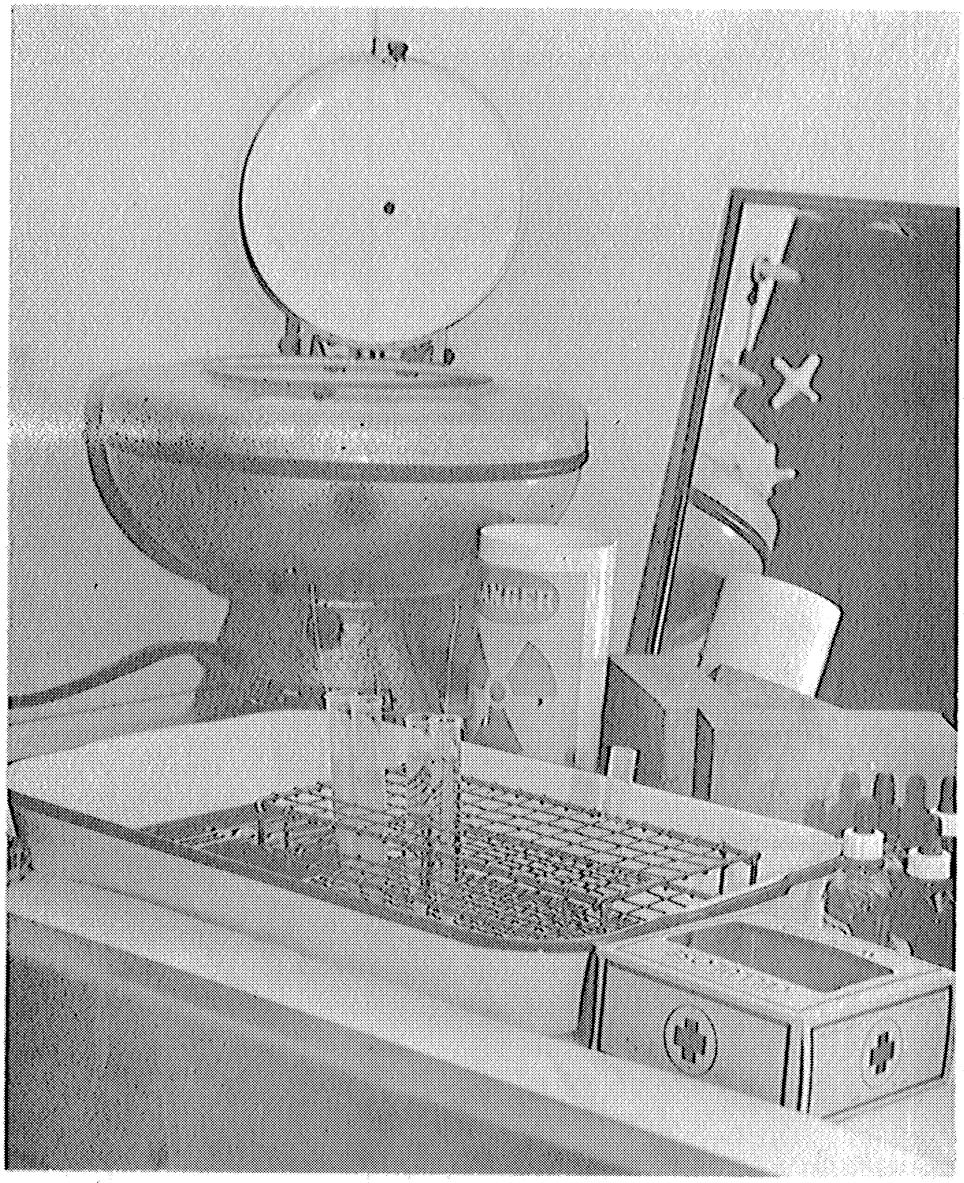


FIGURE 5. Equipment for Laboratory Separations by Precipitation.

radioactive species present as contaminating elements, but very little of the desired constituent. The desired constituent is retained in solution by use of a "holdback carrier", and this technique is discussed thoroughly in Chapter III which reports the evaluation of the scavenging action of the hydrous oxides of iron and lanthanum.

Precipitations conducted for standard analytical purposes generally involve the use of dilute solutions of the desired constituent and the gradual addition of a dilute precipitating reagent to prevent adsorption and coprecipitation. Precipitation is followed by a long period of digestion, again to minimize the coprecipitation, and this might be conducted either at elevated or reduced temperatures depending upon the character of the precipitate. Filtration follows digestion, and washing of the precipitate further reduces contamination by adsorption. The precipitate is at this point reduced to a form suitable for weighing or assay by other methods.

In the case of radiochemical methods the precipitating solutions are generally of higher concentration. This is necessary in order to reduce the volumes handled because of the radiation hazard and the effort to contain the active material. The high decontaminations necessary usually require the use of several separation steps in sequence.

Thus, the time required to perform an individual step is of great importance. The addition of reagents is made rapidly with little possibility of maintaining a homogeneous solution during the addition. Digestion periods are minimized to reduce the time required, and the extra equipment and manipulation necessitated by use of ice, water, or steam baths are avoided if possible. Centrifugation is generally more rapid than filtration and requires less complicated equipment. It is also handy to have the precipitate in the bottom of a suitable reaction vessel, such as a centrifuge cone, for future operations. It may also be found that a subsequent precipitation step gives higher decontamination in the same period of time than a washing step and may thus be substituted for it. A quantitative yield is of less importance in radiochemical work since a determination of the amount of inactive carrier of the desired constituent which was carried through the separation procedure will produce a correction to account for losses of radioactive material by incomplete precipitation or faulty manipulation.

Advantages of a precipitation separation step are its simplicity of operation and the short time required to perform it. Equipment is kept to a minimum. The manipulations are readily performed by persons with little chemical training and are easily reproduced. The

most important disadvantage is its lack of specificity. This is due to two causes; one chemical and the other mechanical. Chemical specificity is becoming less a problem as more is learned about the process of chemical binding. Mechanical specificity is harder to obtain. This lack of specificity is the result of difficulties inherent in the process of formation of a solid in a solution or the transfer of mass from one phase to another. It results in carrying of contaminating material both by coprecipitation and adsorption. The work of Rieman, Neuss and Naiman contains a complete discussion of these processes and it will not be repeated here (121). Another disadvantage is the batch nature of the precipitation process. In large scale work this may be circumvented by use of continuous centrifugation equipment, but this is not practical on a laboratory basis.

Electrodeposition:

Electrodeposition may be considered as a specialized case of precipitation. In this case precipitation is caused by passage of a direct current through the solution at a potential sufficient to deposit the desired constituent in metallic or oxide form on preformed electrodes. Quantitative analytical procedures differ from radiochemical procedures primarily in the current density. Ideally a very low current density would be used for the deposition

and the process would cover a long period of time. However, in radiochemical work the time requirement forces the use of much higher currents and rapid deposition resulting in less adherent deposits and greater contamination through codeposition and occlusion. Many references are available to show where practical use may be made of this method (124, 131). The mercury cathode is an application of electrodeposition very similar to scavenging by precipitation methods. It should certainly be considered for radiochemical work where large quantities of relatively noble metals are present contaminating the more active desired constituent. The equipment necessary to perform a radiochemical separation by electrodeposition is shown in Figure 6.

Advantages of electrodeposition include good decontamination, the presence of the desired constituent in a form which may be readily removed from the solution, and its simplicity which adapts it to remote operation. Decontamination is afforded by the nature of the atom by atom deposition process. The solid phase is generally more compact than that formed by chemical precipitation thus occluding less material and supporting less adsorption. The presence of the desired constituent in a supported form enables the operator to remove it readily and wash

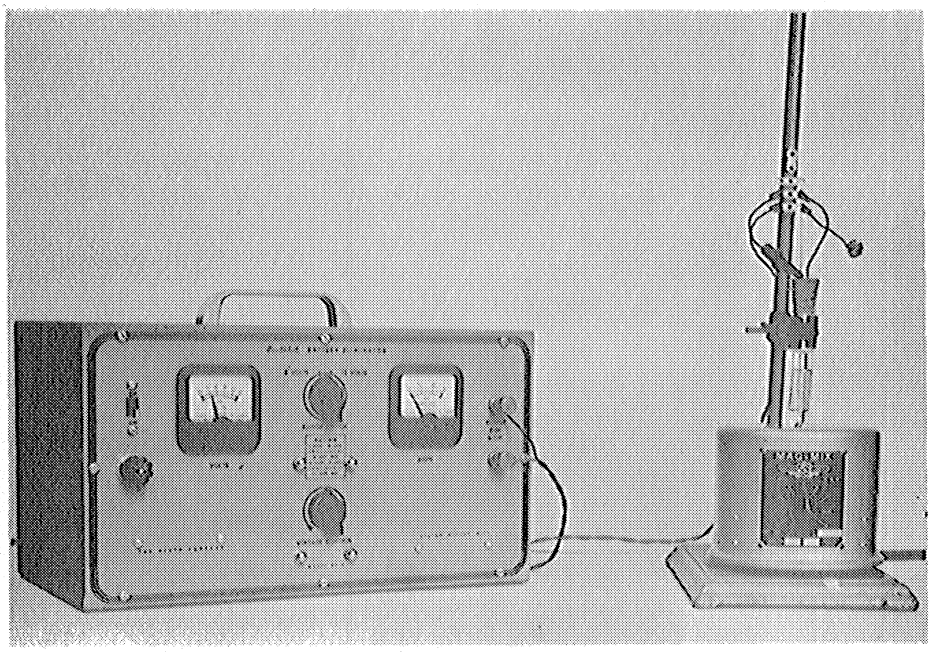


FIGURE 6. Equipment for Laboratory Separations by Electrodeposition.

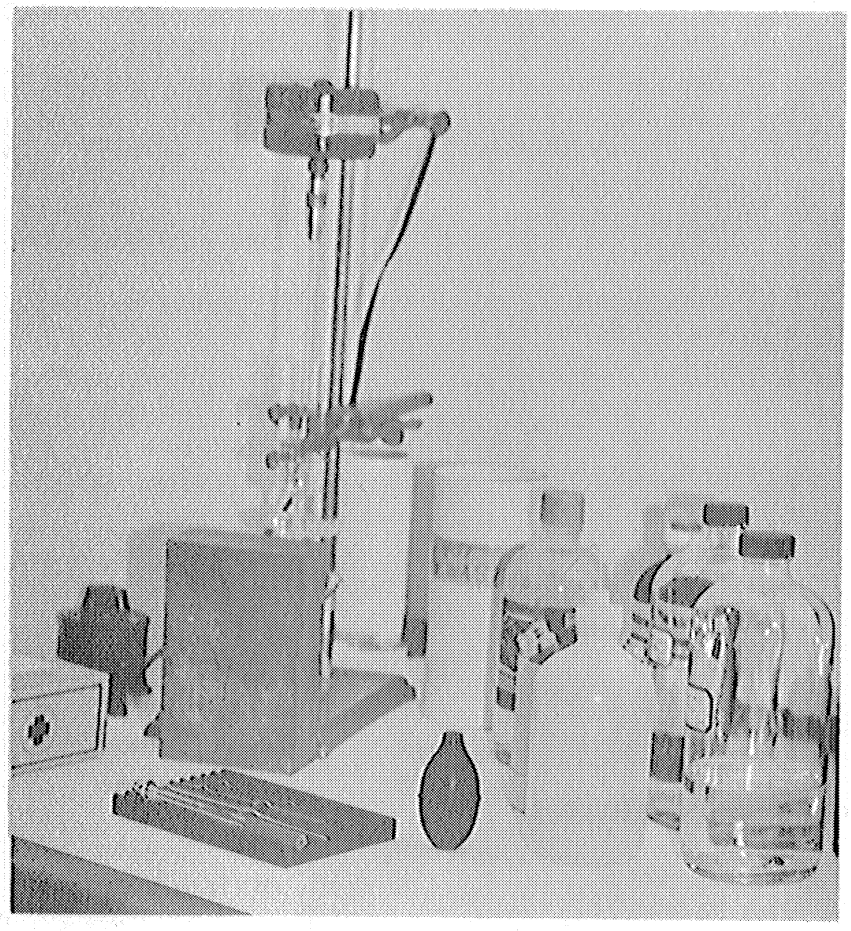


FIGURE 7. Equipment for Laboratory Separations by Solvent Extraction.

it for further decontamination. The preparation of large radioactive sources for industrial use requires simple procedures which are readily adapted to remote control and electrodeposition is quite applicable to such cases, if not as a decontamination step, at least for the preparation of the final source form. Disadvantages include the necessity for high current densities and thus low current efficiencies. It is often necessary to reduce the concentration of the free ions of the desired constituent by adding a complexing agent and this must frequently be done in neutral or basic solution. This results in the use of a solution in which few of the contaminating materials are soluble, thereby increasing contamination of the desired constituent through deposition. The electron is also known for its lack of specificity. Voltage control may be necessary to provide satisfactory separations thus reducing the available current and lengthening the time of the separation. It is also a method in which a large mass transfer is required for separation which increases the possibility of coprecipitation, occlusion and adsorption.

Solvent extraction:

The method of solvent-solvent extraction has been in limited use by the analytical chemist for many years. The familiar separation of iron by extracting the hydrochloric acid solution with diethyl ether has found some application.

In the past fifteen years the increased use of this technique has been based upon applications of several types and these are discussed in the chapter covering the solvent extraction separation of indium. An example of the equipment required for laboratory scale solvent extraction is shown in Figure 7. New industrial applications have depended upon the development of simple, efficient multiple stage contacting equipment. The development of a theory defining the efficiency and operation of such equipment may be found in the works of Treybal and Kortum (74, 144) and both works possess excellent bibliographies. Applications within the atomic energy industry have included the use of "pulse columns" for the separation of uranium and plutonium from fission products and of uranium from plutonium (32). Use of such multiple stage contacting equipment enables one to utilize smaller differences in distribution coefficients and to operate in a continuous manner (12). Large thruput is also obtained.

Advantages of the method of solvent extraction include the ability to obtain very high decontamination factors and the ease of remote control of the continuous process. Extra stages of extraction and scrub may be added to take advantage of small distribution coefficients. Phase separation can be very good if the conditions are well chosen and no emulsification occurs. The major disadvantages

are the lack of specificity and quantitativety in some cases. However, the excellent development within the atomic energy program of the uranium and plutonium separation process resulted in quantitative recovery of the uranium and plutonium and decontamination factors of greater than 10^6 from beta and gamma activities (32). Another disadvantage is the large volume of solution in which the desired constituent is found at the end of the process. This is minimized in the uranium recovery system by the use of a stage of ion exchange following the extraction step, but in laboratory work evaporation is generally required. In some systems organic material is associated with the desired constituent following the separation and this may complicate further operations.

Ion exchange:

It is fortunate with ion exchange to have several general references which describe quite well the work in this rapidly expanding field (79, 104, 123). Cation exchange generally involves chromatographic elution of similar elements because of the low specificity. However, recent work with cation and anion exchange resins enables one to increase the specificity of the ion exchange process by the use of complexing agents which maximize the differences between similar elements. This also increases

greatly the speed of the separation process and its usefulness for radiochemical work. References to these applications may be found in the discussion of anion exchange in Chapter VI reporting the evaluation of the separation of indium in this manner. Examples of the equipment used for laboratory ion exchange separation are shown in Figure 8.

Advantages of this method are its suitability for remote control, due to the simplicity of column operation, and the insensitivity of the method to the weight of material in solution. This second factor is of particular importance in radiochemical work where concentrations of radioactive species may vary by factors of 10^{15} or more. Disadvantages may be the low radiation stability of the resins requiring frequent repacking of columns, the time required for column operation due to low through-puts and flow rates, and the necessity for frequent regeneration of the resin beds because of low capacity.

Isotopic exchange:

Isotopic exchange is a method of very recent application in the field of separation chemistry. The kinetics of isotopic exchange has received wide study for many years in the fields of both inorganic and organic chemistry. The technique has been applied to the production of labeled

compounds and Kolthoff has used it to study the aging of precipitates for analytical purposes (72). However, it was found recently to be of unique interest in the field of separation chemistry. (See Chapter IV and Appendices A, B and C.) For separation purposes its usefulness appears to lie completely within the field of radiochemistry. The process is dependent upon the tendency of atoms of an element, regardless of their atomic weight, to distribute themselves uniformly within a system. If a system is composed of a compound of an inactive form of the desired constituent in contact with a solution in which it is not appreciably soluble, containing trace quantities of an unusual isotope of the desired constituent, this unusual isotope will tend to distribute itself uniformly within the system. This will result in an increase in the concentration of the unusual isotope in the solid phase until, at equilibrium, this concentration will be dependent upon the relative weights of the desired constituent in the solid and liquid phase. If this ratio is very high, the separation of the unusual isotope of the desired constituent from the solution will be very good. An excellent theoretical discussion of this process may be found in the work of Langer (80).

One of the major advantages of isotopic exchange is the simplicity of the methods. Remote operation is readily

possible allowing its use for the preparation of large radioactive sources. The equipment required for laboratory separations by isotopic exchange is shown in Figure 9. In the cases which have been studied in this laboratory, the exchange is very rapid allowing the separation of short lived isotopes from complex mixtures. High decontaminations are possible due to the specificity of the exchange reaction itself. Only an infinitesimal mass transfer is required for complete separation of the desired constituent. A disadvantage is the mechanical instability of the supported solid phase lowering the theoretical distribution factor. Undesirable elements may form less soluble compounds with one of the ions present in the solid phase causing contamination of the desired constituent. It must also be kept in mind that it is a dilution process and that this dilution is an integral part of the motivating force for the separation. Carrier-free separations are impossible by a method of this type, although high specific activity material may be obtained.

Distillation:

Distillation of inorganic materials has also formed an significant part of the atomic energy program separation chemistry. Laboratory methods using this technique for the separation of ruthenium and iodine are routine in

fission-product work. However, since this method was not used thus far in the evaluation program, a more thorough discussion is not warranted at this time.

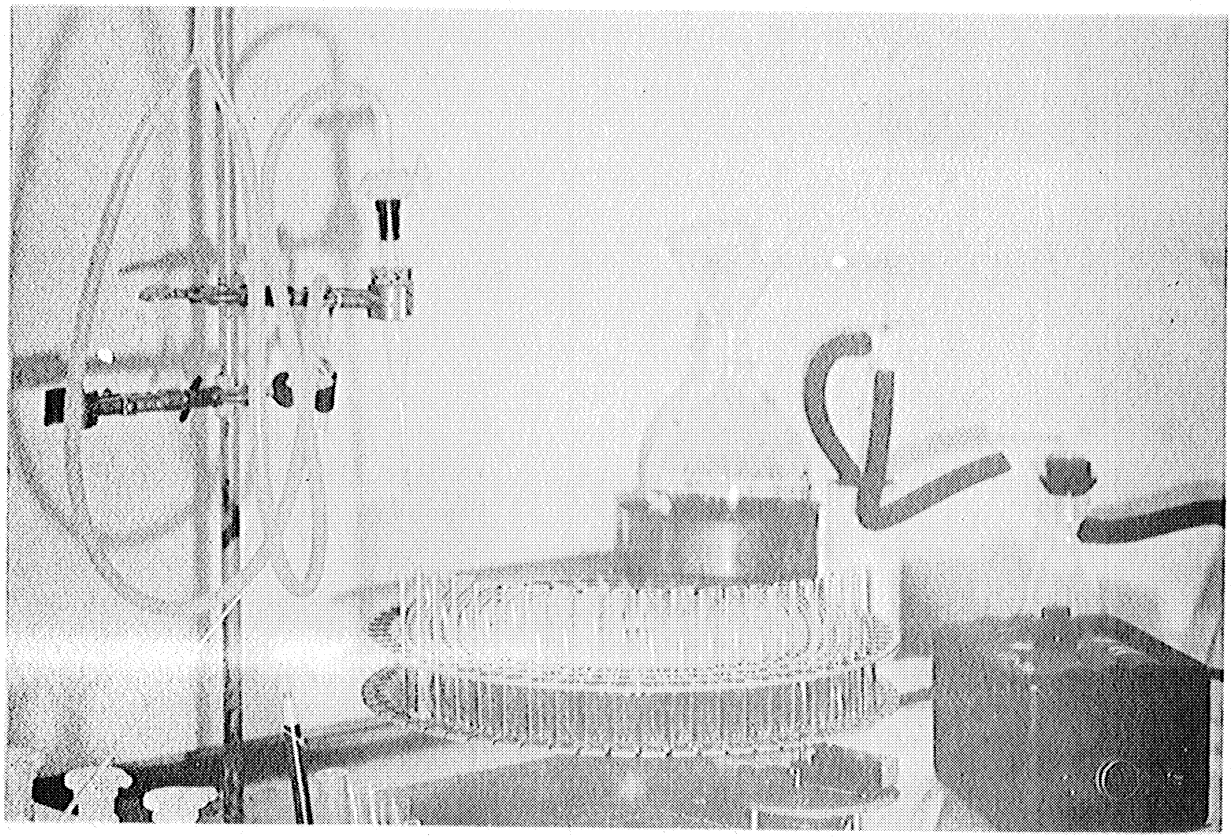


FIGURE 8. Equipment for Laboratory Separations by Ion Exchange.

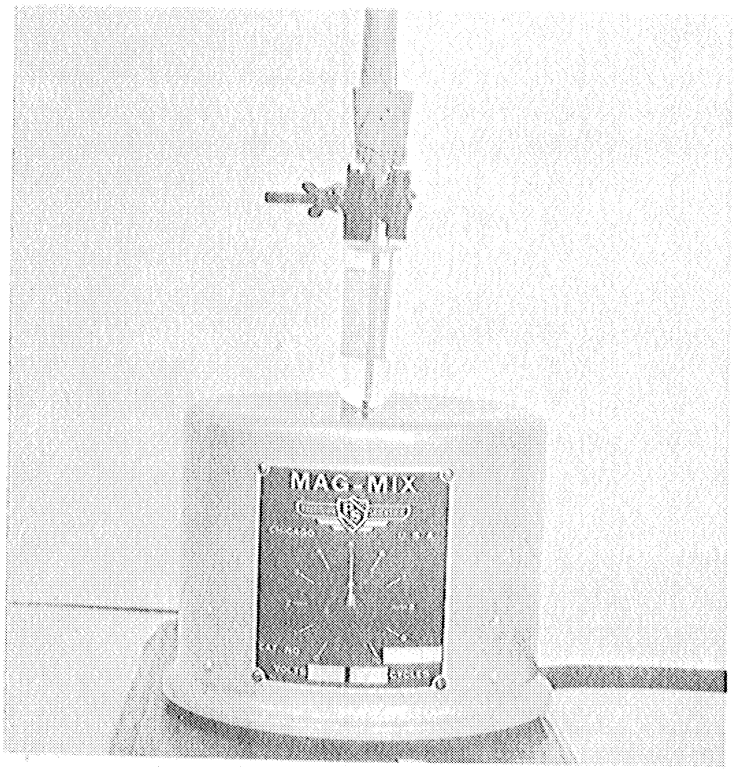


FIGURE 9. Equipment for Laboratory Separations by Isotopic Exchange.

APPARATUS AND REAGENTS

To allow standardization of conditions, an attempt was made to utilize commercially available laboratory equipment. In many cases the equipment was either a duplicate of, or very similar to, that described in the compilations of radiochemical procedures (16, 69, 70, 96). Special equipment, when required, is of simple design, and instructions and diagrams are given to facilitate its duplication.

The reagents described are those which were found satisfactory for the particular operation involved. In some cases this received particular study and these are noted in the text. Commercially available reagents were used in all cases and required no further purification. This was considered important where the methods may be used for routine analysis. Manufacturers names and designations, and in some cases purity, are specified.

Carriers for the radioactive elements were made up to the 10 mg/ml concentration standard in laboratories doing work of this type. Manufacturers names and designations as well as molecular weights are given to aid in reproducing these solutions for personal use. The tracers were obtained from the Isotope Division of the

Oak Ridge National Laboratory and their chemical and nuclear characteristics are described in detail.

Apparatus:

Battery Eliminator, Heathkit Model BE-4, Heath Company, Benton Harbor, Michigan.

Centrifuge Cones, 15 ml, borosilicate glass.

Electric Stirrer, motor manufactured by the Eastern Industries of New Haven, Connecticut. Stirrer was made of 7 mm glass rod which was flattened on the end giving a 1 1/2 in. by 1/2 in. surface which was twisted to 90° turn.

Extraction Vessel, open top Pyrex Brand glass cylinder, 3 cm in diameter, 9 cm high, tapered sharply at bottom to stopcock with 1 mm bore heavy wall, ground to 45° taper at outlet about 1 cm below stopcock. See Figure 19.

Geiger Tube, halogen quenched, 1.4 mg/cm^2 window, Model D-34, Nuclear Instrument and Chemical Corporation, Chicago, Illinois.

Ion Exchange Column, similar to that described by Hicks, Stevenson and Gilbert (51). Made from a 15 ml borosilicate glass centrifuge cone with 4 cm i. d. tube afixed to the apex, 9 cm long tapered in last 3 mm to 2 mm outlet. See Figure 20.

International Clinical Centrifuge.

Lead Housing for Geiger Tube, Technical Associates, Glendale, California, No. Al 14A.

Magnetic Stirrer, manufactured by G. F. Smith Chemical Company, Columbus, Ohio.

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

Platinum Electrodes, 10 mm diameter, 30 mm high, 52 mesh, manufactured by American Platinum Works, Newark, New Jersey.

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

Sample Collection Turntable, similar to that used by University of California Radiation Laboratory, Health Group.

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

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.

Timer for Sample Collection Turntable, Microflex, manufactured by the Eagle Signal Corporation, Moline, Illinois.

Tubes for ion exchange, No. 9446, 100x15 mm, A. H. Thomas Company.

Water Bath, composed of 400 ml beaker containing 300 ml water supported on small hot plate and kept just below boiling point.

Reagents:

Acetic Acid, glacial, (B and A reagent No. 1019).

Aerosol, 1% solution in water.

Aluminum nitrate, (Mallinckrodt reagent No. 3172).

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

Ammonium hydroxide, concentrated (B and A reagent No. 1293).

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

Benzotriazole solution (Eastman reagent No. 2759), 2.5 g in 30 ml conc. NH_4OH, dilute to 100 ml with water.

Bismuth nitrate, (B and A reagent No. 1456).

Buffer solutions, sodium acetate (B and A reagent No. 2191) and acetic acid (B and A reagent No. 1019) (43).

Cupric nitrate, (B and A reagent No. 1641).

Diethyl ether; (Mallinckrodt reagent No. 0848).

Diisopropyl ether, (Eastman Kodak Reagent No. 1193).

Ferric nitrate, (B and A reagent No. 1739).

Fuming nitric acid 90-95% HNO_3 (B and A reagent No. 1121), analyzed by the pycnometer specific gravity method.

Hydriodic Acid, sp gr 1.5, (Merck reagent No. 0246).

Hydrobromic acid, 48% HBr (B and A reagent No. 1085).

Hydrochloric Acid, concentrated, (B and A reagent No. 1090).

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

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

Hydrofluoric Acid, 48%, (B and A reagent No. 1100).

Hydrogen sulfide, 99.9% pure H_2S gas (Matheson Co.).

Ion Exchange Resin, Anion resin AG 2-X8, 200-400 mesh, Bio-Rad Labs, Berkeley, California.

Nitric Acid, concentrated, (B and A reagent No. 1120).

Sodium Acetate, (B and A reagent No. 2191).

Sodium Bisulfate, (Mallinckrodt reagent No. 7437).

Sodium Cyanide, (Mallinckrodt reagent No. 7616), 3 M.

Sodium Hydroxide, (Mallinckrodt reagent No. 7680), 5 M.

Sodium Sulfate, (B and A reagent No. 2294).

Sulfate-bisulfate Buffer Solutions, made to pH of 1, 2, and 3, using 1.15×10^{-2} for K_2 of sulfuric acid with total anion concentration of 0.7 M. Adjusted to pH of 1.0, 2.0 and 3.0 with sodium hydroxide solution and Beckmann Model H pH meter.

Sulfuric Acid, concentrated, (B and A reagent No. 1180).

Sulfuric Acid solution, (B and A reagent No. 1180) H_2SO_4, 10% by volume in water.

Thioacetamide, stabilized, (A. Daigger Co., Chicago, Illinois) 5% in water.

Versene solution, (Bersworth Chemical Co. Anal. Reag.)
diammonium dihydrogen versenate, 400 g/l, ammonia added to dissolve.

Zinc Nitrate, (B and A reagent No. 2445).

Carriers:

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

Barium: $Ba(NO_3)_2$, MW 261.38 (B and A reagent No. 1420), 10 mg/ml Ba(II) in water.

Calcium: $Ca(NO_3)_2 \cdot 4H_2O$, MW 236.16 (Mallinckrodt reagent No. 4236), 10 mg/ml Ca(II) in water.

Cerium: $Ce(NO_3)_3 \cdot 6H_2O$, MW 434.25 (B and A reagent No. 1560), 10 mg/ml Ce(III) in dilute HNO_3.

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

Chromium: $Cr(NO_3)_3 \cdot 9H_2O$, MW 400.18 (B and A reagent No. 1578), 10 mg/ml Cr(III) in dilute HNO_3.

Cobalt: $Co(NO_3)_2 \cdot 6H_2O$, 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.

Indium: $InCl_3$, MW 221.13 (In metal, Indium Corp. of America) 10 mg/ml In(III) in dilute HCl.

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

Iron: $Fe(NO_3)_3 \cdot 9H_2O$, MW 404.02 (B and A reagent No. 1739), 10 mg/ml Fe(III) in dilute HNO_3.

Lanthanum: $La(NO_3)_3$, MW 325.84 (La_2O_3, 99%, Research Chemicals Inc.), 10 mg/ml La(III) in dilute HNO_3.

Niobium: $K_8Nb_6O_{19}\cdot 16H_2O$, MW 1462. (Fansteel Metallurgical Corp.), 10 mg/ml Nb(V) in dilute KOH.

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: $Ag(NO_3)$, MW 169.89 (Merck reagent No. 2169), 10 mg/ml Ag(I) in water.

Strontium: $Sr(NO_3)_2$, 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: $SnCl_2\cdot 2H_2O$, MW 225.65 (Merck reagent No. 7488), 10 mg/ml Sn(II) in 5% HCl.

Zirconium: $ZrO(NO_3)_2\cdot 2H_2O$, 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 (62) 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. More information concerning carrier-tracer exchange may be found in the work of Wilkinson and Grummitt (152).

Cr^{51}

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.

Ir^{192}

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

Ru^{106}

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

Sb^{124}

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.

Sn^{113}

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.

Ta^{182}

Tantalum tracer is present as the potassium tantalate in KOH solutions. The carrier, potassium heptafluotantalate,

Table I. Chemical Characteristics of Tracer Solutions

	Isotope	Received from ORNL* as:	Diluted with	Loss from Hydrol. or Adsorption	For Carrier-Tracer Exchange
1.	Ag-110	$AgNO_3$ in HNO_3 soln.	3M HNO_3	large loss by ads. 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 0.8M 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.	In-114 In-114	$InCl_3$ in HCl soln.	0.1M HCl	none	thorough mixing
10.	Ir-192	$IrCl_6^{=}$ in HCl soln.	0.1M HCl	none	thorough mixing, carrier also in HCl before mixing
11.	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 Adsorption	For Carrier-Tracer Exchange
12. Se-75	$SeCl_4$ in HCl soln.	1M HCl	none	thorough mixing
13. 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
14. Sn-113 In-113	$SnCl_2$ in HCl soln.	5% HCl	none	$SnCl_2$ in 5% HCl plus tracer oxid. in excess NaClO.
15. Sr-89	$SrCl_2$ in HCl soln.	dil. HCl	none	thorough mixing
16. Sr-90 Y-90	$SrCl_2$ in HCl soln.	dil. HCl	none	thorough mixing
17. 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
18. Zr-95 Nb-95	complex in oxalic acid	Dil. oxalic acid	none	Addition of HF and separation as $BaZrF_6$

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

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.

Zr^{95}

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 (70). Complete exchange between carrier and tracer zirconium takes 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 (56). 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.

Table II. Nuclear Characteristics of Tracers (56)

Isotope	Half Life	Primary Radiations β	Primary Radiations γ	Daughter	Spec. Act. Orig. Soln.	Counting
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%) 1.67 (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 1.17 (100%)	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 0.794 (100%) 0.570 (30%) 1.35 (3%) others weak	Ba-134	C.F.	scint. well

Table II (cont.)

Isotope		Half Life	Primary Radiations β	Primary Radiations γ	Daughter	Spec. Act. Orig. Soln.	Counting
14.	Sn-113 In-113m	112 days 105 min		EC-0.393 (100%)	In-113m In-113 (stable)	15.79 mc/gm	scint. well
15.	Sr-89	54 day	1.50		Y-89 (stable)	C.F.	scint. well
16.	Sr-90	19.9 yr	0.61 (100%)		Y-90	C.F.	GM tube 1.4 mg/cm^2
	Y-90	61 hr	2.18 (100%)		Zr-90 (stable)		scint. well
17.	Ta-182	111 day	0.53 1.1	1.2 1.1 0.05-1.0	W-182 (stable)	409 mc/gm	scint. well
18.	Zr-95	65 day	0.371 (99%)	0.721 (99%)	Nb-95	C.F.	scint. well
	Nb-95	35 day	0.16 (100%)	0.745 (100%)	Mo-95 (stable)		

Table II (cont.)

	Isotope	Half Life	Primary Radiations β	Primary Radiations γ	Daughter	Spec. Act. Orig. Soln.	Counting
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.	In-114 In-114	48 day 72 sec	IT 0.192, 1.98	e^-0.162,0.187	In-114 Sn-114 (stable)	86 mc/gm	scint. well
10.	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
11.	Ru-106	1 yr	0.0392 (100%)		Rh-106	C.F.	scint. well
	Rh-106	30 sec	3.53 (68%) 3.1 (11%) 2.44 (12%)	0.513 (23%) 0.624 (12%)	Pd-106 (stable)		
12.	Se-75	127 days		0.10 0.12 0.14 0.26 0.40	As-75 (stable)	49.5 mc/gm	scint. well
13.	Sb-124	60 days	2.29 (21%) 1.69 (7%) 0.95 (7%) 0.68 (26%) 0.50 (39%)	0.121 0.607 (95%) 0.653 (5%) 0.730 (24%) 1.708 (70%) 2.04 (6%)	Te-124 (stable)	1142 mc/gm	scint. well

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 Figures 10-16. 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 niobium daughter, zirconium remained sufficiently pure for counting purposes for several days, while barium and strontium had to be counted within two to four hours.

FIGURES 10 through 16.

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.

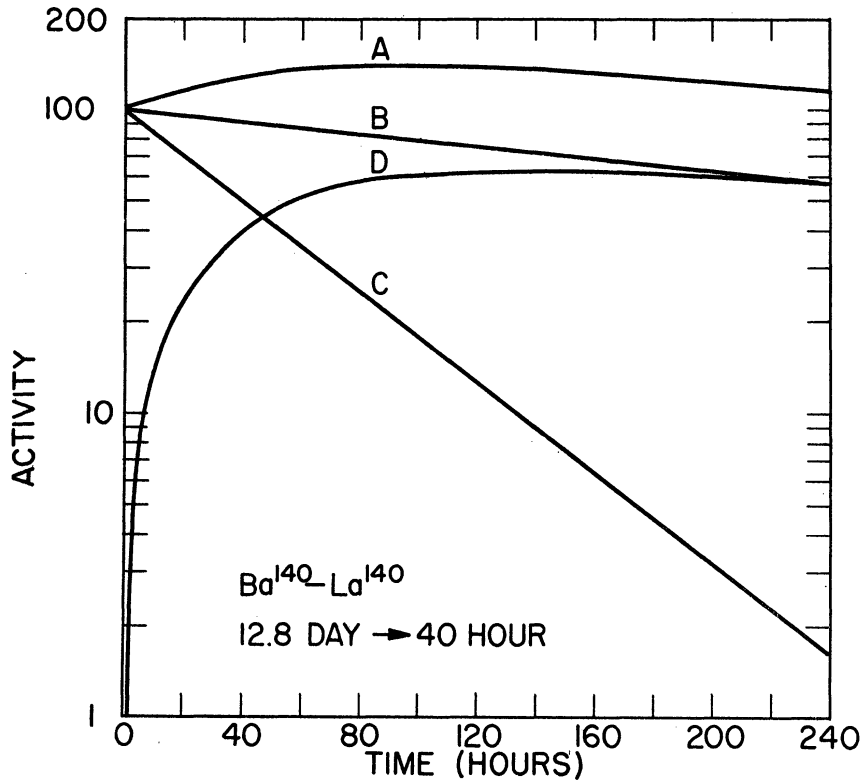


FIGURE 10. Growth and Decay of Tracer Mixture of Ba-140 and La-140.

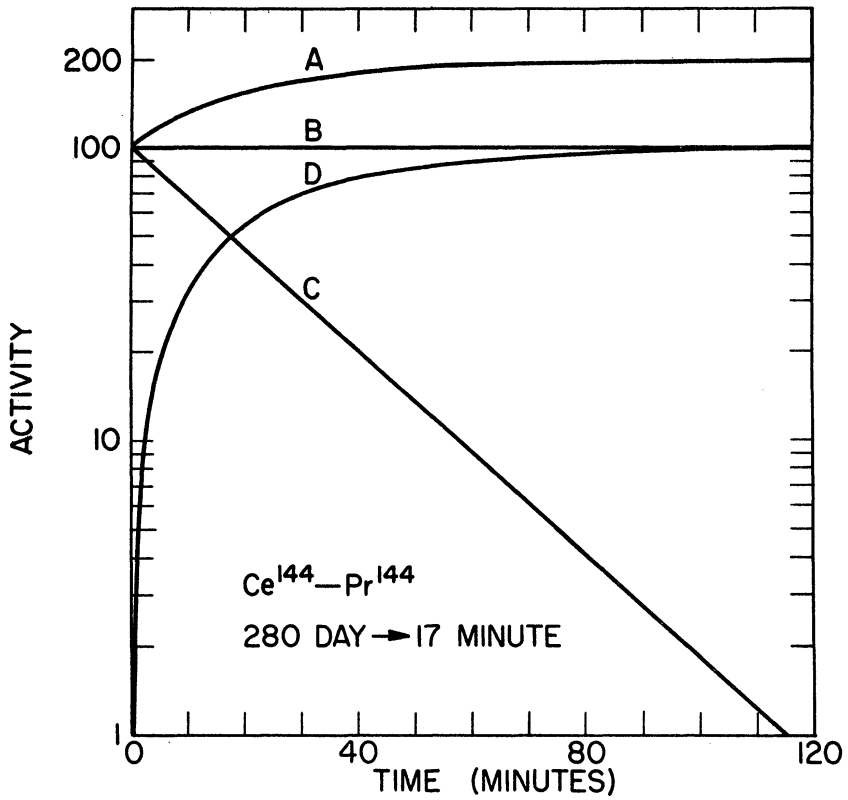


FIGURE 11. Growth and Decay of Tracer Mixture of Ce-144 and Pr-144.

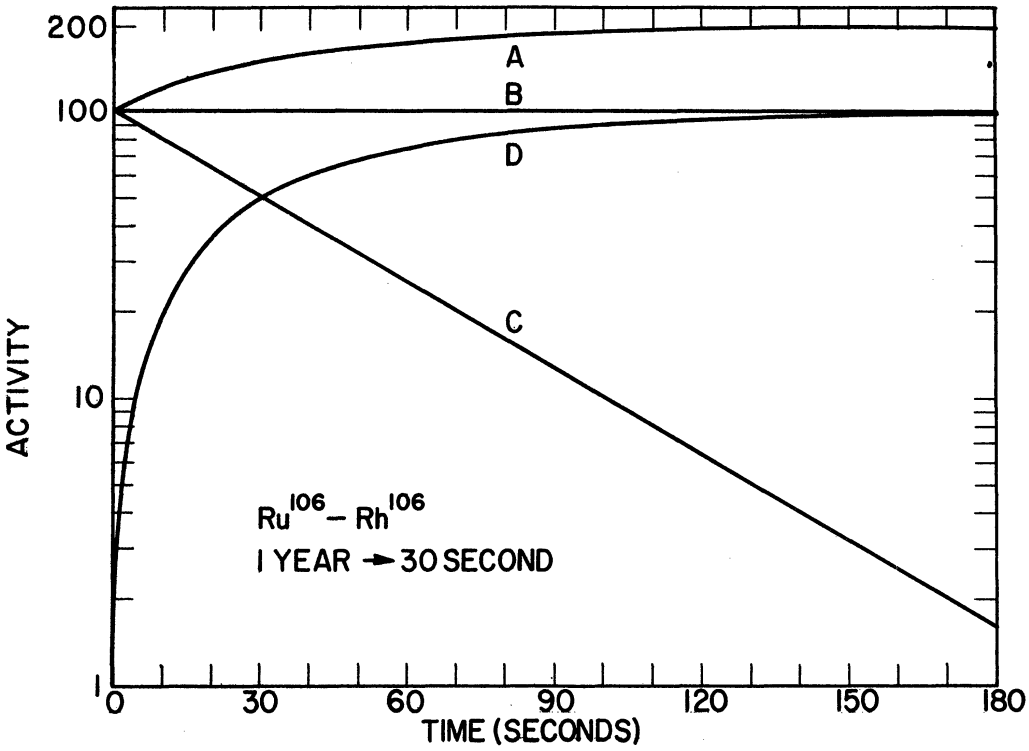


FIGURE 12. Growth and Decay of Tracer Mixture of Ru-106 and Rh-106.

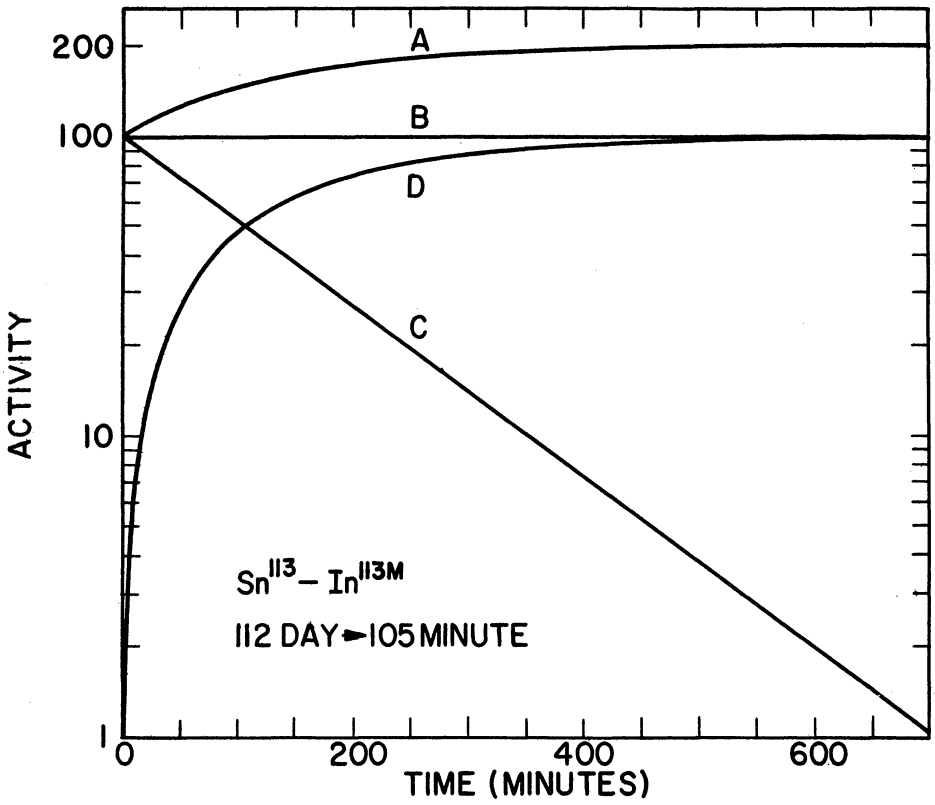


FIGURE 13. Growth and Decay of Tracer Mixture of Sn-113 and In-113.

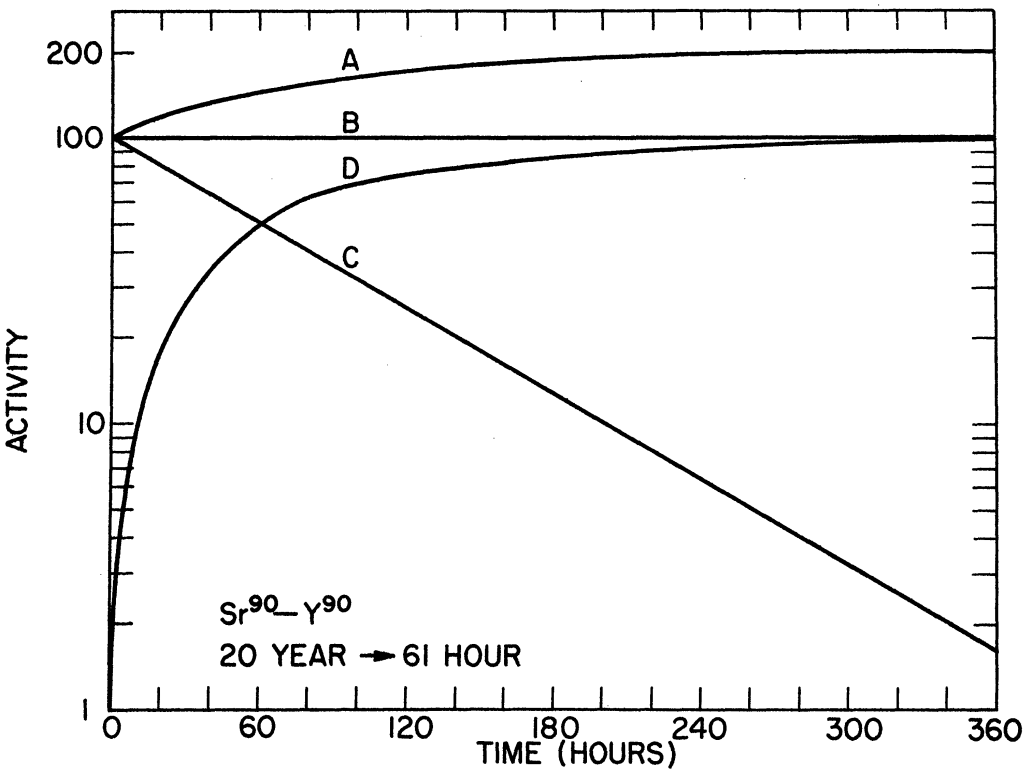


FIGURE 14. Growth and Decay of Tracer Mixture of Sr-90 and Y-90.

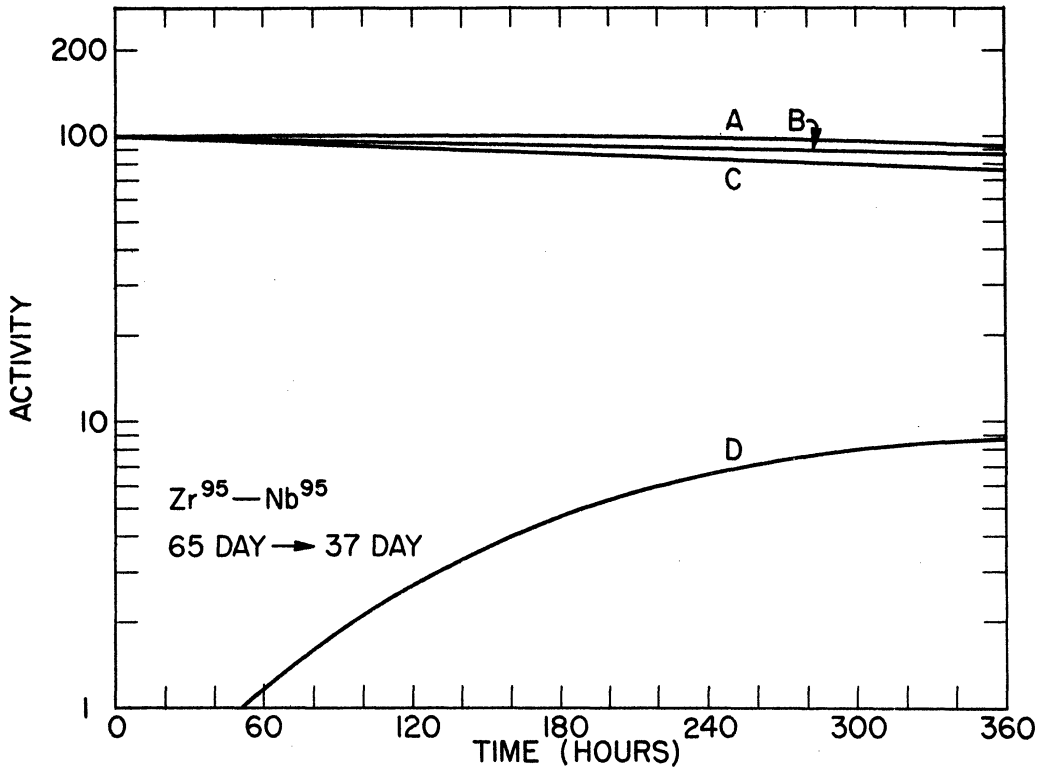


FIGURE 15. Growth and Decay of Tracer Mixture of Zr-95 and Nb-95 Covering 360 Hours.

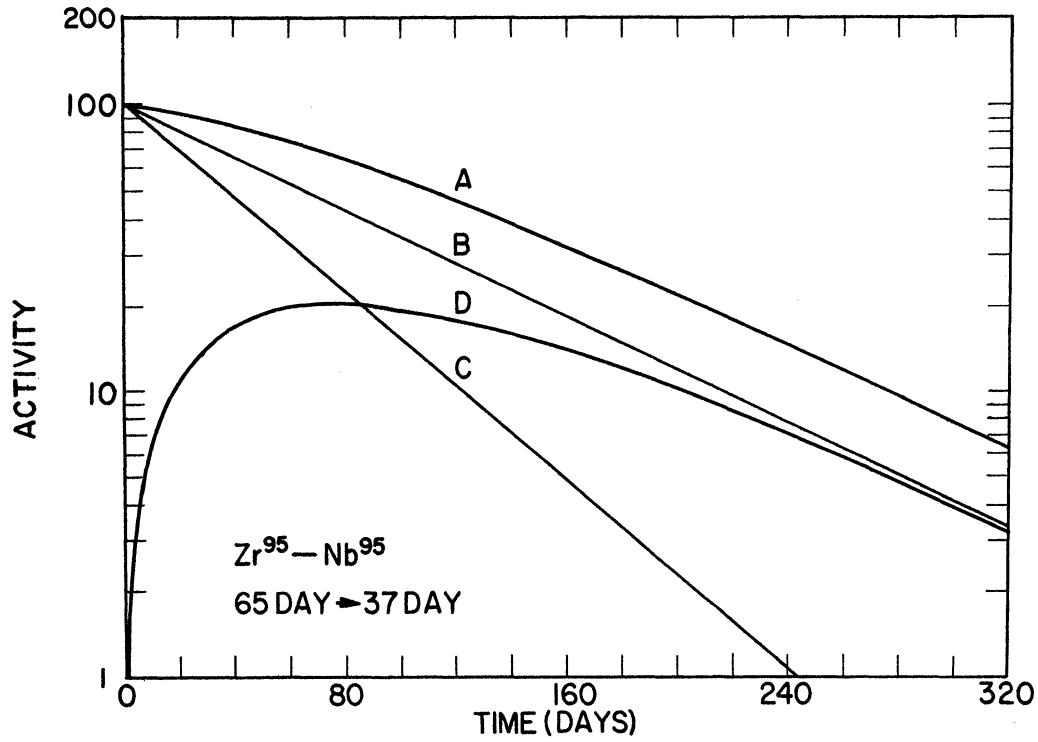


FIGURE 16. Growth and Decay of Tracer Mixture of Zr-95 and Nb-95 Covering 320 Days.

CHAPTER II

BARIUM, CALCIUM, STRONTIUM

The first elements whose radiochemical separations have been explored are the alkaline earths: barium, strontium and calcium. Since barium and strontium are high yield fission products,(16) considerable work has already been done on their radiochemical separations. By comparison, few radiochemical separation procedures are reported in the literature for calcium.

LITERATURE REPORT

Typical procedures for the separation of these elements are suggested by standard analytical references (52, 115, 125). These references have been supplemented by the experimental work of Willard and Goodspeed (154) 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 (16, 38, 64, 69, 70, 96) were consulted for separations involving these three elements. A number of

references were located in the German literature (71), 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 (56) and in "Nuclear Data" compiled by the National Bureau of Standards (150). References to all of these procedures are included in the List of References.

The literature search indicated that the separations of primary interest for these three elements were the precipitations with nitric acid (4, 13, 14, 17, 18, 22, 29, 39, 41, 47, 52, 55, 83, 87, 96, 105, 136, 137, 140, 145), ammonium dichromate (4, 18, 21, 22, 31, 39, 41, 47, 50, 55, 65, 83, 84, 87, 105, 139, 145) and hydrochloric acid (18, 19, 20, 21, 22, 24, 29, 31, 39, 46, 65, 69, 83, 96, 128, 139). Sulfate (46, 50, 109, 111, 133) and oxalate (4, 14, 22, 35, 40, 55, 58, 69, 73, 105, 108, 126, 145, 146) 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 (130) to these separations were not promising, and although good separations have been made by ion exchange (86, 141), time considerations prevent their general applicability to this work at the present time. Certain other minor methods involving precipitation of carbonate or 8-hydroxyquinolate

(8, 25, 60, 90, 112, 113, 129, 142) were also found. Scavenging steps, involving precipitation of hydrous oxides of iron (III) or lanthanum (III), often found in the procedures (4, 18, 21, 22, 25, 35, 39, 40, 41, 46, 55, 58, 69, 87, 105, 108, 126, 137, 139, 145, 146) are discussed in Chapter III.

EXPERIMENTAL PROGRAM

Precipitation separations are conducted under conditions which are standard in laboratories engaged in fission-product and bombardment work (38, 64, 69, 70, 96). 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-

Muller 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 were shown in bold face in Figure 4.

PROCEDURES AND RESULTS

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.

Ammonium Dichromate 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 (52).

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 (61) 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 (43). 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). Tracer plus 10 mg of carrier for the contaminating element were used in these determinations.

The itemized procedure is as follows:

1. Add 10 mg barium carrier and barium tracer to 15 ml glass centrifuge cone. Mix thoroughly to effect exchange.

2. Add 10 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 10 ml of acetic acid-sodium acetate buffer solution of the desired pH. Stir thoroughly.

4. Add 2 ml $(NH_4)Cr_2O_7$ 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 (154) 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 (38, 64, 69, 96).

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 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	3 ml H_2O	82 ± 1.1	2.8 ± 0.9	0.6 ± 0.4	
	1.5 ml H_2O	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_2O_4 15 on CaC_2O_4	99		100
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	Precipitating Solution, Percent Carried							Ions Always Present in Precipitating Soln.
	Chromate pH 4	80% Nitric Acid	60% Nitric Acid	Hydrochloric Acid	Oxalate on SrC_2O_4	Oxalate on CaC_2O_4	Sulfate	
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	2.0	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	99.0	--	57	NO_3^-, Cl^-
Tantalum	10	1	0.7	0.5	49	24	0.6	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.

Three different concentrations of nitric acid (80%, 70% and 60%) were used to determine the effect of nitrate concentrations on the separation from calcium. The following procedure was used.

1. Add 10 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 10 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 Figure 4 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 $BaCl_2 \cdot 2H_2O$ in strong HCl solutions. Many variations of this method have been used in atomic energy work (18, 24, 96). 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 10 ml of the 4:1 HCl:ether reagent was added, (2) 3 ml of aqueous solution containing tracers and carriers to which 10 ml of the HCl:ether

solution was added, (3) 10 ml of aqueous solution containing tracers and carriers into which dry HCl gas is bubbled until the solution is saturated, and (4) 8 ml of aqueous solution containing tracers and carriers to which 3 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 10 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 10 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 10 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 10 ml with water for procedure using plain dry HCl or to 8 ml and add 3 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 H_2O).

Ammonium Oxalate Separations:

Precipitation of strontium and calcium as the oxalates is discussed thoroughly in standard works (52, 125), 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 10 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 10 mg carrier of either strontium of calcium and stir thoroughly. Also add strontium and calcium tracers when determining their yield.

3. Dilute the solution to 8 ml with water.

4. Add sufficient concentrated NH_4OH to obtain an excess. One ml is usually satisfactory.

5. Heat to boiling and add 2 ml of a solution of saturated $(NH_4)_2C_2O_4$, 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.

Sulfuric Acid 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 (125). In more recent work, the sulfate ion is liberated by the thermal decomposition of dimethyl sulfate thus accomplishing homogeneous precipitation (28).

The following procedure was used in this work:

1. Add 10 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 10 mg of barium carrier. Also add barium tracer when determining barium yield.

3. Dilute to 10 ml with 1 M HNO_3 and stir thoroughly.

4. Add 1 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 is 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 statistical significance 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 (84) 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 (154).

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.

Chloride:

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 3 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 10 ml HCl:ether reagent and 3 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 $BaCl_2 \cdot 2H_2O$ 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. (52). The similarity between the crystaline 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 (28) and by heating the solution. 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.

If it 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 (116). 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 oxysulfates 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 hexafluoride of zirconium. This may also cause the high cerium contamination.

An insoluble barium chloroiridate may be induced to precipitate accompanying the barium sulfate, a possible reason for its 5.4% contamination of the $BaCl_2 \cdot 2H_2O$ precipitation.

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 an 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 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

TABLE V. Sample Procedure for the Separation of Barium from Other Activities

HCl:Ether Precipitation of $BaCl_2 \cdot 2H_2O$ — Yield 82%

1. Add carriers to 15 ml cone, secure isotopic exchange.
2. Ppt. $BaCl_2 \cdot 2H_2O$ from 3 ml aq vol by addition of 10 ml 4:1 HCl:Ether sol.
3. Digest 5 min, room temp, centrifuge 5 min, remove supernate.

Decontamination Factors

1-10	Sb
10-100	Ir, Ru, Zr, Sr
100-1000	Ca, Ce, Cs, Cr, Co, Ag, Ta, Sn, Se, I

HCl:Ether Precipitation of $BaCl_2 \cdot 2H_2O$ — Yield 67%

4. Dissolve ppt, add carriers.
5. Ppt as in step (2) above.
6. Digest 5 min, centrifuge 5 min, remove supernate.

Decontamination Factors

10-100	Sb
10^2-10^3	Ir, Sr
10^3-10^4	Ru, Zr
10^4-10^5	Ca, Ce, Cs, Cr, Co, Ag, Ta, Sn, Se, I

HCl:Ether Precipitation of $BaCl_2 \cdot 2H_2O$ — Yield 55%

7. Dissolve ppt, add carriers.
8. Precipitate as in step (2).
9. Digest 5 min, centrifuge 5 min, remove supernate.

Decontamination Factors

10-100	Sb
10^3-10^4	Ir
10^4-10^5	Sr
10^5-10^7	Ca, Ce, Cs, Cr, Co, Ru, Ag, Ta, Sn, Zr, Se, I

H_2SO_4 Precipitation of $BaSO_4$ — Yield 55%

10. Dissolve ppt, add carriers.
11. Make volume to 10 ml with 1 M HNO_3, ppt $BaSO_4$ by addition of 1 ml 10% H_2SO_4.
12. Digest 5 min, centrifuge 5 min, remove supernate.

Decontamination Factors

10^2-10^3	Sb
10^4-10^5	Sr, Ir
10^6-10^8	Ca, Ce, Cs, Ru, Ag, Zr.
10^8-10^9	Cr, Co, Ta, Sn, Se, I

Determination of Yield and Counting

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 discussed in Chapter III.

Calcium

Calcium may also be separated as the nitrate with strontium and barium in 80% HNO_3. 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.

CHAPTER III

FERRIC AND LANTHANUM HYDROXIDE SCAVENGING

Scavenging may be defined as the formation of an insoluble precipitate of the inactive form of an element for the purpose of removing a wide variety of active species from solution which might interfere with or contaminate the further separation of the desired constituent. The scavenging agent may already be present as one of the contaminating activities or it may be a completely dissimilar element. Such a separation step is widely used for the separation of easily hydrolyzed elements from elements such as the alkali metals, alkaline earth metals, halides and noble metals. While removing a number of interfering elements, the scavenging process also removes a portion of the desired constituent. This is the reason for its limited applicability in quantitative analytical work. To retain a major portion of the desired constituent in solution, an inactive carrier is added for it prior to precipitation of the scavenging agent. Materials present only in trace concentrations tend to be carried by mechanical means during precipitation separations making the carrier a necessity. The requirements of radiochemical work, which

are high decontamination and a reasonable yield, do not require that 100% of the desired constituent be recovered. The yield of the desired constituent is determined at the end of the separation procedure by measuring the recovery of the inactive carrier of the element. This number may be used to adjust the counting result to give the total amount of activity due to the desired constituent present in the original solution.

LITERATURE REPORT

The use of scavenging steps is so widespread that no attempt will be made to list all the references which were found. Many procedures using scavenging for various purposes and under varying conditions are found in the manuals of the national laboratories and other compilations of this type (16, 70, 71, 96). Many other applications may be found in the following references (4, 18, 21, 22, 25, 35, 39, 40, 41, 46, 55, 58, 69, 87, 105, 108, 126, 137, 139, 145, 146).

Two methods of scavenging have received more wide use than any others. These are the precipitation of a hydrous oxide of a metal such as iron or lanthanum, and the precipitation of an insoluble sulfide such as silver, mercury, antimony, or tin. The method which is applicable to the purification of the alkaline earth metals and silver is

the precipitation of the hydrous oxides. When iron is used it acts as a nonselective scavenging agent while lanthanum is used to remove rare earth activities. Cerium (III) is also of interest but the character of the precipitate and the pH of precipitation make it quite similar to lanthanum.

EXPERIMENTAL PROGRAM

The method of scavenging which was evaluated in this work is that of the precipitation of either ferric or lanthanum hydroxide by the addition of ammonia. The chemical properties of these two elements and the character of their precipitates differ sufficiently to warrant an evaluation of each.

In radiochemical work scavenging is generally practiced with only trace amounts of the contaminating activities present in solution. However, two series of determinations were made with each element to obtain a comparison of the efficiency of scavenging in the presence and in the absence of macro amounts of the contaminating elements. The first was carried out in the presence of 10 mg of the inactive form of the contaminating element, and the second series in the absence of added carrier. In some cases this second series involved the use of carrier free activities and in others the use of high specific activity material. These tracers are fully described in Table I and Table II.

PROCEDURES AND RESULTS

Ferric Hydroxide Scavenging:

The use of a precipitation of ferric hydroxide for scavenging purposes is based upon its lack of specificity. It is also aided by the gelatinous nature of the hydrous oxide and by the fact that the precipitate is first formed in a slightly acid solution (about pH 3) thereby presenting a ready-formed surface for adsorption of ions which precipitate in less acid solutions. While many methods have been used to produce a precipitate of this nature, by far the most simple and direct is that of addition of ammonium hydroxide to an acid solution containing ferric ion. The precipitate formed in this manner is quite gelatinous and coagulates rapidly.

Scavenging may be performed in the presence or absence of macro amounts of the inactive form of the element whose radioisotope is to be removed from solution. When carriers were added, 10 mg of the element under study was used. In the case of the zirconium-niobium tracer 10 mg of each element was present. In the cases of tin-indium and strontium-yttrium tracers 10 mg of tin carrier was added in the first and 10 mg of strontium carrier added in the second and a sufficient time allowed to elapse after separation and prior to counting to assure that secular

equilibrium was again attained.

The following procedure was used.

1. Add 10 mg carrier of the element under study to a 15 ml centrifuge cone and sufficient tracer activity of this element to obtain a statistically significant count after separation.
2. Perform the necessary steps to secure isotopic exchange between the carrier and tracer. Mix thoroughly.
3. Make up the volume to 8 ml with distilled water.
4. Add 1 ml of ferric carrier and mix thoroughly.
5. Add 1 ml of concentrated ammonium hydroxide and stir.
6. Digest with occasional stirring for five minutes at room temperature.
7. Centrifuge at top speed for five minutes.
8. Remove the supernate with a slurp tube.
9. Transfer the precipitate to a culture tube, stopper and count in the well scintillation counter. In the cases where a major portion of the activity was carried on the precipitate a 1 ml sample of the supernate was counted to determine more accurately the residual activity in the solution.

Table VI shows the results of this procedure in the presence of the elements listed. The procedure was also

run for each element without the addition of inactive carrier to the tracer activity and these results are also given. Each result is the average of duplicate determinations.

TABLE VI. Scavenging by Precipitation of Hydrous Oxides.

Element	Percentage remaining in solution*			
	$Fe(OH)_3$ pptn.		$La(OH)_3$ pptn.	
	Carrier Present	Carrier Absent	Carrier Present	Carrier Absent
Antimony	18.	8.1	0.9	0.8
Cerium	0.045	0.16	0.11	2.4
Cesium	96.	92.	97.8	97.7
Chromium	0.30	0.26	0.46	0.23
Cobalt	83.	23.	89.	79.
Indium	0.12	0.21	0.14	0.20
Iodine	95.8	92.7	86.9	75.
Iridium	15.	3.9	4.4	1.0
Ruthenium	30.	6.5	2.7	1.4
Selenium	71.	36.	9. (var.)	11. (var.)
Silver	91.3	91.4	97.3	96.5
Strontium	96.3	11.	85.	85.
Tantalum	0.03	0.08	0.3	0.1
Tin	1.7	0.3	0.12	0.19
Zirconium-Niobium	0.02	0.14	0.04	4.9

* Results are the average of duplicate determinations.

Lanthanum Hydroxide Scavenging:

The precipitation of lanthanum hydroxide for scavenging purposes seemed from the literature references to be used interchangeably with the precipitation of ferric hydroxide. However, there are marked differences between them. While the ferric ion will begin to precipitate at a pH of three, the pH for the formation of lanthanum hydroxide is in the neutral range, about 7-8. Thus in the first case a precipitate is already formed when many elements have not yet exceeded their solubility product. Carrying in those cases must be due to adsorption rather than coprecipitation. In the second case the solubility product of many hydrous oxides has already been exceeded before the lanthanum hydroxide begins to form, thereby allowing these particles to serve as nuclei for the formation of the lanthanum precipitate. Also, the precipitate of ferric ion is much more voluminous than that of the lanthanum compound. The lanthanum compound is also slower to coagulate, and, when precipitation is complete, fills a volume only about 1/3 that of the ferric hydroxide.

The conditions for formation of lanthanum hydroxide are identical to those used for ferric hydroxide except for the substitution of 10 mg lanthanum carrier for 10 mg ferric carrier prior to addition of the ammonium hydroxide. The data obtained by this procedure are shown in Table VI. The

results are the average of duplicate determinations. As was the case with iron, the procedure was conducted both with and without added carrier for the elements listed in the table.

DISCUSSION OF RESULTS

The value of a given precipitation as a scavenging step depends upon its ability to fulfill two requirements. First, it must remove a sizeable portion of those elements which might contaminate the desired constituent in further separations and secondly it must leave in solution a major portion of the desired constituent. In general we might say that for scavenging to take its place in a series of separation steps and compete with a specific separation step for the desired constituent, the scavenging step must remove more than 99% of the contaminating activities and allow over 80% of the desired constituent to remain in solution. Even under these conditions it is a dilution rather than concentration of the desired constituent.

When scavenging with the hydrous oxides of iron and lanthanum, the contaminants which may be removed to the largest degree are those which form hydrous oxides in slightly acid or neutral solution. These are shown quite clearly in Table VI. Cerium, tantalum, indium, tin, chromium and zirconium-niobium are carried to greater than 99% in most

TABLE VII. Comparison of Scavengers' Ability to Carry Contaminating Elements.

Ferric Hydroxide Scavenge

Extent of Carrying	Elements	
	Carrier Present	Carrier Absent
90 - 99%	Sn.	Ir, Sb, Ru.
99 - 99.9%	Cr, In.	Ce, Cr, In, Sn, Zr-Nb.
99.9 - 99.99%	Ce, Ta, Zr-Nb.	Ta.
over 99.99%	None	None

Lanthanum Hydroxide Scavenge

Extent of Carrying	Elements	
	Carrier Present	Carrier Absent
90 - 99%	Ir, Ru, Se.	Ce, Ir, Ru, Zr-Nb.
99 - 99.9%	Ce, Cr, In, Sb, Sn, Ta.	Cr, In, Sb, Sn, Ta.
99.9 - 99.99%	Zr-Nb.	None
over 99.99%	None	None

cases under study. Those elements forming unstable ammonia complexes such as iridium and ruthenium are carried to a lesser extent. In Table VII the data are arranged so as to compare the ability of the precipitates of iron and lanthanum to remove over 99% of those activities. When the data are arranged in this manner it would appear that lanthanum hydroxide is the better scavenger in that tin and antimony are also included in the group carried to better than 99% when carrier of the element is present. However, when no carrier for the contaminating element is present there is very little difference between the two scavengers. Iron may be less specific in its scavenging action as would be expected by its voluminous nature. Antimony, ruthenium and iridium are carried to greater than 90% when no carrier has been added for these elements, and they are not in this group when carrier is present. There seems to be a general tendency for iron to carry elements to a greater extent when no carrier for these elements is present, but there are notable exceptions. This tendency is not shown with lanthanum.

To compare the scavenging agents' ability to leave more than 80% of the desired constituent in solution, the data were arranged as shown in Table VIII. Results tend to be erratic if carrier is not added for the desired constituent. The elements comprising the 80-100% group are identical

in both cases. Again the specificity of the lanthanum precipitation is evident in that no elements were found in the 10-50% or the 50-80% groups. This definitely enhances its applicability as a scavenger.

These results indicate that in the choice of a scavenging agent, as in the choice of a specific separation for the desired constituent, care must be taken to fit the separation to the requirements of carrier present or carrier free conditions and of decontamination for individual elements present in the sample. No general choice will fit all the possibilities which might be encountered.

TABLE VIII. Comparison of Scavengers Ability to Leave the Desired Constituent in Solution.

Extent remaining in solution.	Elements remaining in solution*	
	$Fe(OH)_3$ pptn.	$La(OH)_3$ pptn.
10 - 50%	Ir, Ru, Sb.	None
50 - 80%	Se.	None
80 - 100%	Ag, Co, Cs, I, Sr.	Ag, Co, Cs, I, Sr.

* Carrier present in all cases.

CHAPTER IV

SEPARATION OF SILVER BY ISOTOPIC EXCHANGE

The exchange of silver ion between a precipitate of silver chloride and a solution of silver nitrate reaches isotopic equilibrium very rapidly. Because of the low solubility of silver chloride, a very favorable ratio exists at equilibrium between the silver atoms in the precipitate and the silver atoms in the solution. For this reason if silver chloride is added to a solution containing only trace amounts of radioactive silver, a high percentage of this silver will have exchanged with the silver in the precipitate by the time equilibrium is attained. Use has been made of this fact to develop a rapid, high decontamination, single-step method for the separation of traces of radioactive silver from a solution containing other radioactive species.

LITERATURE REPORT

By use of the technique of isotopic exchange it is possible to shorten existing procedures for the separation of silver without sacrificing specificity or yield. Isotopic exchange involving silver halides and silver salts in solution has been studied by Langer (80, 81) and in one case

was applied to the determination of macro amounts of silver (82). This method has also been applied to the preparation of beta-ray sources (103), and the separation of I-131 (see Appendix B). A method for the separation of iodine on a base material of AgCl recently reported in the literature (5) is based upon elemental substitution of chloride for iodide by the silver chloride rather than isotopic exchange.

EXPERIMENTAL PROCEDURE

A silver chloride electrode of large surface area is made from an electrode of fifty-two mesh platinum gauze, 10 mm in diameter and 30 mm high. Ten mg of silver metal is deposited on the gauze by electrolysis for ten minutes at four volts from 10 ml of a solution 3 M in NaCN and 0.5 M in NaOH. A simple battery eliminator was used as a source of voltage for these experiments. The whitish surface of silver metal is rinsed with water, inserted in 10 ml of 0.05 M HCl and electrolyzed as the anode for five minutes at one volt, completely converting the silver metal to silver chloride. The electrode is washed with 8 M HNO_3 and is ready for use.

To separate silver by isotopic exchange, the silver chloride electrode is contacted with 10 ml of solution containing a very low concentration of radioactive silver.

The solution is stirred magnetically. The gauze is then removed from the solution and washed with 8 M HNO_3 for one minute. It is rinsed with acetone, placed in a lusteroid cone and counted in the scintillation well counter. If quantitative counting and recovery of the silver is desired, the silver chloride may be dissolved in ammonium hydroxide, acidified, and the silver chloride precipitate separated by centrifugation or filtration and mounted for counting.

The standard method referred to hereafter as the "quantitative procedure" for separating trace silver requires the use of 10 mg of silver as silver chloride on the electrode and fifteen-minute contact with the tracer solution 1 M in HNO_3 at room temperature. The silver chloride is then dissolved, transferred to a culture tube, reprecipitated, centrifuged, the supernate removed and the precipitate counted in the scintillation well counter.

RESULTS AND DISCUSSION

Yields of Silver:

Recovery of silver tracer in the quantitative procedure using 10 mg, 4 mg and 1 mg of silver as AgCl on the gauze is given in Table IX. For each determination 20,000-40,000 d/m of Ag-110 tracer was used. All samples were counted to a probable error of 0.4%. Errors quoted in the table are standard deviations.

TABLE IX. Yield of Radioactive Silver by Exchange with Silver Chloride

Determination	Weight of Silver on Gauze		
	10 mg (%)	4 mg (%)	1 mg (%)
1	99.5	99.0	93.0
2	98.5	99.1	94.3
3	99.8	98.8	94.7
4	99.8	99.0	94.9
5	99.8	98.8	95.8
6	99.2	99.0	
7	100.0	98.7	
Avg. and Std. Deviation	99.5±0.5	98.9±0.2	94.5±1.0

The silver chloride surface prepared in the manner described above is not ideal from the point of view of mechanical stability. During the course of the procedure a small amount of silver chloride is lost, apparently the result of chipping or chalking of the electrode surface in the contacting and washing periods. Experiments indicate that this chalking loss is of the order of 0.05 mg of silver chloride. Thus if only 1 mg of the chloride precipitate is used originally, this loss is an appreciable portion of the total while it is negligible with the 10 mg samples used routinely.

As noted in Table IX, however, reproducible results can be obtained with 4 mg and even 1 mg amounts of silver. Thus it is possible to use such small amounts if, because of self-absorption or other considerations, it is necessary to obtain a high specific activity.

Fifteen minutes contact time under ideal conditions is more than sufficient for complete removal of the radioactive silver from solution, as shown in a later section. Actually at 25°C the 97% removal point occurs at five minutes and over 99% is obtained in six to seven minutes. This range of five to seven minutes, however, is a very sensitive one as far as interfering ions and nonideal conditions are concerned. Thus the fifteen minute time was chosen to minimize the effect of small changes in acidity, stirring, and the character of the silver chloride deposit.

The full one-minute wash of the silver chloride gauze after exchange is necessary where decontamination from other activities by a factor of 10^6 is desired. Washing for a longer period of time had no effect. Eight M HNO_3 proved effective as the wash solution for all the contaminating activities used in this work. If other conditions warrant their use, even organic wash solutions could be applied.

It was found essential to dissolve the silver chloride surface and reprecipitate it for the quantitative recovery

of radioactive silver and its reduction to a reproducible form for counting. This was necessary because it was impossible to reproduce counts of the gauze to better than 2-3%.

When very small amounts of inactive silver are desired on the gauze, the lower limit appears to be dependent upon the manipulatory techniques in making the silver plate. This means first that the more uniform the deposit, the more area is made available for exchange for a given small amount of silver. Secondly, silver in sub-milligram amounts is perhaps dissolved or in any case lost from the electrode in the process of removing it from the cyanide solution. This is shown by Fig. 17 in which the time of electrolysis is plotted against the fraction of metallic silver removed on the platinum gauze from cyanide solution using the standard four-volt cell and varying the amount of silver in solution. Silver-110 was used as the tracer to follow the deposition in these experiments.

Silver iodide surfaces are also quite suitable for the exchange separation of tracer silver. The rate of exchange is not significantly different from that with silver chloride in that 97% is removed in six minutes and 99% in nine minutes with 10 mg silver as AgI. In some cases, the iodide may be considerably better for exchange purposes due to its

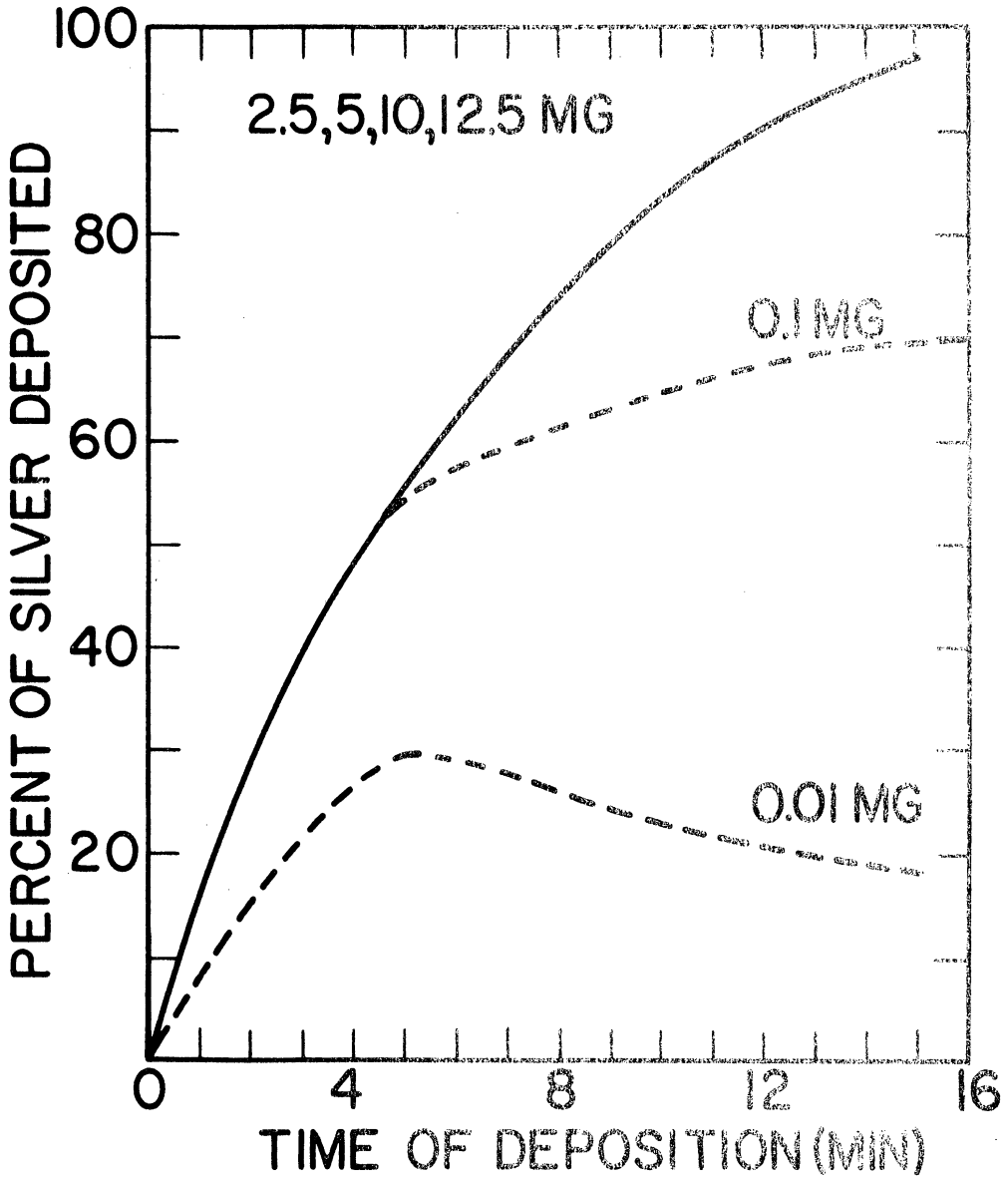


FIGURE 17. Influence of Total Amount of Silver Present on the Yield of Silver Deposited Electrolytically from a Cyanide Solution.

lower solubility, but further separations are often complicated by the presence of the active silver in the form of the difficultly soluble iodide. One method used in this laboratory to by-pass these difficulties was to electrolyze the "AgI gauze" containing the tracer silver as cathode in a neutral conducting solution such as sodium acetate for one minute at a voltage sufficient to decompose the silver iodide. The iodide ion goes into solution and free silver remains as a black deposit on the electrode. This free silver may then be dissolved in nitric acid.

Contamination:

The quantitative procedure was checked with eighteen different representative tracers to determine the levels of contamination which might be expected. Long-lived daughter activities of the tracers were also considered since no carriers were present and no attempt was made to separate parents from daughters. In these experiments the only radioactivity present was that of the element being studied. The contamination of the AgCl gauze by each element is given in Table X. All results are an average of at least two determinations.

TABLE X. Contamination of Silver by Other Activities in Isotopic Exchange Method

Activity	Percentage Carried on Gauze
Ba-140, La-140	0.00005
Ce-144, Pr-144	0.0001
Cs-134	0.0001
Co-60	0.001-0.0001
Cr-51	0.01
I-131	0.01-0.001
Ir-192	0.1-0.01
Ru-106, Rh-106	0.1
Sb-124	0.01
Se-75	0.1
Sn-113, In-113	0.1-0.01
Sr-90, Y-90	0.0001
Ta-182	0.01
Zr-95, Nb-95	0.01-0.001

To obtain more information concerning the mechanism of contamination of the AgCl gauze by foreign activities it is advantageous to arrange the data in the form of Table XI illustrating the similarity of those activities giving the largest contamination.

TABLE XI. Contamination Summary

	Percentage Carried	Elements
Group A	0.1-0.001	Cr, I, Ir, Ru-Rh, Sb, Se, Sn-In, Ta, Zr-Nb
Group B	0.001-0.00001	Ba-La, Ce-Pr, Co, Cs, Sr-Y

The elements in Group A which show some tendency to contaminate are those elements which in general, form very strong halide complexes with chloride and fluoride. (The iodide case is different in that about 10% of the tracer iodide is carried on a silver chloride gauze after a fifteen-minute contact. The 0.01% figure of Table X for iodine is obtained after treatment of the I-131 solution with HNO_3 and $KMnO_4$ to oxidize the iodide to iodate. The iodate is more soluble than the iodide and the chloride by factors of 10^4 and 10^2 respectively so it would not be expected to replace either of them on the gauze surface.) The contamination of the gauze by the complex formers may be caused by adsorption of chloride complexes of the individual elements on the silver chloride surface. Perhaps these complexes actually replace the silver chloride with insoluble compounds of the type Ag_2IrCl_6, similar to the slightly soluble Cs_2PtCl_6 or even $Ag_4Fe(CN)_6$.

If this explanation was correct, a less soluble surface such as AgBr should reduce contamination and a AgI surface reduce it even further. The degree of Ru-Rh contamination of AgBr and AgI surfaces was studied to determine whether this was the case. These results along with the corresponding AgCl data are shown in Table XII and indicate that the availability of silver ions or halide ions or both does indeed influence the contamination by this particular activity.

TABLE XII. Contamination of Silver Halide Surfaces by Ru-Rh Tracer

Surface Material	Percentage of Ru-Rh Activity Carried
AgCl	0.1
AgBr	0.04
AgI	0.003

In the cases of zirconium-niobium and tantalum activities, the contamination is probably due to hydrolytic effects such as radio-colloid formation or adsorption of basic salts.

Three more general determinations of decontamination were made with this procedure. First, the silver chloride gauze was contacted with a solution containing four-year-old fission products in unseparated form. After a fifteen-minute contact, 0.001% of the fission product activity was

found on the gauze. In the second determination, cadmium metal was bombarded with deuterons in the University of Michigan cyclotron, the target was dissolved in nitric and hydrofluoric acids and the silver produced by the (d, α) reaction removed by isotopic exchange. Due to the rapidity of the separation it was possible to detect a two-minute silver isotope which was never seen when precipitation separations were used. The decay was followed in the scintillation well counter as well as a four-pi beta proportional counter and the decay curves showed as clean a separation from cadmium and indium activities as had a series of precipitation separations requiring forty-five minutes. For the third determination a Pd-109 irradiated unit, containing about 300 mc of thirteen-hour Pd activity and 2-3 mc of Ag-111 with a 7.5 day half-life, was obtained from Oak Ridge National Laboratory. The palladium was dissolved in aqua regia, diluted to a 4 M HNO_3 solution and the silver removed by isotopic exchange. The AgCl gauze obtained weighed 10 mg and contained 2 mc of Ag-111 which gave a reading of three "r/hr" at six inches when monitored. Its decay was followed in the scintillation well counter and the GM end-window counter. The semilog plot of the decay was linear over more than five half-lives and no other activity was detected.

TABLE XIII. Effect of Interfering Substances upon Exchange of Silver with Silver Chloride

Specie	Concentration	Percentage Yield of Ag-110
HNO_3	1 M	99
	4	99
	8	93
	12	91
	16	85
HCl	0.05 M	98
	0.5	99
	1.0	98
	3	89
	6	41
H_2SO_4	1.5 M	97
	3	90
	6	79
HF	1.1 M	98
	3.3	98
	6.6	83
	13.2	57
	22	18
$HC_2H_3O_2$	99%	42

TABLE XIII. (cont.)

Specie	Concentration	Percentage Yield of Ag-110
$Al(NO_3)_3$	2 M	86
	1	95
	0.5	99
$Cu(NO_3)_2$	2 M	95
	1	97
	0.5	98
$Zn(NO_3)_2$	2 M	95
	1	97
$Fe(NO_3)_3$	2 M	94
	1	93
	0.5	95
$Bi(NO_3)_3$	2 M	93
	1	97
	0.5	100
$NaC_2H_3O_2$	2 M	95
	1	97
	0.5	98
C_2H_5OH	99%	36
	50	95
	25	98
$(CH_3)_2CO$	99%	70
	50	95
	25	98

Interferences:

A study was made of the effects of inactive species present in varying concentrations and forms in the solution from which tracer silver is to be removed. About 40,000 d/m of Ag-110 were added to solution containing the given concentration of interfering specie, the quantitative procedure used to remove the silver activity, and the yield determined. The species chosen were those which were considered to be of most interest, with the greatest likelihood of appearance in process solutions. The values for the silver tracer yield are given in Table XIII.

This study of the effect of inactive species in high concentrations revealed few specific interferences. The only substance which showed adverse effect on the yield of tracer silver was $Fe(NO_3)_3$. Yield values remained between 93 and 95% for this compound. For other salts and acids included in the study, the effect seems to be one of salt concentration rather than a specific effect of any individual ion or salt. In Table XIV the anionic molarity of each salt is listed opposite the concentration at which that salt first resulted in less than 97% yield of the tracer silver. In this work the AgCl gauzes were counted with an accompanying error of 2-3% as explained earlier.

TABLE XIV. Interference Summary

Specie	Anionic Molarity at Critical Concentration
HNO_3	4-8 M
HCl	1-3
H_2SO_4	1.5-3
HF	3-6
$Al(NO_3)_3$	3
$Bi(NO_3)_3$	3-6
$Cu(NO_3)_2$	4
$Zn(NO_3)_2$	4
$NaC_2H_3O_2$	2

It would appear from these data that a concentration of anion of greater than 2-8 M, depending upon whether it is nitrate, chloride, sulfate, fluoride or acetate, will result in losses of silver under the procedures used. A look at the mechanism of the separation may show the reason for this concentration effect. Silver chloride, as freshly precipitated, is well known for its ability to adsorb either positively or negatively charged ions, depending upon which is in excess. Use is made of this fact by the "Fajans" method for determination of end point in the titration of

chloride with silver nitrate, by use of dichlorofluorescein. To effect the isotopic exchange which is required for separation, high ionic mobility is required in the immediate vicinity of the silver chloride surface. A stable ionic layer adjacent to the exchanging surface might lower this mobility and cause loss of yield. Cognizance should be taken of this possibility before adoption of this method for highly salted solutions.

The effect of the two aqueous-organic systems studied indicates that minor concentrations of either acetone or ethyl alcohol will not prevent quantitative removal of silver tracer since they apparently have no specific de-activating effect on the AgCl surface. "AgCl gauzes" did, however, show lower activity toward exchange if they had been rinsed with acetone and dried prior to exchange.

Dependence of Yield on Time and Temperature:

If for any reason fifteen minutes is too long a contacting time, shorter periods can be used. Experimental determinations of the extent of exchange for a number of temperatures are plotted against time in Figure 18. As would be expected, the exchange is more rapid at the higher temperatures.

It can be seen from this temperature dependence that considerable time economies can be realized by raising the

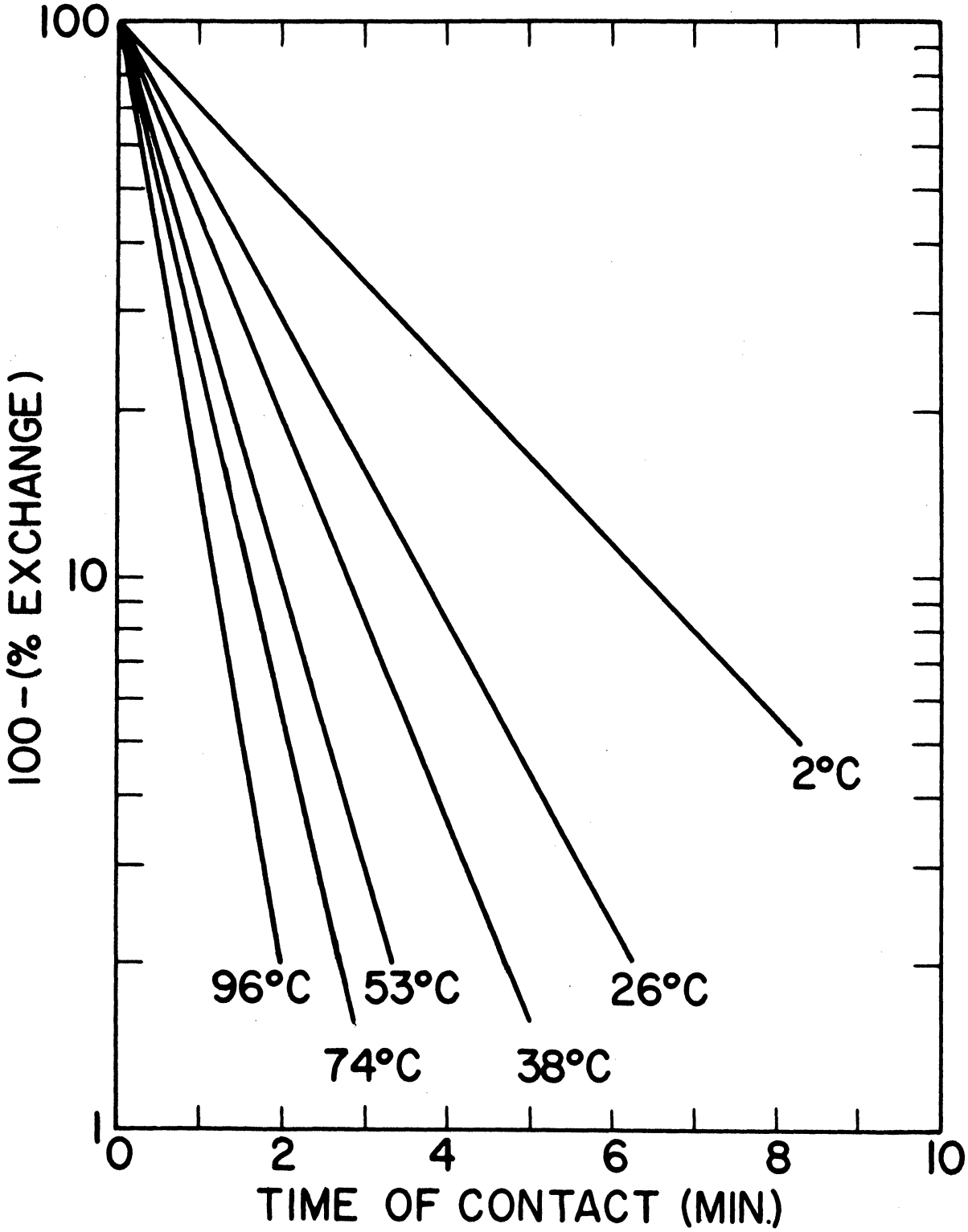


FIGURE 18. Temperature Dependence of Rate of Exchange of Silver Ion with Silver Chloride.

temperature of the contacting solutions. At 96°C, for example, over 95% of the tracer can be separated with only a two-minute contact, the 50% point being reached in twenty seconds. Use was made of this fact to separate silver with sufficient rapidity to measure the rate of decay of a two-minute isotope formed by the (d, α) reaction on cadmium.

Aging of Silver Chloride:

Most of the work described above was carried out with AgCl gauzes prepared within one hour of use. Because of the light sensitivity of AgCl and the fact that isotopic exchange must necessarily occur on the surface of the electrode, time studies were made of the stability of the AgCl surface. Gauzes containing 10 mg of silver as AgCl were prepared, stored in 8 M HNO_3 for varying periods of time and then used for a silver separation. The yields of the exchange determined under quantitative conditions are shown in Table XV. The period of study extended over one week.

TABLE XV. Effect of Aging of the AgCl upon the Efficiency of the Silver Exchange

Time of Aging in 8 M HNO_3	Yield in 15 Minute Contact
2 hrs	99.0
22 hrs	99.8
72 hrs	99.5
7 days	98.7

No attempt was made to keep the gauzes from direct light. However, the only light incident upon the gauzes during this period was that from two 100-watt fluorescent tubes about four feet above them. It appears that the aging of AgCl gauzes in 8 M HNO_3 for periods up to seven days has no effect on their activity with respect to the exchange separation of silver.

CHAPTER V

SILVER

Silver has been of great interest in the atomic energy program. It is one of the important short-lived fission products (16). A great deal of work has been done in characterizing its isotopes as well as in determining its yield from unusual nuclear reactions (48).

LITERATURE REPORT

The condition of the literature with respect to the analytical determination of silver is similar to that described for barium, strontium and calcium. Standard analytical works (52, 115, 125) have well defined the conditions for quantitative separations using standard analytical techniques and these methods have been characterized for yields and contamination by foreign material.

The field of radiochemical separations is not as well organized. Table XVI illustrates the variety of combinations of separation steps used by various workers in many practical applications. In the determination of which separations were to be evaluated an attempt was made not only to pick the most popular methods as indicated by the literature search but also to find new methods capable of high decontamination.

TABLE XVI. Techniques for the Radiochemical Separation of Silver

Ref.	HCl	H_2S	NaOH	HIO_3	HI	Chem. Red.	Elec. Dep.	Ion Exch.	Scav.	Iso. Exch.	Benzo-triazole
15											X
23	X	X							X		
26	X										
40	X	X							X		
45							X				
51								X			
53	X										
54	X	X							X		
55	X	X							X		
67	X				X						
70	X	X	X	X					X		
71	X				X	X					
75	X										
78	X										
88	X	X							X		
97	X	X							X		

TABLE XVI (CONTINUED)

Ref.	HCl	H_2S	NaOH	HIO_3	HI	Chem. Red.	Elec. Dep.	Ion Exch.	Scav.	Iso. Exch.	Benzo-triazole
98	X	X							X		
99	X								X		
100	X		X						X		
101	X	X							X		
103										X	
106	X	X							X		
107	X										
110	X										
114	X						X				
120	X					X					
127	X				X	X			X		
138	X										
145	X										
149	X										
151	X										
152	X						X				

EXPERIMENTAL PROGRAM

Two problems are encountered in radiochemical separations of silver that require, in general, different methods of solution. These are, first, the separation of silver from other metals and, second, its separation from halides, in particular iodine. The four separations that were studied in this laboratory included two methods designed to fulfill each of these requirements. The precipitation of the chloride and precipitation of the benzotriazole compound were studied as members of a possible series when used alternately for the separation of silver from other metals by precipitation. The first is carried out in acid solution and the second in an ammoniacal solution in which the first is soluble. For example, the precipitate of silver chloride may be dissolved by the addition of the ammoniacal versene solution. The addition of the benzotriazole reagent will then reprecipitate the silver for further decontamination.

For the decontamination of silver from halide activities the separations by electrodeposition and isotopic exchange were studied.

The precipitation by sulfide, hydroxide or reduction to the metal by chemical means were insufficiently specific for consideration. The precipitation of the iodide or iodate suffered from the same contaminants as the chloride

while possessing in both cases the added handicap that they may be quite difficult to dissolve, thereby hindering further chemical operations.

The washing of precipitates was not included in this study. It was found that much greater decontamination was afforded by dissolution and reprecipitation than was afforded by washing the already formed precipitate, although the steps required a similar period of time to perform.

PROCEDURES AND RESULTS

Silver chloride precipitation:

The conditions reported in the radiochemical literature for this separation were quite similar to those recommended in the standard analytical works. Precipitation is conducted in dilute nitric acid solution by the addition of hydrochloric acid followed by thorough stirring and a period of digestion. Occasionally the solution is heated to promote coagulation or a wetting agent such as aerosol is added to prevent the precipitate from sticking to the sides of the vessel. When centrifugation is used to collect the precipitate it was found that heating was unnecessary to accomplish complete precipitation and recovery. However, the addition of two drops of a 1% aerosol solution is recommended to prevent loss of precipitate on the sides of the cone.

One of the advantages of this particular separation is the ability to dissolve the precipitate in dilute ammonia and reprecipitate it by the addition of 1 M HNO_3. It was found that no yield was lost by this operation even in the absence of added chloride ion for the second precipitation.

The yield of silver and contamination of this precipitate caused by the presence of thirteen typical tracer activities was determined by use of the following procedure.

1. Add 10 mg carrier for the interfering element to a clean 15 ml centrifuge cone.
2. Add tracer for the interfering element and perform the operations necessary to obtain exchange.
3. Add 10 mg of silver carrier. Add two drops of 1% aerosol solution.
4. Dilute the solution to 10 ml with 1 M HNO_3. Stir.
5. Add 0.1 ml concentrated HCl with stirring and digest at room temperature for five minutes.
6. Centrifuge at top speed for five minutes.
7. Remove the supernate with a slurp tube and transfer the precipitate either to a planchet for drying, mounting and counting or to a glass culture tube to stopper and count.

The use of the above procedure resulted in the yield of silver and contamination by other elements as shown in Table XVII. All silver yield values are the result of

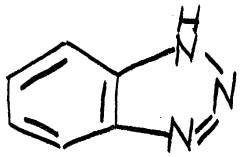
Table XVII. Contamination of Silver Separations by Other Activities

Tracer	Chloride (Carrier added)	Benzotriazole (carrier added)	Electrodeposition (carrier added)	Electrodeposition (carrier free)	Isotopic Exchange (carrier free)
Ag-110	99. ± 1.3	92. ± 5	99. ± 1.3	variable	99.5 ± 0.5
Ce-144, Pr-144	0.5	2.3	insol.	24.	0.0001
Co-60	0.5	2.5	insol.	0.05	0.001-0.0001
Cr-51	0.5	92.	0.4	2.1	0.01
Cs-134	0.5	2.4	0.001	0.004	0.0001
I-131	97.	98.	0.2	0.04	0.01-0.001
Ir-192	27.	29.	0.06	0.2-4.	0.1-0.01
Ru-106, Rh-106	2.5	2.5	0.03	0.1	0.1
Sb-124	22.	52.	26.	5.	0.01
Se-75	0.5	2.7	0.04	0.05	0.1
Sn-113, In-113m	0.8	77.	insol.	10.	0.1-0.01
Sr-90, Y-90	0.7	2.4	insol.	2.5	0.0001
Ta-182	0.6	87.	insol.	6.4	0.01
Zr-95, Nb-95	0.4	3.9	insol.	1.0	0.01-0.001

quadruplicate determinations and contamination values are the result of duplicate determinations.

Silver benzotriazole precipitation:

The use of benzotriazole as a reagent for silver was not wide until recent work (15) recommended the use of an ammoniacal versene precipitating solution. The reagent whose structural formula is as follows:



is not specific except in the presence of a large concentration of some complexing agent such as versene. According to Cheng (15), chloride, bromide, fluoride, sulfate, nitrate, phosphate and acetate do not interfere. Iodide forms a less soluble precipitate; cyanide and thiosulfate dissolve the precipitate and prevent precipitation. Copper (II), nickel (II), iron (III), cadmium (II), zinc (II) and cobalt (II) do not interfere, while tin, antimony, titanium and beryllium precipitate as hydrous oxides unless tartrate is present and the iron (II) versenate reduces silver to the metal. The conditions chosen for the radiochemical separation are quite close to those recommended by Cheng.

The following procedure was used for the determination of yields and contamination:

1. Add 10 mg carrier for the interfering element.
2. Add tracer for the interfering element and perform whatever operations are necessary to obtain exchange.
3. Add 10 mg silver carrier and increase the solution volume to 5 ml with water.
4. Add 5 ml of a solution that is 40% "versene" in ammonia. Stir.
5. Add 1 ml 2.5% benzotriazole solution, stir, digest at room temperature for five minutes.
6. Centrifuge at top speed for five minutes.
7. Remove the supernate by slurp tube and prepare the precipitate for counting.

The yield of silver and the contamination by other activities are shown in Table XVII.

Electrolytic separation of silver:

In spite of the extensive literature concerning the separation of silver by electrodeposition, it has found surprisingly few applications in radiochemical work (45, 114, 152). Although some references recommend the use of an acid solution for the deposition (152), it was found in this laboratory that the high current densities required to deposit 10 mg of silver in a fifteen-minute period from an acid solution resulted in a deposit which was completely

unsuitable for quantitative removal or washing. Thus the solution chosen was that used in the plating industry, with sufficient cyanide to hold in solution those elements which complex with cyanide and suffieient base to assure the solubility of amphoteric elements.

The following procedure was used.

1. Add 10 mg carrier for the interfering element to a test tube about 8 cm high and 15 mm in diameter.
2. Add tracer for the interfering element and perform the necessary operations to secure exchange. In the cases where macro amounts of the interfering element are not soluble in the solution do not add carrier.
3. Add 10 mg silver carrier.
4. Add 7 ml 3 M NaCN solution and 1 ml 5 M NaOH solution and mix thoroughly. Stir magnetically.
5. Insert the platinum gauze cathode and platinum wire anode and center them so they do not touch the walls of the tube or each other.
6. Connect the leads to a source of DC current and electrolyze at 4 v. for fifteen minutes. (It was determined experimentally that this voltage was required to deposit 10 mg silver quantitatively in fifteen minutes, see Figure 17). Stir rapidly.

7. Disconnect the leads when electrolysis is completed and remove the electrodes. Wash the cathode with a stream of water from a wash bottle for a period of one minute.
8. Dry the cathode with acetone and count in the scintillation well counter.

This procedure was found to give quantitative recovery when more than 2.5 mg of silver was present. With smaller amounts of silver the yield was reduced by dissolution of the silver by the plating bath during removal of the cathode.

Contamination of the silver separated in this manner was studied using the thirteen typical tracers. In cases where macro amounts of the contaminating elements were soluble in the plating solution the determinations were made twice, first with carrier and secondly without added carriers. When macro amounts of the contaminants were not soluble, the tracers were used without added carriers. Results of yield and contamination determinations are shown in Table XVII.

Silver separation by isotopic exchange:

The separation of radioactive silver by contacting the active solution with a gauze electrode upon which a surface of silver chloride had been deposited is described in Chapter IV.

The yield and contamination data areincluded in Table XVII for comparison purposes.

DISCUSSION OF RESULTS

Silver chloride precipitation:

As might be expected, the precipitation of silver chloride is a very good method of separating silver from many elements. The largest interference is antimony which is difficult to keep in solution during any change in acidity, particularly when a precipitate is being formed. Iodine is carried quantitatively as the iodide, in this case the major portion of the precipitate. The other interferences which stand out are those of the platinum group, iridium and ruthenium. This agrees with the fact that multiple precipitations are necessary to separate silver from irradiated palladium since a large portion of the palladium is carried on the early precipitations. It is also of note that these are two of the major interferences in the separation of silver by isotopic exchange, 0.1% of each being found as a contaminant. Possibly this contamination is the result of the formation of a compound between silver and the chloride complex of the platinum metals. The presence of zirconium slows considerably the precipitation of silver chloride and precipitation was not quite quantitative under these conditions.

The minimum contamination of a precipitate by a dissimilar material when precipitation is carried out rapidly in a volume of 10 to 15 ml appears to be of the order of 0.5%. This probably is due to the adherence of supernate to the side of the centrifuge cone and inclusion in the precipitate. This minimum is also found in the cases of barium chromate and barium sulfate, two very compact precipitates described in Chapter II. It must be kept in mind that if this is a true minimum, it leads to a maximum decontamination factor of 200 for radiochemical separations by precipitation of 10 mg of carrier under these conditions.

The precipitation of silver chloride is a very useful step as the first of a series for the separation of silver. It may be dissolved in ammonia and reprecipitated by acidification as described earlier. It may be dissolved in cyanide and followed by electrodeposition or it may be dissolved in ammonia and followed by precipitation of the silver-benzotriazole compound from versene solution and thus separated from chloride and bromide.

Silver benzotriazole precipitation:

This was chosen as a separation which would accomplish the removal of chloride and bromide. It also illustrates the use of an organic precipitant giving a bulky precipitate. A chelating agent is used to prevent the precipitation of

normally insoluble hydrous oxides. The separation from chloride and bromide is demonstrated by the fact that one wash with water of the silver benzotriazole precipitate is sufficient to produce a solid which upon dissolution with dilute nitric acid gives a clear solution, even when the original precipitation was made from 0.1 N chloride solution.

The limit of the specificity of this reaction is illustrated by the fact that large quantities of antimony, chromium, iodine, iridium, tantalum and tin are carried with it. However, a separation is possible from cerium, cesium, cobalt, ruthenium, selenium, strontium and zirconium. These results substantiate those reported by Cheng (15). The mechanical limit of decontamination by the precipitation of this bulky organic precipitant under these conditions appears to be in the region of 2.5%. This could not be due to increased adherence of the liquid to the side of the cone and must be considered an occlusion phenomenon. It would also indicate that more efficient use of time would be made by dissolution and reprecipitation rather than by merely washing the precipitate already formed. Washing the benzotriazole precipitate was found to reduce the contamination by a factor of two while dissolution and reprecipitation

reduced it by a factor of forty for a contaminant such as cesium. Attempts were made to dissolve the precipitate in an organic solvent which was immiscible with water and thus allow extraction instead of precipitation. However, no common solvent was found which was capable of dissolving the precipitate. Those which showed promise on the basis of the literature survey were either miscible with water or reactive with it.

The lack of quantitative recovery of the silver by this method indicated in Table XVII is due to slowness of precipitation and coagulation in the highly salted solution. The bulky character of the precipitate caused it to adhere to the sides of the cone. Every effort, however, was made to transfer this portion as well as that in the cone apex to the counting sample.

Electrolytic separation of silver:

Unlike precipitation separations the electrolytic separation of silver can take advantage of the absence of macro amounts of the radioactive elements normally encountered in radiochemical work. To illustrate this the contamination determinations were carried out both with carrier and in the absence of added carrier. In some cases macro amounts of the tracer elements were not soluble in the alkaline cyanide solution. Macro amounts

of antimony caused a competing electrode reaction and resulted in the inclusion of 26% of the antimony present. In the cases where macro amounts of the contaminating elements were soluble, excluding the case of antimony, decontamination was quite good. In the cases where macro amounts of the tracer elements were insoluble contamination varied from 0.05% for cobalt to 24% for cerium.

The importance of the method of electrodeposition lies in its use for separation of silver from halides, particularly iodine. As is shown in Table XVII this contamination varied from 0.2 to 0.04% depending upon the amount present. Only the method of isotopic exchange produces better decontamination. It, however, requires prior oxidation of the iodide to iodate which is not required for electrodeposition. In case a precipitate of silver iodide is presented for separation, it may be dissolved in the cyanide plating solution and the silver may be deposited readily. Electrodeposition may be coupled with the method of isotopic exchange to produce a decontamination factor of 10^7 from iodine by a procedure which may be completed in thirty minutes. An illustration of the application of this procedure is shown in Table XVIII. Use of this procedure will give quantitative recovery of silver and decontaminate it from other activities by factors of from 10^4 to 10^{10}.

TABLE XVIII. Sample Procedure for the Separation of Silver from Other Activities

Isotopic exchange with supported AgCl — Yield 100%

1. Plate 10 mg Ag on platinum gauze.
2. Electrolyze as anode in HCl to change to AgCl.
3. Contact with silver tracer solution for 15 min. at room temperature, stir during contact.
4. Wash gauze with 8 M HNO_3 for 1 min., rinse with water.

Decontamination factors:

Sb	10^4
Ce	10^6
Cs	10^6
Cr	10^4
Co	10^5
I	10^4
Ir	10^3
Ru	10^3
Se	10^3
Sr	10^6
Sn	10^3
Ta	10^4
Zr	10^4

↓

Electrodeposition of silver — Yield 100%

5. Dissolve the silver chloride in 3 M NaCN, 0.5 M NaOH plating solution.
6. Electroplate at 4 v. for 15 min.
7. Wash electrode with water, acetone and dry.

Decontamination factors:

Sb	2×10^5
Ce	4×10^6
Cs	10^{10}
Cr	5×10^5
Co	2×10^8
I	2×10^7
Ir	10^5
Ru	10^6
Se	2×10^6
Sr	4×10^7
Sn	10^4
Ta	2×10^5
Zr	10^6

↓

Weigh gauze to determine yield, prepare for counting.

CHAPTER VI

INDIUM

The methods for the separation and determination of indium for analytical purposes generally involve two different precipitations. The first is the precipitation of the hydrous oxide from a neutral of slightly alkaline solution. This is accomplished by the addition of ammonium hydroxide to the solution containing the soluble indium salt (52, 153). The method is restricted to solutions which do not contain elements which also form hydrous oxides under these conditions or which are otherwise unstable in the precipitating solution. The second method involves the precipitation of the sulfide in a neutral or slightly acid solution. Users of this technique usually suggest the presence of some weak acid such as acetic to increase the specificity of the separation. This method also suffers from many interferences from metals which precipitate as sulfides in acid or neutral solution. To circumvent these interferences it is sometimes suggested that a prior precipitation of a metal sulfide be conducted in a solution with an acidity greater than one molar to remove the less soluble sulfides. This prior precipitation must often be repeated after dissolution of the

sulfide to allow a greater yield of the indium to be made in the subsequent precipitation (52, 153). The work of Lundell and Hoffman (89) describes the action of these separations on other elements for purposes of quantitative analytical determination.

LITERATURE REPORT

The radiochemical literature suggests many modifications of both the hydrous oxide (2, 27, 66, 67, 70, 91, 96, 128) and the sulfide precipitations (2, 66, 70, 91, 96). Two other separation methods are found in the radiochemical literature which have found little application in quantitative analytical work at the present time. These are extraction of the bromide from a strong hydrobromic acid solution with either diisopropyl ether (59) or with diethyl ether (70).

As was mentioned earlier, the precipitation of the hydrous oxide lacks sufficient specificity to be of general applicability. Also it was felt that an evaluation of this method would add little to the work already completed and described in Chapter II concerning the action of the precipitation of hydrous oxides for the purposes of scavenging. The precipitation of the sulfide can be made in a sufficiently acid solution to prevent the interference of easily hydrolyzed elements and those which form sulfides in a neutral or alkaline solution. The sulfide precipitation

may also be useful for the determination of the yield of indium at the end of a series of separation steps and for reducing the volume occupied by the active material for counting purposes. The possibility of causing the precipitation by the "in situ" production of sulfide ion by the hydrolysis of thioacetamide and thus increase the specificity of the separation, contributed to the decision to evaluate it as a method for the separation of indium for radiochemical purposes. The relatively new methods of anion exchange and solvent extraction, being capable of high decontamination and high specificity, were also chosen for evaluation.

While a number of radiochemical procedures recommend the use of a sulfide precipitation step for indium, the most complete study made of its precipitation from slightly acid solution was that of Jeffreys and Swift (63). This work was used as a guide for the development of a method for radiochemical separation of indium and its evaluation.

Methods reported for the separation of indium by solvent extraction concern the solubility of either an inorganic or organic salt of indium in an organic solvent. The soluble inorganic salt is the bromide and the organic phases in which it is soluble are diisopropyl and diethyl ether. The soluble organic salts of indium are either those formed

with acetylacetone or 8-hydroxyquinoline (96, 135). The extraction of the acetylacetone chelate by acetylacetone is strongly dependent upon acid concentration and suffers from a large number of interferences. General information may be found in the work of Steinbach and Freiser (135) and the specific application to indium in a later reference by these authors (134). The extraction of the 8-hydroxyquinoline salt of indium with chloroform was used with cyclotron produced activities and is reported by Meinke (96). The extraction of indium bromide by various ethers has been studied by several investigators (10, 59, 147, 148) and their work has been taken as a basis for the development of a method for the separation of indium and the evaluation of this method.

The separation of indium from other elements by anion exchange was described qualitatively by Hicks, Stevenson Gilbert and Hutchin (51) and quantitative work is given by Krause and his coworkers (77). Krause has also described the general applicability of anion exchange to hydrochloric acid solutions of a large number of other elements (76).

EXPERIMENTAL PROCEDURES AND RESULTS

Precipitation by Hydrogen Sulfide:

Preliminary work on the sulfide precipitation included an investigation of the applicability of sulfide generation by the thermal decomposition of thioacetamide. This reagent is available in a stabilized form from the Daigger Co. under the trade name of "Sulfi-Down". Various procedures for its use have been reported in the literature, using concentrations from 2 to 13% by weight for an aqueous solution of the reagent. Flaschka and Jakobljevich (34) report that a 2% solution was used in the rapid quantitative separation of copper, molybdenum, arsenic, antimony and bismuth. Lehrman and Schneider (85) used a 13% or saturated solution of thioacetamide for the separation of the copper-tin group for qualitative analysis. A 5% solution was used for the purposes of this investigation. A solution containing 10 mg of indium as the chloride in a sulfate-bisulfate buffer of pH 3.0 in a 10 ml volume was heated to 90 to 95° in a water bath and 2 ml of the 5% solution of thioacetamide was added. The solution was allowed to digest for fifteen minutes at this temperature. Visually the precipitation was very slow and did not occur at the same time in samples which were treated in an identical manner. The indium yield in the above procedure for four samples varied from 21 to 60%. This indicated that a much

longer digestion time would be required to obtain a satisfactory yield with sufficient reproducibility to be of value in radiochemical work, and the experiments with thioacetamide were discontinued.

The use of buffer solutions for the precipitation of indium sulfide from acid solutions was thoroughly studied by Jeffreys and Swift (63). Their recommendation for the quantitative precipitation of indium sulfide with hydrogen sulfide was the use of a sulfate-bisulfate buffer of pH 1.6 to 1.8. The total sulfate concentration in the precipitating solution was 0.35 M. These conditions were found by Jeffreys and Swift to be superior to the use of organic acids for buffering purposes. The separation from nickel, cobalt, iron, and alkali and alkaline earth metals was found satisfactory when the precipitation was carried out over a period of time and the precipitate allowed to digest in the hot precipitating solution.

For radiochemical work it was necessary for the precipitation to be conducted in a solution more concentrated with respect to indium and sulfide than that used in standard analytical work, in a shorter time, and with little or no time for digestion. To investigate the effect of these changes in the conditions and to develop an optimum procedure for the separation of indium, buffers of pH 1, 2, and 3 were

prepared similar to these of Jeffreys and Swift. The yield of indium was determined under radiochemical conditions using solutions buffered at these acid values. Cobalt was taken as an element representative of those metals that precipitate in a solution slightly more basic than indium and its interference at these three pH values was investigated.

The following procedure was used:

1. Add 10 mg indium carrier and indium tracer to a 15 ml centrifuge cone. Mix thoroughly to effect exchange.
2. Add 10 mg amounts of carrier of the contaminating element under study and tracer for this element, e.g. Co or Sr, Sn, Ag, etc. Take the steps necessary to secure exchange. In cases where the yield of indium was not to be determined, the indium tracer was not used.
3. Dilute the solution to 5 ml and adjust the acidity roughly to pH 1, 2 or 3 with sodium hydroxide or dilute hydrochloric acid.
4. Add 5 ml of sulfate-bisulfate buffer of the desired pH. Stir thoroughly. Heat the solution to 90 to 95° on a water bath.
5. Pass hydrogen sulfide gas through the solution at a rate which is rapid but not so rapid as to cause

loss of material by spattering. Allow this introduction of hydrogen sulfide to continue for one minute.

6. Allow the solutions to remain in the water bath for digestion of the precipitate for five minutes with occasional stirring.
7. Centrifuge at top speed for five minutes.
8. Remove the supernate with a slurp tube.
9. Transfer the precipitate by pipet to a glass culture tube for counting in the scintillation well counter or to a planchet to dry, mount and count in the geiger counter.

Table XIX shows the results of this procedure for indium yield and cobalt contamination at pH 1, 2, and 3. pH 1 was chosen for evaluation with the fourteen representative radioactive tracers due to the greater specificity obtained at this pH. The results of this evaluation are presented in Table XX.

TABLE XIX. Variation of Yield of Indium and Cobalt with Acid Concentration for Sulfide Precipitation.

Element	Indium	Cobalt
pH	Percentage carried with the indium	
3.0	98.1±1.1	6.2
2.0	98.8±1.8	4.1
1.0	91.8±2.5	1.7

Note: Limits are "standard deviation" of quadruplicate determinations.

Solvent Extraction of Indium Bromide:

Preliminary work on the extraction of indium bromide involved investigation of the methods available for contacting the phases. The possible use of a method of this type with high levels of activity requires the existence of a contacting vessel which will allow equilibrium to be reached quickly with little chance of losing material which might contaminate the operator or his working area. The use of a standard separatory funnel with a stopper and either hand or mechanical shaking results in an operator hazard due to the extensive manipulations required. Also, the use of an ethereal organic phase tends to cause pressure in the flask and increases the

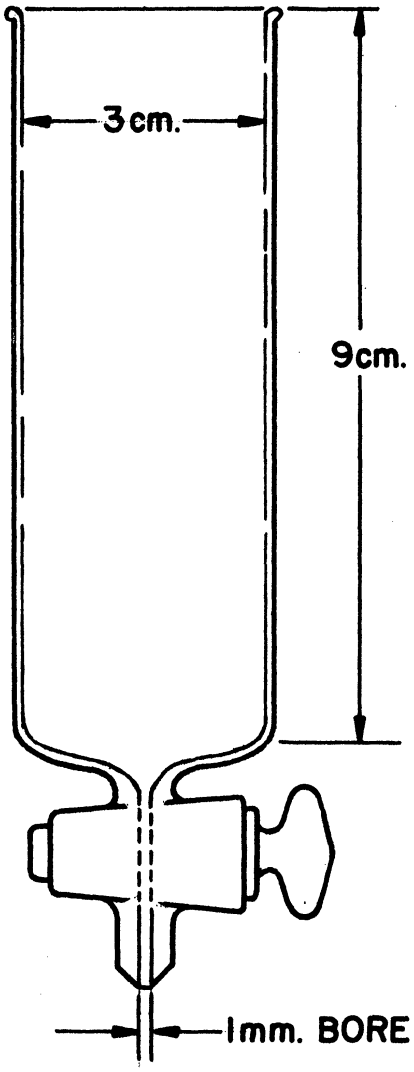
TABLE XX. Yield and Contamination Data for Indium Separation Methods.

Method	H_2S Pptn.	Extraction	Ion Exchange
Element	Percentage carried with the indium		
Antimony	96.	2.2, 0.25*	2.0
Cerium	20-70 (var.)	0.01	0.13
Cesium	2.0	0.015	0.11
Chromium	1.0	0.012	0.6
Cobalt	1.7	0.009	43.
Indium	91.8±2.5	93.0±2.0	95.5±1.2
Iodine	4.3	6.7, 6.8*	1.1
Iridium	4.9	0.017	3.7
Ruthenium	96.	0.015	22.
Selenium	80.	23., 7.*	0.3
Silver	100.	0.055	25.
Strontium	100.	0.006	0.1
Tantalum	1.6	0.08	6.2
Tin	97.	48., 40.*	0.4
Zirconium-Niobium	8.7	0.018	31.

* These values were obtained with a procedure employing two 4.5 M HBr washes.

possibility of loss of material when the stopper is removed. The design of standard separatory funnels prevents the high degree of phase separation which is required for the high decontamination in radiochemical work. Drops of aqueous solution remain on the sloping sides of the vessel and in the wide bore of the outlet tube. A technique reported by Meinke (95) utilizes the inability of an organic phase to pass through a filter paper membrane which has been wetted with an aqueous solution to achieve rapid separation of phases. This method is very rapid and results in complete retention of the organic phase in the extraction flask, but contamination caused by retention of activity in the paper membrane prevented its use in this case.

To circumvent the difficulties in standard separatory funnels, an open top cylindrical funnel shown in Figure 19 was used. The bottom of the cylinder was tapered very sharply (in about 1 cm of length) to a small bore, heavy-wall, ground-glass stopcock. The outlet of this stopcock was about 1 cm long and ground to a 45° taper to the tip. The high perpendicular walls of this funnel allowed rapid stirring with no loss of material and rapid phase separation with a minimum of clinging to the walls by the aqueous phase which was the heavier of the two. It was necessary to watch the outflow very closely due to the sharp taper of



EXTRACTION FUNNEL
(PYREX BRAND GLASS)

FIGURE 19.

the bottom of the funnel, but the small volume of the capillary stopcock permitted excellent phase separation with a minimum of loss of the organic phase. The drops of solution fell clean from the ground tip. The volume of solution used in these experiments extended about 1/2 the heighth of the cylinder. Phase equilibrium was reached in between one and two minutes of rapid stirring.

The composition of the phases was the next point of investigation once the contacting equipment had been decided upon. The work of Hudgens and Nelson (59) concerning the radiochemical separation of indium by solvent extraction recommended the use of diisopropyl ether which had been specially purified as the organic phase. Their work was based upon the investigations of Wada and Ishii (147, 148) with diethyl ether. For the extraction steps they suggested 4.5 M hydrobromic acid. The removal of indium from the organic phase was accomplished by contacting with a 6 M hydrochloric acid solution.

It was felt, however, that to encourage general acceptance of a solvent extraction procedure for routine use, the reagents should be commercially available in a form of sufficient purity to obtain satisfactory results. Thus an attempt was made to reproduce the work of Hudgens and Nelson using reagent grade diisopropyl ether commercially

available from the Eastman Co. It was found that without further purification it was impossible to obtain distribution coefficients greater than five by use of 4.5 M hydrobromic acid and 10 mg of indium carrier. This distribution coefficient was thought to be insufficient since one wash of the organic phase would reduce the possible yield to about 60%. It was then decided to investigate the use of diethyl ether because of the purity with which it is readily available and because of the considerably higher distribution coefficients reported by Wada and Ishii (147, 148) and by Bock and his coworkers (10). The disadvantages of diethyl ether are its higher volatility and higher solubility in the aqueous phase. The use of 10 mg of indium in a system composed of diethyl ether as the organic phase and 4.5 M hydrobromic acid as the aqueous phase resulted in a distribution coefficient of sixty-five which was sufficient to give high yields.

The use of solvent extraction usually enables one to perform separations on carrier free amounts of radioisotopes. Carrier free operation is not practical in precipitation separations due to adsorption and coprecipitation effects. To take advantage of this quality of the solvent extraction technique the study of the separation of indium was conducted without adding carrier amounts of the interfering elements. Indium carrier was added prior to extraction to facilitate

the determination of yield and subsequent manipulations, which may be of a precipitation type, for further purification and preparation of counting samples.

The following procedure was used to determine the yield of indium and the contamination by the fourteen representative tracer elements.

1. Prepare the solution containing 10 mg of indium and tracer for the contaminating element. Make up to 10 ml with a final concentration of 4.5 M hydrobromic acid.
2. Contact this solution with 30 ml of diethyl ether in the cylindrical separatory funnel with rapid stirring for a period of two minutes.
3. Allow the phases to separate and remove the lower aqueous phase, taking care that a very small amount of organic phase is also removed. (This was done by allowing the aqueous phase to drain from the vessel and one drop of organic phase to appear at the tip of the outlet tube.)
4. Add 10 ml 4.5 M hydrobromic acid solution to the organic solution in the vessel and stir rapidly for two minutes. Separate the phases as described in step (3).
5. Repeat step (4) if greater decontamination is required. (See Table XX.)

6. Add 10 ml of 6 M hydrochloric acid to the organic solution in the extraction vessel and stir rapidly for two minutes.
7. Separate the phases and withdraw the aqueous phase but in this case allow one drop of aqueous solution to remain in the tip of the outlet tube.
8. Take a portion of this aqueous solution and transfer to a culture tube for counting in the scintillation well counter.

The results of the evaluation of this procedure for the determination of indium yield and contamination by the fourteen representative tracer elements are shown in Table XX. Yields are the average of quadruplicate determinations. Contamination data are the average of duplicate determinations.

Separation by Anion Exchange:

The emphasis in the development of a method for the separation of indium by anion exchange was placed upon the requirements that the method be simple, require little unusual equipment, be generally applicable and reproducible. The two most frequently used sources of information on anion exchange were the papers of Krause (76, 77) and of Hicks and coworkers (51). The data of Krause are based upon equilibrium conditions in the columns, and the treatment of the data was very thorough. The general method of Kraus

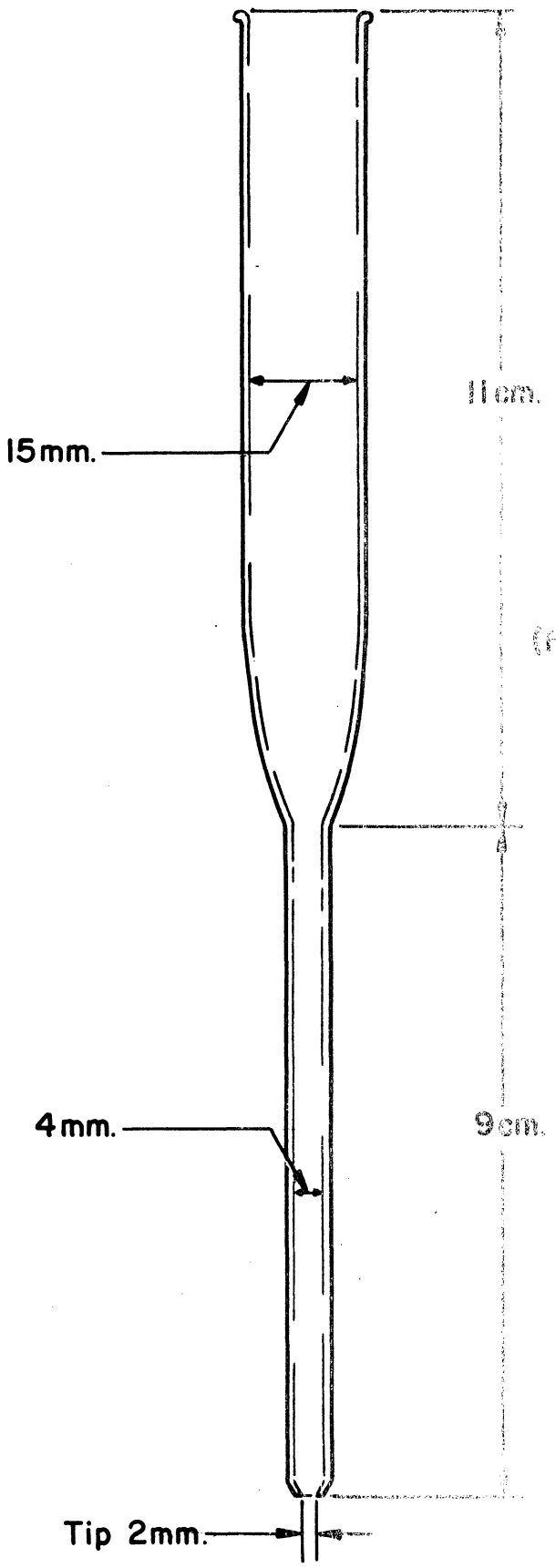


FIGURE 20.

ION EXCHANGE COLUMN

(PYREX BRAND GLASS)

was felt, however, to lack applicability in the case under study due to the low flow rate. It was thought that the method should be sufficiently short to be completed in one hour. This required use of a flow rate closely approximating that used by Hicks. The column itself, shown in Figure 20, was also similar to that used by Hicks. This allowed a column of resin of 8 to 9 cm in length with a sufficiently large capacity for general radiochemical work. The flow rate obtained was about 1 ml in three minutes. This was affected greatly by the method of packing the column and the height of the resin. Very reproducible flow rates (within one percent) were obtained when the column was filled by gravity with the resin in the 6 M hydrochloric acid used as eluant. A linear variation of flow rate with column height was found in the range from 4 to 9 cm of resin. The height of 8.5 cm gave the desired flow rate of 1 ml every three minutes. This resulted in the passage of 20 ml of eluant in one hour which was sufficient to remove a major portion of the indium. The resin used was Dowex 2 with 8% cross-linking, 200 to 400 mesh, which had been processed by the Bio-Rad Laboratories of Berkeley, California, and was supplied in the chloride form. This resin was stored in 6 M hydrochloric acid until used. The elution curves for the contaminating elements

as well as for indium were very reproducible as will be shown by the yield data.

An important variable for the radiochemist to keep in mind is the method of addition of the sample to the column. The volume of the sample should be kept as small as possible. From 0.05 to 0.5 ml of solution was used for these experiments. The sample must be added directly to the top of the resin and not allowed to contaminate the reservoir above the resin. It must then be allowed to seep into the resin bed until the solution level reaches the top of the resin. No air is allowed within the resin bed. If the sample is "pushed" into the resin bed by air or otherwise forced into the resin it will spread itself over the entire column and the separation will be negated. This is particularly important with the small sized column used in this work. The eluant is then allowed to fall dropwise on the top of the resin bed with no more than 1 ml allowed in the reservior immediately above the resin. This prevents contamination of a large volume of eluant and subsequent spreading of the elution band obtained. These manipulatory factors were found to be of great importance with the rapid flow rate and low distribution coefficients used in this work.

Several methods of elution were possible. The work of Hicks showed the effect of changing the concentration of the

eluant to remove the elements selectively while the work of Krause is based upon constant concentration of eluant. For the separation of an element with a distribution coefficient which increases markedly with acid concentration, the method of Hicks would be of value. However, indium was shown by Krause to have a distribution coefficient which increases to a maximum at about 3 M hydrochloric acid and is reduced slowly by increasing the acid concentration to 12 M. The maximum distribution coefficient is about ten. This is sufficient to allow a separation from those elements which are not adsorbed and those which are strongly adsorbed if care is taken in the manipulations. The concentration of acid was taken at 6 M because of the large number of elements which experienced strong adsorption at this concentration, while the distribution coefficient of indium was still sufficiently high to effect a separation from slightly adsorbed elements. The procedure used for the separation of indium was the following.

1. Add the sample in 6 M hydrochloric acid to the top of an 8.5 cm column of resin in the manner previously described and allow it to seep into the resin bed.
2. Elute with 6 M hydrochloric acid using a flow rate of 1 ml in three minutes and saving the 6 through

20 ml portion which contains a majority of the indium.

The yield of indium obtained by this procedure is shown in Table XX. The limit is the standard deviation of quadruplicate determinations. The above procedure was also used to determine the contamination of the indium which would be caused by the presence of any of a number of representative tracer elements and elution curves were obtained from 0 to 20 ml of eluant in which the activity of each milliliter was measured. The percentage of the activity of each tracer which was found in the 6 to 20 ml portion of the eluant is shown in Table XX. No inactive carriers for either indium or the contaminating elements were added.

DISCUSSION OF RESULTS

Precipitation by Hydrogen Sulfide:

The yield of indium by sulfide precipitation from a solution with pH 2 or 3 is over 98%. The yield at a pH 1 appears somewhat lower. This may be due to the characteristics of the precipitate at the lower pH value. The precipitate which forms in a solution of pH 2 or 3 is yellow-orange and begins to form immediately upon addition of hydrogen sulfide. The precipitate which forms in a solution of pH 1 is red-orange and much more dense and crystalline than the yellow-orange variety. It begins to form after

about 0.3 minutes of bubbling hydrogen sulfide through the solution. When centrifuged it fills only one/third the volume of the yellow-orange precipitate. It also shows more tendency to adhere to the sides of the tube thereby contributing to the lower yield and is more difficult to dissolve in acid than the sulfide formed at the higher pH. The more crystalline nature probably contributes to the lower contamination by other activities, as shown in Table XIX for cobalt. For this reason pH 1 was the condition chosen for the contamination study as the optimum one for the precipitation of indium sulfide. A reference to a similar form of indium sulfide which was formed by heating the normal sulfide in an acid solution was found in the work of Bottger (11).

No separation is found or is to be expected for the many metals such as antimony, silver, and tin that precipitate as sulfides in more acid solution than pH 1. The variable high contamination by cerium is unusual and the reason for it is not obvious. It may be the result of the precipitation of $Ce_2(SO_4)_3 \cdot 2Na_2SO_4 \cdot 2H_2O$ from the buffered solution. In dilute acid it is possible to precipitate cerium completely in this manner by the addition of sodium sulfate to a solution of a cerous salt (143). Ruthenium is slow to precipitate but finally forms the brown-black sulfide

resulting in almost quantitative precipitation. The case of iridium is rather interesting in that the color of the solution is changed from brown to colorless with the addition of hydrogen sulfide but the conditions are not right for the further precipitation of the sulfide. Further passage of hydrogen sulfide through the solution would probably result in a larger portion of the iridium being carried due to the precipitation of iridium(III) sulfide. Selenium is carried following reduction to the elemental state with the hydrogen sulfide. Strontium is carried as a result of the insolubility of the sulfate and coprecipitation with the sulfide of indium.

To sum up, the sulfide precipitation has very limited applicability as a separation method for indium. The cases where it is applicable are separations from alkali metals, the less noble transition metals, halides and metals of the zirconium and tantalum group. It is also a high yield method for reducing the indium to a form for counting or the determination of the yield by weighing. (In most cases the sulfide is dissolved and the hydroxide precipitated and ignited to the oxide (89).)

Solvent Extraction of Indium Bromide:

The high distribution coefficient obtained with diethyl ether under the conditions described allows one to obtain

yields of over 90%. The losses of indium experienced with this procedure are due to mechanical rather than chemical effects. The method of separation of phases requires a small loss of indium in each contact. This is generally preferable to a lower decontamination. The distribution factor is so high that very little loss is experienced by a second wash with 4.5 M hydrobromic acid solution. The distribution factor in the final extraction step with 6 M hydrochloric acid was found to be less than 0.005 allowing complete recovery of the indium present in the organic phase. A hydrochloric acid solution was used at this point to prevent the contamination by macro amounts of iron often found as either backing material in bombardment procedures or as a contaminant or reagent in process solutions. It also lowers the contamination by antimony and tin since they are appreciably soluble in the organic phase in this extraction step.

From the contamination data it is seen that the best decontamination possible by this procedure results in 0.01% carrying of the contaminating material. This indicates a decontamination factor of 100 for each separation step. There are two separation steps in the standard procedure given; they are the first extractive contact and the hydrobromic acid wash. The addition of a second hydrobromic acid

wash will increase the decontamination factor by an amount dependent upon the distribution factor for the element being considered. For the elements cerium, cesium, chromium, cobalt, iridium, ruthenium, strontium, and zirconium, which are not appreciably extracted, this increase will be a factor of about 100. The values in Table XX for these elements were obtained with only one wash. For those elements which are appreciably extracted, the value of a second wash will depend upon their distribution factor. For antimony and selenium the second wash was useful, while for iodine and tin little could be gained by it. The data on silver and tantalum indicate greater contamination than the minimum for the method. Silver bromide is soluble in the 4.5 M hydrobromic acid solution.

The solvent extraction method used here is an example of practical use of the technique applicable to routine laboratory operation. Decontamination factors of 10^4 are possible with a procedure requiring about fifteen minutes. By the addition of another wash step requiring about five minutes the decontamination factor can be increased to 10^6. The method is neat, rapid, gives a high yield of the desired constituent, and may be run with materials readily available in sufficient purity to realize the full capability of the method. It requires no technique which

is not possessed by the average laboratory technician.

Separation by Anion Exchange:

One of the prerequisits of any analytical method, whether it be for radiochemical or standard analytical purposes, is that it be reproducible. Prior to the investigation of this anion exchange method there was considerable doubt that it would fulfill this requirement. The elution curve for indium, however, was found to be highly reproducible. An example is shown in Figure 21. As shown in Table XX a standard deviation of 1.2% for four runs, for the volume between 6 and 20 ml, was found. The yield was found to be high enough for radiochemical work although it could be increased by taking a larger portion of the eluant. In most cases this would result in an increase in contamination.

The elements which were studied for contamination purposes were found to fall quite naturally into three groups: first, those which were so slightly adsorbed to be eluted almost entirely before the indium began to appear; second, those elements whose elution curves overlap that of indium to a large extent; and third, those elements which had not yet appeared to any significant degree at the 20 ml point in the elution.

The elements of the first group were cerium, cesium, chromium, iridium, ruthenium, selenium and strontium.

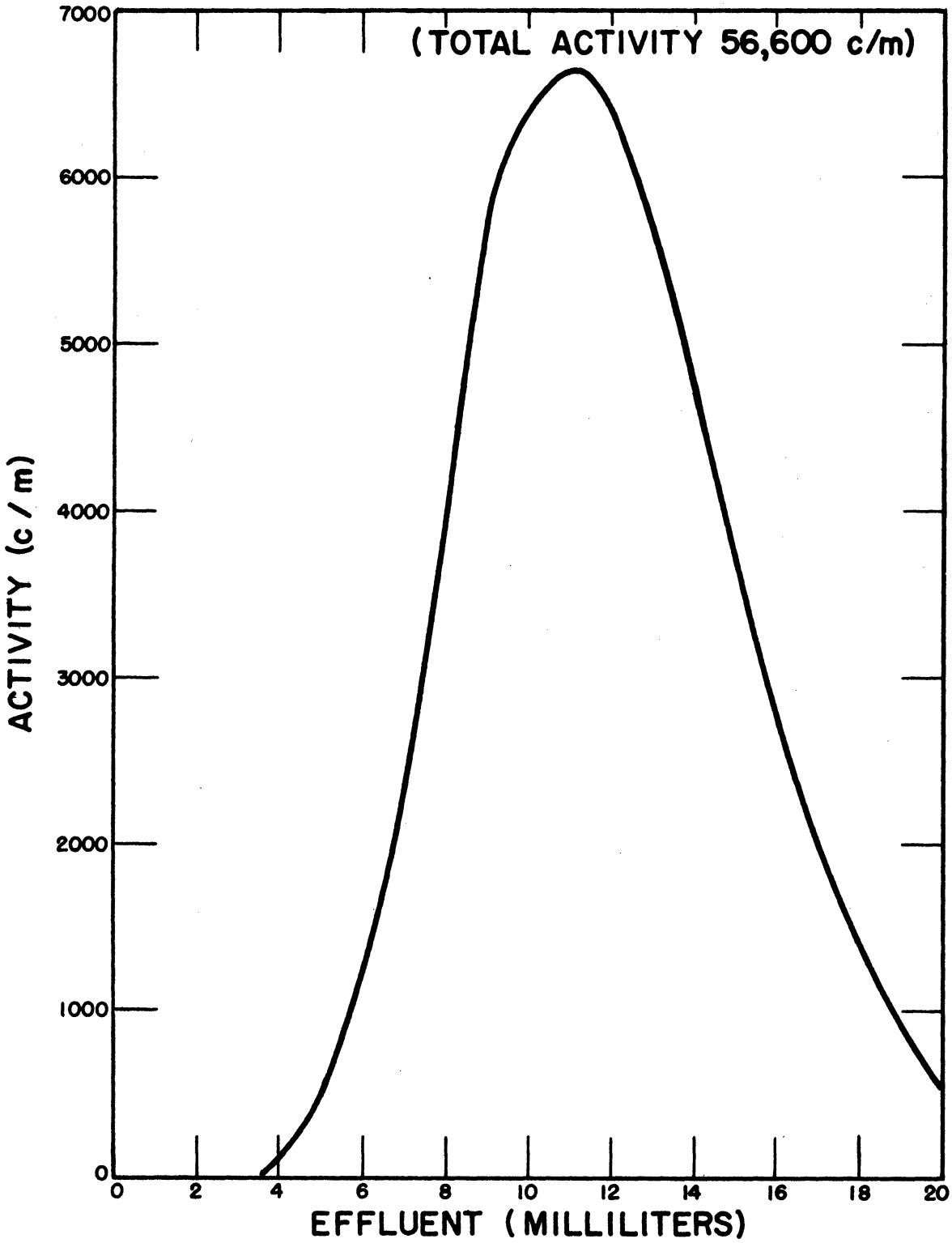


FIGURE 21. Ion Exchange Elution Curve for Indium.

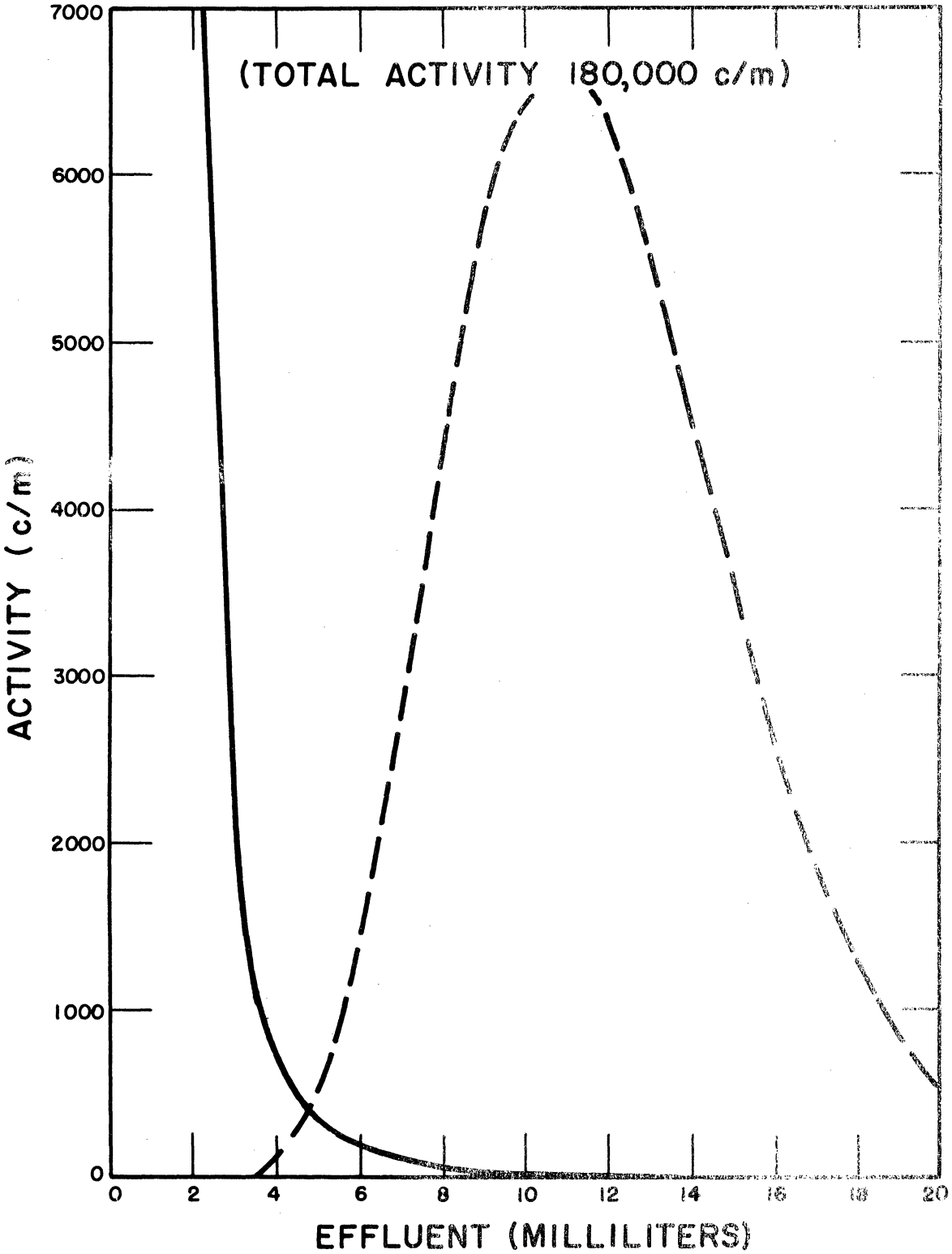


FIGURE 22. Ion Exchange Elution Curve Representing Alkali Metals, Alkaline Earth Metals, and Rare Earths. (Broken Curve is Indium.)

Of these, the contamination caused by cesium, cerium, chromium, selenium and strontium was less than 1%. A minimum of contamination appears to be reached at about 0.1%. An example of this type of elution curve is shown in Figure 22. This minimum contamination is the result of the mechanical problems involved in washing the last portion of the sample through the column. Even though the aqueous volume of the column is about 0.1 ml, a large number of column volumes are necessary for complete change of the solution in the column. The contamination for an element which has a higher distribution coefficient than indium would be lower as a result of the larger volume of eluant prior to its removal. The peaks in the elution curves of iridium and ruthenium occured at 2 ml. The iridium curve is shown in Figure 23. The iridium concentration of the eluant drops very rapidly after the peak is reached while the concentration of ruthenium remains high. This results in a 3.7% contamination of indium by iridium and 22% by ruthenium.

The elements of the second group, those which overlap the indium during elution, are cobalt, silver and zirconium-niobium. Zirconium and niobium must be considered together since they were present in secular equilibrium in the tracer solution, each contributing about 50% of the gamma activity.

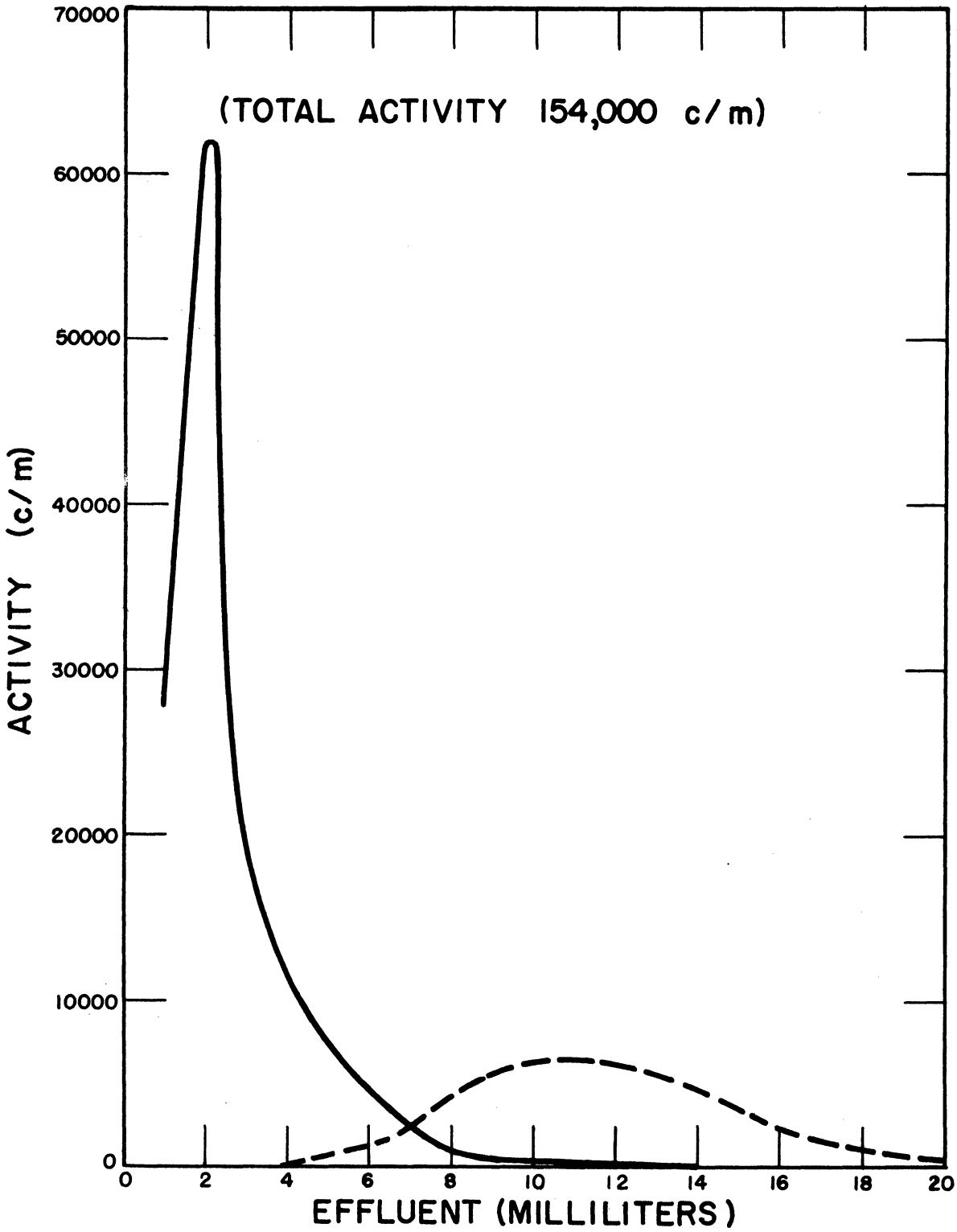


FIGURE 23. Ion Exchange Elution Curve for Iridium.
(Broken Curve is Indium.)

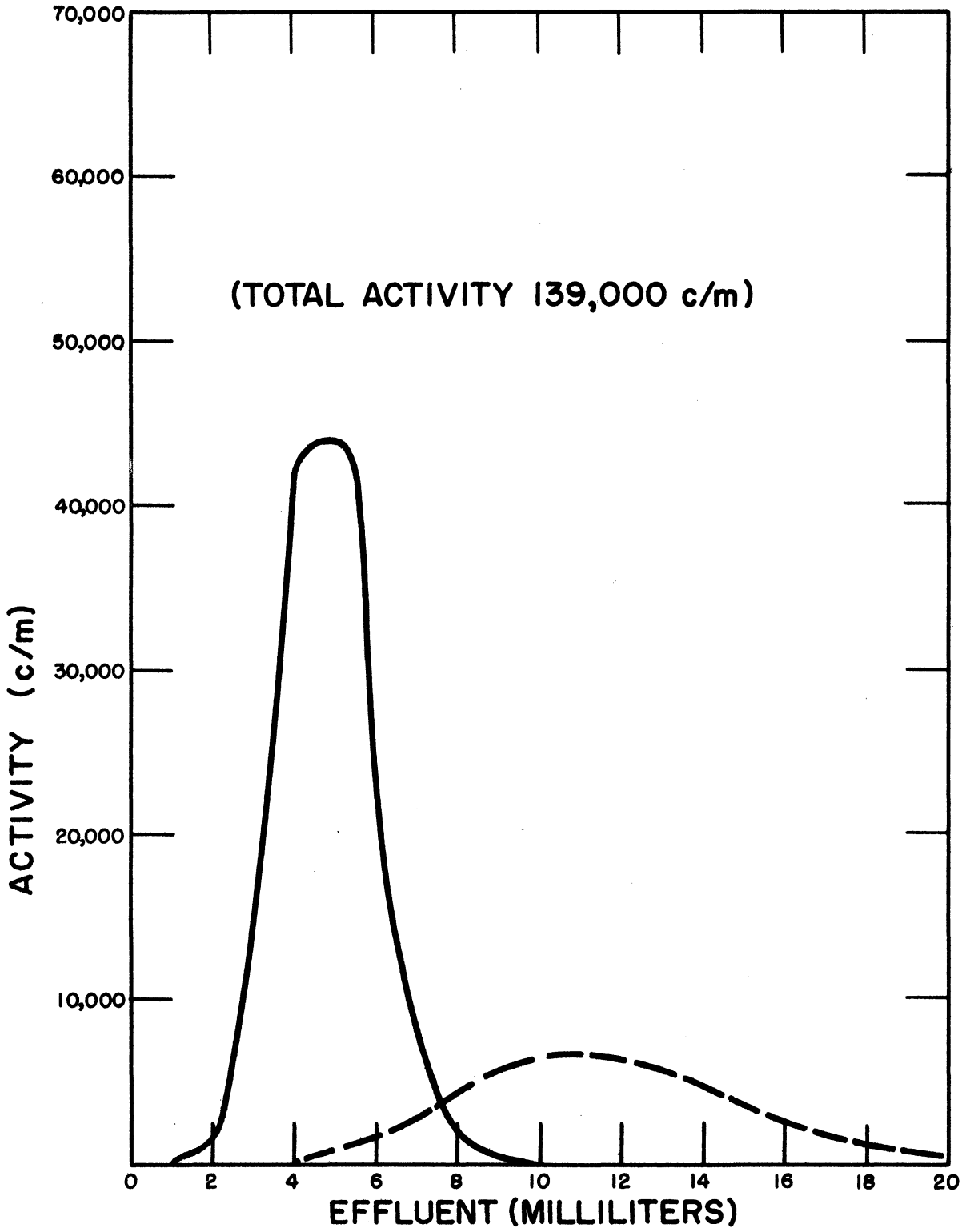


FIGURE 24. Ion Exchange Elution Curve for Silver.
(Broken Curve is Indium.)

The elution curve for silver is shown in Figure 24. The curves of both silver and cobalt reach a peak at 5 ml but the cobalt concentration in the eluant remains high (about 1000 c/m/ml) to 16 ml while the silver is reduced rapidly (to 300 c/m/ml at the 9 ml point). In the cases just described about 140,000 c/m of both silver and cobalt were used. Zirconium and niobium caused general contamination of the entire first 20 ml of the eluant. A slight peak in the elution curve was observed at 15 ml but it was a very broad one.

The elements of the third group, those which have not yet been eluted to a significant degree at the 20 ml point, are antimony, iodine, tantalum and tin. The highest contamination in this group is caused by tantalum which is eluted continually but at a low rate. The elutions of iodine and antimony are similar to this but of lower degree. Tin is held very tightly to the column resulting in the low contamination of 0.4%.

The method of anion exchange with 6 M HCl for the separation of indium is of limited value. It is certainly better than the methods of solvent extraction and sulfide precipitation for the separation of indium from tin and selenium and somewhat better for iodine. However, it cannot compete with solvent extraction for the separation of indium

from antimony, cerium, cesium, chromium, cobalt, iridium, ruthenium, silver, strontium, tantalum and zirconium-niobium.

SUMMARY

A number of methods for the radiochemical separation of barium, calcium, strontium, silver, and indium have been studied. Procedures for individual elements reported in the literature have been collected and subdivided into individual separation steps. Those steps which were found unique and possessing general applicability were studied experimentally to determine optimum conditions (of both yield and contamination) for separation. These procedures were then further evaluated under optimum conditions to determine the effects on the separation of a number of diverse but representative elements and materials.

An entirely new application of the technique of isotopic exchange to radiochemical separations was developed. It was found that radioactive silver in trace concentrations will exchange with a supported surface of inactive silver halide with sufficient rapidity to separate the radioactive silver from other activities quantitatively in a few minutes with decontamination factors of as high as 10^6. This decontamination was shown to be better than a precipitation separation by a factor of 10^4, and better than the separation by ion exchange, electrodeposition and solvent extraction

included in this study by a factor of 10^2 to 10^3. This technique can also be applied to the separation of radioactive iodine. Its future application to the field of separation chemistry may allow more rapid, simple manipulations, higher recovery and higher decontamination factors than are now possible.

A number of other techniques and procedures were also studied. Among these were separations by precipitation, ion exchange, electrodeposition, and solvent extraction. The evaluation of these individual separation steps enables the engineer, biologist, physicist, chemist or medical technician to devise separation procedures which fit his particular needs without further development work. The wide variety of chemical species studied as possible contaminants will cover many situations.

In the future, greater depth must be obtained in the evaluation program than was possible in this work. More information could be obtained on valence transformations of trace concentrations in various solutions. The new method of isotopic exchange should be applied to other elements and new contacting techniques devised. Advantage could be taken of a pulse height analyzer to increase the effective discrimination in the measurement step. More elements should be studied as the desired constituent while the contaminant

list is probably sufficiently large and representative. As new elements are studied, variations in the techniques for an individual separation will appear which will increase its applicability.

This work should be continued and broadened because of its value as an instructional aid as well as its research value. It allows the research student to become familiar with the chemistry of a large number of diverse elements and a broad spectrum of chemical and nuclear techniques.

APPENDIX A

RADIOCHEMICAL SEPARATIONS BY ISOTOPIC EXCHANGE: A RAPID, HIGH-DECONTAMINATION METHOD FOR SILVER.

Duane N. Sunderman and W. Wayne Meinke

(Reprinted from SCIENCE, May 27, 1955, Vol. 121, No. 3152, page 777.)

It has been reported by Langer (80) that the exchange of silver ion between a precipitate of silver chloride and a solution of silver nitrate reaches isotopic equilibrium very rapidly. Because of the low solubility of silver chloride, a very favorable ratio exists at equilibrium between the silver atoms in the precipitate and the silver atoms in the solution. For this reason, if silver chloride is added to a solution containing only trace amounts of radioactive silver, a high percentage of this silver will have exchanged with the silver in the precipitate by the time equilibrium is attained. Use has been made of this fact to develop a rapid, high-decontamination, single-step method for the separation of traces of radioactive silver from a solution containing other radioactive species.

Platinum gauze is coated with metallic silver by plating from an alkaline cyanide bath. The silver is then changed to silver chloride by reversing the current and electrolyzing the silver in an HCl solution.

To separate radioactive silver from other activities (except halides), the "silver chloride electrode" is immersed for 5 min at room temperature in about 10 ml of an acid solution containing the active material. The solution may be stirred magnetically. The electrode is removed and washed with a stream of 1:1 HNO_3 for 1 min.

Yields of radioactive silver from this procedure are given in Table XXI for varying temperatures, amounts of silver chloride, and times of immersion. The exchange rate appears to be independent of the nitric acid concentration in the range of 0.1 to 4M, whereas at 8M HNO_3 only 92 percent and at 16M HNO_3 only 50 percent is exchanged in 5 min at 25°C. The exchange is also independent of hydrochloric acid concentration in the range 0 to 0.6M, whereas in 1.2M HCl only 77 percent and in 6.0M HCl only 30 percent of the silver is exchanged in 5 min at 25°C. This effect of HCl is noted only as long as the silver concentration is so low that the solubility product of silver chloride is not exceeded in the tracer solution before immersion of the electrode. Higher concentrations of silver in hydrochloric acid were not investigated.

Table XXI. Yields of radioactive silver from 1M HNO_3 by exchange procedure.

AgCl (mg)	Immersion time	Temp. (°C)	Recovery (%)
2	5 min	25	> 97
2	2 min	95	> 98
2	20 sec	95	50
0.3	5 min	25	85-90

A study of the decontamination afforded by this procedure showed a decontamination factor of 2×10^4 with 4-yr-old fission products and a factor of at least 10^4 with cadmium freshly bombarded with 7.8-Mev deuterons in the University of Michigan cyclotron. In addition, when carrier-free iodine was oxidized with permanganate and nitric acid, a decontamination of 10^4 was obtained. The advantages of this exchange method include its rapidity, its high decontamination in a single step, and simplicity of manipulation. Greater than 98-percent recovery is possible as long as the weight of solid inactive silver chloride is at least 50 times the weight of tracer silver in the solution.

This method should find use in radiochemical assay work when simplicity and speed are essential. It should be useful

in characterization studies of short-lived silver activities in bombardment work and in the rapid determination of silver in fission products. It should also prove useful in the rapid preparation of high specific activity silver from irradiated materials such as palladium. It is readily adaptable to work with high levels of radiation when handling by remote control is required.

Experiments with this method of separation are continuing, and its applicability in other cases such as the exchange of iodide with silver iodide is being studied.

APPENDIX B

UTILIZATION OF ISOTOPIC EXCHANGE FOR RADIOCHEMICAL SEPARATIONS

Duane N. Sunderman and W. Wayne Meinke

(Presented before the Nuclear Engineering and Science Congress, December, 1955, Cleveland, Ohio. Preprinted by the American Institute of Chemical Engineers)

The problems of analytical control for chemical process systems in the atomic energy industry are often very similar to those of the chemical processes themselves. Very high decontaminations are required for both types of separations. Hence precipitation procedures have, in many cases, given way to the more highly decontaminating techniques of ion exchange of solvent extraction. Batch ion exchange procedures are not very specific and use must be made of column techniques to achieve satisfactory separations. These techniques, however, result in low flow rates and hence low thru-put for separations involving similar elements. Liquid-liquid extraction may, on the other hand, be quite specific

in certain cases when solution composition is closely controlled. The mechanical contacting of two liquid phases leads, however, to occlusion and incomplete phase separation, requiring a number of scrub stages to approach the theoretical capabilities of the method. One further requirement of all methods is that of rapidity of operation whether for the control laboratory or the processing plant.

Existing procedures are not completely satisfactory on a number of these counts and hence we have initiated a program of critical evaluation of radiochemical separations. Separations listed in the literature for one element (or a group of elements) are checked to find several of the most promising. These procedures are then subjected to a large number of exhaustive tests to determine optimum conditions, interference effects of macro amounts of foreign ions, and the actual decontamination values for some sixteen different typical tracer elements.

An early result of this evaluation program was the application of the technique of isotopic exchange to radiochemical separations. This is a technique which is particularly well suited to radiochemical work since it is highly specific, is very rapid, gives very high decontaminations in one step, and suffers few interferences. Thus the procedure requires few solution adjustments, and is readily adaptable to remote handling.

A. Langer (80) of the Westinghouse Research Laboratories in 1942 studied, with the help of a radioactive tracer for silver, the exchange of silver ions between freshly precipitated silver chloride and a solution of silver nitrate. He found the exchange to occur rapidly and to be a predictable function of the temperature. At equilibrium, the distribution of any given isotope of silver between the solid halide and the solution is determined by the relative weights of silver in the solid halide and in the solution. For example, if 1 mg of radioactive silver-110 in solution is equilibrated with solid silver chloride containing 100 mg of silver, none of which is silver-110, the ratio of silver-110 in the solid to that in the solution at equilibrium will be 100:1. If the ratio of these initial weights is much larger than 100:1, as would be the case if only trace amounts of silver-110 existed in the solution and if all the inactive silver were in the form of the solid halide, then the ratio at equilibrium will be correspondingly larger, giving an even better separation yield than the 99% value in the example given above. We have applied this principle to the problem of separating radioactive silver from other activities and also have obtained preliminary information on the separation of iodine by this method.

GENERAL EXPERIMENTAL PROCEDURE

Silver metal is deposited electrolytically from a cyanide solution onto a platinum gauze. It is then electrolysed as the anode in dilute hydrochloric acid solution to convert the silver to silver chloride and, finally, this electrode is contacted with an acid solution containing trace amounts of radioactive silver. After a suitable contact period, the gauze is removed, washed, and counted in a well-type scintillation counter to determine the extent of exchange. For the separation of iodine, a silver iodide electrode is prepared in a similar manner. Iodine solutions containing radioactive iodine are then contacted with the electrode and the exchange assayed with the well counter. For more accurate assay work, the halide surfaces containing the tracer are dissolved from the gauze, reprecipitated and counted in a more reproducible geometry than can be obtained by counting the halide on the gauze.

This method was found to give a very rapid separation of silver. With efficient stirring, about 97% of the radioactive tracer was removed in 5 minutes at room temperature from a solution 1 M in HNO_3. About 98% of the silver was removed in 2 minutes from a similar solution at 95°C. For iodine, the separation is less rapid and in many cases incomplete, even after a contact time of 1 hour. Between 65 and 80% of the iodine-131 is removed from solution under the conditions

described above in a period of 5-15 minutes. Higher yields require the use of a second gauze.

SILVER SEPARATION

For the removal of silver, the method was found to be "quantitative" within the counting error when reproducible standardized conditions were used. For this quantitative procedure 10 mg of silver was plated on the platinum gauze and a 15 minute contact time used with the active solution. For high decontamination work this was followed by a 1.5 minute wash with 1:1 HNO_3. The results of a series of analyses using this method gave an average yield of 99.3±0.7% (standard deviation). No decrease in yield is observed with gauzes which are prepared one week before use and stored in 1:1 HNO_3.

This method was found to suffer little interference from other ions often found in radioactive mixtures. Nitrate solutions of bismuth, aluminum, copper and zinc showed no interference (loss in yield of the silver tracer) in concentrations less than 1 M. Acids such as nitric, hydrochloric and hydrofluoric do not interfere in concentrations less than 2-3 M, and sulfuric acid does not interfere below 1.5 M. These results indicate that the interference is due to the anion concentration rather than to specific cationic interferences. This may be due to the formation of an anionic

layer on the halide surface which restricts the mobility of the silver in the vicinity of this surface.

Sixteen different radioactive species were studied to determine the level of decontamination which could be expected from this procedure. The elements studied fall into two categories; those with decontamination factors greater than 10^6, and those with decontamination factors between 10^3 and 10^5, for a single contact step of 15 minutes. In the first group are the alkaline earths, alkali metals and rare earths. Seven elements were studied in this group. In the second group appear the elements which readily form complexes such as tin, antimony, zirconium, niobium, tantalum, iridium, ruthenium and cobalt. Contamination of the gauze by these elements may be due to the formation of compounds between the silver on the halide surface and the complexes of the trace elements in solution. If this were the case, the contamination would be lowered as one progressed from chloride to bromide to iodide surfaces. This reduction of contamination was demonstrated experimentally for radioactive ruthenium-106.

APPLICATIONS

The rapidity of the method is a particular advantage in the radiochemical laboratory. It is even suitable for the separation of short-lived silver isotopes such as the 2.3-minute silver-108. When yields are not of primary

importance, 50% of the silver can be removed from solution in just 20 seconds at 95°C.

The high decontamination afforded by the procedure is due to the inherent specificity of the isotopic exchange reaction itself. A contribution is made to this decontamination by the fact that a large mass transfer is not involved in the separation. The techniques of precipitation, electrodeposition, distillation and to some extent ion exchange are limited in separation efficiency by the fact that a large mass transfer promotes occlusion, coprecipitation, and entrainment. The technique of isotopic exchange has the lowest mass transfer and hence the possibility for high decontamination in a single step.

The insensitivity of the method to changes in acid and salt concentration necessitates fewer solution adjustments prior to the separation step and hence lessens the possibility of hydrolysis or radiocolloid formation.

This separation technique should prove very useful for the production of radioisotopes. Silver-110 and silver-111 samples could be readily separated from bombardment or fission product mixtures even in the multi-curie region. Iodine-131 could also be readily separated in multi-curie lots of high specific activity. The procedure cannot, however, produce iodine "carrier free". Furthermore, contact with several electrodes or use of a column technique might be required for total recovery.

Silver-111 separated by this method from neutron irradiated palladium is ideal for making intense beta-ray sources. The radioactive silver chloride can be dissolved from the platinum gauze after contact and silver electrolysed on an electrode of any desired shape or form.

The simplicity of the operations involved in this procedure allow its adaptation to remote handling of high radiation levels. Many of the possible contamination problems involved in other types of systems are thus eliminated.

The method described above uses strictly a single contact system. If a multiple contact system were devised, the decontamination should be even more striking. This might be accomplished by packing a column with plates or beads coated with a silver halide for either silver or iodide separations. The softness of the silver halide coating might limit the use of this method, however. Further advancement in these techniques may well give this method a place beside standard engineering operations such as distillation, ion exchange, etc.

To date, separations of this type have been made only on the silver halides. The work may possibly be extended to a number of other elements exhibiting rapid exchange between a solid and the ion in solution.

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APPENDIX C

SILVER-111 BETA-RAY SOURCES

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Multi-millicurie sources of beta emitting materials have found many uses during the past decade. Biological systems have most often been subjected to these radiations (3, 36, 37, 49, 119), although investigators have also used the sources with chemical (92), and physical (102, 155) systems. Investigators report using sources of phosphorous-Bakelite (9, 118), Sr^{90}-Y^{90} (37, 68), Ru^{106}-Rh^{106} (36, 44), Tl^{204}(6), and Pd^{109} (102).

Development in this laboratory of a new, rapid, high decontamination method for the separation of silver by isotopic exchange makes possible the routine production of large beta-ray sources of Ag^{111} from neutron bombarded palladium to supplement this list of sources.

Source Preparation:

Palladium metal, when irradiated in a nuclear reactor, forms 13.6-hr Pd^{109}, 26-min Pd^{111}, and a small amount of 17-day Pd^{103}. The Pd^{111} decays to 7.6-day Ag^{111}. In processing, these Ag^{111} atoms must be separated from grams of palladium--an element which is quite similar chemically to silver. Previous methods of separation proved tedious and not readily adaptable to high level processing.

The separation of silver by isotopic exchange, however, proves to be a very specific type of reaction which suffers little interference from macro amounts of palladium. Silver iodide is the compound used since it suffers less interference from palladium than the silver chloride described previously. A "silver iodide" electrode is prepared and the electrode immersed in the radioactive solution to allow the process of isotopic exchange to occur and thus separate the radioactive silver from impurities. The silver iodide is then dissolved from the electrode and silver electrolysed from this solution as the metal on a platinum electrode of desired shape to form the source. For this final step, the silver may be plated on a variety of basic metals such as copper, brass, steel, nickel, and many ferrous and non-ferrous alloys, as well as platinum. Instructions for such electroplating processes may be found in a book on electroplating by Gray (42).

To prepare the electrode, a platinum gauze about 1-1/4" high and 3/8" in diameter is coated with metallic silver by plating from 10 ml of solution containing 10 mg of silver as the nitrate, in 3 M NaCN and 0.5 M NaOH. The plating process requires about 4 minutes at 3 volts and results in the deposition of about 5 mg of silver. The electrode is washed with water for 30 seconds and immersed in 10 ml of a solution 0.05 M in HI and 0.05 M in $NaHSO_3$. The current is then reversed, the silver surface used as the anode, and electrolysed at 1-1/2 volts for about 5 minutes changing the silver to silver iodide. The finished electrode is washed and can be stored in 1-1 HNO_3.

To separate radioactive silver from other activities (except halides) the "silver iodide electrode" is immersed for 5 minutes at room temperature in about 10 ml of an acid solution containing the active material. The solution may be stirred magnetically. The electrode is then removed and washed with a stream of 1-1 HNO_3 for one minute, the thorough wash being essential when high decontaminations are required. To form the Ag^{111} source the electrode from above is again immersed in the alkaline cyanide bath and the silver iodide coat dissolved and the silver plated as metal on a source holder of platinum or other metal.

Sources prepared in this way give an adherent coat of metallic silver. Contamination by rub-off may be lessened

by plating a thin coat of inactive silver over the active silver. When silver is used as the support for the silver halide surface much poorer deposits are obtained. It is also possible to use the silver iodide electrode directly and eliminate an extra step in the procedure. The silver iodide tends to be somewhat chalky and brittle, however, and would require a heavier coating to prevent it from contaminating materials it touches than does the metal source.

These sources can be prepared in any of a number of shapes and forms from a point to a line or a cube or a gauze, or an irregularly shaped object merely by changing the shape of the cathode in the final plating step.

Yields of the radioactive silver vary with the type of electrode used in the exchange step. For the platinum gauze used in these experiments, greater than 98% yield was obtained in 10 minutes at room temperature. Increasing the temperature decreases the time required to obtain this yield. Smaller amounts of inactive silver may be used on the gauze if a source of very high specific activity is required. When submilligram amounts of silver are used, near quantitative yields are not obtained because of chalking of the silver iodide.

Concentrated solutions of palladium inhibit this exchange process only at concentrations greater than 0.5 M.

Similarly, other foreign ions have an inhibiting effect at concentrations of about 2 M and above. Results of a number of experiments on yields, decontaminations and interferences using this procedure will be reported elsewhere.

Characteristics of the Source:

The only silver isotope present in a freshly bombarded sample of pure palladium would be the short lived isomers of 44-sec Ag^{107} and 39-sec Ag^{109} in addition to the 7.6-day Ag^{111}. Unfortunately "high-purity" palladium often contains some silver metal impurity (see typical analysis (102)) which would give small amounts of 270-day Ag^{110} by neutron capture. A typical impurity of 0.002% silver would give only about 0.002% as much activity of this long-lived isotope as of the 7.6-day activity in a one week's bombardment, and would be negligible. Thus the primary silver activity present in these sources will be Ag^{111}.

A source of pure Ag^{111} would weigh only 6.5×10^{-9} gm/mc but since several mg of silver carrier are required to utilize this exchange method, the silver will not be carrier-free. The Ag^{111} emits several beta rays of about 1 Mev and a small percentage (10%) of gamma rays of about 0.3 Mev. The surface density of silver metal is about 26 mg/cm^2/mil. Thus, the "half-thickness" for the silver beta rays is about 2-1/4 mils of silver. (This term "half-thickness" is useful for our

discussion, although it admittedly is not very exact.) Since in this procedure 10 mg or less of silver carrier is used, at least half of all the beta rays emitted will not be absorbed in most source arrangements. Hence, much less activity is lost by absorption in these silver sources than in the P^{32} plaques.

The most active source made to date in this laboratory has been several millicuries, but the same procedure is suitable for many curies with the same amount of carrier. The graph in Fig. 25 shows the amount of Ag^{111} per gram of Pd which may be obtained in a 1-week irradiation at various reactors. Reactors such as the NRX at Chalk River and the MTR in Idaho can accept up to 50 or more grams of palladium in their high flux position. Thus, multicurie sources could be made by this exchange procedure. Regardless of the activity level of the Ag^{111}, the source can still be kept in an easily handled form.

Comparison of Sources:

Characteristics of a number of kinds of beta-ray sources are listed in Table XXII. Sr^{90} suffers the major disadvantage of difficulty of mounting and of high personnel hazard. P^{32} has been used extensively in Bakelite plaques for many types of irradiations--especially in the biological and medical field, but is inherently bulky and prone to contamination.

Table XXII. Comparison of Beta-Ray Sources

	Half-Life (57)	Radiations (Mev)(57) β^-	γ	Form	Specific Activity used or available (curies/gm)	Personal hazard (93,122)	Combustible?	How Obtained
Pd^{109}-Ag^{109m}	13.6 hr	Pd 0.961 Ag e^-	none 0.087	Metal foil	X-10 - MTR 0.2 - 100	low	no	Irradiation of Pd metal in neutron flux
Ag^{111}	7.60day	1.04(91%) 0.80 (1%) 0.70 (8%)	0.340(8%) 0.243(1%)	Ag metal electroplated on metal cathode. Thin layer of inactive Ag gives protection	1 - 1000	low	no	Formed carrier-free from 26-min Pd^{111} in palladium irradiated with neutrons
P^{32}	14.30day	1.701	none	Red phosphorus mixed with Bakelite	X-10 - 0.0058	low	yes	Irradiation of plaque in neutron flux
Ru^{106}-Rh^{106}	1.0 yr	Ru 0.0392 Rh 3.53(68%) 3.1 (11%) 2.44(12%) 2.0 (3%) others (6%)	none 0.513(23%) 0.624(12%) others(3%)	Ru metal electroplated on Cu, Pt, Au or Ni cathode and covered with thin layer of silver for protection.	~ 20	Intermediate	no	Fission products
Tl^{204}	4.1 yr	0.765(98%) EC (2%)	none	Thallium salt or metal	0.02	low	no	Irradiation of thallium in neutron flux
Sr^{90} - Y^{90}	19.9yr	Sr 0.61 Y 2.18	none none	$SrCl_2$ incorporated in vials or sealed in plastic or metal with thin window	~ 200 (carrier free)	high	no-but easily ruptured	Fission products

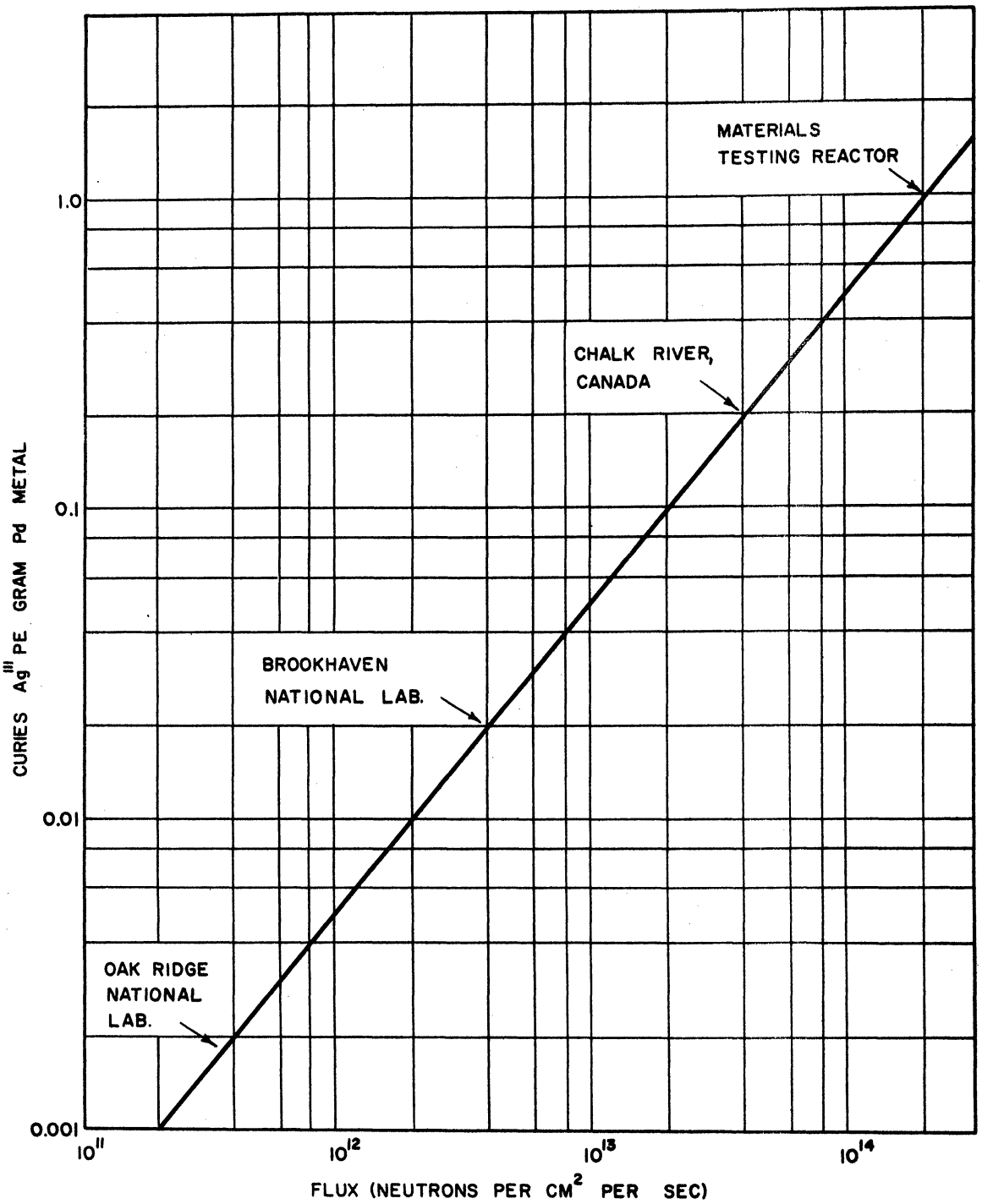

FIGURE 25. Ag-111 Activity Attainable in One Week's Bombardment at Different Neutron Flux Levels.

Sources of Ag^{111} compare favorably with the other sources given in the table. The 7.5-day half life is some disadvantage, but the ease of preparation should offset this. In its favor is the possibility of preparing multicurie sources in any of a multitude of shapes which best fit the material or object being irradiated. Since silver is relatively non-toxic (30) in small concentrations, it does not present the problems of Sr^{90}. The gamma ray associated with the silver beta ray is of low energy and low abundance and should have a negligible effect on the handling problems.

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APPENDIX D

PAPERS ARISING FROM THIS WORK

Published:

1. D. N. Sunderman and W. Wayne Meinke, "Radiochemical Separations by Isotopic Exchange: A Rapid, High-Decontamination Method for Silver," Science 121, 777 (1955).

2. W. Wayne Meinke and D. N. Sunderman, "Silver-111 Beta-Ray Sources," Nucleonics 13, No. 12, 58 (1955).

Submitted for Publication:

1. D. N. Sunderman and W. Wayne Meinke, "Utilization of Isotopic Exchange for Radiochemical Separations," Presented before the Nuclear Engineering and Science Congress, Cleveland, Ohio, December, 1955.

2. D. N. Sunderman and W. Wayne Meinke, "Radiochemical Separations: I. Barium, Calcium and Strontium."

3. D. N. Sunderman and W. Wayne Meinke, "Radiochemical Separations: II. Separation of Silver by Isotopic Exchange."

Prepared for Publication:

1. D. N. Sunderman and W. Wayne Meinke, "Radiochemical Separations: III. Silver."

2. D. N. Sunderman and W. Wayne Meinke, "Radiochemical Separations: IV. Precipitation of Hydrous Oxides for Scavenging Purposes."

3. D. N. Sunderman and W. Wayne Meinke, "Radiochemical Separations: V. Indium."

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