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CHEMICAL PROCEDURES USED IN BOMBARDMENT WORK AT BERKELEY

W. Wayne Meinke

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Chemical Procedures Used in Bombardment Work at Berkeley

UCRL-432

W. Wayne Meinke

Department of Chemistry, Radiation Laboratory
University of California

In the Nuclear Chemistry Group of the University of California Radiation Laboratory, chemists have for the past several years been using many chemical procedures, separating at one time or another about 75 of the 96 elements in the periodic table. These procedures vary from simple single step processes requiring less than a minute to tedious week long separations.

With new high energy accelerators either being planned or being built in many places, it has seemed worth while to compile the procedures used at Berkeley. Many times these procedures can be used exactly as written but more often they will serve only as a starting point from which the individual can develop a procedure more suitable to his particular problem. Their great advantage is that they have actually been used in bombardment work for separating a particular element from all other elements present.

This compilation begins with some general remarks applicable to chemical separations from targets that have been bombarded with high energy particles. The remaining pages are indexed by atomic number and procedure number, e.g., 40-1 is the first procedure for zirconium. Procedures for elements 90 and above are excluded pending declassification.

A brief explanation of the headings used is probably in order. The yield and degree of purification listed for each separation have in many cases been determined experimentally while in other cases they are only the best guess of the chemist. These values are included as a general guide to the person unfamiliar with the chemistry of a particular element to help him judge the applicability of the procedure to his work. The time of

separation in general refers to the time required to perform the operations listed; for fission work it does not include time for solution of the target. Any special equipment required for the procedure has been noted.

The portion of the heading reading "Procedure by" should actually read "Procedure used by". It is not feasible in a report of this kind to acknowledge all the sources of information that have gone into the formulation of these procedures. Many are adaptations of the fission product procedures[1] while others combine experimental data with data

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1. RADIOCHEMICAL STUDIES: THE FISSION PRODUCTS, Volume 9, Div. IV of the National Nuclear Energy Series, McGraw-Hill Publishing Co.(1950).

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presented in standard books on analysis.

The type of bombardment for which each separation has been used is also noted in the heading. Where no energies are indicated, one may assume the procedure applicable to full energy bombardments. The full energy particles of the accelerators used are:

184" cyclotron: 388 Mev alphas, 348 Mev protons, 194 Mev deuterons

60" cyclotron: 37 Mev alphas, 9.5 Mev protons, 19 Mev deuterons

Linear accelerator: 32 Mev protons

37" cyclotron: 16 Mev protons

The purpose of this compilation was to make for our laboratory a working file to which new procedures might be added as they are developed. The procedures were written up by the chemists using them and edited by the author. When there were variations in target material, time for separation, or type of bombardment, separate procedures which may differ only slightly were included. This was done in order that each procedure might be as complete as possible within itself.

The author wishes to express his sincere thanks to the following chemists who have made this compilation possible: N. E. Ballou, George W. Barton, Roger E. Batzel, Daniel P. Brooks, Stanley V. Castner, T. C. Chu, Wm. W. Crane, Richard W. Fink, Robert L. Folger, Al Ghiorso, Robert H. Goeckermann, Harry Hicks, Jack M. Hollander, H. H. Hopkins, Jr., Earl K. Hyde, David G. Karraker, Charles A. Levine, Robert C. Lilly, Manfred Lindner, David Z. Lippmann, L. B. Magnusson, Luis Marquez, Wm. R. McDonell, J. M. Miller, Daniel Miller, Robert A. Naumann, Henry M. Neumann, Amos S. Newton, William C. Orr, Donald A. Orth, Charles A. Prohaska, John O. Rasmussen, Sheldon Softky, Dorothy B. Stewart, Donald C. Stewart, Kenneth Street, Jr., Stanley G. Thompson, Geoffrey Wilkinson and Richard Wolfe.

It is a pleasure to thank Dr. I. Perlman for his advice and assistance in the preparation of this compilation. The careful work of Miss Virginia Hempel in typing the manuscript is also greatly appreciated. This compilation was sponsored by the Atomic Energy Commission.

General chemical separations for the mass spectrograph.

For the m.s., it is necessary to have the material in almost carrier-free form-from .2 ug to 100 ug being the range of stable carrier allowed. Purity is not essential, as far as decontamination is concerned, since the mass spectrograph does this. It is necessary to get the sample in a small volume, with a minimum of carrier and a minimum of accompanying salts.

To accomplish this for most elements is quite difficult, but methods that can be used are suggested. An ion-exchange column gives the ideal product. Nearly all other methods depend on the carrying properties of homologues for initial separation from the target, with subsequent separation of the carrier. For example, Ba may be carried on Pb, and left in soln by ppt PbS. Tri-positive ions may be carried on $Fe(OH)_3$, and the Fe extracted with ether, leaving a carrier free solution.

A very good separation of Bi may be obtained by plating the Bi activity (chemically) on Ni foil, dissolving the Ni in HNO_3, and carrying the Bi away on $La(OH)_3$. Bi is then separated from La by ppt 50 μg of Bi with H_2S from a very small volume of solution.

Electroplating offers many unexploited possibilities, but should certainly not be lost sight of, simply because it has not been used. For many metals, it is possibly the best available method.

D. G. Karraker

7/12/49
P-18-57

Exerpts from Thesis on Spallation Products of Arsenic with 190 Mev Deuterons- (UCRL - 312) H. H. Hopkins, Jr.

Abstract: Purified arsenic has been bombarded with 190 Mev deuterons. Following chemical separation of chlorine and the 11 elements chromium through selenium, an analysis of the radioactivities in each fraction showed the presence of a total of 40 isotopes.

Bombardment Procedure:

For the purpose of bombardment, several hundred milligrams of granular arsenic metal were wrapped with one mil platinum foil. The resulting envelope was approximately 25 mm long, 3 mm wide, and 2 mm thick. This envelope was clamped along one edge to a standard copper mount which is screwed to a water-cooled target head. This head moves into the cyclotron chamber so that the forward edge of the target meets the deuteron beam.

The duration of a bombardment was usually one hour. The beam attainable was about one microampere, but costly experience proved that the dissipation of the effective power caused volatilization of the target. Cutting the beam intensity to 30% eliminated this loss of arsenic as proved by weighings made before and after bombardment.

After bombardment the envelope containing the arsenic was taken from the holder, and the arsenic removed. The pieces were ground in a hand mortar, and the resulting arsenic powder used for chemical operations.

Chemical Separations:

The separation of the isotopes produced by spallation into elemental fractions was accomplished by chemical procedures. First the target was dissolved in nitric acid. Second, inactive carrier ions were added, corresponding to those elements we are concerned with. Finally, separations were conducted by distillations, solvent extractions, and precipitations.

The degree of separation required of the chemical procedures is determined by the radiation characteristics of the isotopes of the different elements and the relative intensities of the radiations. Thus, to identify conclusively two isotopes of different elements, of similar half-life, radiation properties, and yield, a separation of about fifty to one is required. In the case that the isotope of one element decays by electron-capture and the other by beta emission, then for the latter a separation factor of only five is required, due to the relative differences in counting efficiencies. Correspondingly, the elemental fraction of the electron-capturing isotope must be separated by a greater factor, of the order of 500, since small amounts of the beta emitter would introduce considerable error in counting the x-rays of the electron-capturing isotope. For cases where the half-lives differ considerably, other considerations must be applied. For example in the iron fraction only 47 day Fe^{59} is observed, while the longest gallium period is 3.3 days. Thus whereas gallium isotopes are formed in far greater yield than Fe^{59}, no chemical separation is necessary, since all gallium isotopes will be dead before the Fe^{59} has decayed appreciably.

The quantity of a radioelement present is of the order of 10^{-13} mole. Thus, while this amount would undergo distillation and extraction just as milligram amounts of the element, most precipitations could not occur since solubility products would not be exceeded. Therefore milligram amounts of the elements are added to function as carriers. The exchange of the radioactive isotopes with ions of the added carriers is believed to be complete in hot acid solution. No evidence such as cross contamination or widely varying specific activity indicated that this was not the case. Another reason for carriers is to minimize adsorption on precipitates.

A description of the separation of the elements into three groups will be presented, followed by a discussion of specific methods for individual elements.

1. The Germanium, Arsenic, Selenium Group.

These three elements may be distilled from 9 N hydrobromic acid and bromine as the bromides. An alternative is to sublime the arsenic before dissolution in nitric acid. When this is done arsenic and radioselenium separate from the other radioelements. Germanium may subsequently be separated from the residue by distillation with hydrochloric acid.

This group may also be precipitated by hydrogen sulfide in acid solution and subsequently dissolved in ammonium hydroxide. The clear filtrate will contain only the thio-salts of germanium, arsenic, and selenium.

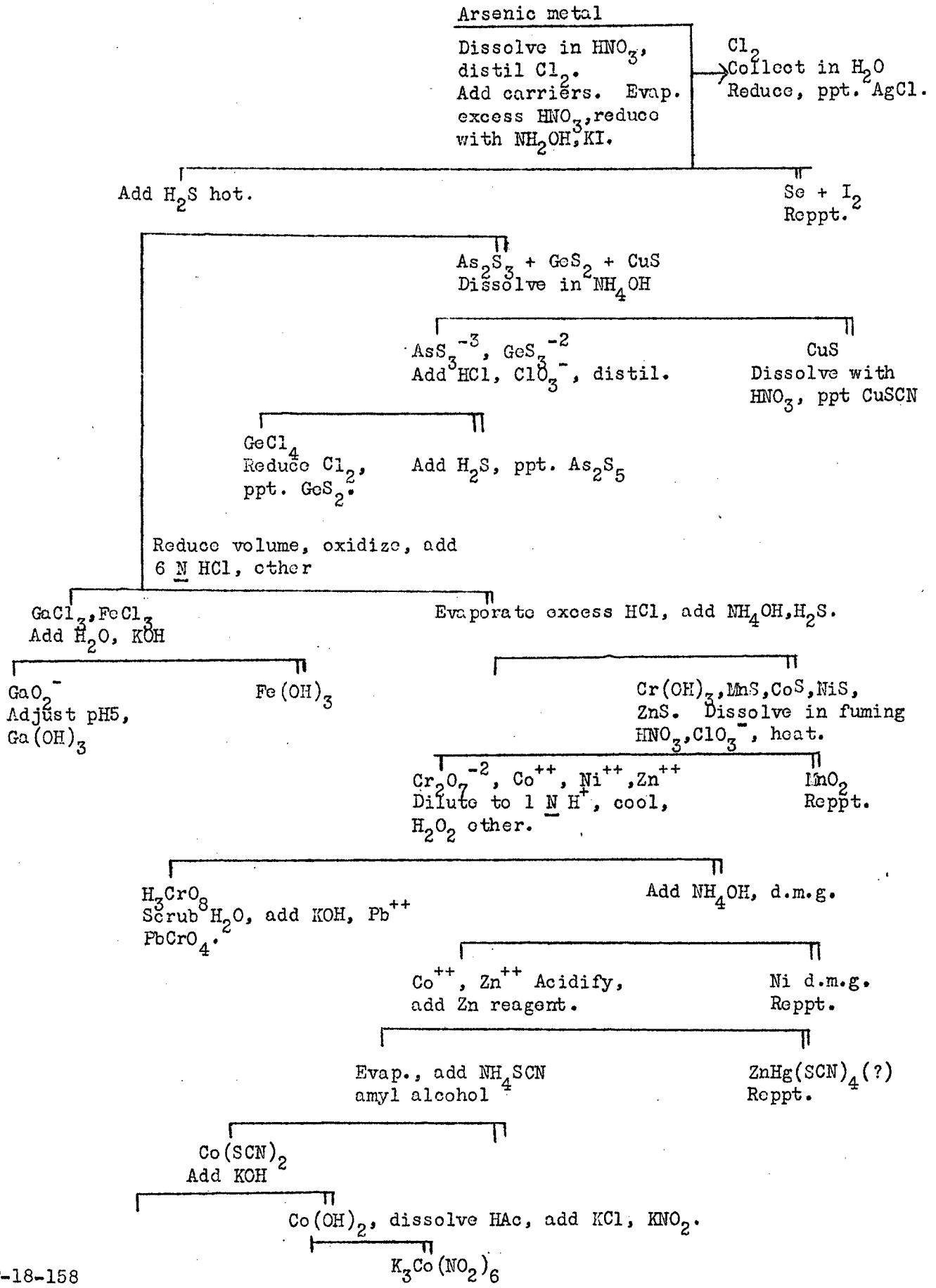
2. Iron and Gallium.

These elements are readily extracted into ether, from 5.5 to 6 N hydrochloric acid. Iron must be in the ferric state. Washing the organic layer with more hydrochloric acid removes other groups which extract to a lesser extent.

3. Chromium, Manganese, Cobalt, Nickel, Copper, and Zinc.

This group can be separated from the first by the use of ammonium sulfide. The sulfides are usually dissolved in concentrated nitric acid in the presence of solid potassium chlorate, and subsequent procedures separate the elements one at a time.

Diagram of Separation Procedures.



Exerpts from Thesis on Characteristics of Bismuth Fission with High Energy Particles - (UCRL 251) - Robert H. Goeckermann

Introduction:

The yields of nuclides resulting from 190 Mev deuteron fission of bismuth were determined by studying the activities of 27 elements from Z = 20 to Z = 63 ---- Ca, Cr, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Cb, Mo, Ru, Pd, Ag, Cd, Sb, Te, I, Cs, Ba, Ce, and Eu.

Bombardment Technique:

The circulating beam of the 184-inch frequency-modulated cyclotron was used almost exclusively because its intensity is much greater than the deflected beams. The average beam is of the order of one microampere, but neither it nor its day-to-day variations were measured or known accurately. Therefore it was necessary to use an internal monitor--in this case 67 hr β^--emitting Mo^{99}---in each bombardment and measure all yields relative to it. The absolute yield of Mo^{99} was later determined using a deflected collimated measured beam (3.0×10^{-5} μa) of 190 Mev deuterons.

Bismuth strips 0.1 x 1 x 3 cm were machined from an ingot obtained from the American Smelting and Refining Company. Spectrographic analyses showed the absence of any impurity that might interfere with the measurements.

Chemical Procedures:

The irradiated portion of the bismuth was dissolved in hot 6 N HNO_3 and stored in a closed calibrated glass container. Aliquots of this solution were used for the study of the activities of a particular element. Liter amounts of carrier solutions had been prepared, by weighing out some suitable compound to contain 10 mg/ml of the element. (A few of these carrier solutions have been standardized and found to be accurate within 10%.) One or two ml of this solution of an element was added to the aliquot of the bismuth solution as carrier for the radioactive isotopes present, precautions to insure exchange of active and inactive atoms taken in some cases, and the element purified from all others which would interfere in the radioactivity measurements. Radioactive isotopes of most of the elements up to astatine are probably produced to some extent but the predominant fission products are in the calcium (20) to europium(63) region and the predominant spallation products are in the hafnium(72) to astatine(85) region. From the determined fission cross section it is estimated that the yield of spallation products is several times as great as the yield of fission products. Part or all of the purified element was then precipitated as a weighable compound, filtered through a Hirsch funnel on a tared ~ 1 cm diameter filter paper and the chemical yield determined. The filter paper is washed and dried like the precipitate it will carry prior to taring. Most of the chemistry used was adapted from fission product procedure reports to appear as part of the National Nuclear Energy Series. The procedures are outlined here primarily because no compilation of them is yet generally available. The amounts of scavengers used are only approximate. All precipitates were separated by centrifugation except the final one in each case.

Exerpts from Thesis on Nuclear Reactions in Antimony with High Energy Particles - (UCRL-143) - Manfred Lindner

Irradiation with 200-Mev deuterons and 400-Mev alpha particles from the 184" cyclotron has, in general, given rise to so large a number of radioactive products that rather elaborate chemical procedures had to be worked out in order to identify these products. Thus it has been found in the case of antimony targets that activities were produced which differ in mass from the target atoms by 36 units, and in atomic number by 15 units. Of course, a multitude of isotopes in between these limits was also formed.

The elements listed below include those which were identified from the complex mixture of spallation products of high-energy deuterons and alpha particles of the 184" cyclotron: $_{39}Y$, $_{40}Zr$, $_{41}Cb$, $_{42}Mo$, $_{43}Tc$, $_{44}Ru$, $_{45}Rh$, $_{46}Pd$, $_{47}Ag$, $_{48}Cd$, $_{49}In$, $_{50}Sn$, $_{51}Sb$, and $_{52}Te$. Zr, Cb, and Tc were not investigated, and rhodium proved too difficult to remove from the complex mixture. However, the remaining elements, Y, Mo, Ru, Pd, Ag, Cd, In, Sn, Sb, and Te were investigated. Since many of the products of lower atomic number (Y, Mo, etc.) were found to be formed in exceedingly low yield, it was necessary to effect complete separation of a given element followed by several repurification steps. A known weight of carrier (usually twenty milligrams in the form of a solution of a readily soluble salt) was always added to the gross mixture of activities before chemical separations were made. This procedure insures against the adsorption of any tracer activity on foreign precipitates. The following procedure was found to work satisfactorily for the separation of those elements listed in table I except for Zr, Cb and Tc.

The dimensions of the metallic antimony targets were about 1 mm x 2 mm x 30 mm, weighing about 0.45 grams.

The procedures given below serve to isolate a given element in a state free from any contaminating activities. In many instances, the procedures were not suitable to the determination of periods of the order of one-hour half-life, due to the time involved in separation and purification. In such instances, it was usually necessary that initial efforts be concentrated in isolation of such a short-lived activity or that the chemical procedure be shortened if the separation and decontamination from other elements is not seriously impaired.

8/11/49
P-18-172

Exerpts from Thesis on Radioactivities Produced in the Platinum Group by Bombardment of Uranium with 400 Mev Helium Ions

(UCRL-123) - Richard D. Wolfe

Abstract:

The purpose of the investigation was to determine the yield of radioactivities of the platinum group metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum) produced when natural uranium is bombarded with 400 Mev helium ions. The reason for interest in the yields of these metals is that the last three lie in a region where the plot of yield vs. mass number may change from a fission-yield curve to a spallation-yield curve. In addition, the first three lie in a region which should indicate whether the center of the curve has a dip (as does the slow-neutron fission-yield curve), or a single maximum indicating symmetrical fission (as in the case of bismuth and thorium).

Radiochemistry of the Platinum Elements

The chemistry of the six platinum elements $_{44}Ru$, $_{45}Rh$, $_{46}Pd$, and $_{76}Os$, $_{77}Ir$, $_{78}Pt$ is notoriously complex. Their separation, purification, and quantitative determination is a classical problem of long standing. The electron configuration of the first three partially fills the 4d orbit, with the possibility of adding 10, 9, and 8 electrons respectively for ruthenium, rhodium, and palladium in order to fill out the 5s and 5p orbits and form the stable noble-gas configuration of $_{54}Xe$. Similarly, osmium, iridium, and platinum partially fill the 5d orbit, and can add 10, 9, and 8 electrons respectively, filling the 6s and 6p orbits to attain the noble gas structure of $_{86}Rn$. Because of this electron structure, all six elements enter into a vast number of coordination complexes, with almost any radical or element, charged or neutral, which can furnish an unpaired electron. Their chemistry is thus characterized first by extensive complex formation in which all six behave very similarly and are therefore difficult to separate; and secondly by difficulty in getting the elements into solution, and once they are in solution, further difficulty in getting them quantitatively out of solution.

A number of satisfactory schemes are presented in the literature for quantitative and qualitative determination of these elements.[4] However,

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4. Analysis of Platinum Metals, Bur. of Standards Sci. Paper No. 532 (1936); Jour. of Res. 3, 993 (1929), 6, 421 (1931), 9, 547 (1932); Jour. Am. Chem. Soc. 48, 2493, 2507 (1926), 51, 175 (1929), 52, 42 (1930); Ind. and Eng. Chem. Anal. Ed. 8, 141 (1936), 9, 420 (1937); Am. Mineral 22, 1016 (1937); Microchem. 24, 20 (1938).

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these schemes are generally inapplicable, without extensive modification, to fission product procedures. In the first place, the classic methods aim at separating the platinum metals from ores or naturally occurring sources, where contaminating substances are relatively few, and are fairly

well known as to type. Secondly, these schemes aim at quantitative determination of the platinum elements, entailing precise, time consuming, cumbersome, and involved chemical procedures.

The fission product procedure for these elements has a different aim. Although 100% recovery of the six elements sought is not required provided their chemical yield can be ascertained, decontamination factors from other radioactive elements must often be as large as 10^6 and sometimes larger, since activities in osmium, iridium, and platinum are very low compared to activities of contaminants. In addition, separation must be made not from a few known elements occurring with these metals in natural ores, but from the majority of the elements in the periodic table. Finally, the separations performed must be relatively specific and rapid, in order to permit observation of the shorter-lived periods.

With the foregoing requirements in mind, the literature was surveyed for reactions which might be combined to achieve the separations desired. Fission-product procedures for ruthenium and palladium are extant. That developed for rhodium was insufficient, in that no separation from iridium had been provided for. No fission-product procedures existed for osmium, iridium, and platinum, although the standard qualitative method of distilling osmium tetroxide seemed adaptable to the requirements. Thus the separation of iridium, rhodium, and platinum comprised the chief problems.

It seemed likely that the pyridine separation for rhodium developed by Ballou[5] might be adaptable also to iridium, since the two metals behave almost

5. Ballou, N. E., Plutonium Project Report CN 1312, An-X (May 1945).

identically in their chemical reactions. Further reference to the old literature[6] established the existence of a number of pyridine complexes

6. Delépine, M., Compt. Rend. 146, 1267 (1908), 153, 60 (1911); Bull Soc. Chim. (4) 3, 906 (1908), (4) 9, 710, 771 (1911); Ann. Chim. Phys. (9), 7, 277 (1917), (9) 19, 5, 145 (1923); A. Gutbeier and D. Hoyermann, Zeit. Anorg. Chem. 89, 340 (1914).

of iridium. After many weeks of trial and error, the proper conditions were discovered for simultaneous formation of pyridine complexes of rhodium and iridium, and for their extraction into excess pyridine. The method was finally tested using active iridium as a tracer, to prove the results. The method is particularly elegant since it separates in one step from the bulk of uranium in the solution, and from all of the non-platinum group fission products except silver. Subsequent separation of rhodium from iridium was achieved by adapting the method of Gilchrist and Wichers[7],

7. Gilchrist, R., and E. Wichers, Jour. Am. Chem. Soc. 57, 2565 (1935).

precipitating rhodium metal from the boiling sulfate solution by addition of titanous chloride, leaving the iridium in solution.

Based on the use of ethyl acetate to extract platinum[8], a number

8. Wobling, H., Ber. 67, 773 (1934).

of experiments were performed to determine optimum conditions for platinum extraction. Clean extraction of platinum reduced by stannous chloride was attained above four normal acid concentration. Butyl acetate was found preferable to ethyl acetate because of lower water solubility.

The target for each bombardment consisted of a small strip of uranium metal, of natural isotopic composition, 0.04 inches thick and about two inches long. It was mounted on a copper holder, which was inserted on a probe into the vacuum chamber of the cyclotron such that the beam struck the leading edge of the target perpendicular to the metal strip. After bombardment and removal of the target from the copper backing plate, the unbombarded portions were cut off in order not to encumber the chemistry with too much inactive material. It was found desirable to clean the target in nitric acid and keep it in an evacuated desiccator until just prior to bombardment, to prevent formation of the difficultly soluble oxides of uranium.

Chemical yield was determined in each case by adding a known amount of standardized carrier at the start (ca 20 mg for each element), and by determining the weight of each element recovered. Osmium, iridium, platinum, ruthenium, and rhodium were determined as the elements by precipitation with magnesium. Palladium was determined as $Pd(C_4H_2N_2O_2)_2$, the palladium compound of dimethylglyoxime. Barium is determined as $BaCl_2.H_2O$.

8/13/49

Spallation of Copper with 350 Mev Protons - R. E. Batzel

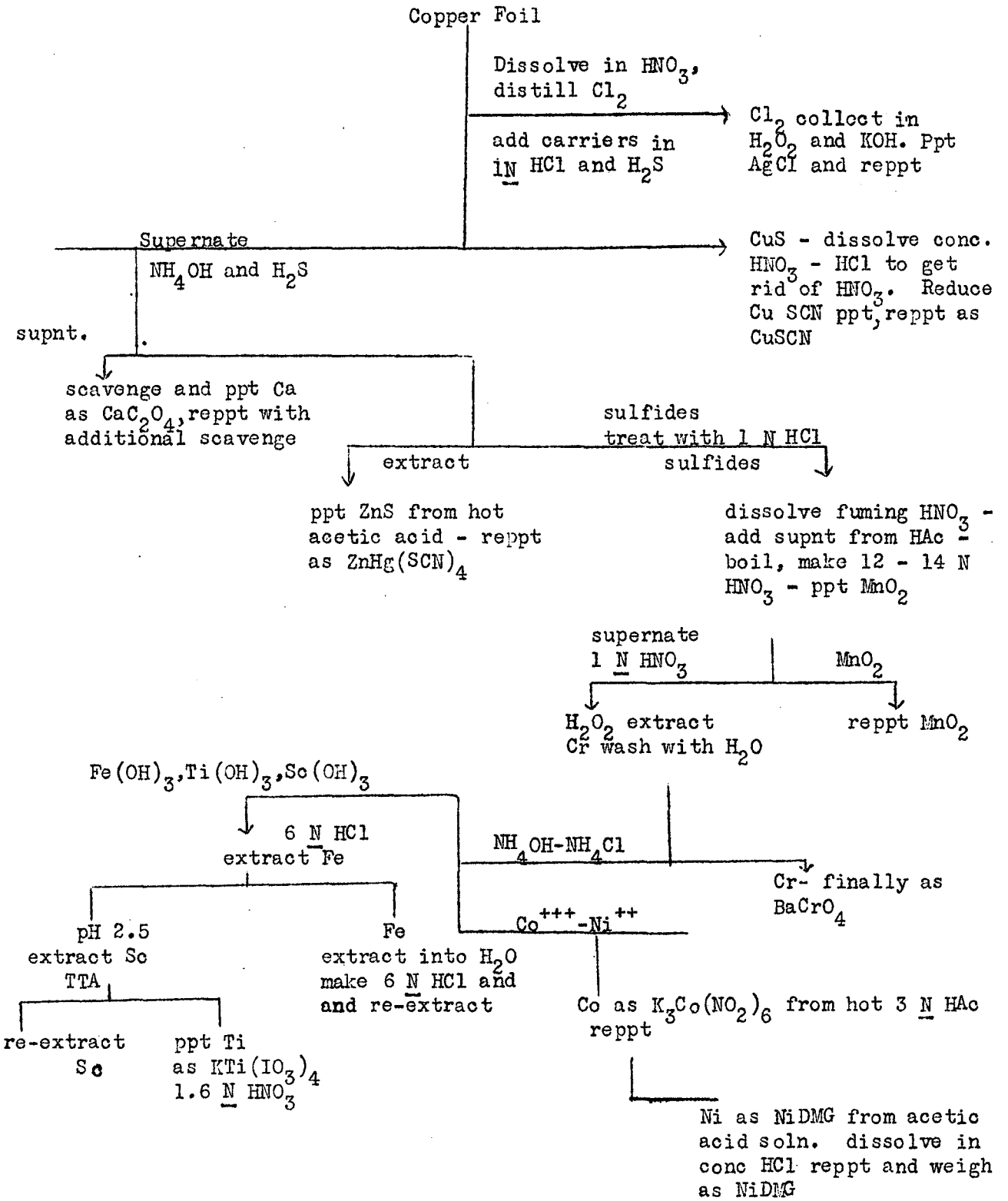
The bombarded copper foil is usually dissolved in the minimum amount of concentrated nitric acid. Known amounts of carriers are added and precipitations are carried out from this solution. The known amounts of carriers are added in order that a quantitative estimation can be made as to the amounts of original carrier lost during chemical separations, this being also a measure of the amount of radioactivity lost.

In general the degree of chemical purification necessary depends on the yield and counting efficiency of the specific isotopes formed during bombardment. If the isotope is formed in high yield and has a high counting efficiency the degree of chemical separation need not be too high, but if the element is formed in low yield or has a low counting efficiency special precautions must be taken. To increase the degree of radiochemical purity holdback carriers are added. The holdback carriers dilute the activity of any elemental fraction which has a tendency to co-precipitate or occlude during precipitation. Another method of increasing radiochemical purity is the use of scavenging agents. With the desired element in solution under conditions which will precipitate one or more of the possible contaminants, small amounts of carriers for the interfering elements are added and repeated precipitations made.

In order to remove the majority of the solids from the solution, the copper is precipitated from a 1 N HCl solution free of oxidizing agents. Sulfide precipitations can be used as a volume reduction step since most of the elements below copper which are of interest are insoluble in ammonical sulfide. The chemical procedures are usually adapted to meet specific conditions depending on the order in which elemental fractions are to be removed.

The following is an example of a separations scheme for one specific bombardment:

SEPARATION PROCEDURE



8/16/49

P-18-193

Fission and Spallation of Uranium with High Energy Particles - R. Folger

General Remarks:

(1) By proper choice of solvents, a number of elements may be removed from a single target soln., e.g., when looking for Os, I, and Br the target should be dissolved in HCl (NO_3^- excluded.) After solution, these elements may be distilled from aqua regia by add'n of HNO_3 and heating.

(2) When looking for Ag, Ge, Sr, the target should be dissolved in conc. HNO_3.

(3) Ppting uranium by passing in NH_3 removes a large group of elements in the form of ammonia complexes (Co, Ni, Cu, Ag, Cd, Pd)

(4) The degree of purification needed depends upon the half-life and the relative fission yield of the isotope sought.

(5) Holdback carriers are added to reduce contamination by diluting the activity mechanically carried along.

(6) Scavenges are useful both to mechanically adsorb normally insoluble compounds present in trace quantities and to co-ppt certain contaminants. Good scavenging agents, easily pptd completely, are $Fe(OH)_3$, AgCl from 4 N HNO_3, CuS from 0.5 N H^+.

(7) Where chemical considerations permit it is usually helpful to add carriers for all elements sought directly to the original target soln. The aliquot taken for a particular element is then measured by the chemical yield of that element. In the case of Ag this procedure is necessary because trace quantities of this element are rapidly adsorbed by glass.

8/15/49

P-18-200

Exerpts from Paper on "The Fission of Thorium with Alpha Particles"

(Phys. Rev. 75 17, 1949) - Amos S. Newton

Experimental Methods

The thorium used in the bombardment was special purity thorium metal produced by the group at the Atomic Research Institute at Iowa State College. In a long bombardment, designated as Bombardment A, of 3020 μah of 39-Mev helium ions (impinging energy as estimated by Dr. J. G. Hamilton) on the Crocker Laboratory cyclotron, a 3 1/2-inch diameter thorium backing plate 1/8 inch thick was used. After bombardment, a radioautograph of the disk was made to determine the active area. The activity was then removed by milling thin layers from the active area, using a milling set-up in which the millings could be quantitatively collected. Eleven layers, varying from 1 to 3 mils in thickness, were removed from this target so the fission product distribution and the excitation curve for fission could be determined. The milling removed about 95 percent of the total beta- and gamma-activity from the target. In addition to this, three shorter bombardments of 24-hour, 2-hour, and 4-hour duration, designated as bombardments B, C, and D, respectively, were obtained on thorium foils of thickness about 30 mg/cm^2 using the interceptor set-up of the Crocker cyclotron. In these cases it was assumed that all of the 2-cm^2 area of the interceptor received bombardment.

The technique used in determining the fission yields was the standard chemical technique as used on the Plutonium Project. The bombarded sample was dissolved in either hydrochloric or nitric acid, a small amount of ammonium fluosilicate being added as a catalyst. The solution was diluted to a known volume and stored in Lusteroid tubes inside a glass tube to prevent loss of activity by adsorption on glass and evaporation of the solution. Aliquots were taken for determination of each desired element. In each fraction, carrier was added for the element to be separated, and the element chemically separated and decontaminated from other activities. The element was then precipitated in a suitable form, weighed, and the chemical yield determined. The samples were mounted on cardboard, covered with Cellophane, and counted on the second shelf of a standard counter set-up.

In all bombardments the 300-hr. Ba^{140} was separated in order to offer a rough check on the bombardment. The chemical methods used in the isolation were modifications of those developed for the fission products by the Plutonium Project.

8/16/49

Procedures for Filtering, Drying, Weighing and Mounting Precipitates

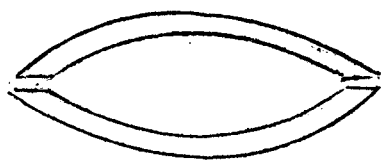
Amos S. Newton

The following procedures are useful in methods where a suitable aliquot of the bombarded material is taken so that the entire precipitate of the element desired can be counted. This is the most accurate procedure for determining chemical yields and allows maximum use of the original bombarded material. A known amount of carrier is added to the aliquot of the original solution, the element chemically purified, and precipitated in a suitable form.

Precipitates which are crystalline or in other easily filtered forms can be filtered on a Hirsch funnel (Coors size 00 or 000A are suitable). A tared piece of filter paper 1 3/16" diameter (a half dollar can be used as a form for cutting filter paper) is placed in the bottom and the precipitate transferred to the paper and distributed evenly on the paper with a transfer pipette, being careful not to allow the precipitate to run off the edges of the paper. Any washing liquids can be transferred to the filter paper in the same manner.

Precipitates are dried by evacuation or in the 110° oven. In general those precipitates which form hydrates are dried by evacuation using a standard procedure for a given precipitate which has been shown to give the desired hydrate. Oven drying or longer evacuation of such precipitates should be avoided as the composition will be different. The filter paper should be treated with the same reagents, washed, and dried in the same manner as the final precipitate, and weighed in order to get the tared weight of the paper.

Since filter paper takes up water rapidly after drying, it will gain weight rapidly on the balance unless means are taken to avoid atmospheric contact. A suitable weighing container for these filter papers can be made by grinding the lips of two thin 50 mm watch glasses flat with 200 mesh carborundum against a flat piece of glass, being careful to rotate pressure points during grinding to keep the ground area perfectly flat. These are then fitted together to form a small chamber. The uptake of water by a filter



paper disc in this should not be over 0.1 mg/10 minutes while a weighing should be completed within 2 minutes after taking the paper from the vacuum desiccator or oven. It is both unnecessary and undesirable to put the watch glass weighing chamber in the oven or desiccator. If it is left in equilibrium with the balance case at all times weights will be more reproducible. Also of course one should avoid chipping the edge of the watch glasses between taring a filter paper and the final weighing.

A convenient method of mounting is to mount the sample in the center of a standard 2 1/2" x 3 1/2" cardboard card. It is held in place by a piece of 2 1/2" x 2" scotch tape in which a cellophane window 1 3/16" diameter has been made, being careful to place the window directly over the sample. The cellophane has a thickness of only $\sim$ 2.6 mg/cm^2 compared to $\sim$9.6 mg/cm^2 for thin scotch tape and $\sim$ 13 mg/cm^2 for the 2" wide material.

The scotch tape with cellophane windows can be prepared ahead of time as follows. A piece of scotch tape 2 1/2" long is cut from a 2" wide roll and placed sticky side down on a piece of plate glass. The hole 1 3/16" diameter is then cut with a large cork borer (one can be made from the holder for 50 ml centrifuge cones if a suitable piece of brass tubing cannot be found). The center hole is lifted out, the outside section lifted up and placed over a piece of cellophane 1 3/8" diameter so that the cellophane is even all around the hole. When one corner of this sample cover is stuck to a bottle for storage, it will keep for about 2 weeks before the stickiness of the scotch tape is lost, probably due to drying out of the adhesive.

Precipitates which are ignited (Sn, Zr) are filtered on ashless filter paper and ignited in a porcelain crucible. The material is then carefully transferred to a tared paper, carefully spread and weighed. The paper is then moistened with a few drops of dilute collodion in ether to hold the ppt in place. It is then mounted like any other precipitate. Only that material which is mounted is weighed as the chemical yield determination is made on the material which is counted.

Examples of Drying and Weighing Methods

Ppts dried at 110°

Element	Ppt.	Time (min.) drying	Weigh as
Ag	AgCl	10	AgCl
Br	AgBr	10	AgBr
I	AgI	10	AgI
Mo	Ag_2MoO_4	15	Ag_2MoO_4
Pd	Pd(dimethyl glyoxime)	10	$Pd(C_8N_4O_4H_{17})$
Cs	$CsClO_4$	10	$CsClO_4$
Te	Te (metal)	10	Te
Ru	Ru (metal)	10	Ru
Cd	$CdNH_4PO_4 \cdot H_2O$	10	$CdNH_4PO_4 \cdot H_2O$

Ppts dried by evacuation

Element	Ppt.	Time Evacuation	Weigh as
Sr	SrC_2O_4	(2 min., release, 5 min.)	$SrC_2O_4 \cdot H_2O$
Ba	$BaCl_2$	(2 min., release, 5 min.)	$BaCl_2 \cdot H_2O$
Rare earths	$R.E._2(C_2O_4)_3$	(2 min., release, 2 min., release, 3 min.)	$La_2(C_2O_4)_3 \cdot 8H_2O$ $Ce_2(C_2O_4)_3 \cdot 10H_2O$ $Pr_2(C_2O_4)_3 \cdot 9H_2O$ $Y_2(C_2O_4)_3 \cdot 7H_2O$ $Eu_2(C_2O_4)_3 \cdot 10H_2O$

8/16/49

CHEMICAL SEPARATIONS

Element separated: Sodium

Procedure by: D. B. Stewart

Target material: Aluminum alloy
95% Al, 2.25% Mg, 0.25% Cr(+Fe & Cu)

Type of bbdt: 184" deuterons

Time for sep'n: ~ 8 hrs.

Equipment required: Centrifuge cone, beaker

Yield: ~ 60%

Degree of purification: 10^4 from Al, others unknown

Procedure:

(1) Dissolve aluminum in 6 N HCl. Add 50 mg Na and 10 - 20 mg Cu carriers.

(2) Precipitate $Al(OH)_3$ with slight excess of NH_4OH. Centrifuge, pour off supernatant. Dissolve first precipitate in HCl and repeat, adding the 2nd supernatant to the original.

(3) Saturate solution with H_2S to precipitate CuS and remaining Al as Al_2S_3. Filter or centrifuge.

(4) Acidify filtrate with HCl or HNO_3 and evaporate to dryness. NH_4^+ salts can be quickly destroyed by boiling with a 1:4 HCl-HNO_3 mixture. Residue is mixture of NaCl and Na_2SO_4.

8/24/49

CHEMICAL SEPARATIONS

Element separated: Magnesium

Procedure by: D. B. Stewart

Target material: Aluminum alloy
95% Al, 2.25% Mg, 0.25% Cr(+Fe & Cu)
Type of bbdt: 184" deuterons

Time for sep'n: 4 hrs.

Equipment required: Beakers, filter funnels

Yield: 90-100%

Degree of purification: 10^4 from Al and Cu

Procedure:

(1) Dissolve aluminum in minimum dilute HCl. Add 25 mg Mg and 5 mg Cu carriers. Dilute to about 0.3N - HCl.

(2) Saturate solution with H_2S to precipitate CuS. Filter. Wash precipitate with 0.1 N - HCl containing a little H_2S

(3) Boil filtrate to expel H_2S. Volume of sol'n should be greater than 50 ml (or to give ~1 mg Mg/2 ml solution). Add 2-5 g tartaric acid, or slight excess over the amount required to complex the aluminum. Neutralize with NH_4OH and make just acid with 1 drop of HCl. Warm slightly.

(4) Add 2 g $(NH_4)_2HPO_4$/100 ml solution and NH_4OH dropwise with stirring, until neutral, and then 10 ml conc. NH_4OH/100 ml solution. Let stand 1 hr. or more to allow formation of $Mg(NH_4)_2PO_4$.

8/24/49

P-18-266

CHEMICAL SEPARATIONS

Element separated: Phosphorous

Procedure by: Batzel

Target material: Cu

Time for sep'n: 2 hrs.

Type of bbdt: All 184" and 60"

Equipment required: Standard

Yield: 60%

Degree of purification: Factor of 100 from all activities present except vanadium. Probably factor of 50 from V.

Procedure:

(1) Dissolve target in HNO_3. Add 5 mg P as PO_4^{-3} and neutralize most of free acid with NH_4OH.

(2) Make 1 N in HNO_3 and add ammonium molybdate to the warm solution (50° C) (add 6 ml of molybdate for every 4 mg of P).

(3) Allow to settle for 15 minutes. Centrifuge and wash with 1% HNO_3.

(4) Dissolve with NH_4OH citrate solution and add HCl until the ppt that forms dissolves with difficulty. Add 5 mg vanadium holdback carrier.

(5) Bubble SO_2 through the solution to reduce VO_3^- to VO^{++}. Add 2 ml of cold $MgCl_2$ mixture - allow to settle 5 minutes and add conc NH_4OH until solution is 1/4 of original volume. Allow to settle for 15 min. Centrifuge and wash precipitate with 1:4 $NH_4OH:H_2O$.

(6) Add 5 mg vanadium holdback carrier and repeat step (5).

(7) Dissolve ppt in 1 N HNO_3.

(8) Repeat (2) and (3).

(9) Weigh as ammonium phosphomolybdate.

Ref. Scott's Standard Methods of Chemical Analysis, Vol. I, page 694.
I. M. Kolthoff & Sandell, E.B., Textbook of Quantitative Inorganic Analysis, page 368.

Remarks:

Vanadium co ppts with phosphorus if it is in V^{+5} state. It should be reduced to VO^{++} state & the cycle repeated two times in order to remove vanadium completely.

8/24/49

CHEMICAL SEPARATIONS

Element separated: Chlorine

Procedure by: Batzel

Target material: Copper

Time for sep'n: 30 minutes

Type of bbdt: All -

Equipment required: standard

Yield: 60%

Degree of purification: 10^3

Procedure:

(1) Dissolve the copper in concentrated HNO_3 containing 5 mg of chlorine carrier (1-2 ml concentrated HNO_3 for 0.1-0.3 grams copper foil)

(2) Distill the chlorine into a centrifuge tube containing 2 cc of water, 2-3 drops of concentrated HNO_3, and sufficient $AgNO_3$ to precipitate the chlorine as AgCl.

(3) Heat almost to boiling, centrifuge the precipitate and wash with 3 cc of 2N HNO_3.

(4) Dissolve the AgCl in 3 cc of 5 N NH_4OH and add a drop of holdback carriers from standard 10 mg/ml solns, for Cu, Ni, Co, Zn, Fe (add as nitrates or sulfates) and then add 2 drops of 0.5 N KI.

(5) Centrifuge and wash the precipitate with 2 cc of 5 N NH_4OH. Add the wash to the supernate and add excess $AgNO_3$ to precipitate the excess iodide (5 drops of 0.5 N $AgNO_3$).

(6) Centrifuge and wash as before saving the supernate and wash.

(7) Make acid with HNO_3 to precipitate the AgCl, centrifuge, and wash the precipitate twice with 3 ml portions of 2 N HNO_3. The precipitate can be plated directly or dissolved in NH_4OH and an aliquot taken.

Remarks: If an appreciable amount of copper is to be dissolved the heat of reaction may drive the chlorine carrier into the receiving vessel before the copper is completely dissolved. If this occurs add 2.5 mg of chlorine carrier as chloride to the water in the receiver and after the copper is in solution add an additional 2.5 mg to the copper solution and distil as stated above. In case bromine is present it may be removed by making the solution 0.5 M in HNO_3 before precipitation, adding 5 mg of Br^- carrier, 0.25 grams of ammonium persulfate and boiling, thus oxidizing the Br^- to Br_2 and volatilizing. The solution should then be reduced with hydrazine and the chlorine precipitated as AgCl.

7/12/49

P-18-58

CHEMICAL SEPARATIONS

Element separated: Potassium

Procedure by: Brooks

Target material: LiCl

Time for sep'n: 1 hr.

Type of bbdt: alpha 20-60 Mev

Equipment required: Small centrifuge tubes, 72% perchloric acid

Yield: Quantitative is possible

Degree of purification: Radio chemically pure possibly.

Advantages: Simplicity and speed.

Procedure:

(1) Dissolve LiCl in about 3 cc water add KCl carrier (~ 20 mg)

(2) Add ~ 5 cc of 72% $HClO_4$ and cool in ice.

(3) Centrifuge.

(4) The $KClO_4$ may be recrystallized as many times as desired by heating it to ~ 90°C with 1 cc of 72% $HClO_4$ and then cooling in ice.

Remarks: 4 recrystallizations can be made in 1 hour of chemistry. About 1/2% is lost per recrystallization by doing it this fast. A trace of P^{32} sometimes was not removed by this chemistry.

NH_4^+ salts interfere. Separation from Na is good. No Rb or Cs contamination was found.

6/16/49

CHEMICAL SEPARATIONS

Element separated: Potassium

Procedure by: Brooks

Target material: LiCl

Time for sep'n: 40 min. or less

Type of bbdt: alpha 20-60 Mev

Equipment required: Napthol yellow S reagent

Yield: 50% or more depending on speed required.

Degree of purification: Radiochemically pure is possible.

Advantages: Fast and simple

Procedure:

(1) Dissolve LiCl in ~5 cc of H_2O

(2) Add 10 cc of Napthol-yellow-S (5% solution) cool and centrifuge.

(3) Recrystallize from about 5 cc of NYS 5% in ice.

(4) The ppt can be dissolved quickly in water or weak acid.

(5) Scavenge with $Fe(OH)_3$.

Remarks: NH_4^+ salts interfere

6/16/49

CHEMICAL SEPARATIONS

Element separated: Calcium

Procedure by: Goeckermann

Target material: ~1g Bi metal

Time for sep'n: Few hrs.

Type of bbdt: 184" bbdt all particles

Equipment required: Centrifuge

Yield: ~ 20%

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

Advantages: Separates Ca from all other elements.

Procedure:

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

(2) Add 10 mg Ru & Bi to supn & repeat H_2S pptn.

(3) Boil out H_2S & ppt with NH_3.

(4) Add 10 mg Fe & Y to supn & repeat NH_3 pptn.

(5) Boil down to ~ 5 ml, add 10 mg Ba & Sr, & ppt with cold fuming HNO_3.

(6) Add more Sr & Ba to supn & repeat pptn three times.

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

(8) Boil down to ~ 5 ml, add 5 ml sat $(NH_4)_2C_2O_4$, & make basic with NH_3.

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

(10) Add more Fe, La, & Y to supn & repeat pptn., centrifuge.

(11) Repeat step (5)

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

6/27/49

P-18-25

CHEMICAL SEPARATIONS

Element separated: Calcium

Procedure by: Batzel

Target material: Copper

Time for sep'n: 45 min.

Type of bbdt: All 60" and 184"

Equipment required: standard

Yield: 95%

Degree of purification: 10^3

Advantages: Pure fraction with good yield.

Procedure:

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

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

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

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

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

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

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

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

Remarks:

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

CHEMICAL SEPARATIONS

Element separated: Calcium

Procedure by: Stewart-Softky

Target material: Copper (up to 10 g)

Time for sep'n: 4 hrs.

Type of bbdt: Neutrons 184"

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

Yield: 60 - 80%

Degree of purification: 10^6 from Cu

Procedure:

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

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

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

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

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

8/24/49

CHEMICAL SEPARATIONS

Element separated: Scandium

Procedure by: Batzel

Target material: Copper

Time for sep'n: 1 1/2 hr.

Type of bbdt: All 60" and 184"

Equipment required: Standard

Yield: 60%

Degree of purification: Factor of 100 from other activities present.

Procedure:

(1) Dissolve copper in minimum amount of HNO_3. Boil to remove excess. Add 5 mg of Sc and other carriers. Adjust to 1 N in HCl and treat with H_2S (CuS out).

(2) Boil to remove H_2S, add NH_4OH and NH_4Cl till ammonical. Centrifuge and wash ppt with hot NH_4Cl solution.

(3) Dissolve ppt in HCl and make 6 N in HCl. Extract Fe 3 times with equal volume ethyl acetate. Add ~3 mg of Fe carrier and again extract Fe.

(4) Make the pH of the solution 2.0 and extract with equal volume TTA (5 ml of 0.5 M in benzene.) Shake for 10 minutes. Wash TTA layer with three 4 ml portions of water.

(5) Extract into 1 N HCl with two 3 ml portions.

(6) Ppt the Sc as hydroxide with NaOH. Wash with H_2O. Repeat the extraction with fresh TTA.

(7) The scandium can be weighed as Sc_2O_3 after precipitation as $Sc(OH)_3$ and ignition.

8/15/49

P-18-203

CHEMICAL SEPARATIONS

Element separated: Vanadium

Procedure by: Batzel

Target material: Copper foil (~ 1 gm.)

Time for sep'n: ~ 2 hours

Type of bbdt: 184-inch, all.

Equipment required: Standard

Yield: Fair (undetermined)

Degree of purification: Undetermined (only probably impurities, Cr and P)

Procedure:

(1) Dissolve target in minimum amount of conc. HNO_3, add carriers, Zn through Cl, boil off HNO_3, and make 1 N in HCl.

(2) Add H_2S, centrifuge off copper. Wash copper with 1 N HCl and resaturate with H_2S. Add wash to supernate.

(3) Boil down to remove H_2S, to 6 ml. add conc. HNO_3 and boil down almost to dryness, and make vol. to 5 ml. with conc. HNO_3; cautiously add $KClO_3$ and boil for one minute.

(4) Centrifuge off MnO_2. Wash MnO_2 with 6 N HNO_3, and add wash to supernate.

(5) Boil down to remove HNO_3 and HCl, and make 1 N in HNO_3. Cool to 5-10° C, and add an equal volume of diethyl ether. Add 5 drops of 30% H_2O_2 and immediately stir vigorously to extract chromium. Draw off ether layer, and wash water layer with one-half volume of ether, stirring vigorously to extract any chromium left. Draw off ether layer and add to original ether layer.

(6) Almost neutralize the water layer with NaOH and pour into 10 ml of a hot solution of 1 N NaOH. (A small amount of Fe^{+++} must be present.) Centrifuge off hydroxides of Ni, Co, Fe, Ti, Sc, and Ca. Wash precipitate with 4 ml. of hot 1 N NaOH. Add wash to supernate.

(7) Scavenge by adding 1 drop of Fe^{+++} carrier (10 mg./ml.) and 500 λ Ti^{++} (10 mg./ml.) to the hot solution. Centrifuge and wash precipitate with 4 ml. of hot 1 N NaOH.

(8) Boil down to 6 ml. Make slightly acid with acetic acid and add 5 ml. of 10% $Pb(Ac)_2$. Centrifuge off $Pb(VO_3)_2$, and wash with slightly acidic, dilute $Pb(Ac)_2$. Add wash to supernate (containing Zn^{++}).

(9) Make 2 N with HNO_3, precipitate Pb as the sulfide by adding H_2S. Centrifuge and wash precipitate with 2 N HNO_3. Add wash to supernate. Boil to remove H_2S.

(10) Neutralize with NaOH, make slightly acid with HAc and reprecipitate vanadium as lead vanadate. Weigh.

Remarks: Reference: Scotts Standard Methods of Chemical Analysis, p. 1036.

8/29/49

CHEMICAL SEPARATIONS

Element separated: Chromium

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 3/4 hr.

Type of bbdt: 190 Mev D^+

Equipment required: standard

Yield: 60%

Degree of purification: ~ factor of 50 from other activities.

Procedure:

(1) Dissolve As in HNO_3. Add 10 mg Cr carrier and evaporate to ~2 cc.

(2) Add 1 cc fuming HNO_3 and several crystals $KClO_3$. B oil several minutes, adding more $KClO_3$.

(3) Cool, add KOH and water to about 25 cc of 1 N H^+. Chill in ice salt bath to near freezing, add 10 cc cold ether. Add 1 dp H_2O_2 and extract deep blue color into ether.

(4) Add a second portion of ether and H_2O_2. Wash the cold ether layers with four quarter volumes of water containing 1 drop conc. HNO_3.

(5) Extract chromate out with dilute KOH, add other holdback carriers and HAc to slightly acid.

(6) Add Ba dropwise to precipitate $BaCrO_4$.

Remarks: Procedure should be practiced so success of the oxidation and extraction can be recognized.

6/27/49
P-18-22

CHEMICAL SEPARATIONS

Element separated: Chromium

Procedure by: Goeckermann

Target material: approx. 1 g Bi metal

Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, cones, 110° oven.

Yield: Approx. 50%

Degree of purification: Few c/m separated from several million counts of fission and spallation products.

Advantages: Fair yield of pure Cr.

Procedure:

(1) To aliquot of HNO_3 soln of target add 10 mg Cr as $Cr_2O_7^{=}$. Add HCl & HCOOH to reduce to Cr^{+3}. Ppt Bi_2S_3 & Sb_2S_3 scavenger from 1 N HCl soln.

(2) Ppt $Cr(OH)_3$ with K_2CO_3 + H_2S, by long boiling.

(3) Oxidize in 10 ml 0.5 N NaOH with H_2O_2, scavenge with $Fe(OH)_3$, & destroy H_2O_2.

(4) Make slightly acid with 6 N H_2SO_4 & wash with ether.

(5) Add H_2O_2 & extract H_3CrO_8 into about equal volume of ether.

(6) Re-oxidize & re-extract aqueous phase.

(7) Evaporate ether over H_2O & repeat H_3CrO_8 extrn.

(8) Evap ether over H_2O, oxidize with H_2O_2 in alkaline soln, scavenge with $Fe(OH)_3$.

(9) Acidify with 6 N HNO_3, add 1 ml 6 N HAc & 2 ml 6 N NH_4Ac, heat, add several ml 50 g/l Ba soln. Filter, wash with hot H_2O & EtOH, dry 10 min. at 110° C. Weigh as $BaCrO_4$ (48.7 mg per 10 mg Cr).

Remarks: H_3CrO_8 extrn tricky, easy to lose Cr by reduction before extraction.

6/27/49

CHEMICAL SEPARATIONS

Element separated: Chromium

Procedure by: Batzel

Target material: Copper

Time for sep'n: 40 minutes

Type of bbdt: All 184" and 60"

Equipment required: standard

Yield: 50%

Degree of purification: 10^2-10^3

Advantages: Very specific - no interfering ions.

Procedure:

(1) Dissolve the copper in the minimum amount of concentrated HNO_3. Boil almost to dryness, add carriers (Zn and below) and make 1 N in HCl.

(2) Precipitate the copper as sulfide, make the supernate alkaline with NH_4OH and precipitate the sulfides including Cr with H_2S.

(3) The Mn is usually removed at this point (see procedure for Mn(25-5). Neutralize the HNO_3 and make 1 N in HNO_3.

(4) Cool in an ice bath to 5° C and add 0.5 cc of 30% H_2O_2. Extract the blue peroxychromic acid with ethyl ether. (two 4 ml portions).

(5) Wash the ether layer with three 4 ml portions of water acidified with a drop of HNO_3.

(6) Extract the chromium from the ether layer with 3 cc of distilled water made distinctly alkaline with NH_4OH.

(7) The Cr may be precipitated and weighed as $BaCrO_4$.

Remarks:

(1) The Mn is usually removed (step 3) so that an estimate can be made of the amount of Cr^{51} formed by decay of the 42 minute Mn^{51}.

8/4/49
P-18-134

CHEMICAL SEPARATIONS

Element separated: Chromium

Procedure by: D. B. Stewart

Target material: Aluminum alloy
95% Al, 2.25% Mg, 0.25% Cr(+Fe & Cu)

Time for sep'n: ~1 hr.

Type of bbdt: 184" deuterons

Equipment required: Standard

Yield: 60-80%

Degree of purification: 10^4 from Al, others unknown

Procedure:

(1) Dissolve aluminum in 6 N HCl. Add 25-50 mg Cr carrier, 5 mg Cu carrier.

(2) Oxidize Cr to dichromate by boiling with 1 g ammonium persulfate and 2-3 drops of 2% $AgNO_3$ solution.

(3) Remove Al, Mg, Fe by precipitation with excess NH_4OH. Centrifuge, & decant supernatant. Dissolve precipitate in HCl and repeat to get out more of the Cr which can be occluded.

(4) Acidify the combined supernatants with HCl (0.1 - 0.3 N acid). Saturate with H_2S to precipitate CuS and reduce chromium to Cr^{+3}. Centrifuge or filter off the CuS.

(5) Boil filtrate to expel H_2S and reduce volume as far as possible. Make solution basic with NH_4OH. A gelatinous green precipitate of $Cr(OH)_3$ forms on boiling off the excess NH_3.

8/24/49

P-18-268

CHEMICAL SEPARATIONS

Element separated: Manganese

Procedure by: W. C. Orr

Target material: Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, or Sr.

Time for sep'n: 2 hrs.

Type of bbdt: 190 Mev deuterons, 30 min.

Equipment required:
sintered glass filters
100 ml beakers
50 ml vol. flask

Yield: 60-80%

Degree of purification: Adequate for determining Mn^{52} and Mn^{56} yields. Recycling should give increased purification.

Advantages: Simplicity.

Procedure:

(1) Target is dissolved in ~ 30 ml conc. HNO_3. (HCl used for Cr).

(2) 25 to 50 mg of standardized Mn carrier is added, i.e., a measured vol. of solution of known concentration.

(3) Several mg of hold-back carriers added, all elements except Mn from Z + 1 to Z - 12 (Z = target at. no.).

(4) Boil to expel oxides of nitrogen.

(5) Solid $KClO_3$ is added SLOWLY! Wait after adding each increment for the evolution of ClO_2, etc. Continue until ppt'n of MnO_2 is complete. Boil continuously.

(6) Filter through a medium sintered glass filter on which a layer of "Supercel" has been laid down. Wash with conc. HNO_3.

(7) MnO_2 is dissolved directly on the filter by conc. HNO_3 to which 30% H_2O_2 is added dropwise. Solution may be drawn through the filter into a clean filtering flask and transferred to a clean 100 ml beaker.

(8) The carriers of step (3) are again added.

(9) The solution is boiled to decompose H_2O_2. Conc. HNO_3 is added to restore vol. to ~ 30 ml.

(10) Repeat steps (5) through (9) two or more times (see remarks, following).

(11) Repeat steps (5), (6), and (7)

(cont'd.)

(12) Boil to decompose H_2O_2; i.e., solution becomes colorless and vol. is less than 50 ml.

(13) Transfer to 50 ml vol. flask and dilute to mark. Samples of 25λ and 100λ should be suitable for counting Mn^{56} (2.59 hrs.) decaying into Mn^{52} (6 days) half-life.

Remarks: The repetition of steps indicated in (10) should give increased purification. The whole procedure should include not less than three precipitations of MnO_2.

In cases where step (9) preceded step (8) good separation was not always achieved, presumably because the active impurity was not in the same oxidation state as the added carrier at the beginning of MnO_2 precipitation.

Presence of sulfate is to be avoided because soluble sulfate complexes of Mn(III) render precipitation incomplete.

According to Scott (Std. Meth. Chem. Anal.) oxides of W, Si, Cb, and Ta are also ppt'd by $KClO_4$ as in this procedure.

DETERMINATION OF Mn CONCENTRATION

For determining chemical yields in a series of separations of Mn activity from other elements the following procedure is particularly easy and of an accuracy comparable with other methods.

Assuming that 2.0 ml of a standard manganous nitrate solution was added as carrier to all starting mixtures, and assuming that after separation from other elements the remaining manganese was in all cases contained in 50.0 ml of solution, take 1.0 ml of the latter 50.0 ml by pipet and transfer to a 50 ml vol. flask.

Add about 40 ml of 3 N HNO_3.

Add enough solid $NaBiO_3$ so that a slight amount of excess solid remains in the flask at all times (but not enough to occupy a significant volume).

Shake for 30 seconds, then dilute with water to 50.0 ml. Shake for one minute.

Let stand overnight (or centrifuge if there is need for hurry).

Decant a portion of the supernatant solution of MnO_4^- and measure its optical density in a one cm cell of the Beckman quartz spectrophotometer. Set the wavelength at the peak near 525 mμ.

Dilute 2.0 ml of the standard carrier solution to 50.0 ml. Take 1.0 ml of this as the starting sample and repeat the procedure just described.

The ratio of the first optical density to the second is the desired chemical yield.

W. C. Orr

6/24/49

P-18-6

CHEMICAL SEPARATIONS

Element separated: Manganese

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 1 hr.

Type of bbdt: 190 Mev D^+

Equipment required: standard

Yield: ~ 60%

Degree of purification: ~ factor of 50 from other activities.

Procedure:

(1) Dissolve As in minimum HNO_3 & HCl, add 5 mg Mn and 1 mg other carriers.

(2) Make alkaline with NH_4OH, pass in H_2S for 1 minute, centrifuge, wash with H_2O.

(3) Dissolve with hot fuming nitric acid and add solid $KClO_3$ to boiling solution to ppt. MnO_2, add fuming HNO_3 and $KClO_3$ until pptn is complete.

(4) Centrifuge and wash with H_2O. Dissolve with 1 dp dilute HCl and 1 dp H_2O_2.

(5) Make to 5 ml volume, 3 N HCl and add 5 mg As.

(6) Pass H_2S into hot solution to ppt As_2S_3.

(7) Repeat pptn of As_2S_3. Make supnt alkaline, pass in H_2S to precipitate MnS. Dissolve as before and ppt. MnO_2 from a solution containing additional holdback carriers.

6/27/49

P-18-21

CHEMICAL SEPARATIONS

Element separated: Manganese

Procedure by: Stewart-Softky

Target material: Copper foil (ca. 300 mg.)

Time for sep'n: 1-2 hrs for 12 samples

Type of bbdt: 60" or 184" deuterons

Equipment required:
100 ml beakers
filter funnels
40 ml centrifuge cones

Yield: 90-100%

Degree of purification: Excellent, factor of approx. 10^6

Advantages: Simplicity & rapidity. (Large number of samples can be run simultaneously).

Procedure:

(1) Dissolve copper in minimum 6N HNO_3. Add 1 mg Mn carrier as nitrate.

(2) Dilute to 1-2 N HNO_3 add about 100 mg of $KBrO_3$ and boil for 5-10 minutes, or until MnO_2 is well coagulated.

(3) Filter through Whatman #42 filter paper. Wash precipitate with 6N HNO_3 until no Cu blue shows in final wash.

(4) Dissolve MnO_2 through filter paper into a 40 ml centrifuge cone, with conc. HCl. Add 2 mg Cu carrier. Make solution strongly ammonical.

(5) Add a few crystals of $(NH_4)_2S_2O_8$ and boil off excess persulfate in a hot water bath. MnO_2 precipitates almost immediately.

(6) Centrifuge, decant supernatant, and wash precipitate with dilute NH_4OH.

CHEMICAL SEPARATIONS

Element separated: Manganese

Procedure by: Batzel

Target material: Copper

Time for sep'n: 30 min.

Type of bbdt: All 184" and 60"

Equipment required: standard

Yield: 75%

Degree of purification: 10^3

Advantages: Pure fraction and is not time consuming.

Procedure:

(1) Dissolve the copper in the minimum amount of concentrated HNO_3. Boil almost to dryness, add carriers (Zn and below) including 5 mg of Mn and make 1 N in HCl.

(2) Precipitate the copper sulfide. Make the supernate alkaline with NH_4OH and precipitate the sulfides including Mn with H_2S.

(3) To the sulfides add concentrated 16 N HNO_3 carefully, to dissolve and make the volume up to 4 cc with fuming HNO_3. Add 2 or 3 crystals of $KClO_3$ and boil gently for 2 minutes to precipitate MnO_2.

(4) Wash the precipitate with H_2O and dissolve in one drop of HNO_3 and H_2O_2.

(5) Again add holdback carriers and make 16 N in HNO_3. Precipitate the MnO_2 with $KClO_3$ as in step 4.

(6) The precipitate may be weighed as MnO_2 and counted.

8/4/49

P-18-132

CHEMICAL SEPARATIONS

Element separated: Iron

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 1/2 hr.

Type of bbdt: 190 Mev D^+

Equipment required: standard

Yield: ~ 60%

Degree of purification: ~ factor of 50 from other activities.

Procedure:

(1) Dissolve As in minimum HNO_3 + HCl, add 2 mg Fe, Ga, adjust to 6 N HCl, extract twice with equal volumes ethyl ether.

(2) Wash ether layer 5 times with 1/3 volumes 6 N HCl.

(3) Wash ether layer twice with 1/4 portions H_2O to remove Fe. Make 1 N KOH and centrifuge off $Fe(OH)_3$.

(4) Dissolve in minimum conc. HCl, dilute to 5 ml, add 1 mg Ga carrier, and reppt. $Fe(OH)_3$ with KOH.

(5) Repeat until supernatants (Gallium fractions) are inactive.

6/27/49

P-18-23

CHEMICAL SEPARATIONS

Element separated: Iron

Procedure by: Goeckermann

Target material: ∿1 g Bi metal

Time for sep'n: few hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, cones

Yield: ∿ 30%

Degree of purification: Decontamination factor ∿ 10^4 from fission & spallation products.

Advantages: Fair yield of pure Fe.

Procedure:

(1) Extract 15 ml of 9 N HCl containing aliquot of HNO_3 sol'n of target and 10 mg Fe^{+3} with 15 ml isopropyl ether. Wash ether twelve times with 10 ml portions of 7.5 N HCl. Extract Fe^{+3} into 10 ml H_2O and evap dissolved ether.

(2) Scavenge with Sb_2S_3 from HCl sol'n. -- repeat.

(3) Scavenge with TeS by H_2S pptn.

(4) Ppt $Fe(OH)_3$ with NH_3 & dissolve in HCl.

(5) Fume twice with few ml $HClO_4$ after adding Ru.

(6) Ppt $Fe(OH)_3$ with NH_3 -- repeat.

(7) Scavenge with $BaSO_4$.

(8) Scavenge with AgI (excess Ag).

(9) Scav. with Cb_2O_5 by adding HNO_3 & $KClO_3$ to oxalate sol'n.

(10) Scav. with Zr phenylarsonate (make precipitation by adding phenylarsenic acid).

(11) Ether ext Fe^{+3} again, ppt as $Fe(OH)_3$ with NH_3, filter & ignite to Fe_2O_3 to weigh.

Remarks: This rather involved procedure was designed to separate a very small amount of Fe activity from a large amount of activity spread over the periodic table. It can be simplified in most cases. There may be an advantage in doing one of the extractions of Fe^{+3} out of the ether by treating the ether layer with 6-9 N HCl containing Hg and thereby reducing the Fe to Fe^{+2} (insol. in ether). A few mg of carriers are used in the scavenges.

7/6/49

P-18-40

CHEMICAL SEPARATIONS

Element separated: Iron

Procedure by: Folger & Hicks

Target material: ∽ 4 g U metal foil

Time for sep'n: few hrs.

Type of bbdt: 184" all high energy particles

Equipment required: Centrifuge cones, crucible, open top cylindrical separatory funnels, stirring motor and glass stirring rods.

Yield: ∽ 30%

Degree of purification: Decontamination factor ∽10^4 from fission & spallation products. ∽10^6 from elements 38 to 56.

Advantages: Fair yield of pure Fe.

Procedure:

(1) Add 10 mg Fe^{+3} to aliquot of target sol'n. Evap. to dryness twice with conc. HCl. Take up in 15 ml of 9 N HCl. Extract twice with 10 ml portions of di-isopropyl ether. Wash ether twelve times with 10 ml portions of 7.5 N HCl. Extract Fe^{+3} into 2,5-ml portions H_2O and evap dissolved ether.

(2) Scavenge with Sb_2S_3 and TeS_2 from 1 N HCl sol'n. -- repeat.

(3) Ppt $Fe(OH)_3$ with NH_3 wash & dissolve in HCl.

(4) Add Ru and fume twice with few ml $HClO_4$.

(5) Ppt $Fe(OH)_3$ with NH_3 wash.

(6) Dissolve in HNO_3 and scavenge with $BaSO_4$.

(7) Scavenge with AgI (excess Ag).

(8) Ppt. $Fe(OH)_3$ with NH_3 (to reduce volume) wash and dissolve in conc. HNO_3.

(9) Add Cb and scavenge with Cb_2O_5 by adding $KBrO_3$ and HNO_3 to oxalate soln.

(10) Make 3N in HNO_3 and HF. Add Ba and scavenge with $BaZrF_6$ twice.

(11) Ppt $Fe(OH)_3$ with NH_3. Wash. Dissolve in 9 N HCl.

(12) Ether ext Fe^{+3} again, re-extract into H_2O, ppt as $Fe(OH)_3$ with NH_3, wash, filter & ignite to Fe_2O_3 to weigh. (14.3 mg Fe_2O_3 = 10 mg Fe)

Remarks: This rather involved procedure was designed to separate a very small amount of Fe activity from a large amount of activity spread over the periodic table. It can be simplified in most cases. There may be an advantage in doing one of the extractions of Fe^{+3} out of the ether by treating the ether layer with 6-9 N HCl containing Hg and thereby reducing the Fe to Fe^{+2} (insol. in ether). 1-2 mg of carriers are used in the scavenges.

CHEMICAL SEPARATIONS

Element separated: Iron

Procedure by: Stewart, Softky

Target material: Copper foils (300-500 mg Cu)

Time for sep'n: 2-3 hrs.

Type of bbdt: Deuterons 60", 184"

Equipment required: beakers, filter funnel, 40 ml centrifuge cones, separatory funnels

Yield: 80-100%

Degree of purification: factor of $\sim 10^6$

Advantages: High purity. Small amount of carrier.

Procedure:

(1) Dissolve copper in minimum 6N HNO_3 and dilute to 1-2 N HNO_3. Add 1 mg Fe and 1 mg Mn carrier as nitrate.

(2) Add about 0.1 g $KBrO_3$ and boil for 5-10 minutes or until MnO_2 is well coagulated. Filter through Whatman #42 filter paper and catch filtrate in a 40 ml centrifuge cone. Wash precipitate with 2N HNO_3 until wash is colorless.

(3) Precipitate $Fe(OH)_3$ with excess NH_4OH, centrifuge, and decant supernatant. Dissolve precipitate in HCl and repeat until supernatant is colorless. Add 2-3 mg Cu carrier as chloride and repeat twice more.

(4) Dissolve final $Fe(OH)_3$ in 1 drop of HCl and transfer to a separatory funnel with 6 N HCl. Add an equal volume of di-ethyl ether pre-saturated with 6N HCl and extract the Fe. Draw aqueous layer into a 2nd separatory funnel and repeat. Do a 3rd extraction after adding 1 mg Fe carrier as chloride.

(5) Collect the ether layers in a 40 ml centrifuge cone with a small amount of water. Evaporate off the solvent in a hot water bath. Recover Fe as $Fe(OH)_3$ by precipitation with NH_4OH.

Remarks:

It was found that unless specific separation for Mn is done, the contamination in the iron fraction is appreciable. (Step 2).

Direct evaporation of an $FeCl_3$ solution gives considerable loss, so it is better to ppt the iron and re-dissolve in some acid other than HCl. (Step 5).

CHEMICAL SEPARATIONS

Element separated: Iron

Procedure by: Batzel

Target material: Copper

Time for sep'n: 40 min.

Type of bbdt: All 184" - 60"

Equipment required: Standard

Yield: 95%

Degree of purification: 10^3

Advantages: Pure fraction with good yield.

Procedure:

(1) The target may be dissolved in the minimum amount of either concentrated HNO_3 or concentrated HCl and H_2O_2.

(2) Five mg of Fe are added as carrier and the solution made 6 N in HCl - total volume 6 cc.

(3) Extract 3 times with ethyl acetate - 3 ml portions. Wash the ethyl acetate 3 times with 1/3 volume of 6 N HCl.

(4) Extract the iron from the ethyl acetate layer with 3 cc of distilled water. Again make 6 N in HCl and re-extract as listed in step 3.

(5) Finally after washing the ethyl acetate thoroughly with 6 N HCl, extract the iron into 3 cc of distilled water and plate.

(6) The chemical yield can be determined calorimetrically by taking aliquots from the final iron solution (See 26-6).

Remarks:

(1) Holdback carriers need not be added for other elements, but will not interfere with this procedure if added.

DETERMINATION OF Fe CONCENTRATION

The following procedure may be used for the colorimetric analysis of iron.

Prepare a curve of iron concentration vs % transmission as follows:

(1) To 10 ml volumetric flasks add 5, 10, 15, 20, 25, and 30 gamma of Fe from the standard solution.

(2) Add 200 λ of a 10% solution of hydroxylamine hydrochloride. Dilute to 5 cc and add 500 λ of a 0.1 percent water solution of orthophenanthraline.

(3) Add one drop NH_4OH to bring the pH to the range of 4 to 9. Dilute to 10 cc and allow color to develop for 5 minutes.

(4) Measure the % transmission of the samples against a blank containing the hydroxylamine and orthophenanthraline at a wave length of 508 millimicrons on a Beckman Spectrophotometer.

(5) The curve follows Beer's Law.

In analyzing the samples duplicates should be run using the above procedure.

R. Batzel

CHEMICAL SEPARATIONS

Element separated: Iron

Procedure by: R. C. Lilly

Target material: Cobalt

Time for sep'n: 6 hours

Type of bbdt: Neutrons - 60"

Equipment required: Beakers, funnels

Yield: ~100%

Degree of purification: excellent at least factor of 100 from other activities present.

Advantages: Simplicity

Procedure:

(1) Dissolve the Co target in HNO_3. Remove the nitrates by boiling with HCl until no brown fumes are evolved.

(2) Add 2 mg Fe, 10 mg Ni, 10 mg Zn and 50 mg U as the chloride solutions. Dilute and ppt with excess NH_4OH. Coagulate the ppt and filter it quickly through quantitative paper. Dissolve the ppt through the filter with warm HCl and repeat the pptn.

(3) Dissolve the ppt through the filter with warm HCl, collecting the sol'n in a 40 ml centrifuge tube. Add hold-back carriers of Cu, Ni, Zn and Co and do three more NH_4OH ppt'ns, dissolving the ppt in HCl each time.

(4) Dissolve the final ppt in HCl so as to give an 8 N HCl sol'n; and extract the Fe with 3 or 4 portions of isopropyl ether. Combine ether layers, add H_2O, boil to a low volume, and fume with H_2SO_4-H_2O_2 until organic matter is destroyed.

(5) Take up in HCl and ppt with NH_4OH - $(NH_4)_2CO_3$ sol'n., discarding the supernatant. Dissolve in HCl and repeat the ppt'n twice. Dissolve the final ppt if desired, or use as is.

Remarks:

The ppt'n of the Fe and U from the bulk of the cobalt is best made by quickly adding a large excess of NH_4OH to the warm dilute Co sol'n.

Nitrates must be avoided throughout to prevent extraction of the U by the ether.

This procedure was used for the preparation of pure compounds of Fe^{59}; for identification of activities alone, it would be advisable to take an aliquot after dissolving the target.

Paper is used for the filtration in (2) because the ppt tends to clog a sintered filter if suction is applied.

8/19/49
P-18-237

CHEMICAL SEPARATIONS

Element separated: Iron

Procedure by: R. C. Lilly

Target material: Manganese

Time for sep'n: 4-6 hours

Type of bbdt: Deuterons - 60"

Equipment required: beakers, funnels, sintered glass funnels and separatory funnels.

Yield: ~ 100%

Degree of purification: excellent at least factor of 100 from other activities present.

Advantages: Large amount of Mn does not prevent purification of the Fe.

Procedure:

(1) Dissolve Mn target in the least possible amount of 6 N HCl. Add 2-5 mg Fe and 25 mg Cu as the chloride solutions.

(2) Make 0.3 N in HCl, heat to boiling, and pass in H_2S to ppt the copper group as sulfides. Filter. Wash the ppt with 0.1 N HCl and discard it. Add wash to filtrate.

(3) Boil filtrate to 50 ml volume, oxidize Fe with 5 ml of 30% H_2O_2 and boil off excess H_2O_2. MnO_2 may ppt at this point, but it will redissolve as the H_2O_2 is expelled.

(4) Make alkaline with NH_4OH and ppt the Fe as $Fe(OH)_3$. Some Mn will also ppt; it can be disregarded and will be removed later in the procedure. This step separates the Fe from any large amounts of salts which may be present to interfere with the ether extraction which follows.

(5) Dissolve ppt through filter with warm 9 N HCl; the resulting volume should be 10-20 ml. Extract the Fe with 3 or 4 portions of isopropyl ether. Combine the ether layers, add H_2O, boil to a low volume, and fume with H_2SO_4-H_2O_2 until organic matter is destroyed.

(6) Take up in HCl and ppt $Fe(OH)_3$ with NH_4OH, discarding the supernatant. Dissolve the ppt if desired, or use as is.

Remarks:

This procedure was used for preparing pure compounds of Fe^{55}; the procedure time could be shortened for use on shorter-lived isotopes.

8/19/49

CHEMICAL SEPARATIONS

Element separated: Iron

Procedure by: R. C. Lilly

Target material: Ni (separated isotopes)

Time for sep'n: 3-5 minutes

Type of bbdt: Neutrons - 60"

Equipment required: small beakers, 5 ml centrifuge tube, Hirsch funnel

Yield: ~ 90%

Degree of purification: factor of 5

Advantages: Speed

Procedure:

(1) Dissolve Ni foil, weighing 3-5 mg in a 10 ml beaker containing 0.5 ml hot conc. HNO_3. Add 2 mg Co, 2 mg Cu, and 2 mg Fe as 2 ml of the chloride sol'ns.

(2) Transfer to a 5 ml centrifuge cone and ppt with NH_4OH. Coagulate the ppt by immersing the cone in a boiling H_2O bath for a few seconds and centrifuge. Remove the supernatant.

(3) Dissolve the $Fe(OH)_3$ ppt in a few drops of conc HCl. Add 2 mg Co, 2 mg Cu, and 2 mg Ni as 2 ml of the chloride sol'ns, and transfer the sample to a second 10 ml beaker.

(4) Ppt with NH_4OH, coagulate the ppt by heating and filter through a #42 Whatman filter paper disc held in a Gooch crucible or Hirsch funnel. Dry with a few drops of acetone and mount under tape.

8/19/49

CHEMICAL SEPARATIONS

Element separated: Iron

Procedure by: R. C. Lilly

Target material: Cu (50-100 mg)

Time for sep'n: 45 minutes

Type of bbdt: Deuterons - 184"

Equipment required: beakers, funnels, 40 ml centrifuge tube, small centrifuge tube.

Yield: ~ 100%

Degree of purification: Factor of 100

Advantages: Simplicity

Procedure:

(1) Dissolve Cu target in conc. HCl containing a few drops of conc HNO_3. Boil off the excess HNO_3. Add 3 mg Fe, 10 mg Co, 10 mg Ni, and 5 mg Zn as the chloride sol'ns.

(2) Dilute to 50 ml with H_2O and heat to boiling. Ppt $Fe(OH)_3$ by adding NH_4OH in excess and coagulate the ppt well by heating. Filter the $Fe(OH)_3$ ppt through #42 Whatman paper in a glass funnel and wash with a small amount of 1% NH_4Cl sol'n.

(The filtrate contains the Cu, Co, Ni and Zn fractions and is worked up separately as described in the procedures for Co and Ni from Cu targets, Nos. 27-5 and 28-6.

(3) Wash the $Fe(OH)_3$ ppt well with 1% NH_4Cl and discard the washings. Dissolve the ppt through the paper with warm 6 N HCl and collect the sol'n in a 40 ml centrifuge cone.

(4) Add 10 mg Co and 10 mg Ni as the chloride sol'ns as hold-back carriers; place the cone in a hot H_2O bath, and ppt with NH_4OH. Coagulate the ppt by heating, centrifuge, and discard the supernatant. Redissolve the ppt in HCl.

(5) Repeat step (4) twice.

(6) After the third ppt'n. cycle above, dissolve the ppt in the correct amount of HCl and H_2O to give 10 ml of sol'n., 8 N in HCl.

(7) Extract Fe with four 10 ml portions of isopropyl ether. Combine ether layers, add H_2O, boil to a low volume, and fume with H_2SO_4-H_2O_2 until organic matter is destroyed.

(8) Take up in HCl, transfer to a small centrifuge cone, and ppt with NH_4OH. Centrifuge and discard the supernatant. Prepare for counting as desired.

Remarks: See Hillebrand and Lundell (Applied Inorganic Analysis) for further information on the extraction of Fe with isopropyl ether.

8/19/49
P-18-239

CHEMICAL SEPARATIONS

Element separated: Cobalt

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 1 hr.

Type of bbdt: 190 Mev D^+

Equipment required: standard

Yield: ~ 70%.

Degree of purification: ~ factor of 100 from other activities.

Procedure:

(1) Dissolve As in minimum HNO_3 + HO, add 2 mg Se & Ge carrier, 5 mg Co.

(2) Make alkaline with NH_4OH, pass in H_2S rapidly for 1 minute only. Centrifuge immediately.

(3) Dissolve in minimum conc. HCl, add 1 mg Cu, ppt CuS from hot 1 N HCl.

(4) Add other carriers, evaporate to small volume, make 6 N HCl, extract 4 times with equal volume ethyl ether.

(5) Evaporate to near dryness, add H_2O to 2 ml volume, add ~ equal volume solid KSCN, extract 4 times with 2 ml amyl alcohol.

(6) Extract out of amyl alcohol with 4 ml 1 N KOH.

(7) Dissolve with HCl and reppt hydroxide with KOH.

(8) Dissolve in minimum acetic acid, dilute to 4 ml, saturate with KCl, and add KNO_2 until pptn of $K_3Co(NO_2)_6$ is complete.

CHEMICAL SEPARATIONS

Element separated: Cobalt

Procedure by: Stewart - Softky

Target material: Copper foils (ca. 300 mg. Cu)

Time for sep'n: 4-6 hrs.

Type of bbdt: Deuterons 60" or 184"

Equipment required:
- Stainless steel strip electrodes to fit 100 ml beakers
- 30 ml tower electrolysis cells
- 1" Pt discs
- Pt spiral stirrers
- D. C. rectifier unit to give current up to 2 amperes
- 100 ml beakers
- filter funnels

Yield: 90-100%

Degree of purification: Complete separation at least by factor of 10^5 from Mn, Fe, Ni, Cu & Zn.

Advantages: Method by which a large number of samples can be run simultaneosly for excitation functions.

Procedure:

(1) Dissolve Cu foil in minimum dilute HNO_3. Add 1 mg. Co, Ni, & Mn carriers as nitrates, and 2 drops conc. H_2SO_4. Dilute to about 20 ml. with distilled water.

(2) Electrodeposit copper on stainless steel strip cathode set into beaker in which the foil was dissolved, using a rotating Pt spiral anode at 2-3 volts, 1-2 amperes.

(3) When solution is water white, remove the electrodes, add 1 ml. conc. H_2SO_4 and evaporate to SO_3 fumes to remove HNO_3.

(4) Dilute to 35-50 ml and saturate with H_2S to precipitate residual Cu. Filter. Boil filtrate to expel H_2S, add 2 mg Cu carrier as chloride and repeat.

(5) Boil filtrate 5 minutes to expel H_2S, make solution slightly ammonical, then add 1-2 ml 1% dimethylglyoxime in ethanol to ppt NiDMG. Filter. Wash ppt with hot water.

(6) Acidify filtrate with HNO_3 & evaporate to SO_3 fumes to destroy alcohol. Add a few drops of conc. HCl and again take to SO_3 fumes to insure removal of NO_3^-.

(7) Transfer solution to a 30 ml tower electrolysis cell fitted with a 1" Pt disc cathode, make strongly ammonical, and electrolyze at 1-2 amperes for about 30 minutes, using a slowly rotating Pt

anode. Cobalt deposits as a smooth adherent plate on the cathode. MnO_2 deposits at the same time on the anode.

(8) When Co is completely deposited, replace the electrolyte with distilled water while the current is still on. Remove the anode quickly to prevent sol'n of the MnO_2, pour off the water and rinse the cobalt plate with alcohol.

Remarks:

(In step (5) if solution is too strongly ammonical at this point, NiDMG will be incompletely precipitated.)

(In step (7) NH_4OH should be added periodically during the electrodeposition. Current should be kept lower than 2 amperes to give a smooth adherent plate.)

CHEMICAL SEPARATIONS

Element separated: Cobalt

Procedure by: Batzel

Target material: Copper

Time for sep'n: 40 min.

Type of bbdt: all - 184" & 60"

Equipment required: Standard

Yield: 30-40%

Degree of purification: Factor of at least 100 from other activities present.

Procedure:

(1) Dissolve copper in minimum amount of concentrated HNO_3, and boil to dryness or with HCl to destroy HNO_3. Add 5 mg Co carrier and 1-2 mg of the neighboring elements to get as holdbacks.

(2) Remove copper as sulfide from a 1 N HCl solution. Wash the precipitate with 1N HCl saturated with H_2S.

(3) Boil supernate to remove H_2S and neutralize with KOH. Make 2-3 N in acetic acid. Saturate about 5 cc of water with KNO_2 and add 0.3 cc of acetic acid. Heat and add to the hot solution of cobalt.

(4) Allow to settle for 5 minutes in a steam bath. Cool, and centrifuge. Wash with a 5% KNO_2 solution acidified with acetic acid.

(5) Dissolve the ppt with concentrated HCl again add 1 mg each of holdback carriers and reprecipitate.

(6) Weigh as the potassium cobaltinitrite.

CHEMICAL SEPARATIONS

Element separated: Cobalt

Procedure by: Folger

Target material: ~ 4 gm. U metal foil

Time for sep'n: ~ 2 1/2 hrs.

Type of bbdt: 184" full energy particles (high energy fission)

Equipment required: Centrifuge, cones, ice bath, 110° oven. NH_3 gas.

Yield: ~ 50% possible

Degree of purification: Separates from all elements by a factor of at least 10^4 separates from elements 38 to 56 by a factor of ~ 10^8.

Advantages: A small amt. of Co may be obtained pure from large yields of contaminants.

Procedure:

(1) Uranium target is dissolved in conc. HCl (plus a small amt. conc. HNO_3 to clear up the sol'n) or in conc. HNO_3 (should be ≥ 10N). Use ~ 1/4 (or more) of target sol'n for aliquot. Add 10-20 mg Co carrier and make basic with NH_3.

(2) Centrifuge and wash ppt twice with sat'd aqueous NH_3. Combine supernatant and washings.

(3) Scavenge twice with $Fe(OH)_3$, twice with $BaCO_3$ & $SrCO_3$ (add sat'd Na_2CO_3 and check pH to be sure sol'n is basic enough, ~ pH 10).

(4) Make 0.7 - 0.8 N in HCl. Scavenge with CuS, CdS, Re_2S_7 (for Tc) HgS, PdS_2 (1-2 mg of carriers).

(5) Make basic with NH_3 and ppt CoS w. H_2S. Wash to remove all NH_4^+. Dissolve in 1 cc conc. HNO_3. Dilute to ~ 4N HNO_3 and scavenge with 1-2 mg AgCl twice.

(6) Make basic with KOH to ppt $Co(OH)_2$ (upon heating goes to $Co(OH)_3$ Centr. and wash. Dissolve ppt in 3 cc 2-3 N HAc. Add 2 mg Ni holdback and heat.

(7) Add 3-4 cc 6 N HAc sat'd with KNO_2 hot (Caution! Beware of foaming over). Digest 10 min hot. Chill in ice bath to retard bubbles and centrifuge $K_3Co(NO_2)_6 \cdot 1\ 1/2\ H_2O$ (yellow).

(8) Wash, and dissolve in conc. HCl (with heating - green sol'n is obtained).

(9) Repeat steps (3) through (8). Then repeat (6) and (7).

(10) Wash twice with H_2O, EtOH, Et_2O. Filter, dry at 110° C for 5 min. Weigh as $K_3Co(NO_2)_6 \cdot H_2O$.

Remarks:

(1) In step (6), the $Co(OH)_2$ ppt becomes grey-brown on heating in the

water bath. This does not interfere with the procedure.

(2) For additional information see Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, Ed. 5 Vol. I, pp 305-14.

CHEMICAL SEPARATIONS

Element separated: Cobalt

Procedure by: R. C. Lilly

Target material: Cu, Ni

Time for sep'n: 1 hour

Type of bbdt: Deuterons - 184"
Neutrons - 60"

Equipment required:
Beakers, funnels, fine sintered glass filter, 50 ml separatory funnels (3)

Yield: ~ 90%

Degree of purification: Factor of 100

Advantages: Purity of Co product

Procedure: A, B & C have steps 4-9 in common.

A. Cobalt from Ni (separated isotopes) + p,d,n - 60"

(1) Dissolve Ni foil, weighing 3-5 mg., in a few drops of conc HNO_3 and boil off HNO_3 with successive portions of HCl. Add 2 mg Co, 2 mg Fe and 5 mg Cu as the chloride sol'ns.

(2) Dilute to 50 ml with H_2O and heat to boiling. Ppt $Fe(OH)_3$ by adding NH_4OH in excess and coagulate the ppt well by heating. Filter the $Fe(OH)_3$ ppt through #42 Whatman paper in a glass funnel and wash with a small amount of 1% NH_4Cl sol'n. (The ppt is worked up separately as described in the procedure for Fe from Cu targets, No. 26-10). Make the filtrate slightly acidic with HCl. Add conc NH_4HSO_3 sol'n dropwise until all of the Cu is reduced (as shown by the lack of any localized blue color when a few drops of conc NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

(3) Coagulate the CuSCN ppt by heating and filter it through a double thickness of #42 Whatman paper in a glass funnel. Discard the ppt. Boil the filtrate to a volume of 10 ml to expel SO_2 and transfer to a 50 ml separatory funnel.

B. Cobalt from Cu (50-100 mg) + d - 184"

(1) Dissolve Cu target in conc. HCl containing a few drops of conc. HNO_3. Boil off the excess HNO_3. Add 2 mg Co, 2 mg Fe, and 2 mg Ni as the chloride sol'ns.

(2) Dilute to 50 ml with H_2O and heat to boiling. Ppt $Fe(OH)_3$ by adding NH_4OH in excess and coagulate the ppt well by heating. Filter the $Fe(OH)_3$ ppt through #42 Whatman paper in a glass funnel and wash with a small amount of 1% NH_4Cl sol'n. (The ppt is worked up separately as described in the procedure for Fe from Cu targets, No. 26-10). Make the filtrate slightly acidic with HCl. Add conc. NH_4HSO_3 sol'n dropwise until all of the Cu is reduced (as shown by the lack of any

localized blue color when a few drops of conc NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

(3) Coagulate the CuSCN ppt by heating and filter it through a double thickness of #42 Whatman paper in a glass funnel. Discard the ppt. Boil the filtrate to a volume of 10 ml to expel SO_2 and transfer to a 50 ml separatory funnel.

C. Cobalt from Cu (0.1-0.5 gms) + n - 184"

(1) Dissolve Cu target in 10 ml of hot 6 N HNO_3 in a small beaker and boil off HNO_3 with successive portions of HCl. Add 2 mg Co and 2 mg Ni as the chloride sol'ns.

(2) Add H_2O and HCl so as to give a volume of 25-30 ml with 0.3 N-0.5 N HCl. Heat to boiling and pass in H_2S to ppt CuS. Coagulate the ppt by heating and filter it through a small fine sintered glass filter. Wash the ppt with a small amount of H_2O and discard it.

(3) Boil the filtrate to a volume of ~10 ml and then transfer it to a 50 ml separatory funnel.

In all three of the above cases continue as follows:

(4) Add 5 gms of solid NH_4SCN and shake until all of the crystals are dissolved. Extract Co from this sol'n by shaking with an equal volume of ethyl ether - amyl alcohol (1:1)

(5) Draw off the H_2O layer from this extraction into a second 50 ml separatory funnel, discarding the few drops of mixed sol'ns which remain in the stopcock.

(The Ni is contained in the H_2O layer and is worked up separately as described in the procedure for Ni from Cu targets. No. 28-6).

(6) Add 10 ml of 6 N NH_4OH to the organic layer in the first separatory funnel to destroy the complex and reextract the Co.

(7) Draw off this ammoniacal layer into a third 50 ml separatory funnel and make it slightly acidic with HCl. Add 2 mg Ni as the chloride sol'n and repeat the extraction as in step (4) above.

(8) Draw off the H_2O layer and discard it. Treat the organic layer with NH_4OH as described in step (6) above.

(9) Draw off the ammoniacal layer into a 50 ml beaker, boil to a volume of 5 ml, and ppt CoS by adding NH_4HS sol'n. Prepare this ppt for counting as desired.

Remarks: See Sandell (Colorimetric Determination of Traces of Metals) for further information on the extraction of Co from thiocyanate sol'ns with ethyl ether - amyl alcohol.

P-18-228

8/19/49

CHEMICAL SEPARATIONS

Element separated: Cobalt

Procedure by: R. C. Lilly

Target material: Cu, Ni

Time for sep'n: 4 hours

Type of bbdt: Neutrons, deuterons - 184"
For calutron separation

Equipment required: Beakers, funnels, chlorination apparatus.

Yield: ~ 90%

Degree of purification: Factor of 100

Advantages: Separation of Co from large amounts of Cu and Ni.

Procedure: A and B have steps 2-8 in common.

A. Cobalt from Cu(10 gms) + neutrons - 184"

(1) Dissolve Cu target in 50-100 ml of hot 6 N HCl containing 5 ml of 30% H_2O_2. Boil off excess H_2O_2 and add 25-50 mg Co and 5 mg Ni as the chloride sol'ns. Dilute the sample to ~ 1 liter and add NH_4OH until the sol'n is neutral or very slightly acidic.

B. Cobalt from Ni (1-2 gms) + deuterons - 184"

(1) Dissolve Ni target in the least possible volume of conc. HNO_3. Convert nitrates to chlorides by adding successive portions of conc HCl and taking to a low volume. Add 25-50 mg Co and 75 mg Cu as the chloride sol'ns. Dilute the sample to ~ 500 ml and add NH_4OH until the sol'n is neutral or very slightly acidic.

In each of the above cases, continue as follows:

(2) Add conc. NH_4HSO_3 sol'n., 1 ml at a time, until all of the Cu is reduced (as shown by the lack of any localized blue color when a few drops of conc. NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

(3) Coagulate the CuSCN ppt by heating and filter it through a double thickness of #42 Whatman paper in a large glass funnel. Discard the ppt.

(4) Boil the filtrate to expel SO_2 and then add 3 ml of conc HCl per 100 ml of volume.

(5) Add a freshly prepared hot sol'n of alpha-nitroso-beta-naphthol, made by dissolving 10 gms of the salt in 100 ml of 50% acetic acid, as long as a ppt is produced.

(6) Filter the ppt through retentive paper. Wash it well with warm 6 N HCl, and then with warm H_2O until free from acid. Ignite the ppt until all of the paper is burned off.

(7) Dissolve the CoO in HCl and add 100 mg Cu and 25 mg Ni as the chloride sol'ns. Adjust the acidity as in step (1) and repeat steps (2) through (6) above.

(8) Convert this CoO to $CoCl_2$ by treating it with anhydrous Cl_2 at 650° C for 30 minutes.

(If desired, part of the CoO in step (7) may be dissolved in HCl and a cobalt fraction purified still further by adding Cu and Ni hold-back carriers and following the procedure for Co from Ni targets, No. 27-5.)

Remarks:

The above procedure was designed for preparing a sample for analysis in the calutron. In case a smaller spectrograph is to be used, the amount and final form of the Co may need changing.

See Scott (Std. Meth. Chem. Anal.) for further information on the ppt'n of Co by alpha-nitroso-beta-napthol.

8/19/49

P-18-233

CHEMICAL SEPARATIONS

Element separated: Cobalt

Procedure by: R. C. Lilly

Target material: Ni (separated isotopes)

Time for sep'n: 10 minutes

Type of bbdt: Protons - 37" and 60"
deuterons - 60"

Equipment required:
Small beakers
50 ml separatory funnels (2)

Yield: ∿ 90%

Degree of purification: Factor of 5

Advantages: speed

Procedure:

(1) Dissolve Ni foil, weighing 3-5 mg., in a 10 ml beaker containing 0.5 ml of hot 6 N HNO_3. Take to dryness on a preheated hot plate.

(2) Add 3-4 drops of hot conc HCl and take to dryness. Repeat.

(3) Add 2 mg Co as the chloride sol'n and warm slightly. Transfer to a 50 ml separatory funnel and dilute to 10 ml with H_2O.

(4) Add 5 gms of solid NH_4SCN and shake until all of the crystals are dissolved. Extract Co from this sol'n by shaking with an equal volume of ethyl ether-amyl alcohol (1:1).

(5) Draw off the H_2O layer from this extraction into a second 50 ml separatory funnel, discarding the few drops of mixed sol'ns which remain in the stopcock.

(The Ni is contained in the H_2O layer and is worked up separately as described in the procedure for Ni from Ni targets, No. 28-6).

(6) Add 10 ml of 6 N NH_4OH to the organic layer in the first separatory funnel to destroy the complex and reextract the Co.

(7) Draw off the ammoniacal layer into a small beaker, heat to boiling, and ppt CoS by adding NH_4HS sol'n. Prepare this ppt for counting as desired.

Remarks:

See Sandell (Colorimetric Determination of Traces of Metals) for further information on the extraction of Co from thiocyanate sol'ns with ethyl ether - amyl alcohol. If time allows, purification from Cu may be obtained by adding 2-3 mg Cu as the chloride sol'n in step (3) and ppting CuSCN as outlined in the procedure for Cu from Ni targets. (No. 29-5). Filter off the CuSCN, collect the filtrate in a 50 ml separatory funnel, and proceed with step (4) above.

8/19/49

P-18-230

CHEMICAL SEPARATIONS

Element separated: Cobalt

Procedure by: Stewart-Softky

Target material: Copper foils (~3 g Cu)

Time for sep'n: 4-6 hrs for 12 foils

Type of bbdt: 60" or 184" deuterons

Equipment required: 100 ml beakers, centrifuge cones, filter funnels, sep. funnels

Yield: 80-100%

Degree of purification: 10^5 from Cu, Zn activities

Advantages: Can be used to separate Co from copper in a large number of samples simultaneously (e.g. for excitation functions)

Procedure:

(1) Dissolve copper foil in 6 N HCl and a few drops of 30% H_2O_2. Boil off the peroxide. Add 2 mg Fe, Zn and Co carrier as chlorides.

(2) Precipitate $Fe(OH)_3$ with excess NH_4OH, centrifuge and pour off supernatant. Dissolve precipitate in HCl and repeat. Add 2nd supernatant to the original.

(3) Make solution about 0.1 N with HCl. Add a few drops of NH_4HSO_3 to reduce Cu^{+2} to Cu^{+1} (shown by decolorized or pale yellow solution). Warm to near boiling. Add NH_4SCN crystals until no further precipitation of CuSCN takes place. Let settle for 15 minutes. Filter through Whatman #42 filter paper directly into a separatory funnel. Wash precipitate with a 1% solution of NH_4SCN containing a little NH_4HSO_3.

(4) Add 5 g NH_4SCN to the solution in the separatory funnel and extract $(NH_4)_2Co(SCN)_4$ with a 1:1 amyl alcohol-diethyl ether solution. Add 2 ml conc. HCl and 1 g NH_4SCN and repeat extraction until solvent layer is colorless (2-3 extractions usually sufficient). Re-extract cobalt from the combined solvent layers with 6N NH_4OH.

(5) Make solution acid (pH 2-3) with HCl and add an additional 1 mg of Zn as $ZnCl_2$. Saturate with H_2S to precipitate ZnS, centrifuge and decant supernatant into another cone. Make slightly ammoniacal and warm to coagulate CoS precipitate.

Remarks:

It was found that Zn extracted partially from the saturated thiocyanate solution with the alcohol-ether mixture.

8/24/49

CHEMICAL SEPARATIONS

Element separated: Cobalt

Procedure by: Stewart-Softky

Target material: Copper foils (2-3 g Cu)

Time for sep'n: 4-6 hrs for 12 foils

Type of bbdt: 60" or 184" deuterons

Equipment required: Filter funnels, beakers

Yield: ~ 80%

Degree of purification: 10^6 from Cu

Advantages: Can be used to separate Co from copper in a large number of samples simultaneously (e.g. for excitation functions.)

Procedure:

(1) Dissolve copper in minimum dilute HCl + a few drops of 30% H_2O_2. Boil off peroxide. Add 2 mg Fe and Co carriers as chloride.

(2) Precipitate $Fe(OH)_3$ with excess NH_4OH. Filter and wash with NH_4OH (dilute).

(3) Acidify filtrate to about 0.1 N HCl, add a few drops of NH_4HSO_3 to reduce Cu^{+2} to Cu^{+} (decolorized solution) and warm to near boiling. Add NH_4SCN crystals until no further precipitation of CuSCN takes place. Let settle for 15 minutes. Filter through #42 filter paper. Wash precipitate with a 1% solution of NH_4SCN.

(4) Add sufficient conc HCl to filtrate to make about 1 N acid and heat to near boiling. Add 5-10 ml of a freshly prepared solution of α-nitroso-β-naphthol reagent. (10 g α-nitroso-β-naphthol in 100 ml 50% acetic acid). Let stand 30 minutes to insure complete precipitation of cobalt.

8/24/49

CHEMICAL SEPARATIONS

Element separated: Nickel

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 45 min.

Type of bbdt: 190 Mev D^+

Equipment required: standard

Yield: 95%

Degree of purification: factor of $\sim 10^3$

Procedure:

(1) Dissolve As in minimum HNO_3 + HCl, add 2 mg Se, Ge carriers, and 5 mg Ni.

(2) Add NH_4OH to alkaline and pass in H_2S rapidly. Centrifuge and wash NiS with H_2O.

(3) Dissolve with conc. HCl and reppt from NH_4OH.

(4) Dissolve in minimum conc. HCl, boil out H_2S, add carriers below Ge, dilute to 10 ml and adjust pH to $\sim$ 3 with HAc.

(5) Add dimethyl glyoxime solution until precipitation is complete. Centrifuge, dissolve ppt in conc HNO_3 and boil.

(6) Dilute to 10 ml, make alkaline with NH_4OH and reppt with dimethyl glyoxime.

6/28/49
P-18-33

CHEMICAL SEPARATIONS

Element separated: Nickel

Procedure by: Goeckermann

Target material: ∿1g Bi metal

Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, cones, 110° oven.

Yield: ∿60%

Degree of purification: Decomtamination factor ∿ 10^4 from fission & spallation products.

Advantages: Separates Ni in good yield from most elements.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg Ni, make neutral, add 5 ml 1% dimethylglyoxime in alcohol, wash with H_2O and EtOH.

(2) Dissolve Ni d-m-g in 1 ml conc. HNO_3, dilute, & scav twice with CuS.

(3) Scav three times with PdS.

(4) Scav with Sb_2S_3.

(5) Boil out H_2S, make basic with NH_3, scav twice with $Fe(OH)_3$.

(6) Make 0.5 N in HCl & scav with Pd d-m-g.

(7) Neutralize supn & ppt Ni d-m-g.

(8) Dissolve in conc HNO_3, reppt Ni d-m-g, filter, wash with H_2O & EtOH, dry 10 min at 110°C. Weigh as Ni d-m-g (29.4 mg per 10 mg Ni).

Remarks: Designed to purify a little Ni from a lot of activity spread over the periodic table. A few mg of carrier are used in the scavenges.

7/6/49

P-18-39

CHEMICAL SEPARATIONS

Element separated: Nickel

Procedure by: Batzel

Target material: Copper

Time for sep'n: 40 min.

Type of bbdt: All - 184" & 60"

Equipment required: Standard

Yield: 70%

Degree of purification: At least factor of 100 from other activities.

Advantages: Quantitative and specific for this region.

Procedure:

(1) Dissolve copper in minimum amount of concentrated nitric acid. Boil to dryness. Add 5 mg of Ni and 1-2 mg of holdback carriers for other elements Zn and below. Remove copper as sulfide from 1N HCl, and wash precipitate with 1N HCl saturated with H_2S.

(2) Boil supernate to remove H_2S. Neutralize with NH_4OH and make slightly acid with acetic acid. Add 1% alcoholic solution of dimethyl-glyoxime (2 ml.). Centrifuge and wash the precipitate twice with 3 cc water containing 2-3 drops of acetic acid.

(3) Dissolve the precipitate in concentrated HCl and again add 1-2 mg of holdback carriers for other elements. Add NH_4OH to neutralize make slightly acid with acetic to reprecipitate.

(4) Weigh as the Ni - dmg.

Remarks:

Reference: Scott's Standard Methods of Chemical Analysis, Volume I, page 619.

7/27/49
P-18-80

CHEMICAL SEPARATIONS

Element separated: Nickel

Procedure by: Stewart-Softky

Target material: Copper foils (300-500 mg Cu.)

Time for sep'n: 3-4 hrs. for 12 samples

Type of bbdt: 60" or 184" deuterons

Equipment required: beakers, filter funnels

Yield: ∾100%

Degree of purification: Complete separation of Ni from Zn, Cu, Fe, Co, Mn factor of ∾ 10^6.

Advantages: Rapid method by which many samples can be run simultaneously. Good yield with small amount of carrier.

Procedure:

(1) Dissolve copper in 6 N HCl + a few drops of 30% H_2O_2 and boil off excess peroxide. Add 0.5 mg - 1 mg Ni carrier as chloride.

(2) Neutralize with NH_4OH and make slightly acid with HCl. Add NH_4HSO_3 to reduce Cu^{+2} to Cu^{+1} (only 1 - 2 ml necessary) and boil off excess SO_2.

(3) Precipitate CuSCN from the warm solution with a few crystals of NH_4SCN, being careful not to add a large excess of NH_4SCN. Let settle for 10 minutes. Filter through Whatman #42 filter paper and wash the precipitate with a 1% solution of NH_4SCN containing a little NH_4SO_3.

(4) Add 1 ml 50% tartaric acid to the filtrate, make very slightly ammonical and warm to near boiling. Add 1-2 ml 1% dimethyl glyoxime in ethanol to precipitate NiDMG.

(5) Filter through Whatman #40 filter paper and wash with hot water.

(6) Dissolve precipitate in dilute HCl and repeat (4) & (5) to reduce Zn & Co contamination.

Remarks:

Step (4): If solution is made too strongly ammonical, NiDMG will be incompletely precipitated.

CHEMICAL SEPARATIONS

Element separated: Nickel

Procedure by: Folger & Hicks

Target material: ~ 4 g U metal foil

Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all high energy particles

Equipment required: Centrifuge, cones, 110° oven, NH_3 gas.

Yield: ~ 60%

Degree of purification: Decontamination factor ~ 10^4 from fission & spallation products, ~ 10^6 from elements 38-56.

Advantages: Separates Ni in good yield from most elements.

Procedure:

(1) To aliquot of target containing ~ 10 mg Ni pass in NH_3. Centrifuge and wash twice with sat'd AqNH_3. Combine supernatant and washings.

(2) Scavenge with $Fe(OH)_3$. Then Sr and Ba carbonates and $Fe(OH)_3$ (to clean the sol'n).

(3) To supernatant add 1-2 ml 1% dimethylglyoxime in alcohol. Centrifuge and wash with H_2O.

(4) Dissolve Ni d-m-g in 1 ml conc. HNO_3, dilute to 3 N and scav twice with CuS.

(5) Dilute to 1 N and scav three times with PdS.

(6) Scav with Sb_2S_3.

(7) Boil out H_2S, make basic with NH_3, scav twice with $Fe(OH)_3$.

(8) Make 0.5 N in HCl & scav with Pd d-m-g.

(9) Neutralize supn & ppt Ni d-m-g, wash with H_2O.

(10) Dissolve in conc. HNO_3 dilute and neutralize, reppt Ni d-m-g, filter, wash with H_2O, dry 15 min at 110° C. Weigh as Ni d-m-g (29.4 mg per 10 mg Ni).

Remarks:

(1) Designed to purify a little Ni from a lot of activity spread over the periodic table. A few mg of carrier are used in the scavenges.

(2) Where carrier amounts of Cu and Co are present in the original target soln, it may be necessary to remove these before ppt'ng Ni-dmg since Co and Cu form dmg complexes.

(3) Ni-dmg is somewhat soluble both in alcohol and in excess d.m.g. There is also a slight solubility in conc. NH_4OH.

8/4/49

P-18-128

CHEMICAL SEPARATIONS

Element separated: Nickel

Procedure by: R. C. Lilly

Target material: Cu, Ni

Time for sep'n: 1 hour

Type of bbdt: Deuterons - 184"
Neutrons - 60"

Equipment required:
Beakers, funnels,
fine sintered glass filter,
50 ml separatory funnels (3),
15 ml centrifuge tube

Yield: ~ 90%

Degree of purification: Factor of 100

Advantages: Purity of Ni product

Procedure: A, B & C have steps 4-7 in common.

A. Nickel from Ni (separated isotopes) + p, d, n - 60"

(1) Dissolve Ni foil, weighing 3-5 mg., in a few drops of conc HNO_3 and boil off HNO_3 with successive portions of HCl. Add 2 mg Co, 2 mg Fe and 5 mg Cu as the chloride sol'ns.

(2) Dilute to 50 ml with H_2O and heat to boiling. Ppt $Fe(OH)_3$ by adding NH_4OH in excess and coagulate the ppt well by heating. Filter the $Fe(OH)_3$ ppt through #42 Whatman paper in a glass funnel and wash with a small amount of 1% NH_4Cl sol'n. (The ppt is worked up separately as described in the procedure for Fe from Cu targets, No. 26-10). Make the filtrate slightly acidic with HCl. Add conc NH_4HSO_3 sol'n dropwise until all of the Cu is reduced (as shown by the lack of any localized blue color when a few drops of conc NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

(3) Coagulate the CuSCN ppt by heating and filter it through a double thickness of #42 Whatman paper in a glass funnel. Discard the ppt. Boil the filtrate to a volume of 10 ml to expel SO_2 and transfer to a 50 ml separatory funnel.

B. Nickel from Cu(50-100 mg) + d - 184"

(1) Dissolve Cu target in conc. HCl containing a few drops of conc. HNO_3. Boil off the excess HNO_3. Add 2 mg Co, 2 mg Fe, and 2 mg Ni as the chloride sol'ns.

(2) Dilute to 50 ml with H_2O and heat to boiling. Ppt $Fe(OH)_3$ by adding NH_4OH in excess and coagulate the ppt well by heating. Filter the $Fe(OH)_3$ ppt through #42 Whatman paper in a glass funnel and wash with a small amount of 1% NH_4Cl sol'n. (The ppt is worked up separately as described in the procedure for Fe from Cu targets, No. 26-10). Make the filtrate slightly acidic with HCl. Add conc. NH_4HSO_3 sol'n dropwise until all of the Cu is reduced (as shown by the lack of any

localized blue color when a few drops of conc NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

(3) Coagulate the CuSCN ppt by heating and filter it through a double thickness of #42 Whatman paper in a glass funnel. Discard the ppt. Boil the filtrate to a volume of 10 ml to expel SO_2 and transfer to a 50 ml separatory funnel.

C. Nickel from Cu (0.1 - 0.5 gms) + n - 60"

(1) Dissolve Cu target in 10 ml of hot 6 N HNO_3 in a small beaker and boil off HNO_3 with successive portions of HCl. Add 2 mg Co and 2 mg Ni as the chloride sol'ns.

(2) Add H_2O and HCl so as to give a volume of 25-30 ml with 0.3 N-0.5 N HCl. Heat to boiling and pass in H_2S to ppt CuS. Coagulate the ppt by heating and filter it through a small fine sintered glass filter. Wash the ppt with a small amount of H_2O and discard it.

(3) Boil the filtrate to a volume of ~ 10 ml and then transfer it to a 50 ml separatory funnel.

In all three of the above cases continue as follows:

(4) Add 5 gms of solid NH_4SCN and shake until all of the crystals are dissolved. Extract Co from this sol'n by shaking with an equal volume of ethyl ether - amyl alcohol (1:1)

(5) Draw off the H_2O layer from this extraction into a second 50 ml separatory funnel, discarding the few drops of mixed sol'ns which remain in the stopcock.

(The Co is contained in the organic fraction and is worked up separately as described in the procedure for Co from Cu targets, No. 27-5).

(6) Add 2 mg of Co as the chloride sol'n to the H_2O layer in the second funnel and reextract with an equal volume of ethyl ether-amyl alcohol (1:1). Draw off the H_2O layer into a 50 ml beaker, boil to a volume of 5 ml, and transfer to a 15 ml. centrifuge cone. Discard the organic layer.

(7) Make the sol'n slightly ammoniacal and add 1 ml of 1% DMG in alcohol to ppt Ni. Centrifuge and discard the supernatant. Wash the ppt with H_2O, centrifuge, and discard the wash. Prepare the ppt for counting as desired.

Remarks: See Sandell (Colorimetric Determination of Traces of Metals) for further information on the extraction of Co from thiocyanate sol'ns with ethyl ether-amyl alcohol.

8/19/49

CHEMICAL SEPARATIONS

Element separated: Nickel

Procedure by: R. C. Lilly

Target material: Cu(10 gms)

Time for sep'n: 3 hours

Type of bbdt: Neutrons - 184"
For calutron separation

Equipment required: beakers, funnels, centrifuge cone

Yield: ~ 90%

Degree of purification: Factor of 100.

Advantages: Separates Ni from large amounts of Cu.

Procedure:

(1) Dissolve Cu target in 50-100 ml of hot 6 N HCl containing 5 ml of 30% H_2O_2. Boil off excess H_2O_2 and add 25-50 mg Co and 5 mg Ni as the chloride sol'ns. Dilute the sample to ~ 1 liter and add NH_4OH until the sol'n is neutral or very slightly acidic.

(2) Add conc. NH_4HSO_3 sol'n., 1 ml at a time, until all of the Cu is reduced (as shown by the lack of any localized blue color when a few drops of conc. NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

(3) Coagulate the CuSCN ppt by heating and filter it through a double thickness of #42 Whatman paper in a large glass funnel. Discard the ppt.

(4) Boil the filtrate to a volume of 200 ml and make the sol'n slightly ammoniacal.

(5) Add 1% DMG in alcohol until no further ppt is produced. Add NH_4OH until the sol'n is distinctly basic.

(6) Coagulate the ppt by heating and then filter it through #42 Whatman paper in a glass funnel. Wash the ppt thoroughly with warm H_2O. Ignite the ppt until all of the paper is burned off.

(7) Dissolve the NiO in HCl and add 100 mg Cu and 10 mg Ni as the chloride sol'ns. Adjust the acidity as in step (1) and repeat steps (2) and (3).

(8) Boil the sol'n to a low volume and transfer to a centrifuge cone. Make slightly ammoniacal and ppt Ni with DMG as in step (5) above. Coagulate the ppt in a hot H_2O bath, centrifuge, and discard the supernatant. Prepare the ppt for counting as desired.

Remarks: The above procedure was designed for preparing a sample for analysis in the calutron. In case a smaller spectrograph is to be used, the amount and final form of the Ni may need changing.

CHEMICAL SEPARATIONS

Element separated: Copper

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 3/4 hr.

Type of bbdt: 190 Mev D^+

Equipment required: standard

Yield: > 90%

Degree of purification: factor of $\sim 10^3$

Procedure:

(1) Dissolve As in HCl + HNO_3, evap off HNO_3, add 5 mg Cu carrier and 1 mg other holdbacks.

(2) Ppt from 1 N HCl with H_2S. Wash with H_2O and treat ppt several times with 1 N KOH. Washes out As & Ge - discard.

(3) Dissolve remaining ppt in minimum conc. HNO_3, evap to dryness with HCl.

(4) Dilute to 1 N HCl, add pinches of solid Na_2SO_3 and NaCNS.

(5) If the precipitate is not pure white add more Na_2SO_3. After two minutes centrifuge.

(6) Dissolve with hot conc. HCl and repeat precipitation.

(7) Weigh as Cu SCN.

Remarks: Holdbacks added Cr through Sc except As & Cu.

6/28/49

P-18-34

CHEMICAL SEPARATIONS

Element separated: Copper

Procedure by: Batzel

Target material: Copper

Time for sep'n: 40 min.

Type of bbdt: 60" 184", linear accelerator - all particles

Equipment required: standard

Yield: 80%

Degree of purification: factor of $\sim 10^3$

Procedure:

(1) Add holdback carriers for the necessary elements. Dissolve the copper in as little HCl as possible adding H_2O_2 to speed up the solution.

(2) Make 1 N in HCl. Reduce the Cu^{++} to Cu^{+} with Na_2SO_3, cool and add NaCNS until precipitation is complete.

(3) Centrifuge and wash the precipitate with cold water.

(4) The precipitate can be dissolved in concentrated HNO_3 or HCl.

(5) Reprecipitation can be accomplished by diluting to 1 N, reducing and reprecipitating with thiocyanate.

Remarks:

(1) Copper can also be precipitated as the sulfide from 0.5 N to 1.0 N acid solution, and the precipitate dissolved in fuming HNO_3.

(2) A drop of wetting agent will prevent the tendency of the precipitate to creep.

(3) In redissolving care must be taken since the evolution of gas is profuse.

(4) Three precipitations of the Cu are enough to give a decontamination factor of $\sim 10^3$.

7/6/49

P-18-43

CHEMICAL SEPARATIONS

Element separated: Copper

Procedure by: Goeckermann

Target material: ∿ 1 g Bi metal

Time for sep'n: 1-2 hrs.

Type of bbdt. 184" all particles

Equipment required: Centrifuge, cones, 110° oven.

Yield: ∿ 60%

Degree of purification: Decontamination factor ∿ 10^4 from fission & spallation products.

Advantages: Good yield of Cu purified from all other elements.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg Cu, make basic with NH_3, centrifuge out $Bi(OH)_3$ & scavenge with $Fe(OH)_3$ and $BaCO_3$ (add K_2CO_3).

(2) Make supn 0.5 N in HCl. Bubble in SO_2, add KCNS until CuCNS ppts (slight excess)

(3) Dissolve Cu CNS in HNO_3 & make neutral. Add KCN & scavenge with CdS.

(4) Acidify & boil off HCN (caution!), add Sr & Y holdback, ppt CuS from 3N HCl.

(5) Dissolve in HNO_3, add HCl & destroy HNO_3. Dilute to 0.5 N HCl & scavenge twice with AgCl.

(6) Ppt CuCNS from supn, filter, wash with H_2O & EtOH, dry 15 min. at 110°C. Weigh as CuCNS (19.2 mg per 10 mg Cu).

Remarks: Scavenges made with 1-5 mg carrier.

CHEMICAL SEPARATIONS

Element separated: Copper

Procedure by: Folger & Hicks

Target material: ~4 g U metal foil

Time for sep'n: 1-2 hrs.

Type of bbdt. 184" all high energy particles

Equipment required: Centrifuge, cones, 110° oven.

Yield: ~ 60%

Degree of purification: Decontamination factor ~ 10^4 from fission & spallation products. ~ 10^6 from elements 38-56.

Advantages: Good yield of Cu purified from all other elements.

Procedure:

(1) To aliquot of HNO_3 or HCl soln of target, add 10 mg Cu, make basic with NH_3, centrifuge out $Bi(OH)_3$ & scavenge with $Fe(OH)_3$ and $BaCO_3$, $SrCO_3$ (add K_2CO_3).

(2) Make supn 0.5 N in HCl. Bubble in SO_2, add KCNS until CuCNS ppts (slight excess)

(3) Dissolve Cu CNS in HNO_3 & make neutral. Add KCN & scavenge with CdS, As_2S_3 and TeS_2.

(4) Acidify & boil off HCN (caution!), add Sr, La & Y holdbacks, ppt CuS from 3N HCl.

(5) Dissolve in minimum HNO_3. Dilute to 0.5 N H^+ & scavenge twice with AgCl. (Boiling helps coagulate AgCl).

(6) Ppt CuCNS from supn, filter, wash with H_2O & EtOH, dry 15 min. at 110° C. Weigh as CuCNS (19.2 mg per 10 mg Cu).

Remarks: Scavenges made with 1-2 mg carrier.

7/28/49
P-18-95

CHEMICAL SEPARATIONS

Element separated: Copper

Procedure by: R. C. Lilly

Target material: Ni (separated isotopes)

Time for sep'n: 4-5 minutes

Type of bbdt: Protons - 37" and 60"
Deuterons - 60"

Equipment required:
Small beakers,
Hirsch funnel

Yield: 50-75%

Degree of purification: Factor of 5

Advantages: speed

Procedure:

(1) Dissolve Ni foil, weighing 3-5 mg., in a 10 ml beaker containing 0.5 ml of hot 6 N HNO_3. Take to dryness on a preheated hot plate.

(2) Add 3-4 drops of hot conc HCl and take to dryness. Repeat.

(3) Add the following in succession, warming after each addition: 2 mg Cu and 2 mg Co as 2 ml of the chloride sol'ns; 0.5 ml conc NH_4HSO_3 sol'n.; and 0.5 ml 10% NH_4SCN sol'n.

(4) Stir and warm slightly. Filter the sample through a #42 Whatman filter paper disc held in a Gooch crucible or Hirsch funnel and prewet with a few drops of 0.1 N NH_4SCN - 0.1 N NH_4HSO_3 wash sol'n.

(5) Wash with a small amount of 0.1 N NH_4SCN - 0.1 N NH_4HSO_3 wash sol'n followed by a few drops of acetone. Mount for counting.

8/19/49

CHEMICAL SEPARATIONS

Element separated: Zinc

Procedure by: Goeckermann

Target material: ~ 1 g Bi metal

Time for sep'n: ~ 1 hr.

Type of bbdt: 184" bbdt all particles

Equipment required: Centrifuge, cones, ice, vacuum dessicator

Yield: ~ 70%

Degree of purification: No detectable contamination from other fission and spallation products.

Advantages: Good yield of pure zinc.

Procedure:

(1) To aliquot of nitric acid soln of Bi, add 10 mg Zn, 1 ml sat. $H_2C_2O_4$, and make 1 N in HNO_3 (10-25 ml). Cool in ice bath, add 3 ml Zn reagent (39 g KSCN dissolved in 200 ml H_2O. Stir in 27 g. $HgCl_2$ while diluting to 1 liter), stir 5 min. (scratch glass to begin pptn.)

(2) Dissolve $ZnHg(SCN)_4$ in 5 ml 2N HNO_3 and dilute to 1 N. Add 1 ml sat $H_2C_2O_4$ and 3 ml Zn reagent.

(3) Repeat (2).

(4) Dissolve ppt in 2 N HNO_3, dilute to 1 N, and ppt HgS. Neutralize supn to 0.3 N HNO_3 with NaOH and ppt Bi_2S_3 (5 mg Bi) three times.

(5) Make 1 M in NH_4Ac and ppt ZnS.

(6) Dissolve ppt in 5 ml conc HBr, evap to dryness several times, take up in 10 ml 0.5 N NaOH, add 1 ml 2 M Na_2CO_3. Ppt $Fe(OH)_3$ (2 mg) and $BaCO_3$ (5 mg) three times from hot soln.

(7) Add HCl to make 1 N and 1 ml sat $H_2C_2O_4$. Add 3 ml Zn reagent to cold soln, stir 3 min, filter, wash three times with 5 ml absolute EtOH and three times with 5 ml ether, dry 7 min in vacuum dessicator. Weigh as $ZnHg(SCN)_4$ (76.2 mg per 10 mgZn).

Remarks: Standardize carrier as $ZnHg(SCN)_4$ also. Final ppt poor if radiations soft because of large self-absorption correction required.

6/27/49

P-18-28

CHEMICAL SEPARATIONS

Element separated: Zinc

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 1 hr.

Type of bbdt: 190 Mev D^+

Equipment required: standard

Yield: ∿60%

Degree of purification: factor of ∿50.

Procedure:

(1) Dissolve As in 10 N HNO_3. Add 10 mg. Zn carrier and dilute to 1 N H^+.

(2) Add 0.03 M ammonium mercuric thiocyanate solution dropwise until pptn of Zn is complete.

(3) Dissolve in conc. HNO_3, add other holdback carriers and reppt.

(4) Dissolve in HNO_3, evap. off HNO_3 with HCl, scavenge with CuS from 2 N HCl.

(5) Ppt ZnS from solution 0.01 M H^+.

(6) Dissolve in 1 drop conc. HCl & dilute.

(7) Ppt from 0.01 M H^+.

Remarks: Holdback carriers that can be added Cr thru Se except As & Zn.

6/27/49
P-18-35

CHEMICAL SEPARATIONS

Element separated: Zinc

Procedure by: Batzel

Target material: Copper

Time for sep'n: 40 min.

Type of bbdt: all particles 184" & 60"

Equipment required: Standard

Yield: 60%

Degree of purification: factor of $\sim 10^3$.

Procedure:

(1) The copper is dissolved in concentrated HNO_3 or HCl and H_2O_2 to speed up solution. Five mg of Zn and 1 or 2 mg of holdback carriers for the necessary elements are added.

(2) The copper is removed as the sulfide from a 1 N acid solution, NH_4OH added to make the soln alkaline and then H_2S added to complete precipitation.

(3) The precipitate is washed with a solution containing a couple of drops of NH_4OH and saturated with H_2S.

(4) After centrifugation 2-3 ml. of 5 N HCl are added, the precipitate, stirred well, and the solution centrifuged almost immediately (after about one minute). The zinc and manganous sulfides are dissolved while the nickel and cobalt sulfides are attacked slowly.

(5) The supernate is boiled to remove H_2S approx 1 ml conc, NH_4OH added to neutralize the HCl and an equal volume (3,4 cc) of conc. HAc added. The solution is heated almost to boiling and saturated with H_2S to precipitate the Zn.

(6) The precipitate is dissolved in 1 N HCl - the H_2S boiled off and 2 mg Fe holdback carrier added. 2 to 3 pellets of NaOH are added and the ppt removed leaving the Zn in solution as zincate.

(7) The solution is made 1 N in HCl and zinc reagent added to perform the final precipitation.

Remarks:

(1) The Zn reagent is made from 32 gm NH_4SCN & 27 gm $HgCl_2$ in 500 ml H_2O. (See Scotts Standard Methods of Chemical Analysis, Vol. I, p.45)

(2) The Zn reagent precipitate can be dissolved in 5-6 N HNO_3.

(3) The Zn reagent is a satisfactory analytical procedure, but the gravimetric factor should be determined experimentally.

7/6/49

P-18-36

CHEMICAL SEPARATIONS

Element separated: Zinc

Target material: Copper foils (ca 300 mg)

Type of bbdt: 60" or 184" deuterons

Procedure by: Stewart-Softky

Time for sep'n: 1-2 hrs. for 12 samples

Equipment required:
100 ml beaker
40 ml centrifuge cone
filter funnel
20 mesh aluminum

Yield: 80-100%

Degree of purification: Decontamination by factor of $\sim 10^4$ from other activities.

Advantages: Simplicity. Can be used to separate Zn from copper rapidly in a large number of samples simultaneously (e.g. for excitation functions).

Procedure:

(1) Dissolve Cu foil in 100 ml beaker with a minimum amount of 6N HNO_3. Add 2-3 mg Zn carrier as nitrate or sulfate.

(2) Add 1 ml conc. H_2SO_4 and evaporate to SO_3 fumes to remove HNO_3.

(3) Dilute to 2-3 N H_2SO_4 and add about 500 mg 20 mesh aluminum. Boil until all Cu is reduced and for about 5 minutes after the solution appears to be water-white. Cool.

(4) Filter through a rapid filter paper and catch filtrate in a 40 ml centrifuge cone. Wash Cu ppt with 0.1 N - H_2SO_4.

(5) Add a drop of methyl orange to the filtrate and adjust to pH 2-3 with NaOH and dilute H_2SO_4.

(6) Saturate with H_2S to precipitate ZnS, centrifuge, and decant supernatant. Wash with 0.01 N H_2SO_4 containing H_2S.

(7) Plate ZnS & count.

Remarks:

Method is designed to give rapid separation of Zn from Cu when doing 6 to 12 samples simultaneously. There is some Cu contamination after only one aluminum reduction, but this is much less than 0.1% when only 300-500 mg of Cu is used for the target. Contamination could be reduced by adding 1-2 mg inert copper carrier as chloride or sulfate after filtering (step 4) & precipitating CuS from 1 N H_2SO_4 with H_2S. After removal, reduce acidity to 0.1 - 0.01 N H_2SO_4 & ppt ZnS.

CHEMICAL SEPARATIONS

Element separated: Zinc

Procedure by: D. B. Stewart

Target material: Copper

Time for sep'n: 2-4 hrs.

Type of bbdt: 60" or 184"

Equipment required:
- 150 ml beaker
- filter funnel, 40 ml centrifuge cone,
- stainless steel electrode to fit 150 ml beaker
- platinum electrode
- D.C. source

Yield: 80-100%

Degree of purification: Complete separation from copper, better than 10^6.

Advantages: Only small amount of carrier needed as compared to copper. (1 mg Zn carrier can be recovered quantitatively from up to 20 g Cu)

Procedure:

(1) Dissolve copper in 6 N - HNO_3 and evaporate off excess acid. Add 1 mg Zn carrier as nitrate and 0.5 ml conc. H_2SO_4. Dilute to about 100 ml with water.

(2) Electrodeposit copper on a stainless steel cathode at 2-3 volts, 5-10 amperes using a rotating Pt anode. Set apparatus in an ice bath during the electrolysis.

(3) When solution is water-white, turn off current and quickly remove electrodes. Evaporate solution to SO_3 fumes to remove HNO_3. (It may be necessary to add a few drops of H_2SO_4). Dilute to 20 ml (or about 1 N H_2SO_4). Saturate with H_2S to precipitate remaining copper.

(4) Filter through Whatman #42 filter paper, wash precipitate with 1 N H_2SO_4 containing a little H_2S. Boil filtrate to expel excess H_2S.

(5) Transfer solution to a 40 ml centrifuge cone. Add a drop of methyl orange indicator and adjust to pH 2-3 with NaOH and dilute H_2SO_4. Saturate with H_2S to precipitate ZnS. Centrifuge, decant supernatant, and wash with 0.01 N H_2SO_4 containing H_2S.

Remarks:

(Step 2) Cathode used was a stainless steel inner jacket for the beaker with a strip extension for outside connection to the electrolysis unit. Exposed surface was about 75 cm^2. Deposit is not very smooth at this current and cooling is necessary.

7/28/49
P-18-113

CHEMICAL SEPARATIONS

Element separated: Zinc

Procedure by: Folger & Hicks

Target material: ~ 4 g U metal

Time for sep'n: ~ 2 hr.

Type of bbdt: 184" bbdt all high energy particles

Equipment required: Centrifuge, cones, ice, 110° oven

Yield: ~70%

Degree of purification: No detectable contamination from other fission and spallation products - factor of ~10^5 decontamination.

Procedure:

(1) To aliquot of nitric acid soln of U containing ~ 10 mg Zn add 1 ml sat. $H_2C_2O_4$, and make 1 N in HNO_3 (10-25 ml). Cool in ice bath, add 3 ml Zn reagent (39 g KSCN dissolved in 200 ml H_2O. Stir in 27 g $HgCl_2$ while diluting to 1 liter), stir 5 min. (scratch glass to begin pptn.)

(2) Dissolve $ZnHg(SCN)_4$ in 3 ml 4 N HNO_3 and dilute to 1 N. Add 1 ml sat. $H_2C_2O_4$ and 3 ml Zn reagent.

(3) Repeat (2), but do not add $H_2C_2O_4$.

(4) Dissolve ppt in 2 N HNO_3, dilute to 1 N, and ppt CuS, Ag_2S, SnS_2, Sb_2S_3, Bi_2S_3. Repeat using CuS as final scavenge.

(5) Make 1 M in NH_4Ac and ppt ZnS.

(6) Dissolve ppt in 5 ml conc. HBr, evap to dryness several times, take up in 5 ml N NaOH, add 1 ml 2 M Na_2CO_3. Ppt $Fe(OH)_3$ (2 mg) and $BaCO_3$ + $SrCO_3$ (2 mg) three times from hot soln.

(7) Add HCl to make 1 N. Add 3 ml Zn reagent to cold soln, stir 3 min, filter, wash three times with 5 ml absolute EtOH and three times with 5 ml ether, dry ~ 15 min. in 110° C oven. Weigh as $ZnHg(SCN)_4$ (76.2 mg per 10 mgZn).

Remarks: Standardize carrier as $ZnHg(SCN)_4$ also. Final ppt poor if radiations soft because of large self-absorption correction required.

8/4/49

P-18-141

CHEMICAL SEPARATIONS

Element separated: Zinc

Target material: Copper

Type of bbdt: Deuterons - 60"

Yield: ~ 100%

Procedure by: R. C. Lilly

Time for sep'n: 6-8 hours

Equipment required: Pt evaporating dish, Pt anode, stirring motor, DC source supplying 2-4 amps at ~ 5 volts, pH meter, beakers and funnels

Degree of purification: excellent - at least factor of 100 from other activities present.

Advantages: Easy method for removing large amounts of Cu

Procedure:

The weight of Cu used should not exceed 2 gms for the quantities and volumes given below. If the amount of Cu is large, it is advisable to dissolve the target and remove an aliquot.

(1) Dissolve Cu target in HNO_3 and take the sol'n to dryness.

(2) Redissolve the $Cu(NO_3)_2$ by warming with H_2O; then add 2 ml conc HNO_3, 2 ml conc H_2SO_4, and 2-5 mg Zn as $ZnSO_4$ sol'n.

(3) Transfer to a Pt evaporating dish; the sol'n volume should be ~ 50 ml. Using a rotating Pt anode, remove Cu by electrolyzing for from one to several hours at 2-4 amps and ~ 5 volts. The sol'n should become colorless. Pour the sol'n from the dish into a beaker; rinse the Cu deposit with several small portions of H_2O and add them to the main sol'n.

(4) Boil the sol'n to a low volume; add 2-5 ml 30% H_2O_2 and boil off excess H_2O_2. Ppt with NH_4OH, filter, and discard the ppt, if any is present.

(5) Make the filtrate 0.3 N in HCl, heat to boiling, and pass in H_2S to ppt CuS. Filter and discard the ppt. Test for complete ppt'n by again passing in H_2S.

(6) Boil the filtrate to drive off excess H_2S. Adjust the sol'n to pH 2-3 with NH_4OH. Pass in H_2S to ppt ZnS. Filter and wash the ppt with H_2O. Dissolve the ZnS in 1 N HCl if desired or use as is.

Remarks:

The ZnS in step (6) should be white. If it is not, further purifications may be necessary for Cu and Fe and perhaps for other metal impurities such as Ni and Cr. This procedure has been used for the preparation of pure compounds of Zn^{65}.

See Hillebrand & Lundell (Applied Inorganic Analysis) for further information on Cu deposition.

P-18-238

8/19/49

CHEMICAL SEPARATIONS

Element separated: Zinc

Procedure by: Newton

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

Time for sep'n: ~3 hrs

Type of bbdt: 60" alphas

Equipment required: Standard

Yield: ~50%

Degree of purification: $> 10^6$

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

(1) Add 10 mg Zn^{++}, 1-2 ml $H_2C_2O_4$ (sat.) and HNO_3 to make 1 M (10 to 25 ml.) Centrifuge out $Th(C_2O_4)_2$. Cool in ice bath and add 3 ml $HgCl_2$-KSCN reagent. Stir and scratch glass to ppt, let stand 3-5 min. Centrifuge out $ZnHg(SCN)_4$ ppt.

(2) To ppt, add 1.5 ml 6 N HNO_3 and 3 ml H_2O. Boil until ppt dissolves and for 1-2 minutes longer to remove decomposition products. Dilute to 10 ml and cool in cold water. Add 1 ml sat $H_2C_2O_4$ and 3 ml $HgCl_2$-KSCN reagent. Stir for 3-5 min to ppt. Centrifuge.

(3) Repeat (2) on ppt.

(4) To the $ZnHg(CNS)_4$ add 15 ml 6 N HNO_3 and 3 ml H_2O. Boil to dissolve and for 12 min. longer. Dilute to 10 ml and saturate with H_2S. Centrifuge. To supernate add 1 ml 6 N NaOH, 5 mg Bi carrier and saturate with H_2S. Centrifuge.

Repeat Bi_2S_3 scavenging twice. Add 2 ml 6 M NH_4Ac (pH ~ 5), saturate with H_2S, centrifuge out the white ZnS.

(5) Dissolve ZnS in 5 ml conc HBr. Evap to dryness over an open flame. Repeat evaporation twice with 5 ml portions of HBr. Take up residue in 10 ml 0.5 M NaOH, add 1 ml 2 M Na_2CO_3 and boil. Keep solution agitated and add 2 mg Fe^{+++} and 5 mg Ba^{++} dropwise. Digest hot solution 1 min., centrifuge. Repeat hydroxide scavenging twice on supernate.

(6) To the clear supernate add 4 ml 6 M HCl and 1 ml sat $H_2C_2O_4$. Cool in cold water and add 3 ml KSCN-$HgCl_2$ reagent. Stir occasionally for 3-5 min. Centrifuge out $ZnHg(SCN)_4$.

(7) Suspend the $ZnHg(SCN)_4$ in about 5 ml H_2O and transfer with aid of wash bottle to a weighed filter paper in a small Hirsch funnel. Filter with suction.

(8) Wash ppt 3 times with 5 ml EtOH (absolute) and three times 5 ml Et_2O. Transfer paper to small watch glass in vacuum desiccator. Evacuate 2 min. Release, evacuate 5 minutes. Weigh as $ZnHg(SCN)_4$.

Remarks: To make $HgCl_2$-KSCN reagent dissolve 39 gms KSCN in 200 ml H_2O. Stir in 27 gms $HgCl_2$ while diluting to one liter.

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

8/23/49

P-18-278

CHEMICAL SEPARATIONS

Element separated: Gallium

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 1/2 hr.

Type of bbdt: 190 Mev D^+

Equipment required: standard

Yield: ∿ 80%

Degree of purification: radiochemically pure by factor of ∿ 10^3

Procedure:

(1) Dissolve As in 10 N HNO_3, add 10 mg Ga carrier & 1 mg Fe^{+++} carrier, evap to near dryness

(2) Add 6 N HCl and when cool extract twice with equal volumes of ethyl ether.

(3) Wash five times with 1/3 volumes 6 N HCl.

(4) Extract into 5 ml H_2O. Add KOH to 1 N and centrifuge.

(5) To supernatant add HCl till just neutral, adjust pH to ∿5.5 with traces of NH_4OH and HAc.

(6) Centrifuge off $Ga(OH)_3$.

Remarks: If want to check chemical yield weigh as the 8 hydroxy quinolate precipitated from slightly alkaline solution.

6/27/49
P-18-30

CHEMICAL SEPARATIONS

Element separated: Gallium

Procedure by: Goeckermann

Target material: ∿ 1 g Bi metal

Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, cones, 110° oven.

Yield: ∿ 80%

Degree of purification: Decontamination factor ∿ 10^4 from fission & spallation products.

Advantages: Good yield of pure Ga.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg Ga & ∿ 2 mg Mo, destroy HNO_3 & make 6 N in HCl. Extract with equal vol of di-ethyl ether, wash with 1/3 vol 6 N HCl. Re-ext Ga into 2/3 vol H_2O.

(2) Boil out ether. Make 0.3 N in HCl & add 1 ml alcohol soln of α-benzoin oxime to ppt Mo.

(3) Ppt Bi_2S_3 (5 mg) three times.

(4) Boil out H_2S. Make 1 N in NaOH, 0.2 M in Na_2CO_3 & ppt $Fe(OH)_3$ & $BaCO_3$ scavenge three times.

(5) Make soln 6 N in HCl & ext with 1 1/2 vol ether. Wash ether with 6 N HCl & re-extract Ga into H_2O.

(6) Boil out ether. Evap to dryness with 5 ml conc. HBr three times. Take up residue in 10 ml 6 N HCl & repeat ether extrn.

(7) Dilute H_2O layer to 35 ml & heat to 60°C. Add 3 ml of 8-hydroxyquinoline soln (50 g/l in 2 M HAc) & 6 M NH_4Ac dropwise until permanent yellow ppt forms, then add 1 ml excess. Add aerosol & filter, wash with 10 ml warm H_2O, twice with 5 ml cold H_2O, dry 15 min. at 110°C. Weigh as Ga 8-hydroxyquinolate (72 mg per 10 mg Ga).

Remarks: Very bulky heavy ppt per mg Ga. Gallium ferrocyanide pptns were included in the original procedure but were tested & discarded as unsatisfactory. HNO_3 can be destroyed in step (1) by adding hydroxylamine and heating.

7/6/49

P-18-37

CHEMICAL SEPARATIONS

Element separated: Germanium

Procedure by: H. Hopkins

Target material: As

Time for sep'n: 1 hr.

Type of bbdt: 190 Mev D^+

Equipment required: centrifuge, 100 cc distillation apparatus

Yield: greater 90%

Degree of purification: radiochemically pure by factor of $\sim 10^3$

Procedure:

(1) Dissolve As in 10 N HNO_3. Add 10 mg Ge carrier and holdback (Cr through Se) carriers.

(2) Distil Ge from 20 ml boiling 6 N HCl in slow stream of Cl_2. Catch distillate vapor in dry ice-acetone-cooled collector.

(3) When 1/4 remains in distilling flask add more HCl and repeat.

(4) Add $NH_2OH \cdot HCl$ to distillate until no further reaction occurs.

(5) Pass H_2S into the still cold solution.

(6) Centrifuge off GeS_2.

Remarks: When looking for a small amount of Ge in presence of a large amount of Se activity, a special separation of Se should be performed. (See 34-1).

6/27/49
P-18-29

CHEMICAL SEPARATIONS

Element separated: Germanium

Procedure by: Newton

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

Time for sep'n: ∿ 2-3 hrs.

Type of bbdt: 60" α's

Equipment required: still

Yield: undetermined

Degree of purification: 10^5 to 10^6

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

(1) Add 10 mg Ge + As. Make to 15 ml, 6 N in HCl. Add crystal of NH_4I and treat with H_2S at ice temp. Wash with 6 N H_2SO_4 saturated with H_2S.

(2) Dissolve ppt in 1 ml conc. NH_4OH. Dilute to 10 ml. Discard any residue. Transfer to glass still and add 10 mg each of Te, Sb and Sn carriers. Add 10 ml conc HCl and a crystal of $KClO_3$. Distill all but 5 ml into 5 ml H_2O in ice bath.

(3) Pass H_2S into $GeCl_4$ solution and centrifuge. Add 10 mg As to ppt of GeS_2 and repeat $GeCl_4$ distillation (step 2).

(4) Reprecipitate GeS_2, wash with H_2O, alcohol, and ether. Dry at 110° C. Weigh as GeS_2.

Remarks: 10 mg Ge = 18.79 mg GeS_2.

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

8/23/49

P-18-291

CHEMICAL SEPARATIONS

Element separated: Arsenic

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 1 hr.

Type of bbdt: 190 Mev D^+

Equipment required: standard distillation apparatus 100 cc

Yield: greater 80%

Degree of purification: radiochemically pure by factor of $\sim$100

Procedure:

(1) Dissolve As in conc. HNO_3 + HCl. Add carriers of Se and elements below, (2 mg).

(2) Separate Se by procedure given under Se (34-1)

(3) To supernatant add HCl to make a 3 N solution containing 10 mg As/ml.

(4) Pass H_2S into hot solution and stir vigorously. Repeat.

(5) Centrifuge off precipitate and wash with H_2O.

(6) Dissolve As and Ge salts with dilute KOH, leaving CuS behind.

(7) Separate Ge by distilling from 20 ml of boiling 6 N HCl in a slow stream of chlorine. When 1/4 volume remains, add 6 N HCl and repeat.

(8) Precipitate As_2S_5 from 3 N HCl.

Remarks: Se and As may first be removed together by volatilizing the elements along a quartz or pyrex tube.

6/27/49
P-18-18

CHEMICAL SEPARATIONS

Element separated: Arsenic

Procedure by: Goeckermann

Target material: ~1 g Bi metal

Time for sep'n: Few hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, all glass distillation flask, tank Cl_2 & HCl, ice, 110° oven.

Degree of purification: Decontamination factor ~ 10^4 from fission & spallation products.

Advantages: Project fission product procedure.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg As & ~ 10 mg Ge, boil nearly to dryness, take up in 15 ml 6 N HCl, add crystal of NH_4I, & sat with H_2S at ice temp. Wash with H_2S-sat 6 N H_2SO_4.

(2) Dissolve ppt in 1 ml conc NH_4OH & dilute to 10 ml (discard any residue). Transfer to a glass still & add ~ 10 mg each Te, Sb, & Sn. Add 10 ml conc HCl & distill all but 5 ml in a Cl_2 stream into 5 ml H_2O in an ice bath. Add 5 ml conc HCl & ~ 10 mg Ge to residue in flask & repeat distillation.

(3) To residue from $GeCl_4$ distillation, pass in HCl gas to remove Cl_2, add 1 ml sat CuCl in conc HCl, and distill over 5 ml in an HCl stream into 10 ml conc HCl in an ice bath. Add CuCl-HCl to residue & distill further.

(4) Pass H_2S into distillate & centrifuge out As_2S_3. Dissolve in 1 ml conc NH_4OH, add ~ 10 mg Te, Sb, & Sn & repeat $AsCl_3$ distillation.

(5) Ppt As_2S_3 again, dissolve in 1 ml conc. NH_4OH, add 10 ml conc. HCl, sat with H_2S, filter, wash with H_2O, EtOH, & ether, dry 10 min. at 110°C. Weigh as As_2S_3 (16.4 mg per 10 mg As).

Remarks: Tank HCl & Cl_2 are rather unpleasant & corrosive to work with. Procedure is fairly slow. Ge can be separated along with the As as indicated.

7/6/49

P-18-41

CHEMICAL SEPARATIONS

Element separated: Arsenic

Procedure by: Newton

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

Time for sep'n: ~ 2-3 hrs.

Type of bbdt: 60" α's

Equipment required: still

Yield: undetermined

Degree of purification: 10^5 to 10^6

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

(1) Add 10 mg Ge + As. Make to 15 ml, 6 N in HCl. Add crystal of NH_4I and treat with H_2S at ice temp. Wash with 6 N H_2SO_4 saturated with H_2S.

(2) Dissolve ppt in 1 ml conc. NH_4OH. Dilute to 10 ml. Discard any residue. Transfer to glass still and add 10 mg each of Te, Sb and Sn carriers. Add 10 ml conc HCl and a crystal of $KClO_3$. Distill all but 5 ml into 5 ml H_2O in ice bath.

(3) Add 5 ml conc. HCl, 10 ml Ge and $KClO_3$ to remaining solution in still and repeat. (Discard).

(4) To residue from $GeCl_4$ distillation, pass in HCl gas to remove Cl_2.

(5) Add 1 ml sat. CuCl soln in conc. HCl and distill over 5 ml in HCl stream into 10 ml conc HCl in ice bath.

(6) Add CuCl - HCl and distill again. Pass H_2S into distillate and ppt As_2S_3.

(7) Dissolve in 1 ml conc NH_4OH, add 10 mg Te, Sb and Sn and repeat distillation. Ppt As_2S_3 again, dissolve in 1 ml conc. NH_4OH. Add 10 ml conc HCl, sat H_2S. Filter, wash with H_2O, EtOH, ether. Dry at 110°. Weigh as As_2S_3.

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

8/23/49

P-18-290

CHEMICAL SEPARATIONS

Element separated: Selenium

Procedure by: H. Hopkins, Jr.

Target material: As

Time for sep'n: 3/4 hr.

Type of bbdt: 190 Mev D^+

Equipment required: centr. tubes, etc.

Yield: > 90%

Degree of purification: radiochemically pure by factor of ∿ 100

Procedure:

(1) Dissolve As metal in minimum 10 N HNO_3.

(2) Add 5 mg Se carrier, evap. to near dryness to remove xs HNO_3.

(3) Make up to 8 ml with 1 N HCl, add $NH_2OH \cdot HCl$ until Se starts to ppt from hot soln.

(4) Add 1 ml 1 N KI, heat 5 min, centrifuge off mixture of Se and I_2.

(5) Dissolve with minimum fuming HNO_3, repeat precipitation.

Remarks: In presence of carriers separates from all elements below Se.

If want to weigh to check chemical yield do not add KI in step 4. This slows down the precipitation considerably, so much more time must be allowed for complete pptn of the Se.

6/27/49

P-18-20

CHEMICAL SEPARATIONS

Element separated: Selenium

Procedure by: Goeckermann

Target material: ~ 1 g Bi metal

Time for sep'n: < 1 hr.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, and glass distillation flasks, cones, tank SO_2, 110° oven, ice.

Yield: ~ 90%

Degree of purification: Decontamination factor ~ 10^4 from fission & spallation products.

Advantages: Good yield of pure Se in relatively short time.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg Se & Te, 10 ml conc. HBr, & 0.5 ml liq Br_2 in a glass still. Distill in air stream to 3 ml residue, into 5 ml sat Br_2 water in ice bath.

(2) Keep at ice temp & reduce to Se (red) with SO_2 or $NH_2OH \cdot HCl$. Add aerosol & centrifuge.

(3) Dissolve Se in few drops conc HNO_3, add 10 ml conc. HCl & reduce with SO_2 in an ice bath. Centrifuge with aerosol.

(4) Repeat $SeBr_4$ distillation & Se pptns as often as necessary for desired purity.

(5) Ppt Se, filter, wash three times with 5 ml H_2O, three times with 5 ml EtOH, three times with 5 ml ether, dry 10 min. at $110^\circ C$. Weigh as Se.

Remarks: Procedure can be made short enough to catch half-lives < 1 hr.

7/6/49

P-13-42

CHEMICAL SEPARATIONS

Element separated: Bromine

Procedure by: Goeckermann

Target material: ~1 g Bi metal

Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, 110° oven

Yield: ~ 60%

Degree of purification: Decontamination factor ~ 10^4 from fission & spallation products.

Advantages: Good yield of pure Br.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg Br^- & I^-, make 1 N in HNO_3, add a few drops of 0.1 M $NaNO_2$, & extract I_2 into equal vol CCl_4.

(2) Add equal vol CCl_4 to aqueous phase & add 0.1 M $KMnO_4$ dropwise until color persists. Make five extractions of Br_2.

(3) Combine CCl_4 layers & wash with 1 N HNO_3 containing $KMnO_4$. Add 10 ml H_2O & 0.1 N $NaHSO_3$ dropwise until both layers are colorless. Wash aq layer with CCl_4.

(4) Make 1 N in HNO_3, add ~10 mg I^-, warm a few min. to oxidize $SO_3^=$, add few drops 0.1 M $NaNO_2$ & extract I_2 five times with 10 ml CCl_4.

(5) Repeat $KMnO_4$ oxidation & Br_2 extrn & reduction.

(6) Repeat I_2 & Br_2 extrn cycles as needed for purity.

(7) Make last aq soln of Br^- 1 N in HNO_3, heat, add 2 ml 0.1 N $AgNO_3$, stir, digest few min., filter, wash three times with 5 ml H_2O, EtOH, & ether, dry 10 min. at 110°C. Weigh as AgBr (23.5 mg per 10 mg Br).

Remarks: The bismuth fission work only required three I_2-Br_2 extrn cycles. To prevent possible losses of trace Br during dissolving of the bismuth, one might dissolve the target in 6 N HNO_3 with the carrier Br^- present in a glass still, and distill Br_2 or HBr directly from this soln into H_2O in an ice bath.

7/6/49

CHEMICAL SEPARATIONS

Element separated: Bromine

Target material: Tantalum

Type of bbdt: Ta + 350 Mev protons

Procedure by: Lindner
Modified by: Naumann
Time for sep'n: 2 hours

Equipment required: Sep. funnel

Yield: ~ 40%

Degree of purification: excellent - factor of $\sim 10^4$ from fission and spallation products.

Advantages: Provides for the separation of Br_2 from targets requiring HF-HNO_3 mixtures for solution of the target. In these cases glass equipment is impossible and the method of distillation of the halogens is impractical.

Procedure:

(1) Freshly precipitated AgBr (well washed to remove xs Ag^+) containing 10 mgs of bromine as silver bromide is added to 15 mls of 48% HF solution contained in a lusteroid test tube. The target foil is placed in solution and conc. HNO_3 is added as required for solution of the foil. (See (a) under remarks.)

(2) After the target has dissolved the solution is allowed to stand for 15 minutes, (See (b) under remarks.) the supernatant target solution is removed, the AgBr washed twice with 10 mls hot water, 10 mls of water is added and the slurry is saturated with H_2S, then centrifuged.

(3) The supernatant solution is boiled to remove H_2S, 10 mgs I^- is added, the solution is made 1 N in HNO_3 a few drops of $NaNO_2$ is added and the iodine extracted into 10 mls of CCl_4. (extract a total of 5 times).

(4) 10 mls of CCl_4 is added to the aqueous phase and 0.1 M $KMnO_4$ solution is added until the Bromine color persists. Extract Br_2 5 times (total)

(5) Combine the Br_2-CCl_4 extract, wash with 1 N HNO_3 containing $KMnO_4$, add 10 mls H_2O and 0.1 N $NaHSO_3$ dropwise until both layers are colorless. (See (c) under remarks.) Wash aqueous layer with CCl_4.

(6) Make 1 N in HNO_3 add 10 mgs I^-, warm for a few minutes to oxidize the $SO_3^=$, add a few drops of 0.1 M $NaNO_2$ and extract the I_2 5 times with CCl_4.

(7) Repeat (4) and (5) as needed (A total of 3 times was used for purification above.)

(8) Make last aqueous solution of Br^- 1 N in HNO_3, heat, add 2 mls 0.1 N $AgNO_3$. Stir, digest a few minutes, wash three times with 5 mls H_2O, 5 mls C_2H_5OH, 5 mls ether. Dry for 10 mins. at 110° C.

Remarks:

(a) This reaction proceeds rapidly and at no time should there be an xs of HNO_3. Heating is not required and lusteroid tube may be ice cooled if necessary.

(b) Procedure depends upon an equilibration between AgBr and tracer bromide ion in the target solution. If the tracer bromine were in a higher oxidation state this equilibration would be impossible. However, since the Ta is being dissolved it may be assumed reductive conditions exist and all the tracer is in the form of bromine or bromide.

(c) Unless the solution is kept acid MnO_2 will precipitate. The MnO_2 precipitation may also be avoided if the solution is warmed before permanganate addition.

(d) Steps (3) to (9) are R.H.Goeckermann's procedure for bromine. (35-1)

(e) I_2 might also be separated by this procedure.

CHEMICAL SEPARATIONS

Element separated: Bromine

Procedure by: Newton

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

Time for sep'n: ~ 1 hr.

Type of bbdt: 60" metal

Equipment required: Standard

Yield: ~ 50%

Degree of purification: ~ 10^6 except from I^- (~ 10^4 from I^-)

Procedure: The Th metal is dissolved in conc. HCl + a few drops .2 M solution $(NH_4)_2SiF_6$ to clear up black residue. The HCl is diluted to 2 N and an aliquot taken. Sample added to 15 ml 1 N HNO_3 in 50 ml separatory funnel. Add 10 mg Br^- carrier and 10 mg I^- carrier.

(1) Add $KMnO_4$ (0.1N) dropwise until color persists (15 drops). Make 5 successive extractions with CCl_4. Discard aqueous. To CCl_4 layer add 10 ml water and 0.1 N $NaHSO_3$ until CCl_4 layer colorless on shaking. Discard the CCl_4.

(2) To aqueous add 2 ml HNO_3 and 10 mg I^-, add 4 drops of 0.1 M $NaNO_2$. Extract five times with CCl_4. Add more I^- and repeat extraction with four more portions of CCl_4.

(3) Add $KMnO_4$ to oxidize Br^-. Extract 5 times with CCl_4.

(4) Extract CCl_4 with $NaHSO_3$. Add Ag^+ to ppt AgBr. Filter, wash three times with 5 ml H_2O and three times with 5 ml EtOH. Dry at 110°, 10 min and weigh. 10 mg Br^- = 23.5 mg AgBr.

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

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P-18-289

CHEMICAL SEPARATIONS

Element separated: Rubidium

Procedure by: Goeckermann

Target material: ∾ 1 g Bi metal

Time for sep'n: Several hrs.

Type of bbdt: 134" all particles

Equipment required: Centrifuge, tubes, small Pt dish, ice, 110° oven

Yield: Rb ∾30%

Degree of purification: Rb looked very clean by a factor of at least 10^3.

Advantages: Supposed to give Rb pure of all elements and separate it from Cs.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 20 mg Rb & Cs & 5 ml conc. $HClO_4$. Evap to fuming, cool, transfer to cent tube with 15 ml absolute EtOH. Cool in ice bath 10 min. with stirring. Wash ppt twice with 10 ml absolute EtOH.

(2) Dissolve in dilute HCl & scav with Te, Ru, Sn, Sb, & Ag sulfides (2 mg each) by adding H_2S.

(3) Scav with NH_3 pptn of La, Ce, Y, Zr, & Cb (2 mg each).

(4) Scav with Sr & Ba carbonates (4 mg)

(5) Acidify with HCl, repeat (2).

(6) Repeat (3).

(7) Scav with $La(OH)_3$.

(8) Scav with Sr & Ba carbonates & Y, Zr, & Cb hydroxides.

(9) Acidify with HCl, evap to dryness in a Pt dish, destroy NH_4Cl by adding a few drops HNO_3 and baking carefully (do not overheat or Cs may be lost).

(10) Dissolve in a minimum of H_2O, transfer to a cone & cent out any residue, evap to dryness in the cone. Add 6 ml H_2PtCl_6 & 6 ml EtOH, wash Rb & Cs chloroplatinates with EtOH.

(11) Dissolve in HCl & repeat Te sulfide scavenging.

(12) Repeat NH_3 pptn of La & Fe hydroxides.

(13) Repeat Sr & Ba carbonate scav

(14) Acidify with HNO_3, add HCl, evap to dryness, bake off ammonium salts carefully again.

(15) Cs - Take up residue in 20 ml 6 N HCl, add 1 ml silicotungstic acid soln & digest. (Save this supn. for Rb fraction).

(16) Rb - Ppt a Cs silicotungstate scav from the supn saved. Evap until crystallization begins, add H_2PtCl_6 & EtOH, filter, wash with EtOH, dry 10 min. at 110°C. Weigh as Rb_2PtCl_6 (33.9 mg per 10 mg Rb).

Remarks: Noyes & Bray recommend ppting the Rb away from the Cs with sodium 6-chloro-5-nitrotoluenemetasulfonate, which we now have on hand, & then ppting the Cs silicotungstate. This may give better Cs-Rb separation. It may be better to weigh the Cs as Cs_2PtCl_6 after purification. It has been alleged that $2BiI_3 \cdot 3CsI$ pptn is specific for Cs. I tried the pptn of Rb away from Cs with cold sat sodium titartrate but the results were very poor. More Cs silicotungstate pptns with Rb holdback present would probably give clean Cs.

The fuming of $HClO_4$ can be done easily in 40 ml pointed centrifuge cones.

For Cs sep'n from same target see (55-1).

7/12/49

CHEMICAL SEPARATIONS

Element separated: Rubidium

Procedure by: Karraker

Target material: NH_4Br

Time for sep'n: ~ 30 min.

Type of bbdt: 40-140 Mev α

Equipment required: No special equipment

Yield: ~ 40%

Degree of purification: Good, at best a factor of 100 except from other alkali metals.

Advantages: Fast, easy, and gives almost carrier-free activity.

Procedure:

(1) NH_4Br in porcelain crucible, add a few drops of dil. HCl, then heat strongly in hood, using burner, NH_4Br sublimes off, Kr activities evaporate. Continue heating till no more solid is visible. Wash crucible with a small amount of dilute HNO_3. (For mass spectrographic purposes, this is sufficiently pure).

(2) Add about 1 mg Rb carrier, and scavenge the solution with few mg of $Te(OH)_3$, $MgCO_3$, AgCl, and any sulfide. This, practically speaking removes all impurities except alkalis.

Remarks: It should be noted that no separation is obtained from other alkalis.

If Rb is not to be used in mass spectrograph, carrier may be added initially.

7/14/49

CHEMICAL SEPARATIONS

Element separated: Rubidium

Procedure by: S. Castner

Parent material: $SrClO_4$ (tracer or with 50 μgm carrier) in 10 M-$HClO_4$

Time for sep'n: 20 Min.

Type of bbdt: Milking experiment

Equipment required: Std, cones, etc.

Yield: ~50%

Degree of purification: Less than 2% Sr carried along.

Procedure:

(1) Sol'n is heated in boiling H_2O. (Sol'n. volume = 1 ml). 50 μ gms $RbNO_3$ are added. Stir.

(2) Cool in ice bath and let stand for 5 minutes. Centrifuge and remove supernatant for later milking. (The $RbClO_4$ may be dissolved in any sol'n if heated).

(3) Add 250 λ sat. $Na_2C_2O_4$ sol'n and heat until just dissolved.

(4) Add 50 μ gms Sr^{++} sol'n and centrifuge the ppt while the sol'n is still hot.

(5) The supernatant containing the Rb is then removed.

Remarks: The majority of the Rb loss is carried away in the Sr scavenge as the sol'n cools rapidly. The Sr parent sol'n contains only approx. 1% of the Rb after the milking.

7/27/49
P-18-78

CHEMICAL SEPARATIONS

Element separated: Strontium

Procedure by: Goeckermann

Target material: ∿ 1 g Bi metal

Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, ice, vacuum dessicator

Yield: ∿ 80%

Degree of purification: Decontamination factor ∿ 10^4 from fission & spallation products. Sr decontaminated > 100 from Ba.

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

Procedure:

(1) To aliquot of HNO_3 sol'n of target, add 10 mg. Sr & Ba, 30 ml fuming HNO_3, digest cold 1-2 min.

(2) Dissolve ppt in 2 ml H_2O & reppt with 15 ml fuming HNO_3.

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

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

(5) Sr - Ppt 5 mg $BaCrO_4$ scav from supn saved from Ba sepn. Add 2 ml conc. NH_4OH, heat, add 5 ml sat $(NH_4)_2Ox$ slowly. Stir 2 min, filter, wash three times with 5 ml H_2O, three times with 5 ml EtOH, three times with 5 ml ether, dry like $BaCl_2$. Weigh as $SrC_2O_4 \cdot H_2O$ (22.1 mg per 10 mg Sr).

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

For Ba sep'n from same target see 56-2.

7/12/49

CHEMICAL SEPARATIONS

Element separated: Strontium

Procedure by: S. Castner

Target material: RbCl (~ 30 mg) finely divided

Time for sep'n: 35 min without column; 1 1/2 hr. with column

Type of bbdt: 184" deuterons and protons

Equipment required: 1 ml cones, pipettes, etc.

Yield: ~ 90%

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

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

Procedure:

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

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

(3) Wash the ppt with $Na_2C_2O_4$ (500 λ), stirring up and then centrifuging and discarding the wash sol'n.

(4) Repeat wash 3 times.

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

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

Remarks:

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

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

$SrCO_3$ carries Rb with it in large quantities.

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CHEMICAL SEPARATIONS

Element separated: Strontium

Procedure by: Folger & Hicks

Target material: ~ 4 g U metal

Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all high energy particles

Equipment required: Centrifuge, tubes, ice, vacuum desiccator

Yield: ~ 80%

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

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

Procedure:

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

(2) Dissolve ppt in 1 ml H_2O & reppt with ~ 13 ml fuming HNO_3.

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

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

(5) Ppt 5 mg $BaCrO_4$ scav from supn saved from Ba sepn. Add 2 ml conc. NH_4OH, heat, and ppt $SrCO_3$ by adding satd Na_2CO_3. Digest 2 min, centrifuge and dissolve in 6 N HCl (minimum). Boil out CO_2.

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

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

For Ba sep'n from same target see 56-1.

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

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P-18-152

CHEMICAL SEPARATIONS

Element separated: Strontium

Procedure by: Lippmann and Goeckermann

Target material: Au foil, about 1 g

Time for sep'n: 1 hr. for Sr

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

Equipment required: Ice bath and hot water bath

Yield: Sr 50%

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

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

Procedure:

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

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

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

Remarks:

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

CHEMICAL SEPARATIONS

Element separated: Strontium Procedure by: Newton

Target material: Thorium metal (.1-1 gm) Time for sep'n: 1 hr.

Type of bbdt: 60" alphas Equipment required: Standard

Yield: 75% on Sr

Degree of purification: 10^6 other F.P. $\sim 10^3$ from barium

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

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

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

(2) Dissolve ppt in 2 ml H_2O. Re-precipitate with 15 ml fuming HNO_3.

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

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

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

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

For separation of Ba from this procedure see (56-7).

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

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

CHEMICAL SEPARATIONS

Element separated: Yttrium (Y-group rare earths) Procedure by: Goeckermann

Target material: ∿ 1 g Bi metal Time for sep'n: ∿ 2 hrs.

Type of bbdt: 184" all particles Equipment required: Centrifuge, tubes, ice, vacuum dessicator, tank SO_2 & NH_3

Yield: ∿ 70%

Degree of purification: Decontamination factor ∿ 10^4 from non-RE fission & spallation products, Y-group separation from La-group probably fair.

Advantages: Designed to separate a lot of Y activity from a hot target which has little rare earth activity, especially Y-group RE.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg Y, La, Ce, & Zr, make 2 N in HCl, & add 2 ml conc. HF. Wash ppt with 10 ml 1 N HCl containing HF.

(2) Dissolve in 1 ml sat H_3BO_3 & 8 ml conc HNO_3. Add 0.2 g $KBrO_3$ & 20 ml 0.35 M HIO_3, digest 3 min in ice bath. Cent $Ce(IO_3)_4$.

(3) Add second portion $KBrO_3$ to supn, 10 mg Ce & Zr, digest 5 min in ice bath.

(4) Add 9 ml 19 M NaOH to supn. Wash ppt with H_2O.

(5) Dissolve ppt in 1 ml conc HCl, dil to 8 ml, reduce with SO_2. Ppt hydroxides with NH_3 & wash with slightly alkaline H_2O.

(6) Dissolve in HCl & scav with Bi_2S_3 twice.

(7) Boil out H_2S, make 2 N in H^+ & add 2 ml conc. HF. Wash with H_2O.

(8) Metathesize with pellet NaOH in a little H_2O & wash hydroxide ppt (watch out for peptization!) Dissolve in HCl & evap to dryness. Add 3 ml 50% K_2CO_3 & heat to dissolve ppt. Add 20 ml H_2O & heat until gelatinous ppt becomes crystalline (occurs suddenly after long heating), then 2 min longer. Cent La-group ppt.

(9) Acidify supn with HCl, ppt $Y(OH)_3$ with NH_3, & wash twice with H_2O. (May repeat La-group separation).

(10) Dissolve $Y(OH)_3$ in 1 ml 6 N HCl, add 15 ml H_2O, boil, add 15 ml sat $H_2C_2O_4$, digest 10 min in ice bath, filter, wash with 3 ml H_2O, three times with 5 ml EtOH, three times with 5 ml ether, dry in vacuum dessicator -- 2 min. evac, release, 2 min evac, release, 2 min evac. Weigh as $Y_2(C_2O_4)_3 \cdot 10H_2O$ (35.0 mg per 10 mg Y).

Remarks: Sometimes no separation from Ce or La-group activities was made in the bismuth fission work. Real separations of Y and the lanthanides can be done with resin columns.

7/12/49

P-18-51

CHEMICAL SEPARATIONS

Element separated: Yttrium

Procedure by: Lindner

Target material: Sb (~.5 gm metal)

Time for sep'n: ~ 2 hour

Type of bbdt: 184" D_2 & α

Equipment required: Lusteroid tubes, centrifuge, cones

Yield: ~ 95%

Degree of purification: At least factor of 100

Procedure:

(1) To dissolve the Sb metal, add 15 drops of 27 N HF to it in a lusteroid tube in a hot water bath. Add conc HNO_3 dropwise until dissolved (~ 10 min). Dilute to ~ 20 ml.

(2) To the SbF_4^- solution add 20 mg each of Te, Sn, In, Cd, Ag, Pd, Ru, Mo and Y carriers as soluble salts. Add 2 drops conc HCl. Centrifuge the YF_3 and AgCl ppts.

(3) Wash the ppt with 1 N HF.

(4) Dissolve out the Ag^+ from the ppt by adding 1 ml conc. NH_4OH. Centrifuge.

(5) Dissolve the YF_3 in 0.5 ml sat H_3BO_3, 1.0 ml conc HNO_3, on a hot water bath. Add 5 ml 6 N NaOH and centrifuge.

(6) Wash the $Y(OH)_3$ ppt with alkaline sol'n and dissolve in one drop conc. HCl. Dilute to 20 ml. Add 1 gm NH_4Ac. Add 2 mg In^{+++} soln. Saturate with H_2S and centrifuge. Discard the In_2S_3 ppt.

(7) Boil the supn to expel H_2S. Add 3 drops 27 N HF.

(8) Dissolve the YF_3 ppt in H_3BO_3-HNO_3 and ppt $Y(OH)_3$ as in (5). Make to 20 ml in 2 N HCl.

(9) Add 2 mg $SbCl_3$ carrier to sol'n. Saturate hot with H_2S. Centrifuge.

(10) Discard the Sb_2S_3 ppt. Repeat the fluoride cycle (7) & (8).

(11) Dilute aliquot to 10 ml. Boil and add 5 ml sat $H_2C_2O_4$. Centrifuge out the $Y_2(C_2O_4)_3 \cdot 10H_2O$ ppt.

(12) Wash with 3 ml H_2O, then 5 ml EtOH, 3 times with ether. Dry in desiccator under vacuum. Weigh as $Y_2(C_2O_4)_3 \cdot 10H_2O$ (35.0 mg per 10 mg Y).

8/18/49

CHEMICAL SEPARATIONS

Element separated: Yttrium

Procedure by: S. V. Castner

Target material: $SrCO_3$

Time for sep'n: 20 min.

Type of bbdt: Protons 184"

Equipment required: Centrifuge, cones, hot water bath

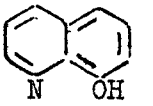
Yield: 100% by radioactivity (see remarks)

Degree of purification: $<$ 1% Sr carried with Y.

Advantages: Crystalline ppt which is easier to centrifuge and/or filter than usual hydroxide curds

Procedure:

(1) Dissolve $SrCO_3$ in YCl_3 soln containing H^+ sufficient to dissolve the carbonate (1/3 mg/ml of YCl_3 & H^+ = .025 N).

(2) Add 1/2 vol of soln made as follows: 0.17 mg 

(8 hydroxy quinoline) dissolved in 12.5 ml of acetone diluted to 50 ml with H_2O. (turns yellow due to acidity of distilled H_2O). Stir.

(3) Add conc NH_4OH dropwise until odor of NH_3 can be detected above soln.

(4) Place in boiling water bath for 10 minutes, centrifuge. Yttrium will ppt as very finely divided grayish green crystals, Sr remains in soln. In chemical yield run, $>$ 99% Sr recovered after yttrium was ppt. Y ppt may be dissolved in H^+ or H^+ + acetone.

Remarks:

(1) On a second ppt of Y from Sr bombardment by above method no activity ($<$ 30 c/m above background) was detected in Y fraction. Initial Y fraction had $>$ 10^6 c/m in less than 1% of the fraction.

(2) All Y rare earths carry with Y .

(3) No expt tried to see if lanthanum rare earths carry or not.

(4) After the yttrium has been coagulated and centrifuged the soln, being basic, is colorless and clear. Filtering through dense filter paper on a Hirsch funnel will also remove all ppt.

8/16/49

CHEMICAL SEPARATIONS

Element separated: Zirconium

Procedure by: Goeckermann

Target material: ~ 1 g Bi metal

Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, lusteroid cones, ice, small porcelain crucible.

Yield: ~ 60%

Degree of purification: Decontamination factor ~ 10^4 from fission and spallation products (no Th & negligible Hf activity present).

Advantages: Good yield of pure Zr, if no Hf activity present.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 10 mg Zr, make sample up to ~ 5 ml of 5 N HNO_3 in a lusteroid cone. Add 2 ml conc. HF & 10 mg La. Repeat LaF_3 pptn.

(2) Add 50 mg Ba to supn. Wash $BaZrF_6$ ppt.

(3) Dissolve ppt in 2 ml 5% H_3BO_3, add 1 ml conc. HNO_3 & 5 ml H_2O, repeat LaF_3 pptn twice (as in (1) and (2)).

(4) Repeat $BaZrF_6$ pptn.

(5) Dissolve with 2 ml H_3BO_3, 2 ml conc. HCl, & 5 ml H_2O. Add 1 drop conc H_2SO_4 & cent out $BaSO_4$.

(6) Dil supn to 20 ml & add 2 ml 6% cupferron in ice bath, filter, wash with cold 1 N HCl containing cupferron, ignite in a porcelain crucible. Weigh as ZrO_2 (13.5 mg per 10 mg Zr).

Remarks: This procedure probably effects no separation from Hf. Th I don't know about. Zr can be separated from Hf by the use of TTA or anion exchange resins.

7/6/49
P-18-47

CHEMICAL SEPARATIONS

Element separated: Zirconium

Procedure by: Newton

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

Time for sep'n: 1-2 hrs.

Type of bbdt: 60" alphas

Equipment required: Standard

Yield: ~ 60%

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

(1) Use a lusteroid tube, add HNO_3 to make 5 ml of soln 4 to 5 molar in HNO_3. Add 20 mg Zr carrier, 2 ml conc HF and mix well. Centrifuge off ThF_4.

(2) Add 10 mg La^{+++} carrier. Mix well and centrifuge. Add a second 10 mg La^{+++} and centrifuge down on top of 1st ppt. Decant.

(3) Add 50 mg Ba^{++} to supn. Mix and let stand 1 min. Centrifuge.

(4) Dissolve ppt by adding 2 ml 5% H_3BO_3 and stirring. Add 1 ml conc HNO_3 and 5 ml H_2O. Add 2 ml 27N HF and 50 mg Ba^{++}. Stir until ppt forms and let stand 1 minute longer.

(5) Repeat (4).

(6) Dissolve with 2 ml H_3BO_3, 2 ml conc HCl and 5 ml H_2O. Add 1 drop conc H_2SO_4 and centrifuge off $BaSO_4$.

(7) Transfer supernate. Dilute to 20 ml and ppt Zr at ice temp with 2 ml 6% cupferron reagent. Centrifuge. Wash ppt with 1 ml cold HCl containing a few drops of cupferron. Filter at once.

(8) Ignite ppt to ZrO_2 in porcelain crucible. Weigh.

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

Preparation of carrier solutions: Dissolve 29.40 gms $ZrO(NO_3)_2.2H_2O$ in water, adding a few drops of HNO_3 if necessary to clarify the solution. Dilute to 1 liter.

Standardization: Take 5 ml carrier. Make 2 M in HCl and cool in ice bath to 10° C. Add a slight excess of 6% cupferron solution. Filter and ignite in a porcelain crucible with care to prevent splattering of oils distilled from cupferron. Final ignition temperature 600° C. Weigh as ZrO_2. (6% cupferron solution: 6 gms cupferron and pinch of $(NH_4)_2CO_3$ in 100 ml H_2O. Solution slowly decomposes.)

8/23/49

CHEMICAL SEPARATIONS

Element separated: Columbium

Procedure by: Goeckermann

Target material: ∿ 1 g Bi metal

Time for sep'n: ∿ 2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, ice, lusteroid cones, crucible

Yield: approx. 50%

Degree of purification: Decontamination factor $>10^3$ from fission & spallation products.

Advantages: Fair yield of pure Cb

Procedure:

1. Add equal volume of concentrated HNO_3 to aliquot of HNO_3 soln of target, 1 ml 6N HCl, 1 ml saturated $H_2C_2O_4$, 20 mg Cb, and 10 mg Zr. Heat and add 0.5 g $KBrO_3$ in small portions. Digest 5 min. and centrifuge Cb_2O_5. Wash precipitate hot with 3 ml 6N HNO_3, 2 ml 6 N NH_4OH, and 5 ml H_2O.

2. Dissolve in 1-2 ml saturated $H_2C_2O_4$ + 10 drops 6 N HCl. Make up to 20 ml of 6N HCl, 0.05M H_2SO_3, and add 10 ml $CHCl_3$. Cool in ice bath, add 2 ml fresh 6% cupferron and shake well. Extract a second time with more $CHCl_3$ and cupferron. Wash $CHCl_3$ with 20 ml cold 6N HCl and 0.05M H_2SO_3 containing more cupferron.

3. Boil with 10 ml concentrated HNO_3, adding $KBrO_3$ until $CHCl_3$ is gone, solution is pale yellow and Cb_2O_5 has precipitated.

4. Transfer to lusteroid with dil. HNO_3. Dissolve by adding 1 ml concentrated HF. Add 2 ml 6N HNO_3, 10 mg Zr, and 5 ml H_2O. Add 50 mg Ba dropwise and centrifuge $BaZrF_6$.

5. Add 6 ml concentrated NH_4OH to supernatant (to pH 8-10). Centrifuge Cb_2O_5, and wash with 3 ml 6N NH_4OH, 1 ml 6N HNO_3, and 5 ml H_2O. Use a second wash to transfer precipitate back to glass.

6. Dissolve hot in 2 ml saturated $H_2C_2O_4$ plus 10 drops 6N HNO_3. Add 3 ml H_2O, 5 ml concentrated HNO_3, heat, add 0.5 g $KBrO_3$ slowly, digest 5 min., centrifuge. Stir precipitate up with 3 ml 6N HNO_3, 2 ml 6N NH_4OH, and 5 ml H_2O, heat, filter, ignite in a crucible 15 min. Weigh as Cb_2O_5 (14.30 mg per 10 mg Cb).

Remarks: The extrn is supposed to separate Cb from Zr, Te, & Mo.

. The extrn separation was substituted for heavy metal sulfide scav. to remove Te and Mo. The extrn procedure can possibly be combined with carrying of the Cb tracer on MnO_2 pptd from 10 N HNO_3 for a carrier free procedure.

7/29/49
P-18-112

CHEMICAL SEPARATIONS

Element separated: Molybdenum

Procedure by: Goeckermann

Target material: ∽ 1 g Bi metal

Time for sep'n: ∽ 1 hr.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, ice, 110° oven

Yield: approx. 50-80%

Degree of purification: Decontamination factor $> 10^4$ from fission and spallation products.

Advantages: Good yield of pure Mo

Procedure:

1. Add 10 mg Mo and concentrated HCl to aliquot of HNO_3 soln of target, destroy HNO_3. Make up to 5 ml 6N HCl, add one drop Br_2 water, extract twice with 15 ml ether. Combine ether layers and wash twice with 2 ml 6N HCl. Evaporate ether over 5 ml H_2O.

2. Boil out ether, dilute to 20 ml, add 5 mg Fe^{+3} and precipitate with NH_3.

3. Add 6 ml concentrated HNO_3 and 1 ml saturated $H_2C_2O_4$ to supernatant, cool, add 5 ml 2% solution of α-benzoin oxime in alcohol, digest 2 min., add aerosol and centrifuge 5 min. (If the Mo oxime does not settle well, dilute the solution with C_2H_5OH). Wash twice with 20 ml 1N HNO_3.

4. Add 2 ml concentrated HNO_3 and 1 ml concentrated $HClO_4$ and boil carefully to fuming. Cool, dilute to 15 ml with H_2O, add 5 mg Fe^{+3} and precipitate with NH_3.

5. Add 1 drop methyl orange to supernatant and make just acid with 6N H_2SO_4. Buffer with 1 ml 10% CH_3COONa, boil, add 10 drops 1M $AgNO_3$, cool slowly with stirring, filter, wash five times with 5 ml 0.03 M $AgNO_3$, three times with 5 ml C_2H_5OH, dry 15 min. at 110° C. Weigh as Ag_2MoO_4 (39.16 mg per 10 mg Mo).

Remarks: More cycles of ether extraction and oxime precipitation may be added if needed for purity. Mo oxime can be dissolved completely by 6N NaOH & repptd by acidifying & adding more α-benzoin oxime.

7/29/49
P-18-109

CHEMICAL SEPARATIONS

Element separated: Molybdenum

Procedure by: Lippmann and Goeckermann

Target material: Au foil, about 1 g

Time for sep'n: 2 hr.

Yield: 65%

Equipment required: Ice bath and hot water bath.

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

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

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

Heat supernatent from precipitation of $Sr(NO_3)_2$ and $Ba(NO_3)_2$ in water bath to destroy HCl. Cool in ice bath and slowly add $K_4Fe(CN)_6$ solution until no further precipitate appears. Centrifuge. Wash precipitate with 10 ml of 6 M HNO_3 containing a few drops of $K_4Fe(CN)_6$ solution and centrifuge again. Dissolve precipitate in 10 ml of 6 M HCl with heating, dilute to 30 ml with alcohol, cool in ice bath, and add 5 ml of 2% solution of α-benzoinoxime in alcohol. Centrifuge. Wash precipitate with 10 ml alcohol and centrifuge again. Dissolve precipitate by slowly adding 4 ml of 16 M HNO_3, heating gently in hot water bath when reaction slows down. When all of precipitate has dissolved add 1 ml concentrated $HClO_4$ and heat cautiously over a flame until thick, white fumes have come off for several minutes. Dilute to 15 ml with H_2O, add 5 mg Fe^{III}, warm in water bath, precipitate $Fe(OH)_3$ with 15 M NH_4OH and centrifuge. To the supernatent add a drop of methyl orange, make just acid with 6 M H_2SO_4, buffer with 1 ml of 1 M $NaC_2H_3O_2$, heat to boiling, add 10 drops of 1 M $AgNO_3$, digest in hot water bath, cool, filter, wash five times with 5 ml of H_2O containing a few drops of $AgNO_3$, five times with 5 ml alcohol, dry 15 minutes at 110°C. Weigh as $AgMoO_4$.

Remarks:

In order to destroy the Mo α-benzoinoxime the solution must be heated until white fumes have boiled off for several minutes. If all of the α-benzoin oxime is not destroyed, Mo α-benzoin oxime will reprecipitate when the solution is made basic.

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

8/12/49
P-18-170

CHEMICAL SEPARATIONS

Element separated: Molybdenum

Procedure by: Newton

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

Time for sep'n: ~ 3 hrs.

Type of bbdt: 60" α's

Equipment required: Standard

Yield: ~ 60%

Degree of purification: ~ 10^5-10^6

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

(1) Add 10 mg Mo to sample in HCl. Add Br_2 to oxidize Mo. Make 6 N HCl. Extract three times with double volume ether. Combine ether layers. Wash twice with 2 ml 6 N HCl. Evaporate ether over water. (May repeat Et_2O extraction after $Fe(OH)_3$ scavenging.

(2) To evaporated solution add 5 ml 6 N HNO_3, 1 ml sat $H_2C_2O_4$ (complex Cb), ppt by stirring with 5 ml 2% α-benzoin oxime. (ppts Mo, Cb & Pd). Let stand 2 min., wash with 20 ml 1 N HNO_3.

(3) Add 2 ml conc HNO_3 & 1 ml 70% $HClO_4$. Heat to fuming, cool, add 20 ml H_2O. Add 5 mg Fe^{+3} & 2 ml conc NH_4OH. To supernate add 6 ml conc HNO_3 & re-ppt with 5 ml α-b-o, wash. Repeat pptn of Fe for higher purity.

(4) Dissolve in 2 ml conc HNO_3 & 1 ml 70% $HClO_4$ & heat to fuming. Dilute to 30 ml, add 1 drop methyl orange, make just alkaline with 0.5 to 1 ml 6 N NH_4OH. Make just acid with 6 N H_2SO_4. Buffer with 2 ml 10% NaAc, boil, add 0.5 ml 1 M $AgNO_3$. Cool with stirring. Filter, wash 7 times with 5 ml 0.03M $AgNO_3$, three times with 5 ml 95% EtOH. Dry 15 min at 110°. Cool in desiccator. Weigh as Ag_2MoO_4.

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

Mo oxime can be dissolved completely by NaOH (6N) and repptd by adding acid and more α-b-o.

Stock solution of carrier - 18.4 g $(NH_4)_6 Mo_7O_{24}.4H_2O$ in 1 liter H_2O.

To standardize carrier: Put 5 ml carrier in 250 ml beaker. Add 150 ml H_2O, methyl orange, several drops 6 N NH_4OH to alkaline, just acid with 6 N H_2SO_4. Add 1 gm NaAc, boil, add 2.5 ml 1 N $AgNO_3$, stir. Cool slowly to 25° C. Filter on tared sintered glass filter. Wash and weigh as mentioned before.

10 mg Mo = 39.15 mg Ag_2MoO_4 (M.W. 375.71)

8/23/49

P-18-288

CHEMICAL SEPARATIONS

Element separated: Molybdenum

Procedure by: Folger

Target material: ~ 4 g U metal

Time for sep'n: ~ 2 hrs.

Type of bbdt: 184" all high energy particles

Equipment required: wide-mouth cylindrical sep. funnels, stirring motor and glass stirring rods, ice bath, centrifuge and cones

Yield: Approx. 50-80%

Degree of purification: ~ 10^4 from all F.P. activities

Advantages: Gives pure Mo in good yield

Procedure: To aliquot of sample in solution:

(1) Add 10 mg Mo and concentrated HCl, destroy HNO_3. Make up to 5 ml 6 N HCl, add one drop Br_2 water, extract twice with 15 ml ether allowing ~ 5 min equilibration. Combine ether layers and wash twice with 2 ml 6 N HCl. Evaporate ether over 5 ml H_2O.

(2) Boil out ether, dilute to 10 ml, add 2 mg Fe^{+3} and 2 mg Cb (as oxalate) and precipitate with NH_3.

(3) Make supernatant 0.5 N in HCl and add 1 ml saturated $H_2C_2O_4$, cool. Add 3 ml 2% solution of α-benzoin oxime in alcohol, digest 2 min. in ice bath, add aerosol and centrifuge 5 min. (If the Mo oxime does not settle well, dilute the solution with C_2H_5OH). Wash twice with ~ 2 ml 0.5 N H_2SO_4.

(4) Add 2 ml concentrated HNO_3 and 1 ml concentrated $HClO_4$ and boil carefully to fuming. Cool, dilute to 10 ml with H_2O, add 2 mg Fe^{+3}, and precipitate with 6 N NaOH.

(5) Repeat (3) by making 0.5 N in H_2SO_4 instead of HCl. Repeat (4).

(6) Add 1 drop methyl orange to supernatant and make just acid with 6 N H_2SO_4. Buffer with 1 ml 10% CH_3COONa, boil, add 10 drops 1 M $AgNO_3$, cool slowly with stirring, filter, wash five times with 5 ml 0.03 M $AgNO_3$, three times with 5 ml C_2H_5OH, dry 15 min. at 110° C. Weigh as Ag_2MoO_4 (39.16 mg per 10 mg Mo).

Remarks:

(1) More cycles of ether extraction and oxime precipitation may be added if needed for purity.

(2) Mo-α-benzoinoxime can be completely dissolved in 6 N NaOH and re-pptd by making the soln 0.5 N in H^+ and adding α-b-o.

(3) Continued fuming with conc HNO_3 and conc $HClO_4$ will ppt a form of molybdic acid which can be dissolved readily in 6 N NaOH.

8/12/49
P-18-161

CHEMICAL SEPARATIONS

Element separated: Ruthenium

Procedure by: Goeckermann

Target material: ~1 g Bi metal

Time for sep'n: ~2 hr.

Type of bbdt: 184" all particles

Equipment required: Distilling flask, ice, centrifuge, tubes, 110° oven

Yield: approx. 60%

Degree of purification: Decontamination factor > 10^4 from fission and spallation products.

Advantages: Fair yield of pure Ru

Procedure:

1. Add 10 mg Ru and Os to aliquot of HNO_3 soln of target, boil 6N HNO_3 solution to volatilize OsO_4. Transfer to glass still, add 10 mg I^-, 0.5 g $NaBiO_3$, 1 ml concentrated H_3PO_4, and 10 ml 70% $HClO_4$. Boil in air stream without bumping and distill over RuO_4 into 12 ml 6N NaOH in an ice bath. Distill until 1-2 ml of $HClO_4$ have distilled (2-3 min. after fuming begins).

2. To distillate, add 3 ml C_2H_5OH and boil 1-2 min. until Ru oxide is coagulated. Wash with 10 ml H_2O and 1 ml 6N NaOH and boil.

3. Distill RuO_4 again, if necessary, and reprecipitate oxide.

4. Dissolve precipitate in 2 ml hot 6N HCl and dilute to 12 ml. Add ~0.2 g Mg chips or coarse powder slowly (add aerosol) until solution passes through blue stage and Ru^o appears. Boil gently until coagulated. Add 5 ml concentrated HCl to remove excess Mg and boil, filter, wash three times with 5 ml hot H_2O, three times with 5 ml C_2H_5OH, three times with 5 ml ether, dry 10 min. at 110° C. Weigh as Ru^o.

Remarks: Some Ru may be lost from boiling a conc. HNO_3 soln. Os & Tc do not ppt with the EtOH. The $NaBiO_3$ converts I to iodate to prevent volatilization. The H_3PO_4 prevents volatilization of small amounts of Mo.

7/29/49

P-18-108

CHEMICAL SEPARATIONS

Element separated: Ruthenium

Procedure by: Folger & Hicks
Also by Wolfe

Target material: ~ 4 g. U metal

Time for sep'n: ~ 1 1/2 -2 hr.

Type of bbdt: 184" all high energy particles

Equipment required:
"Ruthenium still" (all glass)

Yield: approx. 60%

Degree of purification: ~ 10^4 from all F.P. activities.

Advantages: Fairly rapid, simple procedure for obtaining a good yield of Ru.

Procedure:

(1) Add 10 mg Ru and Os, boil 6 N HNO_3 solution to volatilize OsO_4. Transfer to glass still, add 10 mg I^-, 0.5 g $NaBiO_3$, 5 mg Mo hold-back, 1 ml concentrated H_3PO_4, and 10ml 70% $HClO_4$. Boil in air stream without bumping and distill over RuO_4 into 12 ml 6N NaOH in an ice bath. Distill until 3-4 ml of $HClO_4$ have distilled (5 min. after fuming begins).

(2) To distillate, add 3 ml C_2H_5OH and boil 1-2 min. until Ru oxide is coagulated. Wash with 10 ml H_2O and 1 ml 6 N NaOH and boil. (leaves Tc behind).

(3) Distill RuO_4 again, if necessary, and reprecipitate oxide.

(4) Dissolve precipitate in 2 ml hot 6 N HCl and dilute to 12 ml. (Take aliquot for counting here if desired). Add ~ 0.2 g Mg chips or coarse powder slowly (add aerosol) until solution passes through blue stage and Ru^o appears. Boil gently until coagulated. Add 5 ml concentrated HCl to remove excess Mg and boil, filter, wash three times with 5 ml hot H_2O, three times with 5 ml C_2H_5OH, three times with 5 ml ether, dry 10 min. at 110° C. Weigh as Ru^o.

8/16/49

CHEMICAL SEPARATIONS

Element separated: Ruthenium

Procedure by: Lindner

Target material: Sb (~.5 gm metal)

Time for sep'n: ~ 2 hr.

Type of bbdt: 184" D_2 & α

Equipment required: "Ru still" Lusteroid tubes, centrifuge, cones.

Yield: 50% or greater

Degree of purification: At least factor of 100

Procedure:

(1) To dissolve the Sb metal, add 15 drops of 27 N HF to it in a lusteroid tube in a hot water bath. Add conc HNO_3 dropwise until dissolved (~ 10 min.) Dilute to ~ 20 ml.

(2) To the SbF_4^- solution add 20 mg each of Te, Sn, In, Cd, Ag, Pd, Ru, Mo and Y carriers as soluble salts. Add 2 drops conc. HCl. Centrifuge the YF_3 and AgCl ppts.

(3) To half of the supn add 5 ml of 1% dimethyl glyoxime in alcohol. Centrifuge.

(4) Place the supn on an ice bath, add 5 ml 2% α benzoin oxime and digest 2 min. Centrifuge.

(5) Evaporate sup'n to near-dryness on hot plate. Add 10 ml H_2O, 2 ml conc. H_2SO_4 and evap to fuming for 20 min.

(6) Transfer to "Ru distilling flask", add 5 ml 70% $HClO_4$. Boil to fuming for 10 min, catching distillate in 5 ml 6 N NaOH.

(7) Add 2 ml EtOH to the RuO_4 in NaOH, boil and centrifuge.

(8) Dissolve the RuO_2 ppt in a minimum 6 N HCl.

(9) Add 5 ml 70% $HClO_4$. Repeat steps 6-8.

(10) Add 0.2 gm Mg powder to aliquot of the Ru^{+++} sol'n slowly. Boil gently to coagulate Ru.

(11) Add 5 ml conc HCl to dissolve excess Mg and boil.

(12) Plate the Ru metal and count.

8/18/49

P-18-222

CHEMICAL SEPARATIONS

Element separated: Ruthenium

Procedure by: Newton

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

Time for sep'n: 1 hr.

Type of bbdt: 60" alphas

Equipment required: "Ruthenium still"

Yield: $\sim 10^6$

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

(1) Place aliquot in a distilling flask, add 20 mg Ru carrier, 10 mg I^- carrier, 0.5 gm $NaBiO_3$, 1 ml 85% H_3PO_4 and 10 ml 70% $HClO_4$. Heat gently to boiling and distill Ruthenium rapidly, (avoid bumping) into 12 ml of 6 N NaOH in a 50 ml centrifuge tube in an ice bath. Distill till 1-2 ml of $HClO_4$ have distilled (1-2 min after fuming begins).

(2) To distillate add 5 ml EtOH. Heat gently to boiling by swirling over a flame and centrifuge. Suspend pptd Ru in 10 ml H_2O containing 1 ml of 6 M NaOH. Heat to boiling and centrifuge.

(3) Dissolve ppt by heating to boiling in 2 ml 6 M HCl. Add 10 ml H_2O. Add 0.2 gm Mg powder in small portions, shaking with each addition. Add a few drops 0.1% aerosol to minimize frothing. Boil gently until Ru^o in well coagulated. Continue boiling 2 min. Slowly add 5 ml of 12 M HCl to remove excess magnesium and again boil 2 min.

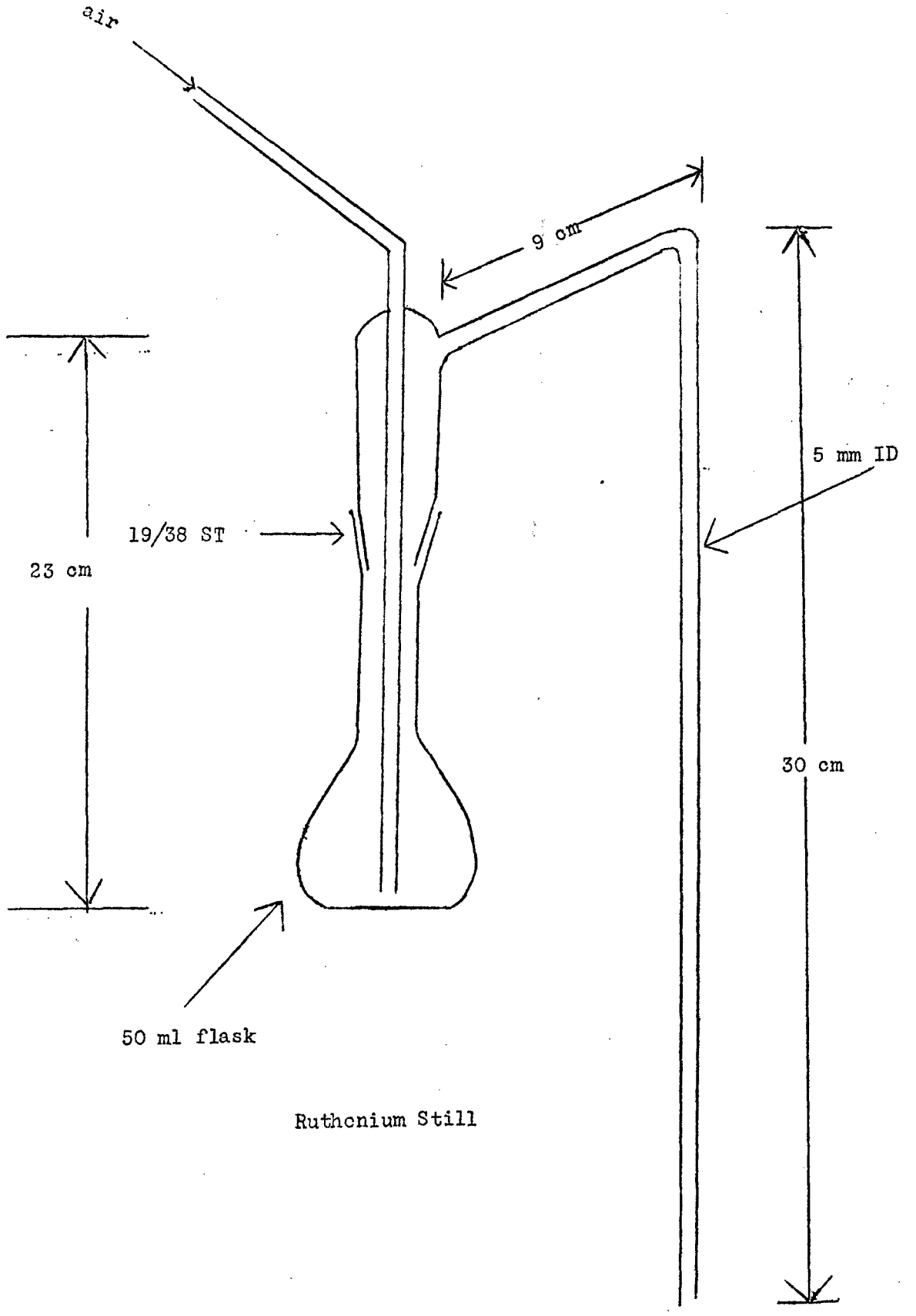
(4) Filter by suction on a weighed filter paper in a small Hirsch funnel. Wash three times with 5 ml hot H_2O, three times with 5 ml 95% EtOH, and three times with 5 ml Et_2O. Dry 10 min. at 110°. Weigh as Ru^o.

Remarks:

Preparation of Carrier Solution: Dissolve 28 gms commercial ruthenium chloride ($RuCl_3RuCl_4$, x H_2O) in water and dilute to 1 liter.

Standardization: Take 5 ml carrier in 250 ml erlenmeyer. Add 25 ml H_2O, 2 ml conc. HCl. Add 0.4 gms powdered magnesium metal in small portions, shaking after each addition. Add a few drops 0.1% aerosol sol to prevent frothing and boil gently till the ruthenium is coagulated and the supernate clear and colorless. Continue to boil 2 min. Add 10 ml 12 N HCl to remove excess Mg and boil 2 min. (Add more Mg if supernate not clear). Filter, wash three times with hot H_2O, three times with 5 ml portions EtOH, three times with Et_2O. Dry at 110° and weigh as Ru metal.

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



Ruthenium Still

8/24/49

P-19-257

CHEMICAL SEPARATIONS

Element separated: Rhodium

Procedure by: Wolfe

Target material: Uranium metal (~ 1 gm)

Time for sep'n: ~ 1 1/2 days when separated with Pt and Ir.

Type of bbdt: 388 Mev alphas

Equipment required: Special distilling flask, centrifuge, sep funnels, Lusteroid tubes, standard.

Yield: 10%

Degree of purification: 10^4 from fission products (None from Ir)

Procedure:

(1) Cut out the central portion of the target and boil with conc HCl to dissolve it and to expel Ge.

(2) Add 5 mg I^- and IO_3^- and boil the solution again to expel iodine.

(3) Add 20 mg Os, Ir, Pt, and Au carriers plus 20 mg Ba, Ru, Rh, and Pd carriers. Withdraw a 20% aliquot for determinations of Ba, Ru and Rh.

(4) To the 20% aliquot add HNO_3, 5 mg Ru carrier and 5 mg I^- and IO_3^-. B oil the solution to expel Os and I. (CAUTION: OsO_4 very poisonous.)

(5) Place the solution in a special all-glass distilling flask like that used for the osmium distillation. Add 0.5 gm $NaBiO_3$, 1 ml conc H_3PO_4, and 10 ml 70% $HClO_4$. Boil in an air stream without bumping and distill over RuO_4 into 12 ml 6 N NaOH in an ice bath. Distill until 1-2 ml of $HClO_4$ have distilled (2-3 min after fuming begins.) See (44-2).

(6) The residue from this Ru distillation is fumed strongly with the $HClO_4$.

(7) Cool the solution, dilute to 4 N and add 20 ml pyridine.

(8) Boil the solution for five minutes, place in a separatory funnel, and add 19 N NaOH to separate the free-base pyridine layer (the high conc of NaOH is merely to keep the volume low.)

(9) Wash the dark blue pyridine layer three times with equal volumes of dilute HCl, separating the layers each time with 6 N NaOH.

(10) Add a few drops of 6 N NaOH to the pyridine layer and evaporate the pyridine off.

(11) Pass H_2S into the boiling alkaline solution for several minutes, while the solution is acidified dropwise with HCl. Sulfides of Rh and Ir ppt.

(12) Dissolve the ppt in a little aqua regia. Add 5 mg of Au, Pt, and Pd carriers.

(13) Make soln 4 N in HCl and extract twice with equal volumes of butyl acetate to decontaminate from Hg and Au.

(14) Dilute the solution to about 0.5 N in H^+, add 5 ml dimethyl-glyoxime solution (1% in alcohol) and filter off the Pd ppt.

(15) Fume the remaining solution with H_2SO_4, dilute, neutralize to the brom cresol purple end point, and add BrO_3^- to ppt the hydrated oxides of Rh and Ir, leaving Pt in solution.

(16) Dissolve the oxides in conc HCl and dilute to known volume.

(17) An aliquot of proper size to give about 5000 c/m is withdrawn and a known amount of Rh carrier is added to it.

(18) Fume with H_2SO_4, dilute twenty to one, boil and ppt Rh metal by adding $TiCl_3$ dropwise until a very slight excess is present.

(19) Plate this Rh metal and count.

Remarks:

In uranium bombardments the activity in step 16 is due almost entirely to Rh, the activity of Ir being about 10^{-3} that of Rh --- even though no separation has been made from Ir. In some other bombarding arrangement where the activities of Ir and Rh are more closely equal, Ir could be separated from the Rh by a procedure similar to the last part of (77-3).

Rh, Ir and Pt should be separated from one bombardment leaving Os, Ru, and Pd for a second bombardment unless several people are cooperating on the procedure.

For other platinum metal - fission product separations see:

Platinum: 78-3
Osmium: 76-1
Ruthenium 44-2
Palladium 46-5
Iridium 77-3

8/16/49

CHEMICAL SEPARATIONS

Element separated: Palladium

Procedure by: Goeckermann

Target material: ~ 1 g Bi metal

Time for sep'n: ~ 2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, 110° oven

Yield: ~ 60%

Degree of purification: Decontamination factor $> 10^4$ from fission and spallation products.

Advantages: Fair yield of pure Pd

Procedure:

1. To aliquot of HNO_3 soln of target add 10 mg Pd^{+2}, make up to 20 ml 0.5N HCl, add 5 ml dimethyl-glyoxime solution (1% in alcohol). Wash with dilute HCl.

2. Dissolve precipitate in 1 ml concentrated HNO_3, dilute with 10 ml H_2O, add 5 mg Fe^{+3} and make basic with NH_3.

3. Add 10 mg Ag to supernatant and enough I^- to precipitate all the Ag. Repeat AgI scavenging.

4. Make supernatant 0.5 N in HCl and centrifuge out any AgCl. Add 5 ml dimethylglyoxime. Wash.

5. Repeat purification cycle if needed for higher purity.

6. Filter last Pd dimethylglyoxime, wash with H_2O and C_2H_5OH, dry 10 min. at 110° C. Weigh as Pd dimethylglyoxime (20.70 mg per 10 mg Pd).

Remarks: Zr and Ag are the principle contaminants of the dimethyl-glyoxime ppt.

7/29/49
P-18-105

CHEMICAL SEPARATIONS

Element separated: Palladium

Procedure by: Folger & Hicks

Target material: ~ 4 g. U metal

Time for sep'n: ~ 2 hr.

Type of bbdt: 184" all high energy particles

Equipment required: Centrifuge, cones, vac. filter

Yield: ~ 60%

Degree of purification: ~ 10^4 from all F.P. activities.

Advantages: Good yield pure Pd.

Procedure:

(1) Add 10 mg Pd^{+2} and 10 mg Ni, make 0.4 N in HNO_3 or HCl, add 3-5 ml dimethyl-glyoxime solution (1% in alcohol). Wash with dilute HCl or HNO_3 (0.2 N)

(2) Dissolve precipitate in 1 ml concentrated HNO_3, dilute with 5 ml H_2O, add 2 mg Fe^{+3} and make basic with NH_3. Centrifuge and repeat $Fe(OH)_3$ scavenge.

(3) Add 10 mg Ag to supernatant and enough I^- to precipitate all the Ag. Centrifuge and repeat AgI scavenging.

(4) Make supernatant 0.4 N in HCl and centrifuge out any AgCl. Add 3-5 ml dimethylglyoxime. Wash.

(5) Repeat purification cycle (steps 2,3,4) if needed for higher purity.

(6) Filter last Pd dimethylglyoxime, wash with H_2O and C_2H_5OH, dry 10 min. at 110° C. Weigh as Pd dimethylglyoxime (20.70 mg per 10 mg Pd).

Remarks:

Pd-d-m-g is quite bulky and may not centrifuge. In such case, filter with suction. The ppt may be dissolved by adding conc HNO_3 and catching the solution which runs through the filter.

8/16/49

P-18-181

CHEMICAL SEPARATIONS

Element separated: Palladium

Procedure by: Lindner

Target material: Sb (~ .5 gm metal)

Time for sep'n: ~ 1 hr.

Type of bbdt: 184" D_2 & α

Equipment required: Lusteroid tubes, centrifuge, cones.

Yield: Greater than 50%

Degree of purification: Factor of at least 100

Procedure:

(1) To dissolve the Sb metal, add 15 drops of 27 N HF to it in a lusteroid tube in a hot water bath. Add conc HNO_3 dropwise until dissolved (~ 10 min.) Dilute to ~ 20 ml.

(2) To the SbF_4^- solution add 20 mg each of Te, Sn, In, Cd, Ag, Pd, Ru, Mo & Y carriers as soluble salts. Add 2 drops conc. HCl. Centrifuge the YF_3 and AgCl ppts.

(3) To half of the supn add 5 ml of 1% dimethyl glyoxime in alcohol. Centrifuge.

(4) Wash the Pd "DMG" ppt with water and dissolve in aqua regia. Evaporate to dryness. Add 10 ml 2 N HCl. Add 1 mg Sb, Sn, In and Cd holdback carriers and 5 ml 1% "DMG" reagent in alcohol.

(5) Repeat (4) twice (do three times altogether).

(6) Wash the ppt with water and then alcohol.

(7) Plate the Pd "DMG" ppt.

8/18/49

P-18-223

CHEMICAL SEPARATIONS

Element separated: Palladium

Procedure by: Newton

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

Time for sep'n: ~ 1 hr.

Type of bbdt: 60" α's

Equipment required: Standard

Yield: ~ 80%

Degree of purification: ~ 10^6 except from Ag^+

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

(1) To sample add 20 mg Pd^{++}. If sample in HCl, must add HNO_3 to oxidize Pd.[1]

(2) Dissolve ppt in 1 ml conc HNO_3, cool, dil with 10 ml H_2O, add 5 mg Fe^{+3}, make basic with excess NH_4OH. Add 10 mg Ag^+ and enough I^- to ppt Ag. Centrifuge and repeat scavenging.

(3) Make 0.4 N in HCl and centrifuge out any AgCl. To supernate add 3-5 ml dimethyl glyoxime, wash.

(4) Repeat purification cycle in 2 & 3 for further purity.

(5) Wash dimethyl glyoxime ppt with H_2O and EtOH. Dry 10 min at 110°. Weigh.

Remarks: Zr and Ag^+ are principal contaminants.
10 mg Pd = 31.6 mg $PdC_8N_4O_4H_{17}$

(1) The Pd is in Th as colloidal metal. Is not oxidized to Pd^{++} by HCl and does not exchange with carrier.

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

8/23/49

P-18-285

CHEMICAL SEPARATIONS

Element separated: Palladium

Procedure by: Wolfe

Target material: Uranium (metal)

Time for sep'n: ~1 day when separated with Os and Ru

Type of bbdt: 388 Mev α's

Equipment required: Special distilling flask, centrifuge, sep funnel, Lusteroid tube, standard

Yield: ~ 50%

Degree of purification: 10^3 from fission products

Procedure:

(1) Cut out the central portion of the target and boil with concentrated HCl to dissolve it and to expel Ge.

(2) Add 5 mg I^- and IO_3^- and boil the solution again to expel iodine.

(3) Add 20 mg Os, Ir, Pt and Au carriers plus 20 mg Ba, Ru, Rh and Pd carriers. Withdraw a 20% aliquot for later determinations of Ba, Ru, and Rh.

(4) Place the remaining solution in a special all-glass distilling flask having a thistle tube entry and an air entry. Add concentrated HNO_3 through the thistle tube, and distill OsO_4 into 6 N NaOH in an ice bath. (Save for Os determination).

(5) Place the residue from the Os distillation in a beaker, add 10 ml 70% $HClO_4$ and boil the solution to fumes of $HClO_4$ to expel Ru.

(6) Dilute the solution, add 5 mg more Ru carrier, and 5 mg more I^- and IO_3^- and repeat the fuming.

(7) Add one ml dilute HCl, dilute the solution to 4 N and extract twice with equal volume butyl acetate to decontaminate from Hg and from Au.

(8) Dilute the solution to ~0.5 N in H^+, add 5 ml dimethylglyoxime solution (1% in alcohol) and filter off the palladium ppt.

(9) Dissolve ppt in HNO_3, dilute to 0.5 N in H^+, and reppt the Pd dmg.

(10) Dissolve ppt in HNO_3, add 2 mg La^{+++} carrier and ppt the hydroxide by adding NH_4OH. Dissolve ppt in HNO_3 and ppt hydroxide twice more.

(11) Add 10 mg Ag^+ to supn and enough Cl^- to ppt all the Ag. Centrifuge and repeat AgCl scavenges twice. Centrifuge off all AgCl.

(12) Dilute supn to known volume, transfer to a plastic lusteroid container (to prevent adsorption of Ag daughter activity on glass walls) and wrap in parafilm to prevent evaporation.

(13) Allow the soln to stand for 12-16 hours until the 3.2 hr Ag^{112} daughter of 21 hour Pd^{112} has grown into equilibrium. Thereafter at intervals of about a day, known aliquots are "milked" of the Ag^{112} daughter by AgCl pptns in order to determine decay of Pd^{112}.

Remarks: Os, Ru and Pd can be taken from one bombardment leaving Rh, Ir and Pt for a second bombardment unless several people are cooperating on the procedure.

For other platinum metal - fission product separations see:

Platinum 78-3	Iridium 77-3	Rhodium 45-1
Osmium 76-1	Ruthenium 44-2	

8/17/49

CHEMICAL SEPARATIONS

Element separated: Silver

Procedure by: Folger & Hicks

Target material: ~ 4 g. U metal foil

Time for sep'n: ~2 hr.

Type of bbdt: 184" all high energy particles

Equipment required: Centrifuge, cones, microburner, 110° oven

Yield: ~ 80%

Degree of purification: $>10^3$ from all F. P. activities

Advantages: Relatively simple procedure giving good separation in high yield.

Procedure:

(1) Dissolve target in > 10 N HNO_3.* Take aliquot and dilute to ~ 5-6 N HNO_3.

(2) Add aerosol and precipitate AgCl with 1 ml 0.5 N HCl.** Wash twice with 10 ml 1 N HNO_3 containing 1 drop 2 N HCl.

(3) Dissolve AgCl in 2 ml 6N NH_4OH, dilute to 10 ml, and add 2 mg Fe^{+3} Centrifuge $Fe(OH)_3$ and repeat scavenge (may be done in same tube.)

(4) Saturate supernatant with H_2S in the cold, wash Ag_2S.

(5) Dissolve Ag_2S in 2 ml concentrated HNO_3, boil, dilute to approx. 4 N (8 ml) and precipitate AgCl with 1 ml 0.5 N HCl. Wash twice with HNO_3 containing 1 drop 2 N HCl.

(6) Repeat (3).

(7) Repeat (4).

(8) Dissolve Ag_2S in 1 ml concentrated HNO_3, boil to destroy or remove all H_2S dilute to 6 ml, add 1 mg Fe^{+3}, and make basic with NH_3.

(9) Add aerosol, make 2N in HNO_3, add 2 drops 6 N HCl and boil to coagulate. Filter, wash three times with 5 ml 0.5 N HNO_3 three times with 5 ml C_2H_5OH, dry 10 min. at 110° C. Weigh as AgCl (13.28 mg per 10 mg Ag).

Remarks:

* Ag carrier should be added to the container in which target is dissolved in order to prevent loss of trace Ag by absorption in the glass. An amount of carrier should be added so that the aliquot will contain 10-20 mg.

**Boiling the solution over a microburner with stirring (being careful to avoid loss by bumping over) causes rapid and complete coagulation of AgCl.

In step 2 addition of a few drops Ba & Sr plus 2 drops 50% K_2CO_3 will provide additional decontamination from these elements.

CHEMICAL SEPARATIONS

Element separated: Silver

Procedure by: Goeckermann

Target material: ~ 1 g Bi metal

Time for sep'n: ~ 2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, ice, 110° oven

Yield: ~ 80%

Degree of purification: Decontamination factor > 10^4 from fission and spallation products

Advantages: Good yield of pure Ag

Procedure:

(1) To aliquot of HNO_3 soln of target add 10 mg Ag, aerosol, dilute to 20 ml, and precipitate AgCl with 1 ml 6N HCl. Wash with 10 ml H_2O.

(2) Dissolve AgCl in 2 ml 6N NH_4OH, dilute to 10 ml, and add 5 mg Fe^{+3}.

(3) Saturate supernatant with H_2S in the cold, wash Ag_2S.

(4) Dissolve Ag_2S in 1 ml concentrated HNO_3, dilute to 20 ml, and precipitate AgCl with 1 ml 6N HCl. Wash with H_2O.

(5) Repeat (2).

(6) Repeat (3).

(7) Dissolve Ag_2S in 1 ml concentrated HNO_3, dilute to 10 ml, add 5 mg Fe^{+3}, and make basic with NH_3.

(8) Add 5 drops 6N HCl to supernatant, add aerosol, make 1N in HNO_3, heat, filter, wash three times with 5 ml H_2O, three times with 5 ml C_2H_5OH, dry 10 min. at 110° C. Weigh as AgCl (13.28 mg per 10 mg Ag).

Remarks: Wilkinson suggested an electrolysis procedure involving plating Ag^0 on the cathode from 2-3 N HNO_3 and then transferring it to the anode in a cyanide bath -- this is good unless Pt, Au, Ir, or Os are present.

7/29/49
P-18-106

CHEMICAL SEPARATIONS

Element separated: Silver

Procedure by: R. C. Lilly

Target material: Cd (separated isotopes)

Time for sep'n: 30-40 minutes

Type of bbdt: Deuterons and protons - 60"

Equipment required: beakers, funnels, Hirsch funnel

Yield: ~ 90%

Degree of purification: good - at least factor of 100 from other activities present.

Advantages: Simplicity

Procedure:

(1) Dissolve the Cd target, weighing 10-15 mg, in a few milliliters of conc. HNO_3 in a small beaker. When all of the material has dissolved, evaporate to dryness to drive off excess HNO_3.

(2) Add 3 - 4 mg In and 3-4 mg. Ag as the nitrate sol'ns and dilute to ~ 10 ml with H_2O.

(3) Add 1 N HCl dropwise until the Ag is completely ppt'd as AgCl. Coagulate the ppt by heating and filter through a small #42 Whatman filter paper in a short-stemmed glass funnel. (The filtrate contains the Cd and In fractions and is worked up separately as described in the procedures for Cd and In from Cd targets, Nos. 48-3 and 49-1.

(4) Wash the AgCl ppt several times with 0.1 N HNO_3, discarding the washes. Dissolve ppt through paper with 6 N NH_4OH, collecting the soln in another small beaker.

(5) To scavange for In, add 2-3 mg Fe as ~5 ml of $FeCl_3$ soln, stirring well during the addition. Coagulate the ppt by heating, filter, and discard it.

(6) Re-acidify the filtrate with HNO_3 and add a few drops of 1 N HCl to make sure that the AgCl is completely ppt'd. Coagulate the ppt by heating and filter through a #42 Whatman paper disc held in a Gooch crucible or Hirsch funnel.

(7) Suck the sample as dry as possible and then pour 1-2 ml acetone through the paper to remove the residual H_2O. When the paper disc is dry, mount under tape.

Remarks: See Scott (Std. Meth. Chem. Anal.) for complete information on the ppt'n of AgCl.

8/17/49

CHEMICAL SEPARATIONS

Element separated: Silver

Procedure by: Lindner

Target material: Sb (~ .5 gm metal)

Time for sep'n: ~ 1 hr.

Type of bbdt: 184" D_2 & α

Equipment required: Lusteroid tubes, centrifuge, cones

Yield: Equal or greater than 50%

Degree of purification: At least factor of 100.

Procedure:

(1) To dissolve the Sb metal, add 15 drops of 27 N HF to it in a lusteroid tube in a hot water bath. Add conc HNO_3 dropwise until dissolved (~ 10 min). Dilute to ~ 20 ml.

(2) To the SbF_4^- solution add 20 mg each of Te, Sn, In, Cd, Ag, Pd, Ru, Mo & Y carriers as soluble salts. Add 2 drops conc. HCl. Centrifuge the YF_3 and AgCl ppts.

(3) Wash the ppt with 1 N HF.

(4) Dissolve out the Ag^+ from the ppt by adding 1 ml conc. NH_4OH. Centrifuge.

(5) Dilute the supn to 5 ml and add 2 mg Fe^{+++} carrier. Centrifuge and discard the ppt of $Fe(OH)_3$.

(6) Add 1 mg each Sb, Sn, In and Cd carriers. Add 1 ml conc. HNO_3 and 1 drop conc. HCl. Centrifuge out the AgCl ppt.

(7) Add 1 ml conc. NH_4OH to the ppt and repeat (6).

(8) Add 2 ml 6 N NaOH to the AgCl ppt. Digest 10 minutes in hot water bath. Dilute to 10 ml & centrifuge.

(9) Wash the Ag_2O ppt with water and then dissolve in 1 drop conc. HNO_3.

(10) This solution can be plated or if chemical yield is to be determined the Ag should be weighed as AgCl.

8/18/49

P-18-224

CHEMICAL SEPARATIONS

Element separated: Silver

Procedure by: Newton

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

Time for sep'n: 1 hr

Type of bbdt: 60" α's

Equipment required: Standard, tank H_2S

Yield: ~85%

Degree of purification: ~ 10^6 except from Pd

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

(1) Add 20 mg Ag^+ to sample after diluting to 0.3 N HCl. Digest a few min. Centrifuge AgCl ppt off and wash with 10 ml H_2O.

(2) Dissolve AgCl in 2 ml 6 N NH_4OH. Dilute to 10 ml and add 5 mg Fe^{+3}. Centrifuge off $Fe(OH)_3$. Add more Fe and recentrifuge. Saturate supernate with H_2S. Precipitate Ag_2S. Wash Ag_2S.

(3) Dissolve ppt in 1 ml conc HNO_3. Dil to 10 ml. Neutralize with 6 N NH_4OH and add 1-2 ml excess. Add 5 mg Fe^{+3}. Discard ppt.

(4) Repeat Ag_2S and $Fe(OH)_3$ pptns.

(5) To last $Ag(NH_3)_4^+$ sol. add 5 drops 6 N HCl, aerosol and 2 ml 6 N HNO_3. Heat and filter. Wash three times 5 ml H_2O, three times 5 ml 95% EtOH. Dry 10 min. at 110° and weigh as AgCl.

Remarks:

10 mg Ag^+ = 13.3 mg AgCl (M.W. 143.34)

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

Ag^+ is adsorbed very rapidly by glass in carrier free solution. Dissolve and treat in quartz or lusteroid till carrier added, otherwise most of active Ag^+ may be lost.

8/23/49

CHEMICAL SEPARATIONS

Element separated: Cadmium

Procedure by: Folger, Hicks, Miller

Target material: ∿ 4 g. U metal foil

Time for sep'n: 2-2.5 hr.

Type of bbdt: 184" all particles

Yield: ∿ 70%

Degree of purification: $>10^3$ from all F. P. activities.

Procedure:

(1) Add 10 mg Cd and Cu as indicator and make basic with NH_3, centrifuge. Wash ppt with NH_4OH and combine washings.

(2) Saturate supernatant with H_2S and centrifuge, wash.

(3) Dissolve precipitate in minimum quantity conc. HCl and evaporate. Dissolve in 10 ml H_2O, add 5 mg Fe^{+++}, La^{+++}, and In^{+++}; add NH_3 and centrifuge. Add more Fe^{+++} and centrifuge on top of first.

(4) Pass H_2S into supernatant and centrifuge.

(5) Dissolve ppt in 3 ml conc. HNO_3 and dilute to 8 ml. Add Ag^+ and Cl^- and centrifuge.

(6) Neutralize supernatant with NH_3, add enough solid KCN to complex Cu and pass in H_2S.

(7) Dissolve CdS in 2 ml 6N HCl, dilute to 6 ml, add 10 mg Pd^{+2}, heat, and saturate with H_2S.

(8) Add Sb^{+3} to supernatant and scavenge with Sb_2S_3.

(9) To supernatant add excess NH_4OH and saturate with H_2S.

(10) Dissolve CdS in a few drops of HCl, evaporate to dryness. Dissolve in 9 ml of a solution containing 3 ml 6 N HAc and 6 ml of 6 N NH_4Ac. Heat, add 2 ml 1.5 M $(NH_4)_2HPO_4$, and digest hot for 15 min. Filter, wash with H_2O, dry 10 min. at 110° C. Weigh as $CdNH_4PO_4 \cdot H_2O$ (21.66 mg per 10 mg Cd).

7/28/49
P-18-104

CHEMICAL SEPARATIONS

Element separated: Cadmium

Procedure by: Goeckermann

Target material: ~ 1 g Bi metal

Time for sep'n: ~ 2 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, H_2S tank, 110° oven

Yield: ~ 70%

Degree of purification: Decontamination factor $\gtrsim 10^4$ from fission and spallation products.

Advantages: Good yield of pure Cd

Procedure:

(1) To aliquot of HNO_3 soln of target add 10 mg Cd and make basic with NH_3, centrifuge out $Bi(OH)_3$.

(2) Add 10 ml concentrated HCl to supernatant and evaporate to dryness. Take up in 20 ml 0.2 N HCl and saturate with H_2S. Wash CdS with H_2S water.

(3) Dissolve CdS in 1 ml 6N HCl, boil out H_2S, dilute to 10 ml, add 5 mg Fe^{+3} and 6N NH_4OH dropwise until $Fe(OH)_3$ precipitation begins. Redissolve 1-2 drops HCl, heat, add 4-5 drops 6N CH_3COONH_4, centrifuge out basic ferric acetate precipitate.

(4) Add 10-15 drops 6N HCl to supernatant and precipitate CdS.

(5) Dissolve CdS in HCl and expel H_2S, add several mg In and precipitate with NH_3.

(6) Re-acidify and precipitate CdS.

(7) Dissolve CdS in 2 ml 6N HCl, dilute to 10 ml, add 10 mg Pd^{+2}, heat, and saturate with H_2S.

(8) Add 5 mg Sb^{+3} to supernatant and scavenge with Sb_2S_3.

(9) To supernatant add excess NH_4OH and saturate with H_2S.

(10) Dissolve CdS in a few drops of HCl, expel H_2S, dilute to 15 ml, add 2 ml 3M HCl, boil, add 2 ml 1M $(NH_4)_2HPO_4$, and digest hot 15 min. Filter, wash with H_2O, dry 10 min. at $110^\circ C$. Weigh as $CdNH_4PO_4 \cdot H_2O$ (21.66 mg per 10 mg Cd).

7/29/49

P-18-103

CHEMICAL SEPARATIONS

Element separated: Cadmium

Procedure by: R. C. Lilly

Target material: Cd(separated isotopes)

Time for sep'n: 2-3 hours

Type of bbdt: Deuterons and protons - 60"

Equipment required: Beakers, funnels, Hirsch funnel, separatory funnels, pH meter.

Yield: ~ 90%

Degree of purification: good - at least factor 100 from other activities present.

Advantages: Good separation

Procedure:

(1) Dissolve the Cd target, weighing 10-15 mg, in a few milliliters of conc HNO_3 in a small beaker. When all of the material has dissolved, evaporate to dryness to drive off excess HNO_3.

(2) Add 3 - 4 mg In and 3-4 mg Ag as the nitrate sol'ns and dilute to ~ 10 ml with H_2O.

(3) Add 1 N HCl dropwise until the Ag is completely ppt'd as AgCl. Coagulate the ppt by heating and filter through a small #42 Whatman filter paper in a short-stemmed glass funnel. The filtrate contains the Cd and In fractions. (The AgCl ppt is worked up separately as described in the procedure for Ag from Cd targets, No. 47-3).

(4) Make the filtrate ammoniacal and add another 3-4 mg Ag as the nitrate sol'n. Acidify with HNO_3 and add a few drops of 1 N HCl to insure complete ppt'n of AgCl. Coagulate the ppt by heating, filter on #42 paper, and discard.

(5) Adjust the pH of the filtrate to 3.5 with NH_4OH and transfer to a 50 ml separatory funnel.

(6) Extract the In by shaking with three portions of 0.02 M 8-hydroxyquinoline in CH_3Cl, drawing the organic layers off into a second separatory funnel after each pass. Discard the few drops of mixed sol'n which remain in the stopcock after separation of layers. (The In is contained in this organic layer and is worked up separately as described in the procedure for In from Cd targets, No. 49-1).

(7) Add 3-4 mg In as the nitrate sol'n to the H_2O layer remaining in the first funnel. Repeat the extractions as outlined in (6) above, but this time discard the three organic layers containing the scavenger In.

(8) Draw the H_2O layer into a beaker, boil off residual CH_3Cl, and add NH_4OH to ppt Cd as the 8-hydroxyquinolate. Filter through a #42 Whatman paper disc held in a Gooch crucible or Hirsch funnel. Suck the sample on the paper as dry as possible and then complete the drying under a heat lamp before mounting under tape.

Remarks:

See Scott (Std. Meth. Chem. Anal.) for complete information on the ppt'n of AgCl.

See Sandell (Colorimetric Determination of Traces of Metals) for further information on the extraction of In with 8-hydroxyquinoline.

8/18/49

P-18-235

CHEMICAL SEPARATIONS

Element separated: Cadmium

Procedure by: Lindner

Target material: Sb(~.5 gm metal)

Time for sep'n: ~ 2 hours

Type of bbdt: 184" α & D_2

Equipment required: Lusteroid tubes, centrifuge, cones, tank H_2S, SO_2

Yield: 50% or greater

Degree of purification: At least factor of 100.

Procedure:

(1) To the target add 15 drops 27 N HF in lusteroid tube in hot water bath. Add conc HNO_3 dropwise until dissolved (10 min.) Dilute to ~ 20 ml.

(2) Add 20 mg each Te, Sn, In, Cd, Ag, Pd, Ru, Mo, Y carriers as soluble salts. Add 2 drops conc HCl. Centrifuge.

(3) Divide supn into two equal parts.

(4) Evaporate one part to near-dryness. Cool, add 20 ml 3 N HCl.

(5) Boil the supn to expel SO_2, add 5 ml H_2O.

(6) Saturate hot with H_2S until Sb_2S_3 pptn complete.

(7) Evaporate the supn to near dryness. Take up in 15 ml 1 N NaOH.

(8) Wash the Cd and In hydroxide with very dilute NaOH, dissolve in HCl. Add 2 mg Sn^{+4} holdback.

(9) Repeat NaOH pptn, dissolve and make to 15 ml in 2 N HCl.

(10) Add 5 mg Sb^{+++}, 2 mg $TeO_3^{=}$ and saturate with H_2S.

(11) Boil supn to expel H_2S. Add excess NH_4OH. Centrifuge.

(12) To the supn containing the Cd $(NH_3)_4^{++}$ complex add 2 mg In^{+++}. Centrifuge off the $In(OH)_3$ ppt.

(13) Saturate sup'n with H_2S. Centrifuge CdS ppt.

(14) Dissolve CdS in HCl.

(15) Dilute an aliquot of solution to 15 ml. Add 11 ml 3 M NH_4Cl, 1 ml 1.5 M $(NH_4)_2HPO_4$ and weigh the $CdNH_4PO_4 \cdot H_2O$ ppt formed.

8/18/49

CHEMICAL SEPARATIONS

Element separated: Cadmium

Procedure by: Newton

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

Time for sep'n: 2 hrs.

Type of bbdt: 60" α's

Equipment required: Standard, tank H_2S

Yield: ~ 50%

Degree of purification: ~ 10^5 from fission products

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

(1) Add 10 mg cadmium carrier. Dilute to 0.2 N HCl, pass in H_2S, ppt CdS. Wash with H_2S water.

(2) Dissolve CdS in 1 ml 6 N HCl. Boil out H_2S. Dilute to 10 ml. Add 5 mg Fe^{+3}, 5 mg La^{+3}, 5 mg In^{+3}, add NH_4OH. Precipitate $Fe(OH)_3$. Centrifuge. Add more Fe^{+3} and scavenge again, centrifuging down on top of first.

(3) Pass H_2S into supernate, ppt CdS.

(4) Dissolve CdS in 1 ml 6 N HCl, boil, dilute to 10 ml, heat, add Ag^+, ppt AgCl, digest a few min., centrifuge.

(5) Add NH_4OH until alkaline, pass in H_2S, ppt CdS.

(6) Dissolve Cd in 2 ml 6 N HCl. Dil to 10 ml. Add 10 mg Pd^{+2} heat and saturate with H_2S, ppt PdS. Repeat sulfide scavenging with 5 mg Sb.

(7) To supernate add 2 ml 6 N NH_4OH saturate H_2S. Ppt CdS.

(8) Dissolve CdS in a few drops HCl. Boil to expel H_2S. Dilute to 15 ml. Add 1.5 ml 3 M NH_4Cl, boil, add 1.5 ml 1.5 M $(NH_4)_2HPO_4$ and digest hot 15 minutes. Filter. Wash with H_2O, dry 10 min. at 110°. Weigh as $Cd(NH_4)PO_4.H_2O$.

Remarks:

10 mg Cd = 21.63 mg $CdNH_4PO_4.H_2O$ (M.W. = 243.45)

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

8/23/49

P-18-284

CHEMICAL SEPARATIONS

Element separated: Indium

Procedure by: R. C. Lilly

Target material: Cd (separated isotopes)

Time for sep'n: 2-3 hours

Type of bbdt: Deuterons and protons - 60"

Equipment required: Beakers, funnels, Hirsch funnel, separatory funnels, pH meter

Yield: ~ 90%

Degree of purification: good - at least factor of 100 from other activities present.

Advantages: Good separation

Procedure:

(1) Dissolve the Cd target, weighing 10-15 mg, in a few milliliters of conc HNO_3 in a small beaker. When all of the material has dissolved, evaporate to dryness to drive off excess HNO_3.

(2) Add 3-4 mg In and 3-4 mg Ag as the nitrate sol'ns and dilute to ~ 10 ml with H_2O.

(3) Add 1 N HCl dropwise until the Ag is completely ppt'd as AgCl. Coagulate the ppt by heating and filter through a small #42 Whatman filter paper in a short-stemmed glass funnel. The filtrate contains the Cd and In fractions. (The AgCl ppt is worked up separately as described in the procedure for Ag from Cd targets, No. 47-3).

(4) Make the filtrate ammoniacal and add another 3-4 mg Ag as the nitrate sol'n. Acidify with HNO_3 and add a few drops of 1 N HCl to insure complete ppt'n of AgCl. Coagulate the ppt by heating, filter on #42 paper, and discard.

(5) Adjust the pH of the filtrate to 3.5 with NH_4OH and transfer to a 50 ml separatory funnel.

(6) Extract the In by shaking with three portions of 0.02 M 8-hydroxyquinoline in CH_3Cl, drawing the organic layers off into a second separatory funnel after each pass. Discard the few drops of mixed sol'n which remain in the stopcock after separation of layers. (The In is contained in this organic layer.)

The Cd remains in the H_2O layer and is worked up separately as described in the procedure for Cd from Cd targets, No. 48-3.

(7) Treat the organic layers in the second funnel with an equal volume of pH 3.5 HCl sol'n to remove traces of Cd.

(8) Draw off the organic layer into a beaker, add dilute HCl and boil off the CH_3Cl. Add NH_4OH to ppt In as the 8-hydroxyquinolate and filter through a #42 Whatman paper disc held in a Gooch crucible or Hirsch funnel. Suck the sample on the paper as dry

as possible and then dry the disc carefully under a lamp and mount under tape.

Remarks:

See Scott (Std. Meth. Chem. Anal.) for complete information on the ppt'n of AgCl.

See Sandell (Colorimetric Determination of Traces of Metals) for further information on the extraction of In with 8-hydroxyquinoline.

8/18/49

P-18-213

CHEMICAL SEPARATIONS

Element separated: Indium

Target material: Cd (separated isotopes)

Type of bbdt: Deuterons and protons - 60"

Yield: 50-75%

Degree of purification: good - at least factor of 10 from other activities

Advantages: speed

Procedure by: R. C. Lilly

Time for sep'n: 10 minutes

Equipment required:
- Small beakers
- Porcelain filter crucible
- Filter flasks
- Gooch crucible & holders
- Glass funnel & filter ring
- Test tube

Procedure:

(1) Dissolve the Cd target material, weighing a few milligrams, in a few drops of hot conc. HNO_3 in a 20 ml beaker. Add 2 mg Ag and 2 mg In as the nitrate sol'ns. The total volume at this point should be $\sim$ 5 ml.

(2) Add a few drops of methyl orange and neutralize with NH_4OH until the sol'n is slightly basic (yellow). Coagulate the ppt for a few seconds on a preheated hot plate.

(3) Filter the sample through a porcelain filter crucible into a 250 ml filter flask, using suction. Wash the ppt with a small amount of 1% NH_4NO_3 sol'n.

(4) Place the crucible containing the ppt on a rubber filter ring in a glass funnel and arrange a test tube in the filter flask in such a way that the tip of the funnel drips into the tube. Dissolve the ppt in HNO_3 and suck it through the filter into the test tube.

(5) Lift the tube out of the flask and pour the sol'n into another 20 ml beaker. Repeat the ppt'n as in (2) and filter the $In(OH)_3$ through a #42 Whatman filter paper disc held in a Gooch crucible or a Hirsch funnel.

(6) Suck the sample as dry as possible and then pour 1-2 ml acetone through the paper to remove the residual H_2O. When the paper disc is dry, mount on a card under tape.

Remarks:

In practice a segment consisting of $\sim$10% of the total was usually cut from the dried paper disc and mounted separately for use in counting the short half lives; the remainder, which was too active to count originally was then used to follow the longer half lives.

8/18/49

P-18-241

CHEMICAL SEPARATIONS

Element separated: Indium

Procedure by: Lindner

Target material: Antimony (~ .5 gm metal)

Time for sep'n: 1-2 hours

Type of bbdt: 184" α & D_2

Equipment required: Lusteroid tube, centrifuge, cones, tank N_2S, SO_2

Yield: 50% or greater

Degree of purification: At least factor of 100

Procedure:

(1) To the target add 15 drops 27 N HF in lusteroid tube in hot water bath. Add conc HNO_3 dropwise until dissolved (10 min.) Dilute to ~ 20 ml.

(2) Add 20 mg each Te, Sn, In, Cd, Ag, Pd, Ru, Mo, Y carriers as soluble salts. Add 2 drops conc HCl. Centrifuge.

(3) Divide supn into two equal parts.

(4) Evaporate one part to near-dryness. Cool, add 20 ml 3 N HCl.

(5) Boil the supn to expel SO_2, add 5 ml H_2O.

(6) Saturate hot with H_2S until Sb_2S_3 pptn complete.

(7) Evaporate the supn to near dryness. Take up in 15 ml 1 N NaOH.

(8) Wash the Cd and In hydroxide with very dilute NaOH, dissolve in HCl. Add 2 mg Sn^{+4} holdback.

(9) Repeat NaOH pptn, dissolve and make to 15 ml in 2 N HCl.

(10) Add 5 mg Sb^{+++}, 2 mg $TeO_3^{=}$ and saturate with H_2S.

(11) Boil supn to expel H_2S. Add excess NH_4OH. Centrifuge.

(12) Dissolve the $In(OH)_3$ ppt in HCl. Add 2 mg Cd^{++}. Repeat NH_4OH treatment.

(13) Dissolve the $In(OH)_3$ ppt in HCl and plate an aliquot.

8/18/49

CHEMICAL SEPARATIONS

Element separated: Indium

Procedure by: Wilkinson

Target material: Uranium (~ 1 gm)

Time for sep'n: ~ 1 hour

Type of bbdt: 184" (high energy fission)

Equipment required: Standard

Yield: 75-80%

Degree of purification: 10^5-10^6 from activities present

Procedure:

(1) To aliquot of target solution add 5 mg of holdback carriers; (Rare Earths, Ba, Sr, Zr, Rb, Cs, Te, Mo and rest of the sulfide group metals) plus 5 mg In and Cd carriers.

(2) Adjust acidity to 0.4 - 0.5 N HCl and saturate with H_2S. Discard ppt.

(3) Repeat steps 1 & 2 twice.

(4) Add NH_4Ac plus acetic acid, ppt In & Cd sulfides.

(5) Dissolve ppt in cold 1 N HCl and repeat steps 1-4 three times or until the acid sulfide fraction is inactive.

(6) Dissolve the In & Cd sulfides from last sulfide pptn in cold 1 N HCl (only Cd & In sulfides soluble in cold 1 N HCl, Sn & Sb soluble in hot 1 N HCl).

(7) Add R. E., Ba & Sr carriers, make slightly alkaline with NH_4OH. Then add HCl until faintly acid.

(8) Add excess NaAc and boil. Centrifuge off the basic indium acetate. (Cd remains in solution)

(9) Dissolve the ppt in dilute HCl. Add 5 mg Cd carrier and repeat steps 7 and 8.

8/24/49

CHEMICAL SEPARATIONS

Element separated: Tin (~ 10 mg)

Procedure by: W.R. McDonell

Target material: Recovery from chemical wastes after bbdt including 50 mg Fe, 30 mg Sb, 20 mg Cu

Time for sep'n: 3-4 hr.

Equipment required: Centrifuge

Yield: 90-95%

Degree of purification: At least factor of 100 from metals present in macro amount.

Advantages: High recovery yield.

Procedure:

(1) Combine wastes, crush and dissolve residues in HCl[1], HNO_3 or aqua regia[1], using alkali fusions (Na_2CO_3 or NaOH) where necessary.

(2) Neutralize with NH_4OH or NaOH, make .25-1.0 N acid with HCl, pass in H_2S to saturation, ppt black (usually) acid sulfide group + sulfur. Centrifuge, decant.

(3) Add 15 cc Na_2S_x soln[2] to ppt. Heat 60-80° C with stirring. Add ~15 ml hot 0.6 N NaOH, centrifuge, decant. Wash with 2nd portion of Na_2S_x. Combine filtrates. Acidify slowly with HCl to neutral litmus, then make .25-1 N acid. Saturate with H_2S. Centrifuge, decant.

(4) Add conc. HCl, warm with stirring to dissolve sulfides and coagulte sulfur[3]. Centrifuge, decant. Wash sulfur with hot 6 N HCl. Combine solutions, which now contain Sn, Sb (and As if any originally present) and only small amounts of Cu group metals.

(5) Do the tin antimony separation as outlined in 50-2 procedure[4] (selective sulfide ppt or ~ Fe reduction, etc.)

Remarks:

(1) Avoid boiling conc. chloride solutions of Sn, since $SnCl_4$ is somewhat volatile.

(2) Na_2S_x is used instead of $(NH_4)_2S_x$ because it affords a better separation from Cu, a major contaminant. (Ref. A System of Chemical Analysis, E. H. Swift, Prentice-Hall, Inc., New York, 1940 p. 215.) Specifications for Na_2S_x soln: dissolve 480 g $Na_2S \cdot 9H_2O$ + 40 g. NaOH in minimum amt of water, dissolve 16 g powdered sulfur in this soln, dilute to 1 liter.

(3) A large quantity of sulfur is present in the ppt. However, it coagulates very well on heating in acid solution, while adsorbing very little of the sulfide, allowing satisfactory extraction.

(4) Traces of Cu are dissolved by Na_2S_x solution. This, however, follows the Sb in the subsequent Sb-Sn separations. (Selective sulfide pptn or Fe reduction).

CHEMICAL SEPARATIONS

Element separated: Tin

Procedure by: Newton & McDonell

Target material: Tin (plus Cu of target holder)

Time for sep'n: 1 1/2 hrs.

Type of bbdt: low energy d,p,n

Equipment required: centrifuge, hot plate, glassware

Yield: 50-70%

Degree of purification: $\sim 10^6$

Advantages: Simpler than oxalate or distillation procedures

Procedure:

(1) Dissolve target in HCl, heating[1] and adding drop Br_2 or few drops of HNO_3 where necessary to effect rapid solution[2]. Add 10 mg Sb, In carriers.

(2) Make 3-4 N HCl. Add iron powder to excess (hydrogen evolution), heat with stirring, ppt Sb and Cu metal (black), filter by vacuum through sintered glass filtering crucible.

(3) To filtrate add drop of Br_2 ($Fe^{++} \longrightarrow Fe^{+++}$, $Sn^{++} \longrightarrow Sn^{++++}$ Neutralize with NH_4OH to appearance of red $Fe(OH)_3$, add just enough HCl to redissolve $Fe(OH)_3$ (acidity $<$ 1 N), pass in H_2S to saturation, ppt yellow SnS_2[3].

(4) Dissolve SnS_2 in HCl (3 cc of 12 N) by heating[1], stirring. Add 10 mg Sb carrier, stirring. Dilute to 2.5 N acid ($\sim$ 14 cc), heat in boiling water bath, pass in H_2S to saturation, ppt orange Sb_2S_3. Centrifuge hot (SnS_2 may ppt in cold), decant. Dilute to 1.5 N ($\sim$ 25 cc), pass in H_2S, ppt SnS_2 (yellow). Repeat step 3 once or twice.

(5) Dissolve SnS_2 in 1 cc 12 N HCl. Add Fe^{+++} carrier (10 mg). Dilute slightly, add excess NaOH with stirring, heat well[4]. Centrifuge. Add further In and Fe (5 mg each) carrier to basic soln, ppting hydroxides. Centrifuge on top of previous ppt, decant. Repeat (4) if necessary.

(6) Acidify to $\sim$ 1 N HCl. Pass in H_2S, ppt SnS_2. Centrifuge, decant. Dissolve ppt in minimum conc HNO_3, add 3-5 cc fuming HNO_3, a knife point of NH_4NO_3. Boil several minutes to ppt white meta-stannic acid. Evaporate aliquots of the slurried soln on watchglass and mount for counting. To determine chemical yield dilute after ppting H_2SnO_3, add filter paper pulp, filter through ashless paper, recycling filtrate till clear, dry, and ignite to SnO_2. Weigh as SnO_2[5]

Remarks:

(1) Avoid boiling concentrated Cl^- solns of Sn; $SnCl_4$ appreciably volatile. (Also $SbCl_3$, $SnCl_3$, etc.)

(2) A black residue replates out on the dissolving Sn, sometimes necessitating a mechanical agitation of the Sn surface.

(3) InS_3 ppts properly only at < .05 N HCl, however, it is partially co-precipitated at higher acidities with other sulfides of the Sn and Cu groups.

(4) $In(OH)_3$ is peptized by fixed alkali hydroxides but reppts on boiling. It is very slightly amphoteric.

(5) Do not use Pt crucible for ignition as Sn metal is produced which alloys badly with Pt. Porcelain crucible should be used.

(6) SnO_2 difficult to dissolve after igniting, has been found to go into HCl soln after fusion with Na_2CO_3 (anhyd.) in Pt crucible.

8/12/49
P-18-156

CHEMICAL SEPARATIONS

Element separated: Tin

Procedure by: Lindner

Target material: Sb (~ .5 gm metal)

Time for sep'n: ~ 1 hr.

Type of bbdt: 184" α and D_2

Equipment required: Lusteroid tubes, centrifuge, cones, tank SO_2, H_2O

Yield: 50% or greater

Degree of purification: At least factor of 100.

Procedure:

(1) To the target add 15 drops 27 N HF in lusteroid tube in hot water bath. Add conc HNO_3 dropwise until dissolved (10 min.) Dilute to ~ 20 ml.

(2) Add 20 mg each Te, Sn, In, Cd, Ag, Pd, Ru, Mo, Y carriers as soluble salts. Add 2 drops conc HCl. Centrifuge.

(3) Divide supn into two equal parts.

(4) Evaporate one part to near-dryness. Cool, add 20 ml 3 N HCl.

(5) Boil the supn to expel SO_2, add 5 ml H_2O.

(6) Saturate hot with H_2S until Sb_2S_3 pptn complete.

(7) Evaporate the supn to near dryness. Take up in 15 ml 1 N NaOH.

(8) Add 2 mg In^{+++} and 2 mg Cd^{++} to the supn containing $SnO_3^{=}$. Centrifuge.

(9) Neutralize the supn dropwise with conc. H_2SO_4, make 0.3 N in HCl, saturate with H_2S.

(10) Dissolve the SnS_2 in 2 ml conc HCl, boil to expel H_2S and dilute to 12 ml. Reject any undissolved material (Sb).

(11) Add 2 mg Sb^{+++} carrier to the Sn^{+4} solution and saturate with H_2S.

(12) Boil to expel H_2S, make 0.3 N in HCl. Re-saturate with H_2S.

(13) Dissolve SnS_2 in minimum HCl.

(14) Evaporate an aliquot to dryness. Take up in 10 ml 16 N HNO_3, boil to near-dryness, repeat several times. Filter.

(15) Transfer the $SnO_2.xH_2O$ ppt to a crucible. Ignite 1 hr to SnO_2 and weigh.

8/18/49

P-18-218

CHEMICAL SEPARATIONS

Element separated: Tin

Procedure by: Newton

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

Time for sep'n: 1 1/2 hrs.

Type of bbdt: 60" α's

Equipment required: Standard, tank H_2S

Yield: ~ 55%

Degree of purification: 10^5 to 10^6

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

(1) To sample add 20 mg Sn^{+4} carrier in 2 N HCl. Dilute solution to 10 ml and 1 N in HCl. Heat and pass in H_2S. Ppt SnS_2.

(2) Dissolve SnS_2 in 1 ml conc HCl. Boil out H_2S. Add 10 mg Sb carrier. Make solution 2-2.5 N HCl, heat and pass in H_2S. Keep hot (if cooled SnS_2 ppts). Centrifuge off Sb_2S_3.

(3) Add 1 ml N NH_4OH to supernate from 2. Heat and pass in H_2S, ppt SnS_2.

(4) Dissolve SnS_2 in conc HCl, dilute, boil out H_2S. Add 5 mg each Ru, Zr, Cb, Cd and Fe. Add 6 N NaOH until quite basic, ppt hydroxides. Add more Fe and centrifuge down on top of first hydroxide ppt.

(5) Make supernate acid, pass in H_2S. Ppt SnS_2.

(6) Repeat Sb scavenging in (2) and (3).

(7) Dissolve SnS_2 in conc HNO_3. Add three drops (~ 2 mg) Ru carrier, 1 gm NH_4NO_3 (solid) boil until SnO_2 ppts.

(8) Filter with aid of filter paper pulp and ignite to SnO_2 in a porcelain crucible. Weigh and mount as SnO_2.

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

To standardize Sn carrier: To 5 ml (50 mg) $SnCl_4$ solution add excess NH_4OH. Centrifuge and wash ppt once with H_2O. Re-centrifuge. Dissolve ppt in HNO_3, boil to ppt H_2SnO_3. Filter and ignite to SnO_2.

8/23/49

CHEMICAL SEPARATIONS

Element separated: Antimony

Procedure by: Goeckermann

Target material: ∽ 1 g Bi metal

Time for sep'n: ∽ 1-3 hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, HCl tank, electrolysis setup, H_2S tank, SO_2 tank

Yield: Variable, low for procedures 1 & 2.

Degree of purification: Unsatisfactory for bismuth bbdt.

Advantages: Procedures 2 & 3 will probably work for other bbdts. No. 2 is fast and may be good with 1-2 mg carrier.

Procedure: Target dissolved in 6N HNO_3.

No satisfactory procedure was found but the following three were tried.

(1) Precipitations of Sb_2O_5 with fuming HNO_3, distillations of $SbCl_3$ from H_2SO_4 in an HCl stream, precipitations of Sb_2S_3 from hot 3N HCl; separations of $AsCl_3$ by distillation, and As_2S_3 precipitation.

(2) Precipitations of Sb_2O_5, electrolysis of SbH_3 from 6N H_2SO_4 with a Pb cathode, reaction of SbH_3 with $AgNO_3$ solution to precipitate $SbAg_3$, reaction of Ag_3Sb with HCl to precipitate Ag and AgCl to give $SbCl_3$, scavenging with As_2S_3, precipitations of Sb_2S_3 from hot 3N HCl.

(3) Precipitations of Sb_2O_5 and Sb_2S_3; scavenging with As_2S_3, MoS_3, Te^0, $Fe(OH)_3$ from KOH solution, and Bi_2B_3 from K_2S solution.

Remarks: Procedure 1 is difficult and purity was unsatisfactory. No. 2 gave poor yields with 10 mg carrier - Sb^0 deposited on the Pb cathode. No. 3 is slow, should clean up the Sb but didn't. Sb^{+5} extracts well into isopropyl ether from 6-9N HCl but not Sb^{+3}.

7/29/49

P-18-102

CHEMICAL SEPARATIONS

Element separated: Antimony

Procedure by: Newton & McDonell

Parent material: Tin

Time for sep'n: 2 hrs.

Milking procedure (Sb from low energy p,d, or n produced Sn activity fractions)

Equipment required: centrifuge, hot plate, glassware

Yield: 60-80%

Degree of purification: At least factor of 10^4 from Sn.

Procedure:

(1) To a 3-4 N HCl soln of the Sn, add 10 mg Sb^{+++} carrier(1). Add iron powder to excess (hydrogen evolution), heat with stirring, ppt Sb metal (black). Filter by vacuum through sintered glass filtering crucible.

(2) Dissolve Sb in aqua regia, dilute to 1 N acid, pass in H_2S and ppt Sb_2S_3 + S. Dissolve the sulfide out of the sulfur with conc. HCl (warming and stirring). Dilute to 3 N HCl heating to expel H_2S if Sb_2S_3 reppts on dilution. Centrifuge, decant.

(3) Add 10 mg Sn^{+4} carrier to filtrate. Heat in boiling water bath, pass in H_2S to saturation, ppt orange Sb_2S_3. Centrifuge hot, decant. Dissolve Sb_2S_3 in conc. HCl. Dilute to 3 N HCl. Repeat step (3) twice more.

(4) Sb_2S_3 mounted after thorough washing with distilled water on small watchglass or on filter paper by suction filtration, followed by gentle heating.(2)

Remarks:

(1) Indium may be scavenged out of this milking by adding 10 mg In carrier to initial Sn solution (step 1), repeating the Fe reduction if the amount of In activity present warrents it.

(2) The Sb sulfide should not be relied upon for accurate yield determination.

8/12/49
P-18-169

CHEMICAL SEPARATIONS

Element separated: Antimony

Procedure by: Lindner

Target material: Antimony (~ .5 gm metal)

Time for sep'n: 1-2 hours

Type of bbdt: 184" α and D_2

Equipment required:
Lusteroid tubes, centrifuge, cones, tank SO_2, H_2S

Yield: ~ 75%

Degree of purification: At least factor of 100

Procedure:

(1) To the target add 15 drops 27 N HF in lusteroid tube in hot water bath. Add conc HNO_3 dropwise until dissolved (10 min). Dilute to ~ 20 ml.

(2) Add 20 mg each Te, Sn, In, Cd, Ag, Pd, Ru, Mo, Y carriers as soluble salts. Add 2 drops conc HCl. Centrifuge.

(3) Divide supn into two equal parts.

(4) Evaporate one part to near-dryness. Cool, add 20 ml 3 N HCl. Saturate with SO_2 gas 10 minutes. Te ppts.

(5) Boil the supn to expel SO_2, add 5 ml H_2O.

(6) Saturate hot with H_2S until Sb_2S_3 pptn complete.

(7) Wash ppt with 2 N HCl sat'd with H_2S. Dissolve in 5 ml conc HCl. Evap to dryness with air stream in hot water bath, add 30 ml 2 N HCl, 2 mg each of Sn, In & Cd carriers.

(8) Saturate hot with H_2S and repeat cycle.

(9) Dissolve the Sb_2S_3 ppt in 2 ml conc. HCl.

(10) Weigh aliquot of sample as Sb_2S_3.

8/18/49

P-18-220

CHEMICAL SEPARATIONS

Element separated: Antimony

Procedure by: Newton

Target material: Th

Time for sep'n: Several hrs. 1-2 hrs. attention

Type of bbdt: α fission, 60"

Equipment required: electrolysis cell

Yield: 0 - 25%

Degree of purification: 10^6 as claimed by Wilkinson

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

(1) Add 10 mg Sb carrier.

(2) Make 2 N in HCl, pass in H_2S, ppt Sb_2S_3.

(3) Wash Sb_2S_3.

(4) Dissolve in conc. H_2SO_4 + few drops HNO_3, fume.

(5) Dilute, make ~ 4 N H_2SO_4. Electrolyze to lead cathode from Pt anode. Collect SbH_3 in $AgNO_3$. Ppt $SbAg_3$.

(6) Centrifuge and wash Ag_3Sb.

(7) Treat ppt with 1 N HCl to dissolve Sb, residue Ag + AgCl. Centrifuge.

(8) From Sb sol. in 1 N HCl ppt Sb_2S_3. Wash three times with 5 ml H_2O, three times with 5 ml EtOH, dry at 110° and weigh.

Remarks:

(1) The less Sb carrier used the better. Add no holdback carriers as these interfere with the operation of the lead cathode.

(2) Electrolysis is very sensitive to condition of lead cathode. SbH_3 evolution can be followed by amount of $SbAg_3$ ppt in $AgNO_3$ solution.

(3) If SbH_3 evolution ceases, more can be brought over if leads are reversed for a while to decontaminate the lead and then re-reversed to make Pb the cathode again. Eventually this procedure fails.

In step (1) make sure the Sb carrier and tracer exchange. One way to insure exchange is to oxidize the Sb with Br_2 to the +5 state and then reduce it to the +3 state with hydrazine before precipitating the sulfide.

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

8/11/49
P-18-174

CHEMICAL SEPARATIONS

Element separated: Te (~100 c/m)

Procedure by: Marquez

Target material: I (~10^8 c/m)

Time for sep'n: 3-4 hrs.

Type of bbdt: Milking experiment

Equipment required: Centrifuge tubes.

Yield: ~80%

Degree of purification: 4 extns give a sample with ~ 300 c/m Te & approx. 100 c/m I.

Procedure:

(1) Add to the I^- sol'n, 10 mg Te carrier as Na_2TeO_4, acidify with H_2SO_4 until brown color of I and add NO_2^- to oxidize to I_2.

(2) Extract the I_2 with equal volume CCl_4.

(3) Add several times more I^- and extract the I_2 with CCl_4.

(4) Ppt Te by bubbling in SO_2 gas.

(5) Repeat the cycle by dissolving Te in conc. HNO_3, adding I^-, etc.

(6) Centrifuge the Te ppt and filter.

(7) Plate and count as Te.

Remarks:

The Te ppts seem to carry each time a little bit of I activity. It requires several cycles to get it pure.

7/27/49
P-18-74

CHEMICAL SEPARATIONS

Element separated: Tellurium

Procedure by: Goeckermann

Target material: ~ 1 g Bi metal

Time for sep'n: ~ 1 hr.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, ice, SO_2 tank, 110° oven

Yield: ~ 60%

Degree of purification: Decontamination factor $>10^4$ from fission and spallation products.

Advantages: Fair yield of pure Te, fairly rapidly.

Procedure:

(1) To aliquot of HNO_3 sol'n of target add 10 mg Te and Se and concentrated HBr, boil nearly to dryness a few times. Take up residue in 10 ml concentrated HCl, add Se, precipitate Se^0 with SO_2 in an ice bath.

(2) Dilute to 3N HCl, heat, and precipitate Te^0 with SO_2, centrifuge with aerosol. Wash with HCl.

(3) Dissolve Te^0 in a few drops HNO_3, evaporate excess acid, dilute to 10 ml, add 6N NaOH dropwise until H_2TeO_3 precipitate forms and then redissolves, 10 drops excess. Scavenge with 1-2 mg $Fe(OH)_3$.

(4) Make supernatant 3N in HCl and precipitate Te^0.

(5) Repeat Se^0, Te^0, and $Fe(OH)_3$ precipitations several times.

(6) Filter last Te^0 precipitate, wash three times with 5 ml H_2O, three times with 5 ml C_2H_5OH, three times with 5 ml ether, dry 10 min. at 110°C. Weigh as Te^0.

Remarks: The evap. with HBr volatilizes $SeBr_4$. Rh carries ~ 25% on Te^0 but the $Fe(OH)_3$ pptn removes it. If NH_3 is used in place of the NaOH, considerable loss of Te in the $Fe(OH)_3$ scavenge may result.

7/29/49

P-18-101

CHEMICAL SEPARATIONS

Element separated: Tellurium

Procedure by: Lindner

Target material: Sb (~.5 gm metal)

Time for sep'n: ~ 1 hour

Type of bbdt: 184" D_2 & α

Equipment required:
Lusteroid tube, centrifuge, cones, tank SO_2

Yield: 90%

Degree of purification: At least factor of 100

Procedure:

(1) To the target add 15 drops 27 N HF in lusteroid tube in hot water bath. Add conc. HNO_3 dropwise until dissolved (10 min). Dilute to ~ 20 ml.

(2) Add 20 mg each Te, Sn, In, Cd, Ag, Pd, Ru, Mo, Y carriers as soluble salts. Add 2 drops conc. HCl. Centrifuge.

(3) Divide supn into two equal parts.

(4) Evaporate one part to near-dryness. Cool, add 20 ml 3 N HCl. Saturate with SO_2 gas 10 minutes. Te ppts.

(5) Wash the ppt with water and dissolve in one drop conc. HNO_3.

(6) Add 15 ml 3 N HCl, 1 mg each, Sb, Sn, In, Cd holdback. Saturate with SO_2 gas.

(7) Repeat steps 5 & 6.

(8) Wash the ppt and weigh as Te.

8/18/49

CHEMICAL SEPARATIONS

Element separated: Tellurium

Procedure by: Newton

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

Time for sep'n: ∿ 1 hour

Type of bbdt: 60" α's

Equipment required: tank SO_2

Yield: ∿ 80%

Degree of purification: ∿ 10^6

Procedure: The Th metal is dissolved in conc HCl + a few drops of .2 N solution $(NH_4)_2SiF_6$ to clear up black residue. The HCl is diluted to 6 N and an aliquot taken.

(1) To sample add 10 mg Te and dilute to 3 N HCl. Heat and ppt Te^o with SO_2.

(2) Dissolve Te in 6 N HNO_3. Add 10 ml conc HCl. Evap to rid of HNO_3. Repeat evaporation. Dilute to 3 N HCl and ppt Te again with SO_2.

(3) Dissolve Te in 6 N HNO_3. Evaporate and dilute to 10 ml. Add 6 N NH_4OH dropwise until H_2TeO_3 ppt dissolves. Then add 10 drops excess. Scavenge twice with 5 mg Fe^{+++}. Make 3 N in HCl and ppt Te with SO_2. Repeat Te pptn (step 2).

(4) Filter final Te ppt. Wash three times with 5 ml H_2O, three times with 5 ml EtOH and three times with 5 ml Et_2O. Dry at 110° and weigh as Te.

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

10 mg Te = 10 mg Te^o

I^- cannot be milked from Te by ppting the Te by this procedure.

Preparation of carrier solution: Add conc. HNO_3 to 10-11 gms Te metal in a 250 ml erlenmeyer and heat until Te ceases to dissolve. Evaporate to a volume of 2-3 ml (residue left) and add 10 ml conc HCl. Evaporate to a volume of 2-3 ml. Add 10 ml more HCl and re-evaporate to expel HNO_3. Take up solution in 1 liter of 3 M HCl. Filter if not clear.

Standardization: Take 5 ml carrier in 125 ml erlenmeyer. Add 40 ml 5 M HCl. Heat nearly to boiling. Saturate with SO_2 until Te is well coagulated. Boil gently for 1 minute. Filter onto a sintered glass crucible, wash three times with hot H_2O, three times with 95% EtOH, three times with Et_2O. Dry at 110° for 10 minutes. Weigh.

8/19/49

CHEMICAL SEPARATIONS

Element separated: I ($\sim 10^{-6}$ barns cross section)

Procedure by: Marquez

Target material: Sn($\sim$ 1 gm)

Time for sep'n: 50 min.

Type of bbdt: 184" α & p

Equipment required:
100 cc distillation flask
separatory funnels
centrifuge tubes

Yield: 70-80%

Degree of purification: Less than 1% impurity in final I sample.

Advantages: Fast. Makes possible sep'n of a very small amount of pure I from large amounts of other activities.

Procedure:

(1) Add 10 mg I^- carrier and target foil to distillation flask.

(2) Add $\sim$ 15 ml conc. H_2SO_4; (H_2SO_4 should be cold) to dissolve the Sn.

(3) Dissolve Sn and distill simultaneously, collecting I_2 in 0.5-1N NaOH soln.

(4) Acidify with H_2SO_4 until iodine turns brown and oxidize with HNO_2, ($NaNO_2$ in acid sol'n). Extract with equal volume CCl_4.

(5) Wash I^- into NaOH sol'n.

(6) Repeat NaOH-CCl_4 cycles as many times as wished. (Three cycles gave purity listed above.)

(7) Acidify last NaOH sol'n with H_2SO_4 and reduce with SO_2 gas. Blow air through soln to expel most of SO_2. Add xs Ag^+ and a few drops of conc. HNO_3.

(8) Heat in water bath and filter.

(9) Plate and count as AgI.

Remarks:

Most of the loss in this procedure comes in the distillation process.

Ice cold H_2SO_4 used in (2) to allow assembly of distillation apparatus before solution of target starts.

SO_2 sol'ns can be used to collect the I_2 from the distillation. The sol'n is then oxidized with HNO_2 and the I_2 extracted went equal volume of CCl_4. The I_2 washed out of the organic layer into SO_2 sol'n and the cycle repeated. This SO_2 procedure is troublesome in the experiment above because the sol'n develops a gas pressure during the extractions.

7/27/49
P-18-79

CHEMICAL SEPARATIONS

Element separated: Iodine

Procedure by: Marquez

Target material: Sb (~ 500 mg)

Time for sep'n: ~ 40 min.

Type of bbdt: 60" α particles

Equipment required:
100 distillation flasks
sep funnels & cent tubes

Yield: 80% or higher

Degree of purification: At least a factor of 10^4 from other activities present.

Advantages: Fast and good separation.

Procedure:

(1) Add target, 10 mg I^- carrier, 10-15 ml of saturated tartaric acid and 10-15 ml of ice cold HNO_3 to distillation apparatus.

(2) Distil and collect I_2 in 0.5-1 N NaOH.

(3) Acidify with H_2SO_4 until iodine turns brown and oxidize with HNO_2, ($NaNO_2$ in acid sol'n). Extract with equal volume CCl_4.

(4) Wash I^- into NaOH sol'n.

(5) Repeat NaOH-CCl_4 cycles as many times as wished. (Three cycles gave purity listed above.)

(6) Acidify last NaOH sol'n with H_2SO_4 and reduce with SO_2 gas. Blow air through soln to expel most of SO_2. Add xs Ag+ and a few drops of conc. HNO_3.

(7) Heat in water bath and filter.

(8) Plate and count as AgI.

Remarks:

Most of the loss in this procedure comes in the distillation process.

Ice cold HNO_3 used in (1) to allow assembly of distillation apparatus before solution of target starts.

Sol'n of Sb in aqua regia interferes with I_2 ext'n.

An I^- sample could be obtained in 15-20 min. by ppting the AgI directly from the distillate of (2). The radioactive purity of the sample, however, will not be as high as above.

SO_2 sol'n can be used to collect the I_2 from the distillation. The sol'n is then oxidized with HNO_2 and the I_2 extracted with equal volume of CCl_4. The I_2 washed out of the organic layer into SO_2 sol'n and the cycle repeated. (See 53-1).

CHEMICAL SEPARATIONS

Element separated: Iodine

Procedure by: Goeckermann

Target material: ∿1 g Bi metal

Time for sep'n: ∿2 hrs.

Type of bbdt: 184" all particles

Equipment required: Distillation flask, centrifuge, tubes, ice, 110° oven.

Yield: approx. 40%

Degree of purification: Decontamination factor $>10^4$ from fission and spallation products.

Advantages: Fair yield of pure I with little if any non-exchange trouble.

Procedure:

(1) Place target in glass still, add 10 mg I^- and 10 ml 6N HNO_3, warm to dissolve. When entirely dissolved, distill over the I_2 and a few ml HNO_3 into H_2O in an ice bath.

(2) Reduce I_2 with a minimum of $NaHSO_3$ in the cold, adjust, to 0.5N HNO_3, add a few drops 0.1M $NaNO_2$, and extract I_2 into an equal volume of CCl_4. Extract aqueous with second portion CCl_4. Wash CCl_4 with dilute HNO_3.

(3) Shake CCl_4 with 10 ml H_2O, adding $NaHSO_3$ until both phases colorless. Wash aqueous with CCl_4.

(4) Repeat extraction cycle several times.

(5) Make last aqueous I^- solution 0.5N in HNO_3, heat to boiling, add 2 ml 0.1N $AgNO_3$, digest, filter, wash three times with H_2O, three times with 5 ml C_2H_5OH, three times with 5 ml ether, dry 10 min. at 110° C. Weigh as AgI (18.50 mg per 10 mg I).

Remarks: Active iodine formed as periodate may not exchange with the carrier by this method, although the I yields were not abnormally low. Reducing condition probably prevail during dissolution of the target.

7/29/49

P-18-100

CHEMICAL SEPARATIONS

Element separated: Iodine

Procedure by: Newton

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

Time for sep'n: 1 hr.

Type of bbdt: 60" α's

Equipment required: Standard

Yield: 90%

Degree of purification: 10^6

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

(1) Add sample to 10 ml 2 M Na_2CO_3 (1) Add 20 mg I^- in 60 ml sep funnels. Add 2 ml 2.5% NaOCl (2) Heat!!! Acidify with 3 ml conc HNO_3, add 3 ml 1 M $NH_2OH.HCl$ (3) Extract with 10 ml CCl_4.

(2) Shake with 10 ml H_2O containing a few drops $NaHSO_3$ until both phases colorless.

(3) To water add 1 ml 6 N HNO_3 and a few drops of 1 M $NaNO_2$. Extract into CCl_4.

(4) Repeat (2).

(5) Add 1 ml 6 N HNO_3. Heat to boiling. Add 2 ml 0.1 N $AgNO_3$. Stir and digest. Filter on tared filter paper. Wash three times with 5 ml H_2O, three times with 5 ml EtOH and three times with 5 ml Et_2O. Dry at 110° C for 10 min. Weigh as AgI.

Remarks: 10 mg I = 18.42 mg AgI

(1) If Bi and La present add 1 ml of 10% tartaric acid and 19 M NaOH.

(2) Oxidize I^- to IO_4^-. Solution must be heated, preferably boiled 5 minutes for complete exchange to occur.

(3) Reduce IO_4^- to I_2.

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

Preparation of carrier solution: Dissolve 13 gms KI in water containing a trace of $NaHCO_3$. Dilute to one liter.

Standardization: Take 5 ml carrier solution in beaker. Add 50 ml H_2O and 1 ml 6 N HNO_3. Heat nearly to boiling and add 5 ml 0.1 N $HgNO_3$ with stirring. Digest 1 minute. Filter into a sintered glass crucible, wash three times with H_2O, three times with 95% EtOH. Dry at 110° C and weigh as AgI

8/23/49

CHEMICAL SEPARATIONS

Element separated: Cesium

Procedure by: Goeckermann

Target material: ∽1 g Bi metal

Time for sep'n: Several hrs.

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, small Pt dish, ice, 110° oven

Yield: Cs ∽40%

Degree of purification: Cs had impurity which was probably Rb.

Advantages: Supposed to give Cs pure of all elements & separate it from Rb.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 20 mg Rb & Cs & 5 ml conc. $HClO_4$. Evap. to fuming, cool, transfer to cent tube with 15 ml absolute EtOH. Cool in ice bath 10 min. with stirring. Wash ppt twice with 10 ml absolute EtOH.

(2) Dissolve in dilute HCl & scav with Te, Ru, Sn, Sb, & Ag sulfides (2 mg each) by adding H_2S.

(3) Scav with NH_3 pptn of La, Ce, Y, Zr, & Cb (2 mg each).

(4) Scav with Sr & Ba carbonates (4 mg)

(5) Acidify with HCl, repeat (2).

(6) Repeat (3).

(7) Scav with $La(OH)_3$.

(8) Scav with Sr & Ba carbonates & Y, Zr, & Cb hydroxides.

(9) Acidify with HCl, evap to dryness in a Pt dish, destroy NH_4Cl by adding a few drops HNO_3 and baking carefully (do not overheat or Cs may be lost).

(10) Dissolve in a minimum of H_2O, transfer to a cone & cent out any residue, evap to dryness in the cone. Add 6 ml H_2PtCl_6 & 6 ml EtOH, wash Rb & Cs chloroplatinates with EtOH.

(11) Dissolve in HCl & repeat Te sulfide scavenging.

(12) Repeat NH_3 pptn of La & Fe hydroxides.

(13) Repeat Sr & Ba carbonate scav.

(14) Acidify with HNO_3, add HCl, evap to dryness, bake off ammonium salts carefully again.

(15) Cs - Take up residue in 20 ml 6 N HCl, add 1 ml silicotungstic acid soln & digest. (Save this supn. for Rb fraction).

Wash twice with 5 ml 6 N HCl (discard). Dissolve Cs silicotungstate in dil NaOH, add 20 ml 6 N HCl & discard yellow ppt. Add 1 ml silicotungstic acid soln, digest, filter, wash with 6 N HCl, three times with 5 ml acetone, dry 10 min at 110° C. Weigh as $Cs_8SiW_{12}O_{42}$ (37.3 mg per 10 mg Cs) -- standardize the Cs carrier solution by the same procedure.

Remarks: Noyes & Bray recommend ppting the Rb away from the Cs with sodium 6-chloro-5-nitrotoluenemetasulfonate, which we now have on hand, & then ppting the Cs silicotungstate. This may give better Cs-Rb separation. It may be better to weigh the Cs as Cs_2PtCl_6 after purification is complete. It has been alleged that $2BiI_3 \cdot 3CsI$ pptn is specific for Cs. I tried the pptn of Rb away from Cs with cold sat. sodium bitartrate but the results were very poor. More Cs silicotungstate pptns with Rb holdback present would probably give clean Cs.

The fuming of $HClO_4$ can be done easily in 40 ml pointed centrifuge cones.

For Rb sep'n from same target see (37-1).

7/12/49

CHEMICAL SEPARATIONS

Element separated: Cesium

Procedure by: R. W. Fink, D. G. Karraker

Target material: NH_4I

Time for sep'n: 45 minutes

Type of bbdt: 60 Mev α-particles for one to four hours.

Equipment required:
porcelain dishes
pipettes
centrifuge

Yield: ~40%

Degree of purification: Excellent, factor of ~ 10^6 from activity present except alkali metals.

Advantages: Good radiopurity although yield is low due to CsCl volatility in step (2).

Procedure:

(1) NH_4I target dissolved in small volume (~ 3 cc) (1:1) HCl, a few drops conc. HNO_3 added, and 20 mg of Cs carrier added. Soln is boiled in porcelain dish to expell volatile radioxenons, etc.

(2) Residue, after evap. to dryness, is ignited to disappearance of I_2 and ammonium salts, but not hot enough to volatilize excessive Cs.

(3) The residue is then taken up in (1:1) HNO_3, a drop of (1:1) HCl added and pptd thrice with a few drops 0.1-N $AgNO_3$ to scavange for any remaining halogen (iodine) impurities.

(4) To the remaining soln is added a few drops Te carrier and then excess $SnCl_2$. This ppts Te and any radiotellurium. (In omitting the tellurium step, no change was noted, indicating Te was not formed.)

(5) The remaining soln is made alkaline with conc. NH_4OH and $FeCl_3$ soln added dropwise to ppt $Fe(OH)_3$ twice.

(6) The final soln contains radiocesium in pure form.

Remarks:

(a) Any alkali metal, e.g., Na, K, Rb, will not be separated, but will appear with the final cesium soln.

(b) Step (2) results in a loss of over 50% of the Cs by volatilization, if the temp. is too high. The minimum temp. consistent with decomposing and expelling ammonium salts should be used. If H_2SO_4 is used in place of HCl, the volatility will be reduced considerably.

7/12/49

P-18-53

CHEMICAL SEPARATIONS

Element separated: Cesium

Procedure by: R. W. Fink

Target material: NH_4I

Time for sep'n: 30 minutes

Type of bbdt: 60 Mev α-particles for one to four hours

Equipment required: Iodine Sublimator

Yield: > 95%

Degree of purification: Factor of at least 5 or 10. Good enough for mass spectrograph work.

Advantages: Full yield of carrier-free radiocesium for mass spectrograph work.

Procedure: Special method for carrier-free, high activity samples for the mass spectrograph.

(1) NH_4I target is placed in a sublimator together with a few drops 0.3 - N H_2SO_4 and conc. HNO_3. CO_2 snow is packed into the cold-finger, and a low vacuum is pulled. Heat is then applied to the NH_4I, which decomposes and condenses on the cold-finger.

(2) The liquid is boiled until colorless, indicating complete volatilization of I_2 and decomposition of NH_4I. The remaining liquid is almost pure in cesium, but if desired it can be put through further purification, starting with step (3) of (55-2).

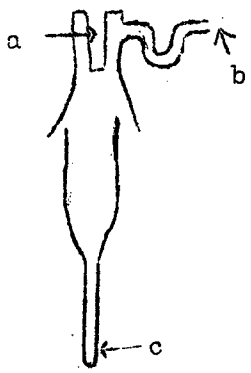


Fig. 1 - Iodine Sublimator

a = crushed CO_2 snow

b = low vacuum

c = target NH_4I + drop H_2SO_4 + drop HNO_3

Remarks:

(a) Any alkali metal, e.g., Na., K, Rb will appear with the Cs.

(b) For mass spectrograph work, the sol'n is used as it comes from the sublimator directly.

7/12/49

P-18-54

CHEMICAL SEPARATIONS

Element separated: Cesium

Procedure by: Folger & Hicks

Target material: ~4g U metal foil

Time for sep'n: Several hrs.

Type of bbdt: 184" all high energy particles

Equipment required: Centrifuge, tubes, ice, 110° oven

Yield: Cs ~60%

Degree of purification: Small amt of some impurity detected by means of Al abs. Decay curve shows pure Cs for ~ 3 half-lives.

Advantages: Supposed to give Cs pure of all elements & separate it from Rb.

Procedure:

(1) To aliquot of HNO_3 soln of target, add 20 mg Rb & Cs & 5 ml conc. $HClO_4$. Evap. to fuming, cool, transfer to cent tube with 15 ml absolute EtOH. Cool in ice bath 10 min. with stirring. Wash ppt twice with 10 ml absolute EtOH.

(2) Dissolve in 0.2 N HCl & scav with AgCl, then Te, Ru, Sn, Sb, & Ag sulfides (2 mg each) by adding H_2S.

(3) Scav with NaOH pptn of La, Ce, Y, Fe, Zr, & Cb (2 mg each).

(4) Scav with Sr & Ba carbonates (4 mg)

(5) Acidify with HCl, repeat (2), (3) and (4).

(6) Repeat (3) and (4).

(7) Add $HClO_4$ and evap to fuming. Transfer to cent. cone with 15 ml abs. EtOH. Cool in ice bath 10 min. with stirring. Wash ppt. with 10 ml abs. EtOH.

(8) Repeat (2), (3) and (4).

(9) Repeat (7).

(10) Cs - Take up residue in 10 ml 6 N HCl, add 1 ml silicotungstic acid soln & digest hot. (Save this supn. for Rb fraction). Chill and centrifuge.

(11) Wash twice with 5 ml 6 N HCl (discard). Dissolve Cs silicotungstate in dil. NaOH, add 10 ml 6 N HCl & discard yellow ppt. (WO_3).

(12) Repeat (10) with Rb holdback. Wash & dissolve as in (11).

(13) Add 1 ml silicotungstic acid soln, digest, filter, wash with 6 N HCl, three times with 5 ml acetone, dry 10 min at 110° C. Weigh as $Cs_8SiW_{12}O_{42}$ (37.3 mg per 10 mg Cs) -- standardize the Cs carrier solution by the same procedure.

Remarks:

(1) See (55-1)

(2) The above procedure is for use when Rb is desired from the same aliquot. If rubidium is not desired, replace step (7) by step (10) including Rb holdback. Step (8) should be included, but step (9) may be omitted.

Steps (10) through (13) should then follow in regular sequence, with Rb holdback being used in (10).

(3) If it is desired to count a weighed sample, Cs should be weighed as Cs_2PtCl_6 instead of $Cs_8SiW_{12}O_{42}$ in order to reduce self-absorption counting corrections. In such a case add to the above procedure,

(14) Dissolve ppt in minimum amt. 1 N NaOH with warming. Neutralize keeping volume low. Add 4 cc H_2PtCl_6 and 4 cc EtOH. Digest ~ 3 min. with stirring in an ice bath, then let stand 5 min. in ice.

(15) Centrifuge and wash w. 6 cc abs. EtOH.

(16) Filter, wash w. 5 cc abs. EtOH, dry in 110° C oven for 5 min. Weigh as Cs_2PtCl_6.

CHEMICAL SEPARATIONS

Element separated: Cesium

Procedure by: Newton

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

Time for sep'n: ~ 1 hr.

Type of bbdt: 60" α's

Yield: ~ 80%

Degree of purification: 10^6 except from Rb

Procedure:

The Th metal is dissolved in conc HCl + a few drops of .2 M sol'n $(NH_4)_2SiF_6$ to clear up black residue. The HCl is diluted to 2 N and an aliquot taken.

(1) In 50 ml beaker + sample add 20 mg Cs, 5 ml $HClO_4$ and evaporate to fuming. Cool and transfer to centrifuge tube with 15 ml absolute EtOH. Cool in ice bath 10 min. and centrifuge. Wash ppt two times with 10 ml absolute EtOH.

(2) Dissolve in 10 ml H_2O. Add 5 mg Fe and ppt hot with NH_4OH. Repeat.

(3) (Optional) Add drop sat. $(NH_4)_2CO_3$ and 5 mg each Ba and Sr. Ppt Ba and Sr carbonates. Centrifuge.

(4) Evaporate supernate to dryness in beaker, flame to decompose NH_4 salts. Dissolve in a few mls hot H_2O, add 4 ml $HClO_4$, evap to fumes. Reppt as $CsClO_4$.

(5) Centrifuge and wash ppt once with absolute EtOH by decantation. Slurry ppt with EtOH and filter. Wash with EtOH. Dry 10 min. at 110° C. Weigh as $CsClO_4$.

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

Preparation of carrier solution: Dissolve 12.7 gms CsCl in 1 liter of water.

Standardization: Take 5 ml carrier. Add 3 ml 70% $HClO_4$. Evaporate to dense fumes of $HClO_4$. Cool in an ice bath and add 10 ml absolute EtOH. Cool and stir occasionally for 15 minutes. Filter onto a sintered glass crucible. Use 3-5 ml portions of abs EtOH to transfer and wash. Dry 10 minutes at 110° C. Weigh as $CsClO_4$.

8/19/49

CHEMICAL SEPARATIONS

Element separated: Barium

Procedure by: Hicks-Folger-Goeckermann

Target material: U or Th or Bi

Time for sep'n: 30-45 min.

Type of bbdt: Fission

Equipment required: ice bath

Yield: ~ 100%

Degree of purification: excellent

Advantages: Fast and easy

Procedure:

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

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

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

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

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

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

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

6/25/49

P-18-9

CHEMICAL SEPARATIONS

Element separated: Barium

Procedure by: Goeckermann

Target material: ~1 g Bi metal

Time for sep'n: 1-2 hrs.

Type of bbdt: 184" all particles

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

Yield: ~80%

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

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

Procedure:

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

(2) Dissolve ppt in 2 ml H_2O & reppt with 15 ml fuming HNO_3.

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

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

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

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

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

For Sr sep'n from same target see 38-1.

7/12/49

CHEMICAL SEPARATIONS

Element separated: Barium

Procedure by: R. W. Fink

Target material: CsCl

Time for sep'n: 90 min.

Type of bbdt: 85 Mev Protons for 1 hour

Equipment required: Standard

Yield: Sufficient for mass spectrograph work.

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

Advantages:

Carrier free Ba for mass spectrograph.

Procedure:

(1) Target CsCl is dissolved in 2 cc 0.1-N HAc, 1 cc NH_4Ac sat'd added, and 10 mg. Pb carrier added. K_2CrO_4 soln. is then added until complete pptn. This ppt. is then washed with 1% NH_4Ac until free from Cesium. If necessary, the ppt may be dissolved in 0.1 - N HCl and repptd. to free it from Cs.

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

(3) The sol'n. from (2) containing radiobarium, is made alkaline, after boiling to expell H_2S and radioargons, and some $Fe(Cl)_3$ added to help ppt. $Cr(OH)_3$.

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

Remarks:

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

CHEMICAL SEPARATIONS

Element separated: Barium

Procedure by: Lippmann & Goeckermann

Target material: Au foil, about 1 g

Time for sep'n: 1 hr. for barium.

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

Equipment required: Ice bath and hot water bath.

Yield: Ba 25%

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

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

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

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

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

Remarks:

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

8/12/49
P-18-176

CHEMICAL SEPARATIONS

Element separated: Barium

Procedure by: Folger

Target material: ~ 3 g U metal

Time for sep'n: ~ 1-1 1/2 hr.

Type of bbdt: 184" high energy particles

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

Yield: 50-75%

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

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

Procedure:

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

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

(3) Dissolve in H_2O, transfer to 15 ml cone and buffer with HAc + NH_4Ac (1 ml 6 N HAc and 2 ml 6 N NH_4Ac or pH 5-6). Add ~ 5 mg Pb and ppt $PbCrO_4$ by add'n of 1.5 M Na_2CrO_4 to hot sol'n. Wash with hot HAc & NH_4Ac buffer (1 ml to 2 ml as above) containing 1 drop 1.5 M Na_2CrO_4.

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

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

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

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

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

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

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

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

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

To remove excess alkali salts add:

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

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

CHEMICAL SEPARATIONS

Element separated: Barium

Procedure by: Newton

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

Time for sep'n: 45 min.

Type of bbdt: 60" alphas

Equipment required: Standard

Yield: 90%

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

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

(1) 1-5 ml sample in 50 ml centrifuge tube. Add 20 mg Ba^{++} carrier. If total volume is > 5 ml, boil down to 5 ml or less. To cold solution add 30-35 ml HCl-ether reagent. Stir 1-2 min while cooling in ice bath. Centrifuge. Wash ppt with 5 ml HCl - Et_2O. Centrifuge.

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

(3) Repeat (2).

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

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

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

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

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

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

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

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

8/23/49

P-18-283

CHEMICAL SEPARATIONS

Element separated: Barium

Procedure by: Newton

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

Time for sep'n: 1 hr.

Type of bbdt: 60" alphas

Equipment required: Standard

Yield: ~ 60% on Ba

Degree of purification: 10^6 other F.P. ~ 10^3 from Strontium

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

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

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

(2) Dissolve ppt in 2 ml H_2O. Re-precipitate with 15 ml fuming HNO_3.

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

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

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

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

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

For separation of Sr from this procedure see (38-5).

8/23/49

CHEMICAL SEPARATIONS

Element separated: Lanthanum

Procedure by: Naumann

Target material: $CsNO_3$

Time for sep'n: 1-1 1/2 hrs.

Type of bbdt: $CsNO_3$ + α(25-50 Mev)

Equipment required: 5 ml sep. funnels

Yield: At least 50%.

Degree of purification: Excellent at least factor of 10^3 from Cs, Ba, F, etc.

Advantages: Affords a sample free of fluorine and containing less than 0.1 μ g La suitable for mass spectrograph work.

Procedure:

(1) The target (0.8 g) $CsNO_3$ is dissolved in 5 ml of hot 0.5 N HNO_3 containing 1 mg of F^-, 1 mg of Ba^{++}, 1 mg of Fe^{+++} and 1/10 μ g La^{+++}. (See (a) under remarks below.)

(2) The solution is made basic with NH_3 and the solution centrifuged.

(3) The $Fe(OH)_3$ ppt is washed three times with boiling water redissolved in 5 cc 0.5 N HNO_3 and 1 mg of F^- and Ba^{++} is added as holdback carriers.

(4) The solution is again made basic with NH_3, the precipitate centrifuged, washed and dissolved as in step (3) but only 1 mg of F^- is added, the Ba^{++} being omitted.

(5) $Fe(OH)_3$ is again precipitated with NH_3, the precipitate centrifuged and washed 3 x with boiling water. The precipitate is dissolved in 2 ml 6 N HCl (See (b) under remarks below.) and extracted twice with 2 ml ether. (See (c) under remarks below.) The aqueous HCl solution is evaporated to 1/4 cc, 1 ml concentrated nitric acid is added and the solution evaporated to about 50 λ. This solution is placed on the filament of the mass spectrograph.

Remarks:

(a) If xs Ba^{++} & F^- are added BaF_2 will precipitate. The 0.1 μ g La serves to give a line at mass number 139 on the mass spectrograph plate.

(b) At this point an aliquot is taken for counting, etc.

(c) Some La is extracted into the ether but this apparently is unavoidable.

(d) Rare earths if present from bombarding a mixture of target materials would not be separated in this procedure.

7/27/49
P-18-127

CHEMICAL SEPARATIONS

Element separated: Rare earths

Procedure by: Hicks, Wilkinson

Target material: Rare earth oxides

Time for sep'n: 1/2 hr.-1 hr.

Type of bbdt: 60"

Equipment required: lusteroid tubes

Yield: ∽ 100%

Degree of purification: 100% from all other elements besides rare earths themselves.

Procedure:

(1) Dissolve rare earth oxides in conc. HNO_3, ppt hydroxides with conc. NH_4OH.

(2) Wash hydroxides until wash is neutral. This increases yield markedly.

(3) Dissolve in HNO_3, transfer to lusteroid, add 5 cc conc. HF, digest in hot water bath, centrifuge, and wash fluorides with water.

(4) Dissolve fluorides in HNO_3 - H_3BO_3 mixture (8-10 M HNO_3 saturated with H_3BO_3)

(5) Repeat 2-4 twice.

(6) Dissolve final hydroxides in HCl pH 1-1.5 and transfer to ion exchange resin column.

6/25/49

P-18-11

Exerpts from Paper on "Radioactive Isotopes of the Rare Earths. I. Experimental Technique and Thulium Isotopes" - Phys Rev 75 1370 (1949)

Geoffrey Wilkinson and Harry Hicks

Abstract:

The experimental techniques used in the chemical separation and identification of radioactive isotopes of the rare earth elements are described. The isotopes are produced by bombardment of rare earth oxides with α-particles deuterons, and protons from the 60-inch Crocker Laboratory cyclotron, and also by bombardment of tantalum with 200 Mev deuterons from the 184-inch cyclotron.

I. Introduction

The extreme difficulty in achieving separation of the rare earth elements in a very pure state has been overcome in recent years by two main advances in experimental techniques. These have meant that not only macro, but tracer, amounts of rare earths can be reliably separated from each other in a few hours.

Methods of separation based on multiple oxidation states of the rare earth elements have been developed for europium, samarium, and other rare earths, particularly by McCoy[1] and Marsh,[2] using zinc and sodium

1. H. N. McCoy, J. Am. Chem. Soc. 57, 1756 (1935); 59, 1131 (1937); 63, 3422 (1941)

2. J. K. Marsh, J. Chem. Soc. 398, 523 (1942).

amalgam reduction procedures, while the separation of rare earths by the use of columns of ion-exchange resins has been developed in the Manhattan Project, and has been described in a comprehensive series of papers.[3]

3. E. R. Tompkins, J. X. Khym and W. E. Cohn, J. Am. Chem. Soc. 69, 2769 (1947); F. H. Spedding et al., J. Am. Chem. Soc. 69, 2777, 2786, 2812 (1947); E. R. Tompkins and S. W. Mayer, J. Am. Chem. Soc. 69, 2859, 2866 (1947).

These procedures have given a great impetus to research on rare earth isotopes formed in fission of uranium and also by neutron capture.[4] Little

4. E. R. Tompkins, J. X. Khym and W. E. Cohn, J. Am. Chem. Soc. 69, 2769 (1947); J. A. Marinsky, L. E. Glendenin, and C. D. Coryell, J. Am. Chem. Soc. 69, 2781 (1947); D. H. Harris and E. R. Tompkins, J. Am. Chem. Soc. 69, 2792 (1947); B. H. Ketelle and G. E. Boyd, J. Am. Chem. Soc. 69, 2800 (1947); W. E. Cohn, G. W. Parker and E. R. Tompkins, Nucleonics 3, 22 (1948).

work, however, has been done on neutron deficient isotopes formed by proton, deuteron, and α-particle bombardment of the rare earths. A systematic study has, therefore, been undertaken to remedy this deficiency in the knowledge of such isotopes, and further, to allow interpretation of the results of

high energy particle bombardments of elements above the rare earths using the 184-inch cyclotron. In a previous note,[5] a list of new rare earth

5. G. Wilkinson and H. G. Hicks, Phys. Rev. 74, 1733 (1948).

activities and their properties was given; the present paper describes the experimental procedures used, and the properties of the new thulium activities.

II. Experimental

A. Bombardments

Where comparatively large quantities of material were available, hundred milligram amounts of rare earth oxide were spread on a ridged copper target plate, which was then covered with 0.2 mil tantalum foil. In all other cases, ten to twenty milligram samples of the oxides were bombarded on interceptor targets placed in the beam of the 60-inch Crocker Laboratory cyclotron. The finely powdered oxide was spread evenly on a small platinum tray with a grooved inner surface, which was silver soldered to a water-cooled copper holder. The oxide layer was wetted, and a few drops of dilute sodium silicate solution dropped on top of it. After evaporation and drying under an infra-red heat lamp, the oxide was very firmly bound in an even layer. Targets so prepared have withstood over a hundred microampere-hours of 20 Mev deuterons without loss. The targets were covered with 0.2 mil tantalum foil as additional protection.

Bombardments of rare earth oxides have been made with 38 Mev α-particles, 19 Mev deuterons, and 10 Mev protons from the 60-inch Crocker Laboratory cyclotron; runs with low energy α-particles were made by placing suitable thicknesses of tantalum foil over the interceptor target. Tantalum, as the metal foil, was bombarded with 200 Mev deuterons from the 184-inch cyclotron.

B. Chemical Separations

After bombardment, the rare earth oxide was dissolved in nitric acid, and insoluble matter removed by centrifugation. Carriers for contaminating activities likely to be formed from the target materials -- copper, tantalum, platinum, sodium silicate, etc. were added, and the rare earth fluoride precipitated from hot 2 N nitric acid solution by addition of hydrofluoric acid. The washed fluoride was dissolved in a mixture of concentrated nitric acid and saturated boric acid; from this solution, the rare earth hydroxide was precipitated by addition of ammonium hydroxide. The washed hydroxide was dissolved in nitric acid and a further fluoride precipitation made as before. Three or four such cycles were made, after which, the hydroxide was dissolved in a minimum of hydrochloric acid and the solution accurately adjusted to a known volume. Aliquots of this solution were taken for direct measurement of radioactivities, for chemical separation of the individual rare earth elements, and for estimation of the chemical yield of the bombarded oxide. Rare earths were determined for chemical yield measurement, by the precipitation of oxalate, followed by ignition to the oxide, and weighing.

The tantalum, after bombardment with 200 Mev deuterons, was dissolved in the minimum of nitric and hydrofluoric acids. To the boiling solution was

added boric acid, to complex the fluoride, followed by cerium III solution as a carrier for the rare earth activities. After dilution, excess hydrofluoric acid was added to precipitate cerium III fluoride. The cerium was purified by hydroxide-fluoride cycles as above. To the final solution in strong nitric acid was added a small quantity of lanthanum (ca. 0.1 mg) and the cerium oxidized to the IV oxidation state by addition of sodium bismuthate. The cerium was then removed by precipitation of cerium IV phosphate from 3 N nitric acid solution. The lanthanum, with the rare earth activities, was recovered as the fluroide, which was then converted to the chloride for subsequent separations on the ion-exchange columns.

C. Chemical Separation of the Rare Earth Elements

Chemical separation of the individual rare earth elements was made by ion-exchange resin columns, or for europium, by an amalgam reduction method. The principle of column separation involves first the adsorption of the rare earth ions in dilute acid solution on a small quantity of ion-exchange resin. This resin is then placed at the top of a resin column, through which is then passed a solution of a complexing agent for the rare earths, e.g., ammonium citrate. The rare earths are eluted under strictly controlled conditions and pass through the column at various rates; lutecium is the first to appear in the eluate, followed in succession by ytterbium, thulium, erbium, etc.

In preliminary experiments to determine the characteristics of column separations and optimum separation conditions for the rare earths, both inactive rare earths in milligram amounts, and Y^{91} radioactive tracer were used. The former were determined spectroscopically[6] and the Y^{91} determined by its radioactivity.

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1. Preparation of the Column. - All column separations were made using Dowex-50,[7] an aromatic hydrocarbon polymer containing many nuclear

7. W. C. Bauman, Ind. Eng. Chem. 38, 46 (1946); W. C. Bauman and J. Eichhorn J. Am. Chem. Soc. 69 2830 (1947).

sulfonic acid groups. The resin used was the colloidal agglomerates, Batch 19891M supplied as the sodium form. The ammonium form of the resin was prepared by stirring with saturated ammonium chloride solution; excess ammonium chloride was removed by washing with water. The resin was graded to have a settling time of less than five minutes for five centimeters in water at room temperature. The length of the preliminary resin column was 50 cm, with a diameter of 0.4 cm, but in subsequent runs, it was found that 20 cm x 0.4 cm and 20 cm x 1.0 cm columns gave adequate separation.

2. Adsorption of Rare Earths on Resin. - The rare earth solution in hydrochloric acid was adjusted to give a pH between 0.5 and 1.5, the ionic strength being kept at a minimum; this solution was then agitated with about 0.2 ml of resin added in two or three successive portions. The solution and resin were agitated at about 70°C, but were not allowed to stand in contact for more than 15 minutes. This prevents diffusion of ions into the interior of the agglomerates, and subsequent slow elution with poor separations.

3. Operation of the Column. - The resin, with the rare earth adsorbed on it, was transferred to the top of the resin column, and the eluting agent passed through. The eluting agent used was a 0.25 M solution of C.P. citric acid, accurately adjusted to pH 3.05 with ammonium hydroxide. Care was taken to approach this value from the acid side, so that readjustment with acid was not necessary, since it is important for good separations to keep the ionic strength at a minimum. The flow rate was approximately 0.03 milliliter per square centimeter column area per minute; with the columns used, of diameter 0.4 cm, and with a drop size of about 0.03 ml, this flow rate corresponded to one drop in 3.5-4 minutes.

The eluate was collected in 10 x 75 mm rimless test tubes placed in a perforated turntable, which was rotated automatically at various time settings, to place succeeding tubes under the column. Samples were normally collected for 15 minutes. In runs with active materials, aliquots were taken with micropipettes and evaporated on stainless steel disks for counting. Aliquots were also taken for spectroscopic analysis of macro amounts of rare earths present. The amount of rare earth, determined either spectroscopically or by activity measurements, was then plotted against the sample number. This allows estimation of the degree of separation achieved. In all column runs, samples collected before the elution of one "free column volume" were disregarded. After completion of a column run, any residual activity or rare earth was stripped from the column with 0.25 M ammonium citrate of pH 7 as eluting agent. After thoroughly washing with water, the column was again ready for use.

After separation on the column, the rare earths were recovered by evaporation of the citrate solution with nitric and perchloric acids with subsequent ignition. The rare earth residue was then extracted with nitric acid and the hydroxide precipitated with ammonium hydroxide. If the

solution contained only tracer amounts, a small amount of lanthanum was added as a carrier.

In addition to strict control of the conditions mentioned above, it is also important for successful separations, that the capacity of the resin for adsorption of rare earth ions is not exceeded. For the columns described, the maximum capacity corresponds to approximately 10 mg and 100 mg of rare earth oxide, respectively. Where the starting materials contained significant amounts of other rare earth impurities, and purification was necessary before bombardment, a larger column, which had a capacity for about 1 g rare earth oxide was used. The area of the column and the drop rate were scaled up from the values used in the 0.4 cm and 1.0 cm diameter column runs, the amount of citrate flowing through unit cross-sectional area of resin being kept constant. The progress of any particular inactive rare earth through the column could be checked by using radioactive tracer for a neighboring heavier rare earth. After elution of the active tracer, the sample numbers of the desired inactive rare earth were estimated by comparison with the standard elution curve (Fig. 1). Aliquots of the samples were then examined spectroscopically to allow the pure rare earth fractions to be isolated.

4. Results in Column Separations. - In Fig. 1 is shown the "standard elution curve" obtained with inactive materials and Y^{91} tracer. It should be noted that while the lutecium and ytterbium are very close together, samples from the peaks of these curves have no detectable lines of each other or of other rare earths in their spectra. Thus samples of these neighboring elements can be obtained in which the separation factor is at least a thousand.

A typical column run on a bombarded sample is shown in Fig. 2, where the broken line shows the distribution of radioactivity produced by 38 Mev alpha-particle bombardment of holmium oxide. The solid lines show the distribution of inactive carriers of lutecium, ytterbium, erbium, and dysprosium, added as references, and determined spectrographically.

A further example of a column separation is shown in Fig. 3, where the rare earths are present in tracer quantities only. In such cases, separation is generally cleaner and there is less "tailing" of the peaks, than where macro amounts of rare earths are separated. The activities shown in Fig. 3 were spallation products, obtained by the bombardment of tantalum with 200 Mev deuterons from the 184-inch cyclotron. Lanthanum was used as a carrier for the radioisotopes. A study of the radiation characteristics and decays of the peak samples has shown no evidence of contamination.

D. Separation of Europium

Europium has been purified prior to, and recovered after bombardment by a modification of McCoy's method.[1] The europium in 6 N hydrochloric acid solution was reduced to the divalent state by boiling with zinc amalgam. Rare earths other than europium were precipitated by carbonate-free ammonia using cerium as a carrier. After centrifuging, the supernatant solution was withdrawn, the europium oxidized by ozone, and then precipitated by ammonia. The procedure was repeated with both fractions to ensure complete separation.

0 0 1 0 0 7 0 3 5 2 8

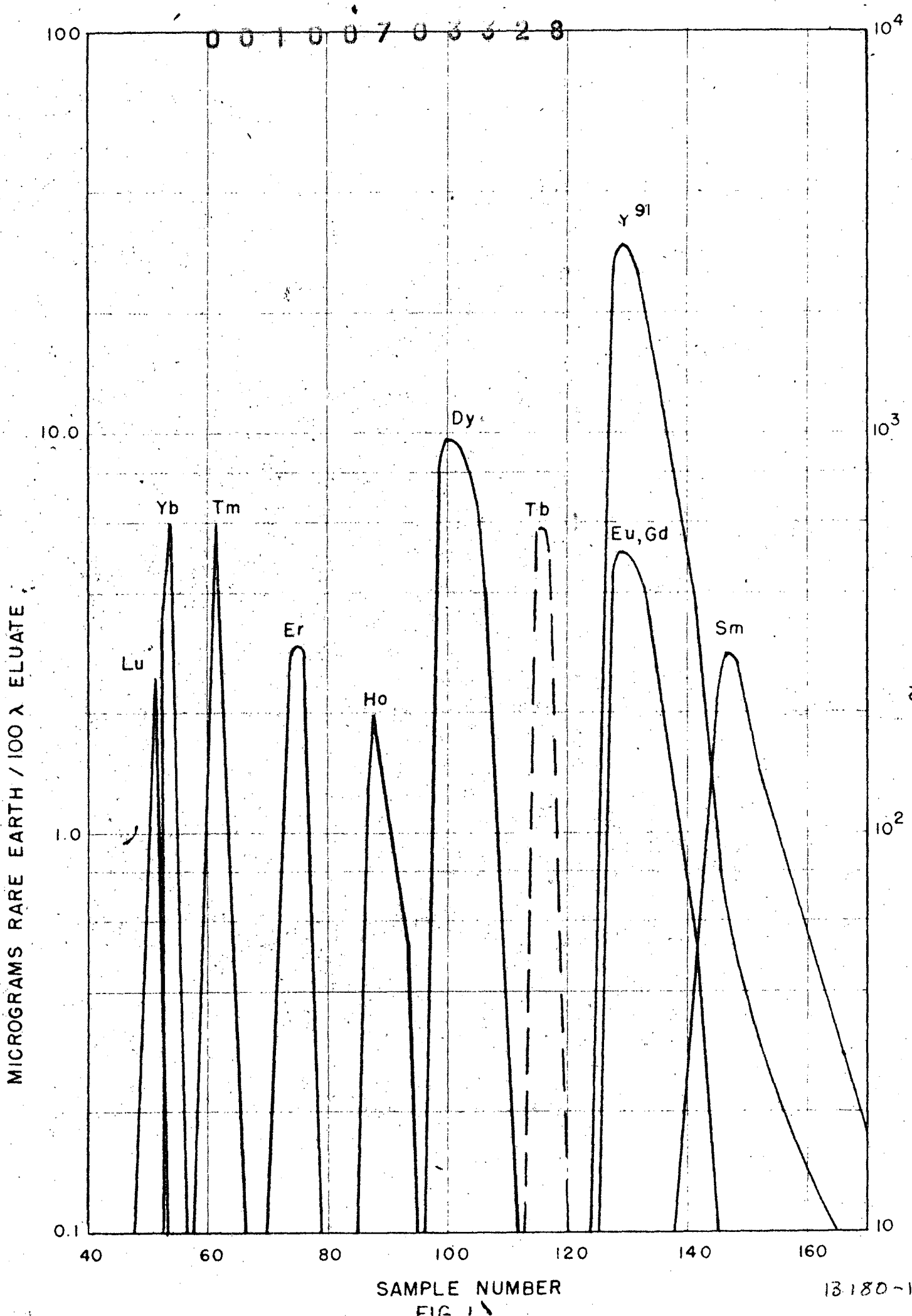
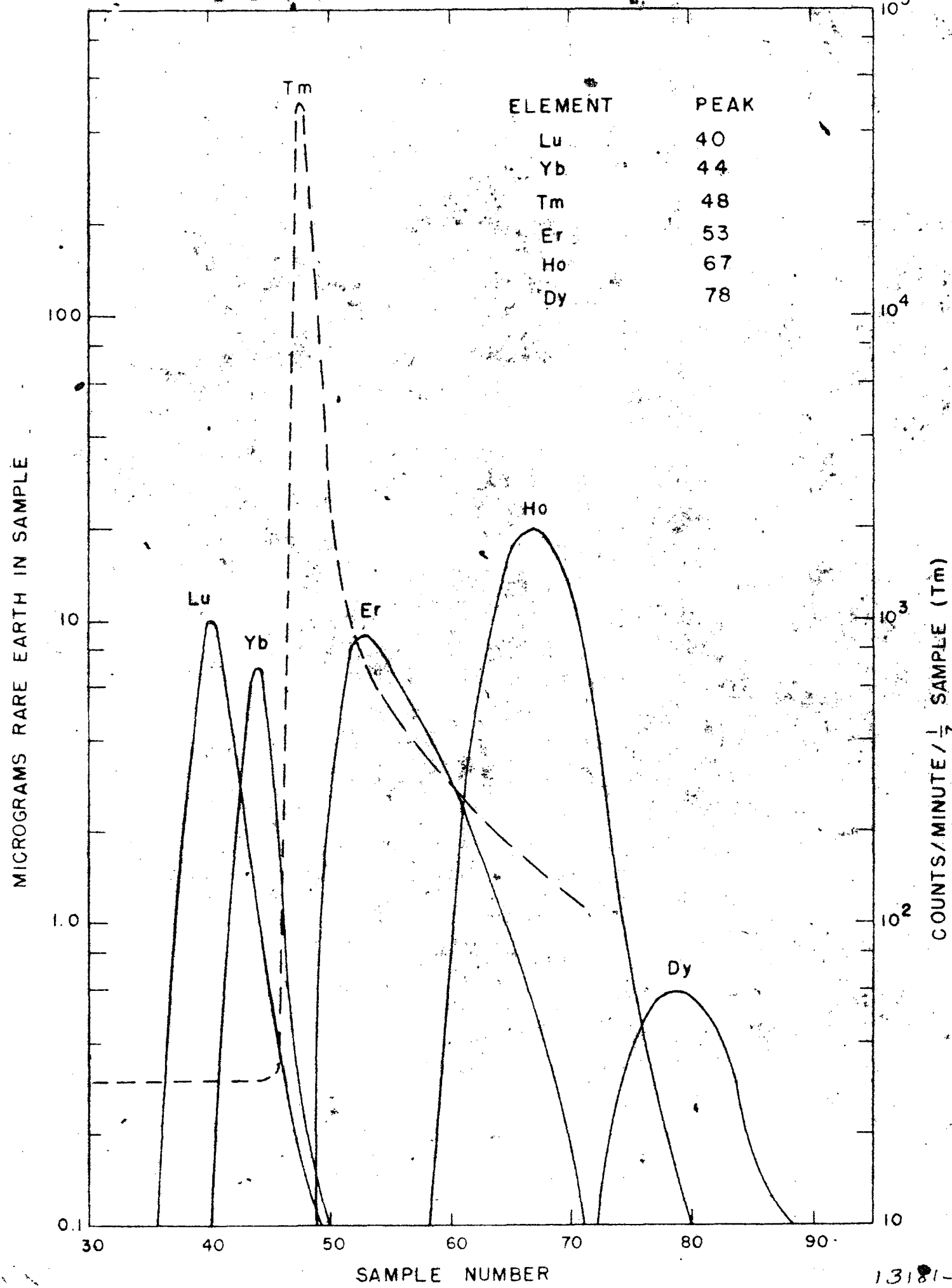


FIG. 1

13180-1


ELEMENT PEAK
Lu 40
Yb 44
Tm 48
Er 53
Ho 67
Dy 78
Tm
Lu
Yb
Er
Ho
Dy
MICROGRAMS RARE EARTH IN SAMPLE
COUNTS/MINUTE/1/7 SAMPLE (Tm)
SAMPLE NUMBER
100
10
1.0
0.1
10^5
10^4
10^3
10^2
10
30
40
50
60
70
80
90

13181-1

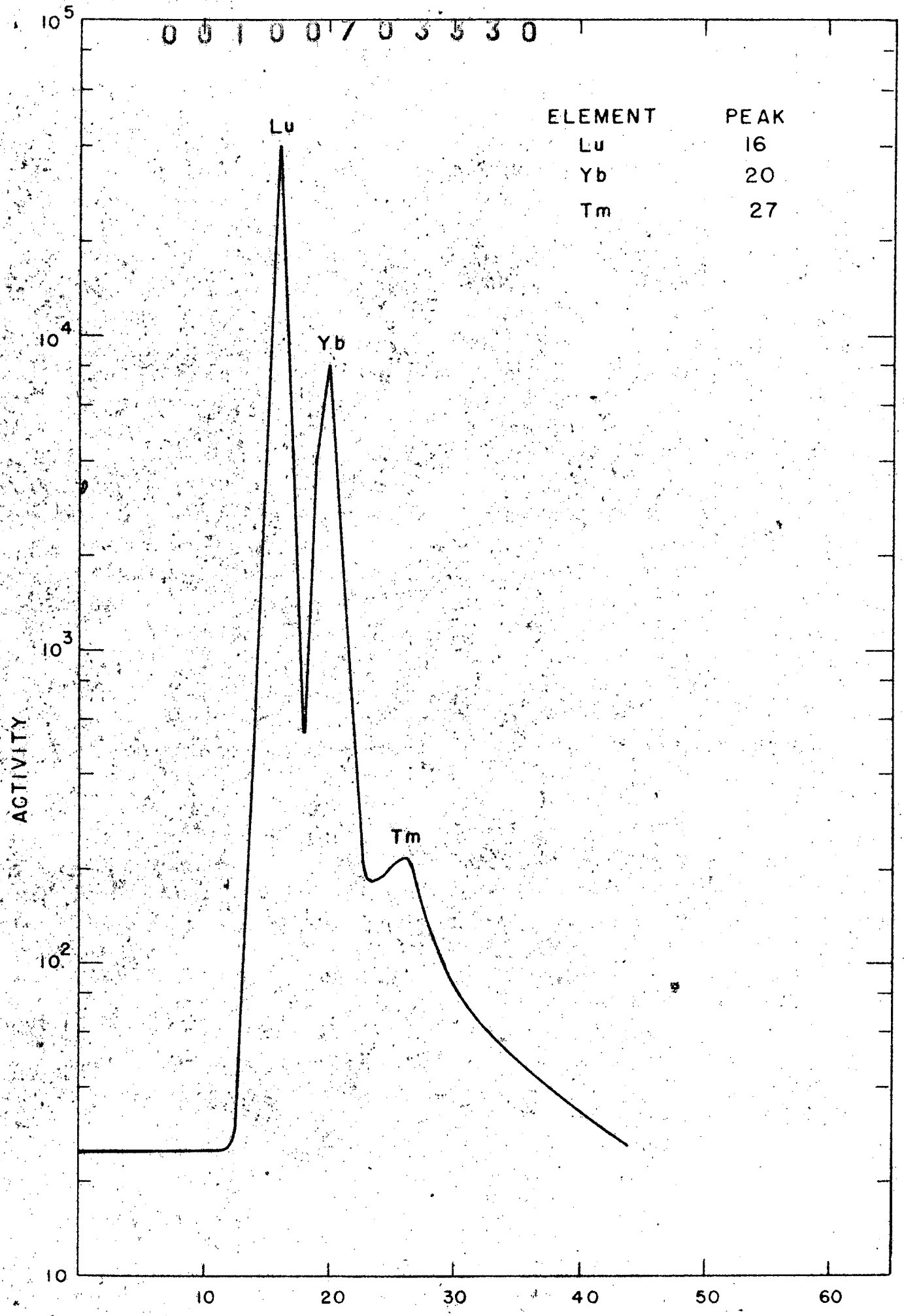


FIG III

13182-1

The Preparation of Gram Amounts of Spectroscopically Pure Rare Earths Using Dowex 50

Elements Purified: Pr, Nd, Eu, Gd, Dy.

Starting Material: The best material commercially available in gram amounts. The starting material usually contained ~99% of the desired constituent.

Procedure by: R. C. Lilly, D. C. Stewart. Based on original data given in JACS, 69, 2769-2879 (1947).

Time for Purification: 2-3 weeks

Equipment required: Large column setup (see below)
automatic sampler
12 dozen 100 ml centrifuge tubes
large beakers
sol'n bottles (12 liter size)

Yield: ~90%

Degree of Purification: In the case of rare earths from Ce through Gd, samples can be obtained which contain no other rare earth lines. Above Gd, the separation is less complete.

Advantages: Large capacity allows preparation of 5 gms of material in one run.

Description of Apparatus Used:-

A. Column

(1) The column is constructed of Pyrex tubing, 4-6 cm. i.d. and from 50-75 cm in length. The lower end of the tube is rounded out slightly and fitted with a piece of capillary tubing 3 cm long, 7 mm o.d., and 1 mm i.d. A small well is left in the large tube just above the start of the capillary to hold a glass wool plug.

(2) The upper end of the column is equipped with a rubber stopper which has been fitted with a 5 cm piece of 10-12 mm glass tubing and hollowed out underneath to give a dome-shaped space whose top is flush with the end of the glass tubing. This type of stopper prevents the accumulation of air at the top of the column.

(3) The glass tube extending up from the stopper is connected to a reservoir bottle by a length of tygon tubing. Provision is made for raising or lower the reservoir to regulate the flow rate.

B. Automatic Sampling Mechanism

(1) The usual automatic sampler, providing holes for 60 small tubes, is revised by substituting a lucite top disc equipped with 30 holes large enough for a 100 ml centrifuge tube. Since these samplers

have 60 stops in one complete revolution, the column is set up so that each tube takes up two turns of the wheel and is under the column for 1/30 of a cycle.

(2) The sampler is also modified by the inclusion of a large aluminum separator between the two discs so that the large centrifuge tubes are supported near the top and will not fall out of position.

General Operations and Information: -

A. Preparation of NH_4^+ resin.

(1) Use 250-500 mesh Dowex 50*. Heat three times at 100°C with 1 1/2 volumes of 4 M NH_4Cl. Wash 8 times with 2 1/2 volumes of distilled H_2O. After each wash discard the supernatant and any fine material suspended in it.

(2) Density of Dowex 50 = 1.5 gms/ml dry) given for resin
1.4 gms/ml wet)

Apparent density in column = 0.58 gms/ml dry) from experimental results
0.72 gms/ml wet)

Thus ~ 40% of the column volume is resin.

* Also referred to as "Nalcite" and "Ionex". The effective Molecular weight is 184.

B. Preparation of Ammonium Citrate Stock Sol'n.

(1) Combine the following:
12 gms Bakers C.P. phenol
600 gms Merck Reagent grade citric acid
116 ml Reagent grade NH_4OH

(2) Dilute to 12 liters with H_2O, mixing well.

(3) Remove a small sample and test the acidity with a pH meter. It should be between pH 3.00 and 3.10. If it is not, add NH_4OH or $HClO_4$.

(4) Citric acid data.
Molecular weight of monohydrate = 192
$K_1 = 8.2 \times 10^{-4}$; $K_2 = 1.77 \times 10^{-5}$; $K_3 = 3.9 \times 10^{-7}$

C. Adsorption of Rare Earths on Dowex 50.

(1) Dissolve the material to be purified in the least possible amount of $HClO_4$ and dilute to 50 ml. If the sol'n does not remain clear on dilution, add several milliliters of conc. HCl and heat the sample further.

(2) Transfer the sol'n, having a volume of 50 ml, to a 250 ml glass-stoppered bottle. Add enough Eu^{154} tracer in $HClO_4$ or HCl soln to give a total of ~ 500,000 c/m of Eu on shelf 1 of counter. Mix the sol'n well and pipette out 100 λ . Dry and count.

(3) Air dry some of the resin prepared as in (A) above, and weigh out 10 gms for each gram of rare earth oxide which has been dissolved.

(4) Add this resin to the sol'n from step (2). Paraffin the bottle and shake it mechanically for 1-2 hours. Allow the resin to settle; remove 100 λ of the supernatant soln, dry, and count. Compare with the count obtained in step (2) to determine the percentage adsorbed. If it is less than 95%, add more $HClO_4$ or more resin, or both, and shake again.

(5) When the count shows enough of the material to have been adsorbed, draw off the supernatant. Wash the resin with 50 ml of H_2O and discard the wash. Then wash with 50 ml of pH 2 ammonium citrate soln (prepared by adding conc HCl to some of the soln prepared in (B)), and discard this wash. The resin is now ready to be slurried onto the prepared resin bed.

Procedure: -

(1) Place a small Pyrex glass wool plug in the well above the capillary tube and wet it with H_2O. Add a slurry of the resin in H_2O prepared as in (A) above, filling the tube to a height of

~ 20 cm for Pr, Nd
~ 40 cm for Sm, Eu
at least 60 cm for Gd and higher rare earths.

(2) After making sure that the glass wool plug has not beem misplaced, allow the resin to settle for several hours and form a well-packed bed.

(3) Transfer the "hot" resin containing the adsorbed rare earth material as prepared in C above to the top of the column by slurrying it on with a small amount of pH 2 ammonium citrate sol'n. Make sure that the resin settles out in a level band.

(4) Carefully fill the column with H_2O and put the rubber stopper in place so that all of the air bubbles are forced up into the glass tube in the middle of the stopper and finally out through the reservoir bottle.

(5) Fill the reservoir bottle with the pH 3.05 ammonium citrate sol'n and allow the liquid to fill the tygon tubing leading to the column. Clamp the tubing until ready for the flow to begin. (Caution!) Do not manipulate the tubing in such a way that a partial vacuum is ever created at the top of the column or the whole resin bed will be sucked upward, and the glass wool plug will be dislodged.)

(6) After the automatic sampler has been put in place, start the flow and regulate it by raising or lowering the reservoir so that the rate is from 4-5 sec/drop (75-90 ml/hr) for Pr and Nd to not faster than 8 sec/drop (40 ml/hr) for Gd and higher rare earths. These rates, 40-90 ml/hr, correspond to figures of 0.033-0.075 ml/cm^2 for a 5 cm i.d. column.

(7) Collect samples as desired. The progress of the rare earths through the column can be followed roughly by checking the position of the Eu tracer with a sensitive survey meter.

(8) The material being purified is best detected by removing 1-2 ml from each of several selected tubes, placing the samples in a small beaker and adding a few crystals of oxalic acid. When weighable amounts of rare earths come through, this test will result in a turbidity or a sizeable white ppt., depending on the amount of material.

(9) When all of the desired material has been eluted, as shown by the above test, and an additional volume has been run through as a safety factor, stop the ammonium citrate flow and the sampler.

(10) Determine the beginning and end of the elution peak by testing as above. Prepare samples for spectroscopic analysis as desired, either at both ends of the peak or at regular intervals throughout its length. In each case pipette 50 λ of the soln onto a Cu spectroscope electrode and dry.

(11) On the basis of the spectroscopic analysis combine the tubes into fractions according to purity. In each case, transfer the solns and washings to a beaker of appropriate size and boil to $\sim$ 1/3 the volume. Add oxalic acid (1 gm for each 25 ml of soln) which has been dissolved in H_2O and heated to boiling, pouring it into the boiling sample soln and stirring well. Digest the sample over low heat with continued stirring for one hour. Allow the ppt to settle, preferably overnight.

(12) Draw off the supernatant and concentrate the ppt by successive centrifugings. Transfer the material to a Pt dish by slurrying with H_2O, dry it, and ignite to constant weight at 700° C.

Remarks:

(1) In order to secure spectroscopically pure material it is important that special care be taken at all times to see that all equipment is clean and that all reagents used are from fresh containers of known purity. Since it is difficult to remove all traces of dichromate cleaning solution from glassware, the centrifuge tubes and beakers used were cleaned with aqua regia instead of cleaning soln and rinsed very thoroughly. During the run the sampler and tubes were covered with a large shield to prevent dust from dropping into the samples; and during subsequent steps all containers were kept well covered.

(2) The rare earths, in general, are eluted in the reverse order from their periodic table arrangement, i.e., lutecium comes off first and lanthanum last. If the same eluting agent is used throughout, the concentration vs time peaks become progressively broader and further apart as the lighter rare earths are approached. This means that praeseodymium, for example, is relatively easy to purify, but will be spread through a number of fractions; whereas the heavy rare earths are difficult to purify and are distributed through fewer tubes per peak.

(3) The Tompkins-Mayer equations (JACS 69, 2859 (1947)) can be used to calculate theoretical separation curves. They require that the plates per centimeter be known for the resin, and that the "C" values (number of free volumes of elutant at the peak) be known for the individual rare earth elements. The experimental data taken are not complete enough to give very accurate figures, but it is estimated that the 250-500 mesh Dowex 50 used as described is equivalent to $\sim$ 15-20 plates per centimeter of column length. Some "C" values are as follows: Eu $\cong$ 16; Sm $\cong$ 20; and Pr $\cong$ 55.

8/16/49

CHEMICAL SEPARATIONS

Element separated: Cerium

Procedure by: Newton

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

Time for sep'n: 1 1/2 hours

Type of bbdt: 60" alphas

Equipment required: Standard

Yield: 80%

Degree of purification: 10^6 except from other R.E.; probably 10^3-10^4 from other R.E.

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

(1) Add 10 mg Ce, La and Y carriers, 8 ml conc. HNO_3 and 15-20 ml .35 M HIO_3 solution. Centrifuge.

(2) Add 11 ml of 15 N NaOH, ppt $Ce(OH)_3$. Wash once with dil NaOH.

(3) Dissolve ppt in 2 ml 6 N HCl. Dil to 10 ml. Add 2 ml 27 N HF. Ppt CeF_3, discard supernate.

(4) Add 1 ml sat H_3BO_3 and 8 ml conc. HNO_3. When dissolved add 1/4 gm $KBrO_3$. Ppt iodate by adding 20 ml HIO_3 sol'n.

(5) Dissolve ppt in 1 drop conc HCl and 3 drops H_2O_2 and repeat iodate pptn.

(6) Dissolve iodate in 1 drop HCl and add 8 ml conc. HNO_3 and 10 mg Zr carrier. Add HIO_3 to ppt $Zr(IO_3)_4$, let stand 5 min. Centrifuge.

(7) Add 10 ml 15 N NaOH, ppt $Ce(OH)_3$.

(8) Dissolve $Ce(OH)_3$ in 1 ml 6 N HCl. Add H_2SO_3 to reduce all IO_3^- to I^-. Add NH_4OH to ppt $Ce(OH)_3$.

(9) Dissolve $Ce(OH)_3$ in 1 ml 6 M HCl. Dil to 15 ml H_2O, boil. Add 15 ml sat H_2CrO_4 with stirring. Cool in ice bath just 10 min.

(10) Filter, wash three times with 5 ml H_2O, three times with 5 ml EtOH, three times with 5 ml Et_2O. Dry by evac. 2 min., release, 2 min., release, 3 min., weigh as $Ce_2(C_2O_4)_3 \cdot 10H_2O$.

Remarks:

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

Preparation of carrier solution: Dissolve 31.0 gms $Ce(NO_3)_3 \cdot 6H_2O$ in water and dilute to one liter.

Standardization: Take 5 ml carrier. Add 20 ml H_2O. Heat to boiling and add 5 ml saturated oxalic acid. Cool in an ice bath for just 10 minutes.

Filter through a fine sintered glass crucible. Wash and dry with 5 ml H_2O, 3-5 ml portions 95% EtOH, 3-5 ml portions Et_2O. Evacuate 2 minutes, release to air, evacuate 2 min., release, evacuate, release (evacuate three minutes). Weigh as $Ce_2(C_2O_4)_3 \cdot 10H_2O$.

The method is quite empirical. The Rare Earth ppts are weighed as the following compositions when dried in the above standard manner.

$La_2(C_2O_4)_3 \cdot 8H_2O$

$Ce_2(C_2O_4)_3 \cdot 10H_2O$

$Pr_2(C_2O_4)_3 \cdot 9H_2O$

$Y_2(C_2O_4)_3 \cdot 7H_2O$

$Eu_2(C_2O_4)_3 \cdot 10H_2O$

8/23/49

P-18-276

CHEMICAL SEPARATIONS

Element separated: Cerium

Procedure by: Goeckermann

Target material: ∿ 1 g Bi metal

Time for sep'n: few hours

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, lusteroid cones, H_2S tank, NH_3 tank, ozone generator.

Yield: Ce approx. 30%

Degree of purification: Ce decontamination factor > 10^4 from fission & spallation products.

Advantages: Good for separating small amounts of Ce & Eu activity from large amts of non-RE activities.

Procedure: Cerium and europium were purified together and then separated from the other rare earths.

(1) To aliquot of HNO_3 soln of target add 20 mg Ce, Eu, and Y. Make 2N in HCl with Zr, Cb, and Sr present and precipitate RE fluorides.

(2) Dissolve and reprecipitate RE fluorides from 2 N HNO_3 with Zr and Cb present.

(3) Scavenge twice with Bi_2S_3 and RuS from 0.5 N HCl.

(4) Precipitate RE hydroxides twice with NH_3(CO_3^{-2} free) and Sr present.

(5) Precipitate RE fluorides from 2N HCl twice with Zr and Cb present.

(6) Scavenge with Bi_2S_3 and RuS from 0.3N HCl.

(7) Precipitate RE hydroxides with NH_3 three times with Sr present.

(8) Precipitate RE oxalates from dilute HCl.

(9) Precipitate RE fluorides from HNO_3.

(10) Repeat (7).

(11) Displace air with O_2 and CO_2 free N_2, reduce with Zn amalgam, precipitate $Y(OH)_3$ and $Ce(OH)_3$ with NH_3. Dissolve and reduce again, reprecipitate hydroxides.

(12) Dissolve hydroxides, precipitate $Ce(IO_3)_4$ twice, then $Ce_3(PO_4)_4$ three times. Precipitate CeF_3 from HCl, metathesize to $Ce(OH)_3$, dissolve in HCl, precipitate $Ce(OH)_3$ with NH_3. Dissolve in HCl. Weigh as $Ce_2(C_2O_4)_3 \cdot 10H_2O$ (25.84 mg per 10 mg Ce).

Remarks: In these bbdts, the amount of Y activity produced was > 10^3 times the RE activity. 1-2 mg of holdback carriers or scavengers are used. See (63-3) for Europium separation from same target.

P-18-262

8/24/49

CHEMICAL SEPARATIONS

Element separated: Samarium

Procedure by: Ballou, Newton

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

Time for sep'n: ~ 2 hours

Type of bbdt: 60" alphas

Equipment required: Purified tank N_2 (O_2 & CO_2 free)

Yield: 5-25%

Degree of purification: undetermined

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

(1) Add 10 mg Ce^{+3} and Eu^{+3} carrier + 10 mg Sm^{+3} carrier, 5 ml conc. HNO_3 and 4 ml 27 M HF; dilute to 35 ml, centrifuge and wash with ~ 10 ml H_2O + several drops HF.

(2) Dissolve ppt in 1 ml sat H_3BO_3 + 3 ml conc HNO_3, dilute to ~ 20 ml, add 2 ml 27 M HF, centrifuge and wash as in (1).

(3) Slurry ppt of (2) with 1 ml sat H_3BO_3 solution and dissolve in 8 ml conc HNO_3. Add 0.2 gm $KBrO_3$ + 20 ml 0.35 M KIO_3 sol'n; cool and stir 2 minutes. Centrifuge & wash with H_2O. (Ppt contains Ce and Th.)

(4) Add 12 ml 19 M NaOH to supn, cool and centrifuge. Dissolve ppt in conc. HCl + H_2SO_3, dilute to 30 ml, add conc. NH_4OH, centrifuge and wash.

(5) Dissolve ppt in 3 ml 6 N HCl, dilute, add 5 mg La holdback carrier, and reppt with NH_4OH; centrifuge and wash.

(6) Dissolve the $Sm(OH)_3$ & $Eu(OH)_3$ with a minimum of 6 N HCl (not more than a few drops) and transfer to a separatory funnel with 10-20 ml water. Add 8 drops of glacial HAc and 3 to 4 ml Na amalgam (0.3%) (Note 1).

(7) Shake for 5-10 seconds (Note 2) and transfer the Hg layer to a second separatory funnel containing ~ 30 ml water. Shake and then transfer to a third funnel also containing ~ 30 ml water (Note 3). Shake and transfer to a fourth funnel containing ~ 20 ml 2 N HCl. Shake until H_2 evolution ceases (Note 4)

(8) Collect the Hg in a recovery bottle and pass the water layer into a centrifuge tube. Add 5 mg La holdback carrier and precipitate with concentrated NH_4OH.

(9) Repeat steps (6-8) twice (Note 5).

(10) Dissolve the $Sm(OH)_3$ and $Eu(OH)_3$ with 1 ml 6 N HCl and transfer to a 50 ml constricted neck centrifuge tube (BKH # 20972) containing 0.5 gm amalgamated Zn.

(11) Dilute to ~8 ml, and heat the mixture with stirring using as a stirring rod a drawn out tube through which is passing a stream of carbon-dioxide free and oxygen free nitrogen (Note 6).

(12) Using the same tube as a stirring rod, place the centrifuge tube in an ice bath and add carbonate-free NH_4OH to precipitate the $Sm(OH)_3$. Close the tube with a tight fitting rubber stopper and centrifuge.

(13) Decant into another tube and test for Eu by passing in ozone. Continue extracting Eu from the Sm as described above until no more Eu appears in the centrifugate.

(14) Add 1 mg more Eu to the $Sm(OH)_3$ and repeat steps (10-13). (Save all Eu residues.)

(15) Dissolve the final $Sm(OH)_3$ with a minimum of 6 N HCl (not over 1 ml), dilute to ~15 ml, heat with stirring, and add 10-15 ml hot saturated oxalic acid with stirring. Filter through a filter circle on a Hirsch funnel, and wash twice with dilute oxalic acid, once with water, and once with alcohol. Ignite the sample and mount for counting.

Notes

1. The Na should be cleaned with ether and be allowed to dry before adding to the Hg. The amalgamation of the Na proceeds with considerable heat evolution, causing some volatilization of the Hg. Consequently, the preparation of the amalgam should be done in the hood under nitrogen. The residue which is also formed can be removed by filtering the amalgam through a small hole in a filter paper. This residue which contains some amalgam can be washed several times with water and used. Once formed, Na amalgam is relatively stable to water and air but decomposes readily in acid solutions.

2. Shaking much longer causes complete destruction of the Na. This should be avoided. On the other hand, sufficient time must be allowed for the Sm to amalgamate completely.

3. No Sm is lost in the water washings. Hence these may be discarded.

4. Sm (and Eu) are completely removed by 2 N HCl. None of the other rare earth fission products are extracted in this step. If the yield of Sm appears low, add more amalgam to the first funnel and repeat the separation. Any Sm remaining in the first funnel should be saved.

5. It is probably necessary to repeat paragraph (2) only once. However, this has not been tested.

6. The nitrogen from the tank is passed through a tube containing Cu heated to ~400° C. CO_2 is removed by passing the N_2 through an Ascarite tube. Reduced Eu is readily oxidized by oxygen and hence oxygen must be excluded. Carbon dioxide forms insoluble carbonates and must also be avoided.

See: L. Winsberg, Paper 195 Radiochemical Studies: The Fission Products, Volume 9, Div. IV, of the National Nuclear Energy Series, McGraw-Hill Publishing Co. (1950).

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

8/23/49

P-18-269

CHEMICAL SEPARATIONS

Element separated: Europium

Procedure by: Newton

Target material: Thorium (metal)

Time for sep'n: 4 hrs.

Type of bbdt: 60" α's

Equipment required: Tank N_2 (O_2 and CO_2 free)

Yield: 40%

Degree of purification: 10^6 except from R. E.; ~ 10^4 from R. E.

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

(1) To aliquot add 10 mg Eu^{+++} and 10 mg Ce^{+++} carriers. Add 8 ml conc HNO_3 and 20 ml 0.35 M HIO_3 soln. Ppt $Th(IO_3)_4$. Discard ppt.

(2) To centrifugate add 19 M NaOH ppt $Ce(OH)_3$ and $Eu(OH)_3$. Centrifuge and wash ppt once with H_2O.

(3) Dissolve ppt in 8 ml conc HNO_3, add 2 ml Zr and 20 ml HIO_3 ppt $Zr(IO_3)_4$. Centrifuge and discard ppt.

(4) Add 19 M NaOH to ppt $Eu(OH)_3$ and $Ce(OH)_3$. Discard supernate. Wash ppt once with H_2O.

(5) Dissolve hydroxides in 1 ml 6 N HCl. Add 10 mg each Ba and Sr carriers. Pass in CO_2 free NH_3, ppt hydroxides.

(6) Repeat (5).

(7) Dissolve ppt in 1 ml HCl. Add Cb and Zr carrier and 3 ml 27 NHF. Ppt CeF_3 + EuF_3. Wash ppts once.

(8) Dissolve ppt in 1 ml 6 N HCl and 1 ml sat H_3BO_3. Dilute, pass in NH_3, ppt $RE(OH)_3$.

(9) Dissolve $RE(OH)_3$ in 1 ml 6 N HCl. Pass in NH_3 ppt $RE(OH)_3$.

(10) Dissolve $RE(OH)_3$ in 1 ml 6 N HCl. Add 0.5 gm Zn(Hg). Dilute to 5 ml, pass in pure N_2 through stirring rod. Heat, stirring with rod through which gas is passing. Place in ice bath and pass in NH_3 to ppt Ce(OH). Stopper tube and centrifuge. Pipette off supernate to another tube.

(11) Dissolve ppt in 1 ml 6 N HCl, dilute and repeat (10).

(12) To combined supernates of 10 and 11 add 1 drop NaOCl (6%) or pass in ozone. Ppt $Eu(OH)_3$. Centrifuge. Dissolve in 6 N HCl and repeat 10, 11, and 12.

(13) Dissolve $Eu(OH)_3$ from (12) in 1 ml 6 N HCl. Dilute to 10 ml. Heat. Add 10 ml saturated $H_2C_2O_4$ and place in ice bath 10 min. Filter on weighed filter paper and wash three times with 5 ml H_2O, three times with 5 ml EtOH and three times with 5 ml Et_2O. Evacuate and weigh.

Remarks:

(1) N_2 gas must be O_2 and CO_2 free.

(2) Save all Eu residues, active or not. Eu is extremely rare and hard to get.

This method has been described previously in Phys. Rev. 75, 17 (1949).

8/11/49
P-18-160

Preparation of Europium Carrier

~1.5 gms of europium oxalate originally prepared by McCoy was purified. There are both α and β^- activities associated with this Eu and it is necessary to separate it in order to obtain a good carrier solution.

The process was:

(1) $Eu_2(C_2O_4)_3$ ignited and dissolved in HCl.

(2) NH_4OH passed in to ppt $Eu(OH)_3$.

(3) $Eu(OH)_3$ dissolved in 10 ml 16 N HNO_3, Zr^{++++} carrier added.

(4) HIO_3 added to ppt $Zr(IO_3)_4$ carrying all Th impurities.

(5) 19 N NaOH added to ppt $Eu(OH)_3$.

(6) $Eu(OH)_3$ dissolved in 6 N HCl. Ba^{++} added and H_2SO_4 added while hot to ppt $BaSO_4$, carrying Ra and MsTh activities.

(7) $Eu(OH)_3$ pptd with NH_4OH, washed and dissolved in dilute HCl.

(8) Zn(Hg) added to reduce Eu with N_2 bubbling through solution. Then NH_3 passed into ppt R. E. and Ac hydroxides. Ppt redissolved in acid and recycled since some Eu not reduced.

(9) Eu^{++} oxidized with NaOCl and ppt'd as hydroxide, washed and dissolved in HCl as carrier.

Standardization of Carrier

Take 2 ml carrier solution, heat and ppt oxalate with $H_2C_2O_4$. Cool 10 min in ice bath, filter. Wash three times with 5 ml H_2O, three times with 5 ml EtOH and three times with 5 ml Et_2O. Dry by evacuation. Weigh as the oxalate. Ignite to oxide and weigh as the oxide.

$Eu_2(C_2O_4)_3 \cdot 10\ H_2O$ (24.6 mg per 10 mg Eu).

A. S. Newton

8/11/49
P-18-163

CHEMICAL SEPARATIONS

Element separated: Europium

Procedure by: Goeckermann

Target material: ~ 1 g Bi metal

Time for sep'n: few hours

Type of bbdt: 184" all particles

Equipment required: Centrifuge, tubes, lusteroid cones, H_2S tank, NH_3 tank, ozone generator.

Yield: Eu approx. 15%

Degree of purification: Eu decontamination factor > 10^4 from non-RE fission and spallation products.

Advantages: Good for separating small amounts of Ce & Eu activity from large amts of non-RE activities.

Procedure: Cerium and europium were purified together and then separated from the other rare earths.

(1) To aliquot of HNO_3 soln of target add 20 mg Ce, Eu and Y. Make 2N in HCl with Zr, Cb, and Sr present and precipitate RE fluorides.

(2) Dissolve and reprecipitate RE fluorides from 2N HNO_3 with Zr and Cb present.

(3) Scavenge twice with Bi_2S_3 and RuS from 0.5 N HCl.

(4) Precipitate RE hydroxides twice with NH_3(CO_3^{-2} free) and Sr present.

(5) Precipitate RE fluorides from 2N HCl twice with Zr and Cb present.

(6) Scavenge with Bi_2S_3 and RuS from 0.3N HCl.

(7) Precipitate RE hydroxides with NH_3 three times with Sr present.

(8) Precipitate RE oxalates from dilute HCl.

(9) Precipitate RE fluorides from HNO_3.

(10) Repeat (7).

(11) Displace air with O_2 and CO_2 free N_2, reduce with Zn amalgam, precipitate $Y(OH)_3$ and $Ce(OH)_3$ with NH_3. Dissolve and reduce again, reprecipitate hydroxides.

(12) Eu - Oxidize supernatants from hydroxide precipitations with ozone, precipitate $Eu(OH)_3$ with NH_3. Dissolve in HCl, add Ce, reduce to Eu^{+2} and precipitate $Ce(OH)_3$. Repeat separation cycle three times. Precipitate $Eu_2(C_2O_4)_3$ like $Y_2(C_2O_4)_3$ and treat similarly. Weigh as $Eu_2(C_2O_4)_3 \cdot 10H_2O$ (24.6 mg per 10 mg Eu). See (58-2) for cerium separation from the same target. In these bbdts, the amount of Y activity produced was > 10^3 times the RE activity. 1-2 mg of holdback carriers or scavengers are used.

CHEMICAL SEPARATIONS

Element separated: Hafnium

Procedure by: Hicks, Wilkinson

Target material: Lu_2O_3

Time for sep'n: 1/2 hr.-1 hr.

Type of bbdt: 60" or 184"

Equipment required: lusteroid tubes

Yield: Very good

Degree of purification: very good

Procedure:

(1) Dissolve Lu_2O_3 in HNO_3, add carriers (see remarks), transfer to lusteroid, heat in water bath and add 5 cc conc. HF.

(2) Digest LuF_3, centrifuge, add several mg La^{+++} to ppt LaF_3, digest, centrifuge.

(3) Make 3 N in HNO_3 and HF (sol'n at room temp, since $BaHfF_6$ will not dissolve if precipitated hot.) and add enough Ba^{++} in the cold to ppt $BaHfF_6$. Wash with water.

(4) Dissolve in HNO_3-H_3BO_3 mixture (8-10 M HNO_3 saturated with H_3BO_3), precipitate HfO_2 with NH_4OH, centrifuge and wash.

Remarks: About 20 mg samples of Lu_2O_3 have been bombarded. Holdback carriers added in (1) can include 1 mg portions of as many elements forming soluble fluorides as thought necessary by the conditions of the bombardment. Zr can be used as carrier for Hf.

The $BaHfF_6$ precipitation described here is specific for Hf and Zr.

6/25/49

P-18-13

CHEMICAL SEPARATIONS

Element separated: Hafnium

Procedure by: Hicks, Wilkinson

Target material: Ta, HfO_2, W

Time for sep'n: 1/2 hr.-1 hr.

Type of bbdt: 60" or 184"

Equipment required:
Platinum dish
lusteroid tubes

Yield: very good

Degree of purification: very good

Procedure:

(1) Dissolve W, Ta, and HfO_2 in HF and HNO_3, transfer to lusteroid tube and add carriers. (See remarks.)

(2) Heat in hot water bath, add several mg La^{+++} to ppt LaF_3, centrifuge, repeat LaF_3 ppt.

(3) Make supn 3 N in HNO_3 and HF, making sure solution is at room temperature for $BaHfF_6$ will not dissolve if precipitated hot. Add enough Ba^{++} to completely precipitate $BaHfF_6$. Wash with dilute HF and then water.

(4) Dissolve $BaHfF_6$ in HNO_3-H_3BO_3 mixture (8-10 M HNO_3 saturated with H_3BO_3), precipitate HfO_2 with NH_4OH, centrifuge and wash with water.

Remarks: Gram amounts of W and Ta are usually bombarded. HfO_2 is bombarded in about 20 or 30 mg samples.

Add any holdback carriers (of elements forming soluble fluorides and Zr) necessary here in mg amounts. Zr can be used as carrier for Hf.

The $BaHfF_6$ precipitation described here is specific for Hf and Zr.

6/25/49

P-18-12

CHEMICAL SEPARATIONS

Element separated: Tantalum

Procedure by: Hicks, Wilkinson

Target material: Lu_2O_3

Time for sep'n: 1/2 hr-1 hr.

Type of bbdt: 60" or 184"

Equipment required: lusteroid tubes

Yield: very good

Degree of purification: very good

Procedure:

(1) Dissolve Lu_2O_3 in HNO_3, transfer to lusteroid tube and add Ta carrier. (Ta_2O_5 may ppt but will dissolve in HF)

(2) Heat sol'n in water bath, add 5 cc conc. HF, digest for 2 - 3 minutes until Ta_2O_5 dissolves and flocculent WF_3 precipitates.

(3) Centrifuge, add several mg La^{+++}, digest flouride as above and centrifuge.

(4) Make basic with NH_4OH to ppt Ta_2O_5.

6/25/49

P-18-15

CHEMICAL SEPARATIONS

Element separated: Tantalum

Procedure by: Hicks, Wilkinson

Target material: W, Ta, Hf

Time for sep'n: 1/2 hr.-1 hr.

Type of bbdt: 60" or 184"

Equipment required: Pt dish, lusteroid tubes

Yield: very good

Degree of purification: very good

Procedure:

(1) Dissolve W, Ta or HfO_2 in HF and HNO_3 in Pt dish.

(2) Transfer solution to lusteroid tube and add any holdback carriers necessary. (Zr works well as carrier for Hf). Make solution 3N in HNO_3 and HF. Add enough Ba^{++} to ppt white $BaHfF_6$ completely, centrifuge, and repeat.

(3) Saturate solution with solid KF or KHF_2 to ppt K_2TaF_7 (white), centrifuge, and wash with conc. KF sol'n.

Remarks: W and Ta usually bombarded in gram amounts, Hf usually in lots of 20-30 mg.

This K_2TaF_7 pptn specific for Ta and will not carry down Cb.

6/25/49

P-18-10

CHEMICAL SEPARATIONS

Element separated: Tungsten

Procedure by: Hicks, Wilkinson

Target material: Tantalum

Time for sep'n: 1/2 hr.

Type of bbdt: 60" or 184"

Equipment required:
Sep. funnel
Pt dish

Yield: ~ 100%

Degree of purification: Separates 10^5 c/m completely from Ta and spallation products.

Procedure:

(1) Dissolve Ta in HF and minimum of HNO_3. Add 20-30 mg W carrier (No less).

(2) Destroy all HNO_3 with hydroxylamine or hydrazine. Make about 2N in HCl, add 0.1 gm solid $SnCl_2$, 0.5 gm NH_4SCN, and H_3BO_3 to complex all HF as HBF_4 in that order.

(3) Heat until a bright apple green complex appears, transfer to a sep. funnel, and extract twice with at least equal volume ethyl acetate.

(4) Wash organic layer twice with equal volume 2 N HCl, and evaporate organic layer to dryness.

(5) Take up the blue residue with 6 N HCl and 1 drop 30% H_2O_2 (or conc HNO_3) and 1 drop aerosol. Bright yellow WO_3 precipitates after digestion on a hot water bath.

(6) Centrifuge and wash WO_3 with 6 N acid. Then dissolve in 1 cc 6 N NH_4OH, centrifuge and discard any ppt. Ferric hydroxide scavenges (with 1/2-1 mg Fe^{+++}) may now be used for further purity but usually are not necessary.

(7) Add 5 cc conc. HNO_3 and 1 drop of aerosol, digest on a hot water bath, centrifuge and wash WO_3 formed with 6 N acid.

Remarks: WF_6 boils at 19° C so don't boil target sol'n any more than necessary.

6/25/49

P-18-16

CHEMICAL SEPARATIONS

Element separated: Rhenium

Procedure by: Hicks, Wilkinson

Target material: Ta, W

Time for sep'n: 1/2 hr.

Type of bbdt: 60" or 184"

Equipment required:
Pt dish
lusteroid test tubes

Yield: ~ 100%

Degree of purification: very good

Advantages: Fast and easy with good purification

Procedure:

(1) Dissolve W and Ta in HF with a minimum of HNO_3 in platinum disk, and Re carrier added.

(2) H_2S is passed into the boiling solution for 15 minutes precipitating black Re_2S_7. Centrifuge and wash in a lusteroid test tube.

(3) Dissolve Re_2S_7 in 3 cc 1 M NaOH and 1 drop 30% H_2O_2 and transfer to glass centrifuge cone.

(4) Scavenge twice or three times with $Fe(OH)_3$ (~ 1 mg Fe^{+++}).

(5) Reprecipitate Re_2S_7 from strong HCl solution (add 10 cc conc. HCl), centrifuge and wash.

(6) This procedure gives excellent purity, but for additional purity, the sulfide can be transferred to a still with H_2SO_4 and the volatile oxide distilled in a current of air and catching the distillate in concentrated NaOH.

CHEMICAL SEPARATIONS

Element separated: Osmium

Procedure by: Folger & Hicks

Target material: ∾ 4 g uranium metal

Time for sep'n: ∾ 2 1/2 hr.

Type of bbdt: 184" all high energy particles

Equipment required: Glass stills ("Ruthenium Stills"). centrifuge, cones, ice bath, reflux condenser.

Yield: ∾ 30%

Degree of purification: ∾ 10^4-10^5 from other fission products.

Advantages: Fairly rapid, simple method of obtaining Os from bulk of F.P. activities. Operations are readily adaptable to semi-remote control, and the activity level drops rapidly after the first separation.

Procedure: HAVE NO NO_3^- PRESENT BEFORE STEP 3.

(1) Use ∾ 20 mg. Os carrier and dissolve target in conc. HCl under reflux. Add ∾ 5 mg Ge carrier and boil with conc. HCl ($GeCl_4$ is driven off.).

(2) Add I^- and IO_3^- (slight x's I^-) and boil to remove I_2.

(3) Add conc. HNO_3 (Sol'n is already ∾ 10 N in H^+. Add HNO_3 to make it ∾ 6 N in NO_3^-) and distill in an air stream. Catch OsO_4 in 6 N NaOH in an ice bath. (Gives orange sol'n).

(4) Pass in H_2S to ppt OsS_2 (black). Acidify with conc. HCl to ∾ 1 N and centrifuge. Wash (Use Aerosol and heat to aid coagulation. Addition of KNO_3 might help).

(5) Dissolve sulfide in conc. HNO_3 and redistill (distillation should proceed from 8-10 N HNO_3 in an air stream). Catch OsO_4 in 6 N NaOH in an ice bath.

(6) Repeat 4. (The wash may be made with ∾ 1 N HCl if desired).

(7) Dissolve the sulfide in conc. $HClO_4$. Add Mo holdback (∾ 5 mg) and 2 cc conc. H_3PO_4 (complexes Mo). Distill in an air stream, catching OsO_4 in 6 N NaOH in an ice bath.

(8) Repeat 6 and 7.

(9) Make slightly acid with HCl. Reduce with Mg metal to some lower oxidation state of Os (to prevent loss of OsO_4). Boil. Add Mg and HCl as needed to completely ppt Os metal. Excess Mg may be removed by washing with warm 2-6 N HCl. Weigh as Os metal.

Remarks:

(1) CAUTION OsO_4 is extremely toxic!

(2) In step 4 an attempt is made to remove most of the Cl^- from the sulfide so that upon dissolving and distilling, $GeCl_4$ will not be carried over. This should no longer be necessary in step 6.

(3) Any Ru contaminant remaining after step 5 will likely be carried through the rest of the procedure. For additional purification repeat steps 4 and 5.

(4) If Iodine is a likely contaminant, repeat step 2.

CHEMICAL SEPARATIONS

Element separated: Osmium

Procedure by: Chu

Target material: Rhenium

Time for sep'n: ~ 20 min.

Type of bbdt: 60"

Equipment required: Distilling flask

Yield: ~ 100%

Degree of purification: Factor of 100 from other activities present.

Advantages: Simple

Procedure:

(1) Pour the Re powder into the distilling flask.

(2) Add 10 mg Os carrier and close the flask.

(3) Insert the outlet tube of the flask into ice cold 6 N NaOH soln (10 cc)

(4) Introduce 3 cc conc HNO_3 through the inlet tube of the flask.

(5) Supply a little air through the inlet tube and heat the flask gently for the solution of Re and the distillation of OsO_4 for about 10 min.

(6) Neutralize and then acidify the NaOH soln with 6 N HCl.

(7) Add 3 cc 10% sodium thiosulfate and heat in water bath.

(8) Filter and count as the brown osmium sulfide.

Remarks:

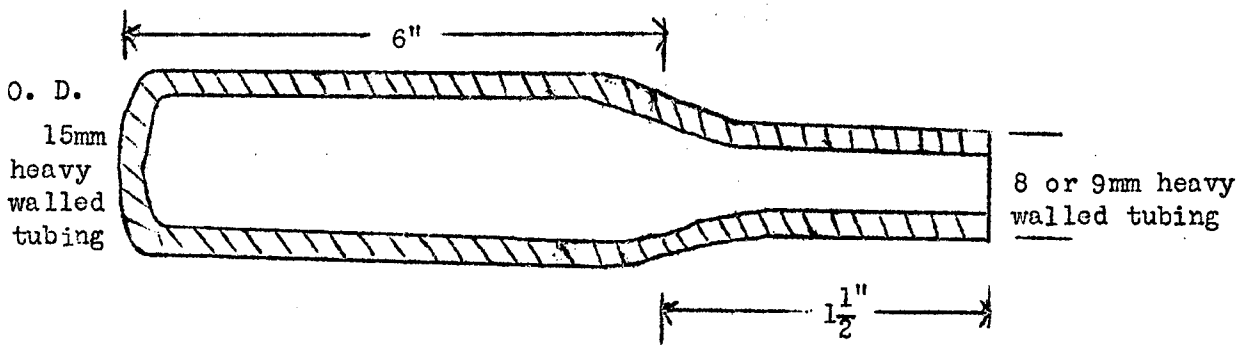
For iridium separation from same target see (77-4).

8/17/49

Solution of Iridium metal

Place Ir in glass bomb tube of 10 cc. volume cooled in liquid N_2. Add 5 cc conc. HCl and 0.5 gm $NaClO_3$. Seal tube with other end in liquid N_2 and allow to warm to room temperature. Heat in furnace 300°C for 3 hours. Ir metal is dissolved to the deep red $IrCl_6^{=}$.

Approximate tube dimensions:



Caution: Place tube in iron pipe plugged at both ends upon removal from liquid N_2. Danger of tube exploding during the heating.

Remarks: See E. Wickers, W. G. Schlect & C. L. Gordon
J. Nat. Bur. Stand. Research 33, 363 (1944)

Hicks and Wilkinson

CHEMICAL SEPARATIONS

Element separated: Iridium

Procedure by: Thompson & Rasmussen

Target material: Iridium foil

Time for sep'n: 1 hr.

Type of bbdt: 184" protons (any energy)

Equipment required: Small porcelain crucible. transfer pipettes, centrifuge tubes

Yield: ~50% (depending on step 3)

Degree of purification: At least factor of 100.

Advantages: A simple, reasonably fast procedure for solution and separation with a target metal (Ir) extremely resistant to dissolution in aqua regia.

Procedure:

(1) Make a melt of KOH and KNO_3 (approx. 50-50, not critical) in a small porcelain crucible, heating strongly over a Fisher burner.

(2) To this hot flux add the target Ir metal, continuing to heat (and adding KOH if volume of flux gets too small) until the metal is completely dissolved. (For a small strip of 1 mil foil this should take no longer than 5-10 min.)

(3) Allow flux to cool, then leach for ~5 min. with conc. HCl, adding Au and Pt carriers in small amount. (Ir gives strong blue colored sol'n)

(4) Extract twice with ethyl acetate to remove Au.

(5) Add a little $SnCl_2$ solution in HCl to the aqueous phase until a dark red coloration (H_2PtCl_4) indicates the reduction of Pt from +4 to +2 state is complete. (See remarks.)

(6) Extract the red coloration (Pt) into ethyl acetate. Wash organic layer twice with equal volume of 3N HCl.

After complete removal of Au and Pt, Ir can be extracted as follows:

(7) Reoxidize the aqueous phase from above by addition of a small amount of 30% H_2O_2. (Reappearance of blue Ir^{VI} coloration.)

(8) Add a little NH_4 SCN solution. (Blue changes to beautiful pink.) A precipitate of $(Ir)_x(SCN)_y$ forms slowly. (The rate of pptn is slow enough that one may make use of the fact that the pink compound is extractable into ethyl acetate.)

The extraction of the pink compound has the advantage of quickly removing the Ir from the original solution, which usually has enough silica dissolved (from crucible) that the whole solution will gel if allowed to stand.

The pink compound ppts from the ethyl acetate on standing.

Remarks:

As most Ir foil contains about ~1% Pt impurity, it is well to provide a step for extraction of Au activities, whether or not the Au is desired for later work, even if it is simply a proton bombarded Ir foil.

On $SnCl_2$ reduction the strong blue coloration of Ir(+6?) disappears, permitting the red of reduced H_2PtCl_4 to be seen.

By spending more time leaching the melt in (3) and by using several portions of leaching agent the chemical yields might be made almost quantitative.

7/27/49
P-18-115

CHEMICAL SEPARATIONS

Element separated: Iridium

Procedure by: Wolfe

Target material: Uranium metal (~ 1 gm)

Time for sep'n: ~1 1/2 days when separated with Pt and Rh

Type of bbdt: 388 Mev alphas

Equipment required: Special distilling flask, centrifuge, sep. funnels

Yield: 3-5%

Degree of purification: At least 10^4 from all fission products except rhodium.

Procedure:

(1) Cut out the central portion of the target and boil with conc HCl to dissolve it and to expel Ge.

(2) Add 5 mg I^- and IO_3^- and boil the solution again to expel iodine.

(3) Add 20 mg Os, Ir, Pt and Au carriers plus 20 mg Ba, Ru, Rh and Pd carriers. Withdraw a 20% aliquot for later determinations of Ba, Ru, and Rh.

(4) Place the remaining solution in a special all-glass distilling flask having a thistle tube entry and an air entry. Add concentrated HNO_3 through the thistle tube, and distill OsO_4 into 6 N NaOH in an ice bath. (Save for Os determination (76-1).

(5) Place the residue from the Os distillation in a beaker, add 10 ml 70% $HClO_4$ and boil the solution to fumes of $HClO_4$ to expel Ru.

(6) Dilute the solution, add 5 mg more Ru carrier, and 5 mg more I^- and IO_3^- and repeat the fuming.

(7) Add one ml dilute HCl, dilute the solution to 4 N and extract twice with equal volume butyl acetate to decontaminate from Hg and from Au.

(8) Dilute the solution to ~0.5 N in H^+, add 5 ml dimethylglyoxime solution (1% in alcohol) and filter off the palladium ppt.

(9) Add conc HCl to supn to make ~5N. Add $SnCl_2$ dropwise until the cherryred of Pt^{++} is apparent.

(10) Extract the Pt with three equal portions of butyl acetate.

(11) Fume the aqueous layer with $HClO_4$ to prepare for the pyridine extraction of Rh and Ir. (CAUTION: Since the solution contains organic material (dimethylglyoxime and butyl acetate), care must be taken to avoid an explosion. Following the method of Noyes and Bray for destroying organic material with $HClO_4$ add HNO_3 to the solution, evaporate on a steam bath for one-half hour, then

heat gently to fumes of $HClO_4$. Add an additional 10 ml of $HClO_4$ and fume the solution strongly for several minutes to destroy the chloride complex of Rh and Ir.

(12) Cool the solution, dilute to 4 N and add 20 ml pyridine.

(13) Boil the solution for five minutes, place in a separatory funnel, and add 19 N NaOH to separate the free-base pyridine layer (the high concentration of NaOH is merely to keep the volume low.)

(14) Wash the dark blue pyridine layer three times with equal volumes of dilute HCl, separating the layers each time with 6 N NaOH.

(15) Add a few drops of 6 N NaOH to the pyridine layer and evaporate the pyridine off.

(16) Pass H_2S into the boiling alkaline solution for several minutes, while the solution is acidified dropwise with HCl. Sulfides of Rh and Ir ppt.

(17) Dissolve the ppt in a little aqua regia, and fume strongly with conc H_2SO_4 to convert completely to the sulfate complex.

(18) Dilute the solution with water twenty to one, boil and ppt Rh metal by adding $TiCl_3$ dropwise until a very slight excess is present.

(19) Dilute the supn (containing Ir) to 0.5 N in H^+; cool in ice and ppt Ti with cupferron. Filter off.

(20) Add 5 mg Pd and Pt carriers and ppt the Pd dmg. Discard.

(21) Heat the supernatant to boiling and neutralize to the brom cresol purple end-point with $NaHCO_3$ solution, adding bromate to oxidize the iridium up to the plus four state. Hydrated IrO_2 is precipitated leaving Pt in solution.

(22) Dissolve the ppt in a little conc HCl, and add a few mg of Rh carrier.

(23) Fume with H_2SO_4 and repeat the Rh pptn with $TiCl_3$ (steps 18-21). Although the $TiCl_3$ pptn of Rh leaves only about 0.1% of the Rh in solution, Rh activity may be 10^4 times as high as that of Ir and hence a single separation may still leave several times as much Rh activity in solution as Ir activity.)

(24) After the Rh pptn, ppt metallic Ir from the HCl solution of the IrO_2 by addition of powdered magnesium.

(25) Weigh the Ir to determine chemical yield and count.

Remarks:

Rh, Ir, and Pt should be separated from one bombardment leaving Os, Ru and Pd for a second bombardment unless several people are cooperating on the procedure.

The yield of activity of Os, Ir, and Pt is very low in comparison with

that of the other platinum metals and many other fission products formed in the bombardment. This fact necessitates, for Ir and Pt, rigorous and repeated decontamination procedures which result in low chemical yields.

For other platinum metal-fission product separations see:

Platinum; 78-3
Osmium; 76-1
Ruthenium; 44-2
Rhodium; 45-1
Palladium;46-5

This procedure should be practiced several times before actually applying it to a bombardment, since in several of the steps the conditions for separation are quite critical. For this reason and for its poor chemical yield, this procedure is not considered a good procedure. To date, however, it is the best procedure that has been worked out for making the required separations. It is an acceptable procedure from which some radioactivity data may be obtained and can serve as a starting point for work on other, better procedures.

CHEMICAL SEPARATIONS

Element separated: Iridium

Procedure by: Chu

Target material: Rhenium

Time for sep'n: ~1 hour

Type of bbdt: 60"

Equipment required: distilling flask

Yield: 70%

Degree of purification: Factor of 100 from other activities present

Advantages: Simple

Procedure:

(1) Pour the Re powder into the distilling flask.

(2) Add 10 mg Os carrier and close the flask.

(3) Insert the outlet tube of the flask into ice cold 6 N NaOH soln (10 cc).

(4) Introduce 3 cc conc HNO_3 through the inlet tube of the flask.

(5) Supply a little air through the inlet tube and heat the flask gently for the solution of Re and the distillation of OsO_4 for about 10 min.

(6) Add 10 mg Ir carrier to the Os-removed "target" soln and evaporate to dryness.

(7) Take up the residue with 3 cc H_2O and add 5-6 cc conc. formic acid.

(8) Heat in boiling H_2O bath for 10-15 min.

(9) Centrifuge the pptd Ir. Reprecipitation may be used for further purity but usually is not necessary.

Remarks: For osmium separation from same target see (76-2).

CHEMICAL SEPARATIONS

Element separated: Platinum

Procedure by: Wilkinson, Hicks

Target material: Pt, Ir, Au, Hg

Time for sep'n: 1 hr.- 4 hrs.

Type of bbdt: 60", 184" bombardments

Equipment required: sep. funnel

Yield: ∽ 100%

Degree of purification: Decontaminates well from Au, Ir, & Hg

Advantages: Carrier free Pt can be obtained pure.

Procedure:

(1) Dissolve targets (except Ir) in HCl with minimum of HNO_3. (For Ir see 77-1).

(2) Add Au, Hg, Pt & Ir carriers as needed. Extract the solution with at least equal volume ethyl acetate twice to get rid of Au (chloride concentration need only be above 1 N), with gold added for the second extraction.

(3) Destroy all nitrate with hydroxylamine, or hydrazine, then add 0.1 gm. $SnCl_2$. Centrifuge out any ppt (Hg_2Cl_2). The red color is $PtCl_4^{=}$ which is extracted into ethyl acetate.

(4) Organic layer is washed twice with equal volume 6 N HCl, then evaporated to dryness.

(5) Residue is taken up in 2 N HCl, Pt metal is precipitated with magnesium metal in form of powder or dust. (Don't use Zn since forms slow dissolving sponge.)

Remarks: See G. Wilkinson, Phys. Rev., 73, 252 (1948). Also see G. Wilkinson, Phys. Rev. 75, 1019 (1949).

6/25/49

CHEMICAL SEPARATIONS

Element separated: Platinum

Procedure by: Thompson & Rasmussen

Target material: Iridium foil

Time for sep'n: 1/2 hr.

Type of bbdt: 184" protons (any energy)

Equipment required:
small porcelain crucible
transfer pipettes
centrifuge tube

Yield: ∿ 70% depending upon step (3)

Degree of purification: at least factor of 100

Advantages: A simple, reasonably fast procedure for solution and separation with a target metal (Ir) extremely resistant to dissolution in aqua regia.

Procedure:

(1) Make a melt of KOH and KNO_3 (∿ 50-50, not critical) in a small porcelain curcible, heating strongly over a Fisher burner.

(2) To this hot flux add the target Ir metal, continuing to heat (and adding KOH if volume of flux gets too small) until the metal is completely dissolved. (for a small strip of 1 mil foil this should take no longer than 5-10 min.)

(3) Allow flux to cool, then leach for ∿5 min. with conc. HCl, adding Au and Pt carriers in small amount. (Ir gives strong blue colored sol'n)

(4) Extract twice with ethyl acetate to remove Au.

(5) Add a little $SnCl_2$ solution in HCl to the aqueous phase until a dark red coloration (H_2PtCl_4) indicates the reduction of Pt from +4 to +2 state is complete (See remarks.)

(6) Extract the red coloration (Pt) into ethyl acetate. Wash organic layer twice with equal volume of 3N HCl.

(7) Plate organic layer & flame.

Remarks:

As most Ir foil contains about ∿ 1% Pt inpurity, it is well to provide a step for extraction of Au activities, whether or not the Au is desired for later work, even if it is simply a proton bombarded Ir.

On $SnCl_2$ reduction the strong blue coloration of Ir(+6?) disappears, permitting the red of reduced H_2PtCl_4 to be seen.

By spending more time leaching the melt in (3) and by using several portions of leaching agent the chemical yields might be made almost quantitative.

For Au sep'n from same target see (79-4).

For Ir sep'n from same target see (77-2).

Tl if present should be checked for interference with this procedure.

CHEMICAL SEPARATIONS

Element separated: Platinum

Procedure by: Wolfe

Target material: Uranium metal (~1 gm)

Time for sep'n: ~1 1/2 days when separated with Ir & Rh.

Type of bbdt: 388 Mev alphas

Equipment required: Special distilling flask, centrifuge, sep. funnels, standard

Yield: ~ 5 %

Degree of purification: At least 10^4 from all fission products. No impurities detected in radioactivities.

Procedure:

(1) Cut out the central portion of the target and boil with concentrated HCl to dissolve it and to expel Ge.

(2) Add 5 mg I^- and IO_3^- and boil the solution again to expel iodine.

(3) Add 20 mg Os, Ir, Pt, and Au carriers plus 20 mg Ba, Ru, Rh and Pd carriers. Withdraw a 20% aliquot for later determinations of Ba, Ru and Rh.

(4) Place the remaining solution in a special all-glass distilling flask having a thistle tube entry and an air entry. Add concentrated HNO_3 through the thistle tube, and distill OsO_4 into 6 N NaOH in an ice bath. (Save for Os determination (76-1)).

(5) Place the residue from the Os distillation in a beaker, add 10 ml 70% $HClO_4$ and boil the solution to fumes of $HClO_4$ to expel Ru.

(6) Dilute the solution, add 5 mg more Ru carrier, and 5 mg more I^- and IO_3^- and repeat the fuming.

(7) Add one ml dilute HCl, dilute the solution to 4 N and extract twice with equal volume butyl acetate to decontaminate from Hg and from Au.

(8) Dilute the solution to ~ 0.5 N in H^+, add 5 ml dimethylglyoxime solution (1% in alcohol) and filter off the palladium ppt.

(9) Add conc HCl to supn to make ~ 5 N. Add $SnCl_2$ dropwise until the cherryred of Pt^{++} is apparent.

(10) Extract the Pt with three equal portions of butyl acetate.

(11) Wash the platinum out of the organic layer with 6 N NaOH, acidify to 5 N HCl and reextract into butyl acetate. Repeat cycle.

(12) Wash Pt from organic layer into 6 N NaOH and ppt PtS from this alkaline solution gradually acidified to 6 N.

(13) Dissolve the sulfide ppt in aqua regia, make alkaline and scavenge

twice with 5 mg pptns of $La(OH)_3$.

(14) Buffer the supn with acetate and scavenge three times with 1 mg pptns of Mo and Pd with 8-hydroxy quinoline.

(15) Make solution acid and ppt platinum metal with powdered magnesium. Weigh the metal to determine chemical yield and plate.

Remarks:

Rh, Ir and Pt should be separated from one bombardment leaving Os, Ru and Pd for a second bombardment unless several people are cooperating on the procedure.

The yield of activity of Os, Ir, and Pt is very low in comparison with that of the other platinum metals and many other fission products formed in the bombardment. This fact necessitates, for Ir and Pt, rigorous and repeated decontamination procedures which result in low chemical yields.

For other platinum metal-fission product separations see:

Iridium: 77-3
Osmium: 76-1
Ruthenium: 44-2
Rhodium; 45-1
Palladium; 46-5

8/16/49

CHEMICAL SEPARATIONS

Element separated: Gold

Procedure by: Wilkinson, Hicks

Target material: Pt, Ir, Hg, Au

Time for sep'n: 1/2 hr - 4 hrs.

Type of bbdt: 60" or 184" cyclotron

Equipment required: sep. funnel

Yield: ~ 100%

Degree of purification: Decontaminates well from Pt, Ir & Hg.

Advantages: Carrier free Au can be obtained pure within 15-20 min. after solution of target.

Procedure:

(1) Dissolve Pt, Au, or Hg in aqua regia.
To dissolve Ir metal: (see 77-1).
($AuCl_3$ carrier may be added here)

(2) Chloride ion must be greater than 6 N (Hg extracts), and the solution shaken with an equal volume of ethyl acetate (gold in organic layer) and layers separated.

(3) Wash ethyl acetate layer twice with equal volume 6 N HCl.

(4) Evaporate ethyl acetate layer to dryness & take up residue in 1 N HCl.

(5) Bubble in SO_2 to reduce Au^{+3} to Au in the hot.

Remarks: See: G. Wilkinson, Phys. Rev. 73, 252 (1948)
See also: G. Wilkinson, Phys. Rev. 75, 1019 (1949)

CHEMICAL SEPARATIONS

Element separated: Gold

Procedure by: R. W. Fink

Target material: Tracer mercury

Time for sep'n: ∽ 10 min.

Type of bbdt: Milking experiment

Yield: Can be quantitative if several extractions made.

Degree of purification: at least 10^3 from Hg activity present.

Procedure:

(1) Take Hg tracer in 4 ml of ∽ 3 N HCl and extract with 500 λ of isoamyl acetate. (The presence of at least 0.1 N Cl^- is required for a sepn from Hg.) - Au into the organic layer.

(2) Wash the organic layer with equal volume sat NH_4Cl sol'n to insure sep'n from Hg.

(3) Plate organic layer for Au sample.

Remarks: Tl if present will follow Au in the solvent extraction.

7/12/49
P-18-52

CHEMICAL SEPARATIONS

Element separated: Gold (quick procedure)

Procedure by: Thompson & Rasmussen

Target material: Gold in leaf form (.004 mil)

Time for sep'n: 4-10 min.

Type of bbdt: 184" High energy protons.

Equipment required: Centrifuge tube. Micro-pipettes

Yield: ~100%

Degree of purification: Adequate separation from Hg and spallation products, at least factor of 50.

Advantages: Extreme speed and simplicity combined with reasonable purification.

Procedure:

(1) Dissolve Au in warm 6N aqua regia (2N HNO_3, 4N HCl) in centrifuge tube. Work in small volume (1-2 ml.)

(2) Add hold-back carriers for Hg, Pt, Ir, and Os (~1 mg each).

(3) Add (1 to 1/2 ml.) ethyl acetate. Agitate, mixing phases with transfer pipette. (Yellow color of gold quantitatively extracts into organic phase.)

(4) Wash the separated ethyl acetate phase once or twice with 6 N aqua regia. (Any wash of high chloride concentration serves to remove Hg, although Tl if present may not be entirely washed out.)

(5) The solution of Au in ethyl acetate may now be rapidly evaporated on a plate for counting or subjected to further specific gold chemistry.

Remarks: A further procedure of very specific gold chemistry, according to Wilkinson, but of lower yield ~50% is as follows: Precipitation of Au as the metal by SO_2 reduction, bubbling SO_2 through a warm 2N HNO_3 solution of the dissolved gold. The ppted Au can be redissolved in aqua regia & extracted with ethyl acetate for counting.

Getting the Au from ethyl acetate into 2 N HNO_3 preliminary to the SO_2 ppt'n can be done in several ways, such as, (a) evaporation of ethyl acetate - Au sol'n (Use hot plate for ethyl acetate is flammable) and taking residue up with 2N HNO_3, or (b) adding 1 N KOH to ethyl acetate - Au sol'n, taking Au back into aqueous phase (and also introducing loss by formation of some insoluble Au oxide), then separating the phases and making the aqueous about 2N acid by adding HNO_3.

7/27/49
P-18-77

CHEMICAL SEPARATIONS

Element separated: Gold

Procedure by: Thompson & Rasmussen

Target material: Iridium foil

Time for sep'n: 20 min-1/2 hr.

Type of bbdt: 184" (any energy)

Yield: ~70%, depending on leach

Degree of purification: at least 100

Advantages: A simple, reasonably fast procedure for solution and separation with a target metal (Ir) extremely resistant to dissolution in aqua regia.

Procedure:

(1) Make a melt of KOH and KNO_3 (~50-50, not critical) in a small porcelain crucible, heating strongly over a Fisher burner.

(2) To this hot flux add the target Ir metal, continuing to heat (and adding KOH if volume of flux gets too small) until the metal is completely dissolved. (for a small strip of 1 mil foil this should take no longer than 5-10 min.)

(3) Allow flux to cool, then leach for ~5 min. with conc. HCl, adding Au and Pt carriers in small amount. (Ir gives strong blue colored sol'n)

(4) Extract twice with ethyl acetate to remove Au.

(5) Combine organic layers and wash twice with equal volume 3N HCl.

(6) Plate organic layer and flame.

Remarks:

As most Ir foil contains about ~1% Pt impurity, it is well to provide a step for extraction of Au activities, whether or not the Au is desired for later work, even if it is simply a proton bombarded Ir.

On $SnCl_2$ reduction the strong blue coloration of Ir(+6?) disappears, permitting the red of reduced H_2PtCl_4 to be seen.

By spending more time leaching the melt in (3) and by using several portions of leaching agent the chemical yields might be made almost quantitative.

For Ir sep'n from same target see (77-2).

For Pt sep'n from same target see (78-2).

Tl if present should be checked for interference with this procedure.

7/27/49

P-18-118

CHEMICAL SEPARATIONS

Element separated: Mercury

Procedure by: R. W. Fink & D. G. Karraker

Target material: Platinium

Time for sep'n: 60 minutes

Type of bbdt: 65 Mev α-particles for 3 hours

Equipment required: Standard

Yield: ~ 70%

Degree of purification: Excellent - factor of at least 100 from activities present.

Procedure:

(1) Pt target dissolved in 4 cc aqua regia in a porcelain crucible. 50 μgr Au and Hg carriers added. Sol'n evaporated to expell HNO_3.

(2) Extracted 5 times with 1/5 volume of isoamyl acetate in presence of at least 0.1-N HCl. The isoamyl acetate layer contains gold free from mercury.

(3) The aqueous layer has excess $SnCl_2$ added to ppt Hg_2Cl_2. The Pt is reduced to a beautiful red Pt^{++} color. The ppt is washed until free of this color.

(4) The ppt is dissolved in dil. aqua regia and used as the mercury fraction.

Remarks: (a) Recycling will improve purity, although this method has been shown to give excellent radiochemical purity.

7/14/49

CHEMICAL SEPARATIONS

Element separated: Mercury

Procedure by: R. W. Fink

Target material: Gold

Time for sep'n: 70 min.

Type of bbdt: 60 Mev protons

Equipment required: Standard

Yield: Near 80-90%

Degree of purification: Excellent - factor of 100 from activities present.

Procedure:

(1) The gold target is dissolved by heating in 4 cc hot, conc. aqua regia. Pt and Hg carrier (50 µg) are added. Five or more extractions with isoamylacetate, 3 cc each portion are made. The Gold will be found in the organic layer.

(2) The aqueous layer is boiled to near dryness with conc. HCl to expell HNO_3, and excess $SnCl_2$ added to ppt. Hg_2Cl_2, which is then washed until free from red Pt^{++} color.

(3) The Hg_2Cl_2 ppt is then redissolved in 2 cc dil. aqua regia, and used as the mercury fraction.

Remarks:

(a) The isoamyl acetate extraction of gold from mercury is quantitative in presence of 0.1 N or more chloride. This is the method used to milk gold daughters from the mercury fraction.

7/12/49

P-18-49

CHEMICAL SEPARATIONS

Element separated: Mercury

Procedure by: R.W. Fink & S. G. Thompson

Target material: Gold or platinum

Time for sep'n: from 1 to 5 min.

Type of bbdt: Protons on gold or α-particles on Pt, but not vice versa

Equipment required: mercury volatilizer (see astatine boiler)

Yield: Enough activity to work with but by no means quantitative. For more yield heat longer.

Degree of purification: Extremely pure.

Advantages: For short Hg half-lives when quick samples are desired for counting. Definitive purity.

Procedure:

(1) The target is introduced into the chamber of the Mercury vaporizer. A thin Pt collecting plate is put on the bottom of the water-cooled cold-finger with duco cement.

(2) The Hg is then vaporized by a bunsen flame, and is collected in high specific activity on the plate.

Remarks:

(a) Caution must be exercised not to open the vaporizer until it has thoroughly cooled, lest the hands become covered with unwashable mercury activity which spews forth when the vaporizer is hot.

(b) The vapor pressure of Hg at only 400°C is 1574.1 mm of Hg, over 2 atm.; while that of molten gold at 1292° C is only 0.001 mm. Hence, at 1000° K, a complete separation is attained.

Tl if present will follow the Hg in this procedure

7/12/49

P-18-55

CHEMICAL SEPARATIONS

Element separated: Mercury

Procedure by: Prohaska

Target material: Au

Time for sep'n: Two or more days

Type of bbdt: Neutron capture in pile

Equipment required: separatory funnels, + ordinary beakers, flask, etc.

Yield: ? probably 60-80%

Degree of purification: ~ 95-98%

Advantages: Will separate 5-10 mg of Hg from 100 g of Au.

Procedure:

(1) Dissolve sample (assume 100 gms of Au) in 250 ml hot conc. HCl and minimum HNO_3 under (air cooled) reflux condenser.

(2) When sample completely dissolved, dilute to 500 ml (approx 6 M H^+). Extract with four successive 200 ml portions of ether.

(3) Add NaOH to H_2O portion until pH $\cong$ 1. Add H_2S and ppt Au_2S_3 + HgS. Centrifuge.

(4) Dissolve HgS + Au_2S_3 in (minimum) 6 N HCl + drops conc. HNO_3, volume of solution should be less than 100 ml at this point.

(5) Extract with successive 50 ml portions of ether until no yellow color of $AuCl_4^-$ observable in H_2O portion.

(6) Extract with 2 additional 50 ml portions of ether.

(7) Again reduce pH to $\cong$ 1 with NaOH and ppt HgS with H_2S.

(8) Repeat the solution and extraction procedure.

Remarks:

In the three ether extractions, an estimated 20%-30% of the $HgCl_2$ would be extracted along with the $AuCl_3$. Working up these extracts for Hg would probably increase total yield of Hg separated.

It appears doubtful that purity of Hg reported would be increased by further solution and extraction.

8/24/49

P-18-260

CHEMICAL SEPARATIONS

Element separated: Thallium

Procedure by: Brooks

Target material: $HgNO_3$

Time for sep'n: 5 min.

Type of bbdt: Linac 2 min. of 30 Mev protons

Equipment required: 40 cc test tube

Yield: 20%

Degree of purification: good

Advantages: Fast -

Procedure:

(1) Dissolve target in 20 cc sat. KI (hot)

(2) Add 2 cc of H_2O containing 20 mg Tl NO_3. Shake well.

(3) Pour off $HgI_4^{=}$ sol'n, dry ppt and count.

Remarks: $HgNO_3$ decomposes somewhat even in a 2 min. bombardment. Don't use it in a cyclotron! The Linac targets are not in a vacuum.

6/16/49

CHEMICAL SEPARATIONS

Element separated: Thallium

Procedure by: Orth & Meinke

Target material: Gold foil

Time for sep'n: ∿ 30 min.

Type of bbdt: 60" α bbdt.

Equipment required: Standard

Yield: ∿ 90%

Degree of purification: At least factor of 10 from other activities present.

Procedure:

(1) Dissolve Au target in aqua regia (1:9 HNO_3 to HCl) add (5 mg. Tl^+ carrier and 5 mg Hg^{++} carrier.

(2) Add $NH_2OH \cdot HCl$, ppt Au metal & reduce to Hg_2^{++}, Tl^+.

(3) Neutralize with Na_2CO_3 (keep cool!) ppt Hg_2CO_3.

(4) To sup'n add sat. soln of KI or few drops of HI, precipitating TlI.

Remarks: The 90% yield can readily be obtained if the Tl is plated from the sol'n of (3). If the Tl is ppt as TlI yield may be only ∿ 75%.

7/12/49
P-18-48

CHEMICAL SEPARATIONS

Element separated: Thallium

Parent material: Lead

Milking experiment

Procedure by: Neumann

Time for sep'n: 10 min.

Equipment required: no special equipment

Yield: ~ 96%

Degree of purification: < 0.01% Pb contamination

Advantages: Extremely good Pb-Tl separation

Procedure:

(1) Pb to be milked kept in 10 ml of 6 N HCl solution. Tl carrier may be added if desired, but is not necessary. Add 3 or 4 drops of $KMnO_4$ solution to insure oxidation of Tl to Tl^{+++}. Stir solution until loss of brown color.

(2) Add 10 ml of HCl saturated diethyl ether. (The ether can be conveniently prepared by shaking with conc. HCl and allowing the two layers to stand in contact until ether is needed). Stir about 3 min. Centrifuge. Remove ether layer containing the Tl^{+++}.

(3) Extract a second time by same method. Combine ether layers.

(4) Wash ether with 10 ml portion of 6 N HCl. Centrifuge. Transfer ether to new tube.

(5) Evaporate ether with jet of air to convenient volume. If entire sample is to be counted, the remaining ether can be evaporated on counting plate. If only an aliquot is desired, evaporate to dryness and take up residue in desired volume of water. Addition of a drop HNO_3 and heating will help in obtaining complete solution.

Remarks:

Tl^+ does not extract. Addition of $KMnO_4$ to insure oxidation to Tl^{+++} is important.

Since the time for separation is quite long for a milking procedure, the steps prior to final separation should be done at the same relative time intervals in each milking.

Two extractions give > 99% yield. The washing with HCl removes ~4% of Tl. The overall yield of Tl is reproducible. 3 yr Tl^{204} can be used conveniently as a tracer to determine chemical yield.

8/12/49
P-18-145

CHEMICAL SEPARATIONS

Element separated: Lead

Procedure by: Karraker

Target material: Thallium

Time for sep'n: ~ 1 hour

Type of bbdt: 60-80 Mev D^+ or H^+

Equipment required: No special equipment

Yield: ~ 95%

Degree of purification: Good, factor of at least 100.

Advantages: One-step is usually sufficient purification.

Procedure:

(1) Dissolve Tl target in 6 M H_2SO_4 the smallest amount possible. Add 5 mg Pb carrier, also 5 mg Hg carrier as hold-back.

(2) Evaporate solution over a hot plate, with an air-jet blowing on the top of the solution, till fumes of SO_2 appear and the solution is quite concentrated.

(3) Dilute carefully with 2 volumes of H_2O. $PbSO_4$, white ppt, appears. Wash ppt with 2 M H_2SO_4, then with H_2O. If desired, this may be dissolved in NH_4Ac and reppted as $PbCrO_4$. However, it is usually sufficiently pure without further steps.

Remarks: Add conc H_2SO_4 to water, not water to acid!!

7/14/49

CHEMICAL SEPARATIONS

Element separated: Lead

Procedure by: Neumann

Parent material: Bismuth (20 mg or less carrier)

Time for sep'n: 5 min for separation, 15 min. for purification

Milking experiment

Equipment required: no special equipment

Yield: ~ 85%

Degree of purification: <0.05% Bi contamination

Procedure:

Bi purified, final step being precipitation as BiOCl (obtainable by method listed in steps 1-3.) (Can dissolve Bi from Ni foil of 83-1 and proceed with BiOCl pptn and step (1) below.)

(1) Dissolve in few drops conc. HNO_3. Add 10 mg Pb carrier (preferably $Pb(NO_3)_2$. Add 3 drops conc. HCl. Dilute to ~ 8 ml.

(2) Add NH_3 dropwise until permanent precipitate just forms, and then HNO_3 dropwise until solution just clears.

(3) At desired time for milking dilute to 45 ml and heat in water bath for a few minutes. Fine crystals of BiOCl should form. Centrifuge, and retain BiOCl for future milkings.

(4) To the supernatent add a drop of NH_3. If the solution remains clear you have obtained a good separation.

(5) Add 2-3 ml of $Na_2Cr_2O_7$ solution to cause precipitation of $PbCrO_4$. Centrifuge, and discard supernatent.

(6) Dissolve $PbCrO_4$ by addition of 2 ml 4 N HCl and one drop 30% H_2O_2. Heat in water bath to destroy excess H_2O_2.

(7) Add 20 mg inactive Bi carrier and repeat BiOCl separation by above methods. Repeat precipitation of $PbCrO_4$.

(8) Dissolve $PbCrO_4$ as in step (6).

(9) Dilute to any desired volume and mount aliquots for counting. The results are reproducible, and chemical yield determinations are not necessary. If the latter are desired, proceed with step 10:

(10) Add 5 ml conc H_2SO_4. Evaporate to fumes of SO_3. Resulting volume will be 2-3 ml. Cool. Dilute carefully to ~ 40 ml. Cool. Filter, dry, and weigh $PbSO_4$.

Remarks:

Any single precipitation of BiOCl under these conditions gives a yield of 98-99% Bi, with 8% of the Pb retained with the Bi. One Bi scavenge of the separated Pb should be sufficient purification from the parent.

In calculating the life of the parent from consecutive milkings of the same Bi solution correction should be made for the 8% of the daughter retained with the parent.

Purification of Pb as $PbSO_4$ gives varying yields, and determination of chemical yield by weighing is necessary.

Where the Pb fractions will be further milked for Tl (81-3) stop at step (8).

CHEMICAL SEPARATIONS

Element separated: Lead

Parent material: Polonium

Milking Experiment

Yield: 95-100%

Procedure by: Karraker

Time for sep'n: 5 min.

Equipment required: Standard

Degree of purification: factor of 10^6 from Po with two washes.

Procedure:

Po is in 20% tributyl phosphate in dibutyl ether mixture. To milk solution:

(1) Extract with equal volume of 6 N HCl. Bi & Pb go into water phase.

(2) Wash HCl extract twice with 1/10 its volume of tributyl phosphate solvent. Add the first portion to the Po sol'n, then discard 2nd portion.

(3) Add 1/2 mg Bi and 1/2 mg Pb carrier, (pptn made from ~ 4 cc volumes.)

(4) To separate Bi and Pb, the procedure is almost identical with that of Neumann. (82-2).

(5) Thallium daughters of the Pb may be separated by oxidation and extraction with ether. (81-3).

CHEMICAL SEPARATIONS

Element separated: Bismuth

Procedure by: Neumann

Target material: Pb

Time for sep'n: 15 min from solution of target up to plating step

Type of bbdt: protons or deuterons 184" or 60"

Equipment required: no special equipment

Yield: see remarks

Degree of purification: Good separation from Pb and Tl at least factor of 10^4. Interference from noble metals.

Advantages: Rapid separation when looking for short half-lives. Prepares carrierless samples for pulse analysis, or high specific activity samples for mass spectrograph or β-ray spectrometer.

Procedure:

(1) Dissolve Pb target in 6 N HNO_3. Keep volume as small as possible. Add water if necessary to give complete solution.

(2) Add 8 N NaOH dropwise until formation of $Pb(OH)_2$. Add HNO_3 dropwise until solution just clears.

(3) Place Ni foil in solution. Bi will electrochemically replace Ni on foil. Keep solution warm, and stir continuously to obtain highest yields. See remarks.

(4) α counting and pulse analysis can be done directly from Ni foil after washing well and drying. Ni foil should be given protective coating (label shellac is satisfactory) on one side so that activity plates on only the unprotected side.

(5) To prepare sample for mass spectrograph or β-ray spectrometer, remove Ni foil from solution when desired amount of activity is obtained and wash well. Dissolve Ni foil in HNO_3. Add 50 μ grams Bi carrier and 20 mg La carrier. Precipitate $La(OH)_3$ and $Bi(OH)_3$ by addition of NH_3. Wash precipitate with water and 1 drop NH_3. Dissolve in few drops HCl, dilute to 0.3 N HCl, and pass H_2S into solution. Bi_2S_3 precipitates. Further disposition of sample depends on type of mounting necessary for instrument.

Remarks: As a rough indication of yields to be expected, a volume of ~40 ml, heated to ~ 85°C, and stirred slowly with mechanical stirrer gives these yields at various time intervals: 5 Min. 10%; 15 min. 25%; 45 min. 65%.

This procedure does not give separation from metals more easily reduced than Bi. Among spallation product impurities will be Au, Hg, and Pt metals. Among fission product impurities will be Cu, Ag, Pt metals, and Sb. Separation from Po will also not be made if it is produced in bombardment.

8/12/49
P-18-148

CHEMICAL SEPARATIONS

Element separated: Bismuth

Procedure by: Karraker

Parent material: Polonium

Time for sep'n: 5 min.

Milking experiment

Equipment required: Standard

Yield: 95-100%

Degree of purification: Factor of 10^6 from Po with two washes

Procedure:

Polonium is in 20% tributyl phosphate, 80% dibutyl ether mixture. To milk solution:

(1) Extract with equal volume of 6 N HCl. Bi and Pb go into acid phase.

(2) Wash HCl extract twice with 1/10 its volume of tributyl phosphate solvent. Add the first portion to the Po soln, discard the second portions.

(3) Add 1/2 mg Bi and 1/2 mg Pb carrier (pptns made from ~ 4 cc volumes).

(4) To separate Bi and Pb, the procedure is almost identical with that used by Neumann (82-2).

(5) Thallium daughters of the lead may be separated by oxidation and extraction with ether (81-3).

CHEMICAL SEPARATIONS

Element separated: Bismuth

Parent material: Tracer Pa^{228} and daughters

Milking experiment

Procedure by: Meinke

Time for sep'n: ~ 1 1/2 hours

Equipment required: Centrifuge, stirrers, tank H_2S

Yield: ~ 60%

Degree of purification: Factor of at least 10^3 from Pa and at least 100 from other activities. Factor of at least 5 from Pb.

Disadvantages: Gives a thick plate - rather bad for alpha pulse analysis.

Procedure: Purified tracer Pa in benzene - TTA solution (procedure 91-1 with DIPK and TTA extractions only).

(1) Stir organic layer 10 min with equal volume 6 N HCl (daughtor into acid layer - most of Pa remains with organic layer).

(2) Wash the acid layer three times with double volume .4 M TTA in benzene, stirring 5 min each. (Removes Pa).

(3) Dilute acid layer to ~ 2 N and add ~ 1/2 mg Bi carrier. Bubble in H_2S gas to ppt Bi and Pb sulfides. Centrifuge.

(4) Again add 1/2 mg Bi carrier and repeat sulfide pptn. Centrifuge and combine ppts of (3) and (4).

(5) Dissolve sulfide ppts in few drops hot conc. HCl. Dilute to at least 1 N acid and reppt sulfides by bubbling in H_2S. Centrifuge.

(6) Repeat step (5), four times.

(7) Dissolve sulfide ppt in few drops conc HCl, dilute to ~ 6 cc and boil to rid solution of H_2S.

(8) Add 1 mg Pb carrier and ppt $PbSO_4$ by adding some SO_4^{-2} (H_2SO_4, $(NH_4)_2SO_4$, etc.) Discard prepicitate.

(9) Repeat step (8) three times.

(10) Add H_2S to supn from last pptn and centrifuge out the Bi_2S_3 formed.

(11) Dissolve the Bi_2S_3 in hot conc. HCl, dilute to known volume and plate aliquot for counting. Caution: Do not flame the $BiCl_3$ plate or much of the activity may be lost.

Remarks:

In step (3) if the acidity is greater than 2 N the Bi will not ppt.

See Prescott and Johnson's Qualitative Chemical Analysis (1933) p 157 for notes on $PbSO_4$.

In some experiments no Bi - Pb sepn is required and the solution of step (7) can be plated directly.

CHEMICAL SEPARATIONS

Element separated: Polonium

Procedure by: Karraker

Target material: Lead

Time for sep'n: 1 1/2 - 2 hrs.

Type of bbdt: 380 Mev He^{++}

Equipment required: SO_2 tank

Yield: 80-90%

Degree of purification: Very good - less than 1% impurity.

Advantages: Po is separated in a carrier-free state.(1)

Procedure:

(1) Dissolve target in 6 N HNO_3.

(2) Heat over a burner until the solution is evaporated to conc. HNO_3 (fuming). $Pb(NO_3)_2$ ppts and may be centrifuged off. Extract twice with equal volume amyl acetate. This removes Tl, Hg, & Au.

(3) Add 1-2 mg Bi & Tl holdback, then fume with HCl (over a burner) till HNO_3 is destroyed. It will be necessary to take the solution down to a very small volume, add about 8 or so portions of conc. HCl to accomplish this. Dilute the solution by adding 2 volumes of H_2O.

(4) Add ~ 1 mg Te carrier. Ppt Te with a few drops of conc $SnCl_2$ soln. Centrifuge the Te off. This ppt carries Po and At.

(5) Dissolve Te in 1 drop conc. HNO_3, then add 1/2 cc conc. HCl.

(6) Pass in SO_2 from tank into sol'n in a hot water-bath. Te ppts, carrying At. The sol'n now is about 6 N in HCl (constant boiling mixture), and contains the Po.

(7) Centrifuge off Te. It may be necessary to use Aerosol to coagulate or transfer sol'n to several test tubes to eliminate Te.

(8) Extract sol'n with an equal volume of 20% tributylphosphate in dibutyl ether. Po goes into the organic layer. Wash organic layer twice with 6 N HCl to thoroughly decontaminate from Bi.

(9) Sample may be prepared by plating a drop of organic sol'n, or by extracting Po back out with conc HNO_3. Then dilute the HNO_3, and chemically plate Po on a small piece of clean Ag.

Remarks: Step (3) is very slow and tedious, but cannot be avoided, since Pb metal can be dissolved only in HNO_3. It should be noted the Pb is almost untouched in conc. HNO_3, due to the extreme insolubility of $Pb(NO_3)_2$ in fuming HNO_3. About 60% of the Po can be chemically plated on Ag in 10 min.

7/14/49

P-18-71

CHEMICAL SEPARATIONS

Element separated: Polonium

Procedure by: Karraker

Target material: Bismuth

Time for sep'n: 40 min to 1 1/2 hrs.

Type of bbdt: 180 Mev D^+, or 350 Mev H^+

Equipment required: Standard

Yield: 80-90%

Degree of purification: less than 1% impurity in sample

Advantages: Po separated in carrier-free state.

Procedure:

Procedure in general is the same as with Pb, except for inability to ppt Bi as the nitrate. So step (2) in Pb procedure is eliminated. It is necessary to dissolve Bi metal in HNO_3, but if Bi_2O_3 is used, this can be dissolved in HCl, and necessity for destroying HNO_3 is removed. This shortens the procedure to where it can be done as rapidly as 30 minutes.

See (84-1) for Po sep'n from Pb.

7/14/49

CHEMICAL SEPARATIONS

Element separated: Polonium

Procedure by: Barton

Milkings from At

Time for sep'n: 40 min.

Yield: ~ 90%

Equipment required: test tubes

Degree of purification: At least factor of 10

Advantages: Simplicity.

Procedure:

(1) Astatine fraction dissolved in 1-5 ml organic solvent (benzene, carbon tet., di-isopropyl ether, etc.)

(2) Wash with 1/2 ml of 2 N H_2SO_4, 0.25 N $FeSO_4$ soln. (to keep At in zero state.)

(3) Wash H_2SO_4-$FeSO_4$ layer twice with di-isopropyl ether.

(4) Extract the Po from the H_2SO_4-$FeSO_4$ layer with 20% tributyl phosphate, 80% dibutyl ether mixture.

(5) Evaporate organic layer on plate with heat lamp. Do not flame or Po will be lost.

8/11/49
P-18-175

CHEMICAL SEPARATIONS

Element separated: Astatine

Procedure by: Barton

Target material: Bi_2O_3 (~ 1/2 gm) (or thorium metal)

Time for sep'n: 15 min.

Type of bbdt: Any 184" or 60"

Equipment required: Test tube

Yield: Unknown, ~ 10%

Degree of purification: Excellent, from all α emitters formed - at least greater than 10^2.

Advantages: Simplicity

Procedure:

(1) Dissolve Bi_2O_3 sample in 1/2-1 ml conc. HCl or H_2SO_4.

(2) Add small (< 0.5 ml sufficient) amount di-isopropyl ether, mix, separate phases.

(3) Plate out organic phase and count or save for milkings.

(Use no more heat than heat lamp or 30 volts on an induction heater while working with the plate or At will be lost.)

Remarks:

Step 1. Do not use HNO_3 unless you want a small-scale explosion.

Thorium metal can be dissolved in conc. HCl and .01 N $(NH_4)_2SiF_6$ soln (Vigorous reaction once started).[1] (See 90-4).

See also AECD 1952 (Chemical Properties of Astatine; G. L. Johnson, R. F. Leiniger, E. Segrè.)

(1) See Phys. Rev. 75, 18 (1949).

8/18/49
P-18-162

CHEMICAL SEPARATIONS

Element separated: Emanation

Procedure by: Ghiorso, Meinke

Target material: Thorium metal (1 mil)

Time for sep'n: 5-15 min.

Type of bbdt: 184" protons

Equipment required: special emanation closed system with traps

Yield: Small from metal; up to 50% from solutions

Degree of purification: Free from other α activity - does not separate from other rare gases.

Procedure:

(1) Metallic strips of Th which have been bombarded with the full energy proton beam are placed in a small closed flask and heated to red heat with an induction heater for a period of one or two minutes.

(2) Argon carrier is then passed through the flask and through a trap cooled with an ice bath.

(3) The carrier and Em are then frozen out in another trap cooled with a liquid N_2 bath.

(4) The activity can be then introduced into a sealed counting chamber and counted for alpha activity.

(5) The activity can be shown to be a rare gas by transferring it back and forth from counter to trap using the liquid N_2 bath to freeze out the activity and carrier.

Remarks:

The procedure described is simple but effective in purifying the Em. If further purification is required additional traps may be used.

The same type of apparatus may be used when: (a) separating Em from a solution or (b) milking Em isotopes from other elements, e.g., Fr and At.

Care should be taken to check separation from At in these separations since in many cases, at least a small fraction of the At present acts much like a gas and may pass through the traps. A special trap to specifically remove At may be necessary in some cases.

8/12/49
P-18-177

CHEMICAL SEPARATIONS

Element separated: Francium - Element 87

Procedure by: Hyde

Target material: Thorium metal foil. Typical target - 3 foils 1/2" x 1 3/4" x .005".

Time for sep'n: 40 min. - 80 min.

Type of bbdt: 184" bbdt with 100 Mev protons to make Fr^{222} and Fr^{223}. 350 Mev proton bbdt to make 30 minute Fr^{213}

Equipment required:
centrifuge
stirrers
50 ml centrifuge cones

Yield: estimated 10-50%

Degree of purification: Clean separation from all elements except cesium

Procedure: *

(1) Drop thorium metal strips into 10 ml of hot 6 N HCl.** Add a few drops $(NH_4)_2SiF_6$ sol'n to clear up black residue. Heat with infra-red lamp until dissolved. Evaporate down to 5 ml or less.

(2) Transfer to 50 ml centrifuge cone. Cool in ice bath. Add 15 ml 6 N HCl. Centrifuge off undissolved particles.

(3) To clear supernate add 4 drops cesium carrier (20 mg Cs/ml) stir and add 1 ml 1/8 M silicotungstic acid. Stir occasionally 1 to 4 minutes. Centrifuge down ppt of cesium silicotungstate. This precipitation eliminates > 90% of total radiation.

(4) Wash ppt twice with 5 ml 6 N HCl. From here on can use either of two procedures. Procedure A is a short one useful when Fr^{222} or Fr^{223} is being studied. Procedure B is recommended for preparing 30 minute Fr^{213}.

Procedure A - For short-lived francium isotopes.

(1) A portion of or all of the silicotungstate ppt is evaporated in a small circle in the center of a platinum plate. This plate is set upon an aluminum plate and centered above a 1/2 in. hole in this plate. An asbestos washer is placed above. On top of the asbestos washer and covering the hole just above the sample plate is placed a second platinum disc, scotch taped to a 1/8 inch aluminum disc. The aluminum disc, platinum disc combination is cooled with a lump of dry ice while an oxygen torch with a small flame is touched to the bottom of the sample plate heating it strongly to red heat for 5 seconds. The cooled collector plate then bears a smooth deposit

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* This procedure is modeled quite closely after the fission product procedure for cesium described by Glendenin & Nelson in AECD 2556-C.

** HNO_3 interfers with the subsequent pptn of cesium silicotungstate.

For Th sol'n see Phys. Rev. 75 18 (1949).

of cesium as well as considerable silica and tungsten.***

(2) This deposit is slurried off the plate with dilute HCl. The silica and tungsten being insoluble are centrifuged off. The clear supernate contains the francium and can be used for chemical studies or evaporated on platinum disc for counting measurements. Usually such samples are flamed again as described above. The resulting collector plates are quite even and clean of everything except cesium. The amount of cesium originally added determines the amount of solid on the plates.

Procedure B - For further purification of 30 minute francium.

(1) Dissolve silicotungstate ppt in 1 ml of 6 N NaOH. Add 2-3 drops ferric chloride carrier. (10 mg/ml) Stir. Centrifuge down the scavenger $Fe(OH)_3$.

(2) To clear hydroxide supernate in 50 ml cone add with caution 5 ml of 70% perchloric acid. Put on safety glasses or face shield and evaporate solution by swirling over a bunsen flame until dense white fumes appear. Continue gentle heating one minute. Cool. Dilute to 10 ml. Stir. Centrifuge off silica ppt.

(3) Evaporate supernate to dense white fumes again. Cool. Cautiously add 15 ml absolute alcohol.**** Cool in ice bath. Centrifuge. Dispose of supernate immediately as it contains ethyl perchlorate which is explosive when heated. Wash ppt twice with 5 ml absolute alcohol.

(4) Cesium perchlorate ppt may be dissolved in distilled water. This is the final francium fraction. If plates are made it pays to volatilize the francium to a second plate by the technique described in A(1) in order to get very smooth deposits.

A 30 minute bombardment of 3 thorium foils 1/2" x 1 3/4" x .005" worked up by Procedure B has produced 10^7-10^{10} c/m of 30 minute francium 60 minutes after bombardment.

*** The volatility of cesium and of francium is believed to be caused by a disproportionation of the oxide to peroxide and metal. The metal distills; the peroxide decomposes to oxide and is ready for a new disproportionation.

Yields on the volatilization step vary from 25% to 90% depending on amount of solid present and other factors. With plates containing only cesium, 75% higher yields are usually obtained.

**** Alcohol is added because of the insolubility of cesium perchlorate in this solvent.

6/28/49

P-18-32

CHEMICAL SEPARATIONS

Element separated: Francium (carrier free)

Parent material: Ac^{227} in equilibrium with Th^{227}, Ra^{223}, Pb^{211}, etc.

Milking Procedure

Yield: 40-50%

Procedure by: J.M.Hollander

Time for sep'n: 1-2 hrs.

Equipment required:
(1) Ion exchange column, 2 cm long, 2 mm in diameter.
(2) Dowex-50 acid form resin.
(3) Two Al"sample mounting" plates, 3 1/2" x 2 1/2", with a 5/8" hole in the center.

Degree of purification: At least a factor of 50 from Pb. Other purifications not determined (α's not counted.)

Procedure:

(1) The Ac should be in 0.5 - 1.0 cc of 2 N HNO_3 solution. Allow this solution to pass through the column, to adsorb the Th, Ac, and partially the Ra.

(2) Elute with ~ 4 cc's of 2 N HNO_3 (to bring off any Ra which had adsorbed on the resin) at a flow rate of about 0.5 ml/min./cm^2.

(3) Then elute with ~ 2 cc's of 4 N HNO_3 to bring off the Ac.

(4) Evap this 4 N Ac fraction to dryness in a centrifuge cone, then dissolve the residue in water. Allow to stand 50-60 min.

(5) Add ~ 5 mg Pb^{++} carrier, heat the soln, ppt PbS by passing in H_2S gas to this solution as it cools.

(6) Centrifuge, reppt PbS from the supernate.

(7) Evaporate supernate to dryness onto a Pt disc.

(8) This disc is set upon an aluminum plate and centered above a 5/8" hole in this plate. An asbestos washer is placed above. On top of the asbestos washer and covering the hole just above the sample plate is placed a second platinum disc, scotch taped to a 1/8 in. Al disc. The Al disc, Pt disc combination is cooled with dry ice while an oxygen torch with a small flame is touched to the bottom of the sample plate, heating it strongly to red heat for 5 seconds. The cooled collector plate should then contain most of the Fr.

CHEMICAL SEPARATIONS

Element separated: Radium

Procedure by: Meinke

Target material: Thorium (~10 gm metal)

Time for sep'n: ~ 8 hrs.

Type of bbdt: 184" full energy particles

Equipment required: Standard plus centrifuges of:
250 ml capacity
50 ml capacity
15 ml capacity
Tank HCl

Yield: 25-50%

Degree of purification: At least 10^7 from Thorium, and at least 10^4 from other alpha activities present in high yield.

Advantages: Can be used to separate Ra with Ba carrier from large amounts of target material and (if coupled with column separation) to give weightless fraction of Ra.

Procedure:

(1) Dissolve the thorium metal target in concentrated HNO_3 with drops of .2 M $(NH_4)_2SiF_6$ soln added to make the sol'n ~ .01 M SiF_6^{-2}. (A large beaker should be used to prevent bubbling over in the vigorous reaction. The solution needs to be heated to start the reaction but once started the reaction proceeds vigorously.) Continue adding conc. HNO_3 and $(NH_4)_2SiF_6$ solution until target completely dissolves (may be an hour or two for 25 mil pieces of Th.)

(2) Evaporate off most of HNO_3 leaving $Th(NO_3)_4$ crystals. Caution: Do not evaporate to dryness or the nitrate will turn to ThO_2 which is harder than the original Th metal to dissolve. If some ThO_2 is accidentally formed use the same combination of conc. HNO_3, $(NH_4)_2SiF_6$ and heat to dissolve it. ThO_2 is considerably easier to dissolve immediately after forming than after prolonged heating and standing. (See 90- 4).

(3) Add 6 mg Ba^{++} carrier to the crystals and dilute with water to ~30 cc. Transfer to 250 ml centrifuge bottle.

(4) Add ~ 16 cc conc. NH_4OH (precipitating $Th(OH)_4$) dilute to 200 cc with water and digest for several minutes.

(5) Centrifuge and pour off supn (containing Ba and Ra plus other activities.)

(6) Dissolve ppt (amounting to ~125 cc volume) in ~ 16 cc conc. HNO_3.

(7) Add 3 mg Ba^{++} carrier, dilute to ~ 30 cc.

(8) Add ~ 20 cc conc. NH_4OH ppting the $Th(OH)_4$ dilute to ~ 200 cc with water and digest for several minutes.

(9) Centrifuge and pour off supn.

(10) Repeat steps 6 through 9.

(11) Combine the three supernatants from steps 5, 9 and 10. Evaporate combined solutions until ~ 200 cc. volume and transfer to 250 ml cent. bottle.

(12) Add 5 mg La^{+++} carrier and precipitate the $La(OH)_3$ plus $Th(OH)_4$ from any Th^{+4} remaining by the addition of conc NH_4OH. Discard ppt.

(13) Evaporate the supn to ~ 40 cc and repeat step 12.

(14) Add Na_2CO_3 solution to the supn to ppt $BaCO_3$ (carries Ra) digest for several minutes. Centrifuge.

(15) Dissolve $BaCO_3$ ppt in minimum of conc. HCl (one or two cc's probably enough).

(16) Place in ice bath. Add double or triple volume of ether and bubble in HCl gas until water and organic layers become miscible and the Ba ppts out as the $BaCl_2$. Centrifuge.

(17) Dissolve the ppt in minimum of H_2O.

(18) Repeat steps 16 and 17 twice (total of 3 $BaCl_2$ pptns). Caution: HCl-ether mixtures spatter readily when warmed.

(19) The $BaCl_2$ can be used for α counting or further purification can be made using a resin column.

Remarks:

Usually about 50 gms of Th metal can be bombarded at once in the cyclotron to produce the Ra^{225}. Hence the large centrifuge is necessary for the separation of the original $Th(OH)_4$ pptns and purifications.

The $Th(OH)_4$ ppt is very bulky-occupying more than half of the tube in step 4. However, with the Ba^{++} carrier added and the two reprecipitations of the thorium it is believed much of the Ra is recovered in the supernates.

The amounts of NH_4OH and HNO_3 used should be calculated rather closely so as to allow little excess, otherwise when the supn's are evaporated to ~ 40 cc (step 13) the solution will be saturated with NH_4NO_3 and interfere with the $BaCO_3$ pptns.

In step 13 some of the yield is lost through the solubility of some of the $BaCO_3$. This might be recovered by destroying the NH_4NO_3 and reducing the volume drastically before the carbonate precipitation.

Originally Ba and Ca were added as holdback carriers in the $Th(OH)_4$ ppts. The Ca, however, did not separate as well from the Ba as expected in the later parts of the procedure.

When working up 50 gms of Th, 10 gms at a time, residues might be combined and further recovery of Ba lost in the original procedure might be made. Also the $BaCO_3$ ppt of step 14 (first 10 gms) can be dissolved in conc. HNO_3 and used as carrier for the various steps of succeeding 10 gm portions - thus reducing the total amount of Ba in the final sample.

10 grams is about the maximum amount of thorium practical to work up at one time by this procedure using 250 ml centrifuge bottles.

If carrier free Ra is needed, $BaCO_3$ can be pptd from the water soln of the end of step 18. This $BaCO_3$ can be dissolved in acid pH 1-2 and absorbed on Dowex 50 resin. The Sr, Ba & Ra can then be eluted in that order by citrate at pH 7.5-8.0 (See E. R. Tompkins AECD-1998). This column procedure, however, has not been included in the runs made to date.

8/24/49

CHEMICAL SEPARATIONS

Element separated: Radium

Procedure by: Folger

Target material: ~3 g U metal

Time for sep'n: ~ 1-1 1/2 hr.

Type of bbdt: 184" high energy particles

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

Yield: 50-75%

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

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

Procedure:

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

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

(3) Dissolve in H_2O, transfer to 15 ml cone and buffer with HAc + NH_4Ac (1 ml 6 N HAc and 2 ml 6 N NH_4Ac or pH 5-6). Add ~ 5 mg Pb and ppt $PbCrO_4$ by add'n of 1.5 M Na_2CrO_4 to hot sol'n. Wash with hot HAc & NH_4Ac buffer (1 ml to 2 ml as above) containing 1 drop 1.5 M Na_2CrO_4.

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

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

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

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

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

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

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

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

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

To remove excess alkali salts add:

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

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

8/23/49

P-18-274

CHEMICAL SEPARATIONS

Element separated: Actinium
(Procedure designed for Ac^{225} & Ac^{226})

Procedure by: Hyde

Target material: Thorium metal
(Two 25 mil foils 1 1/2" square bombarded on edge) About 25 grams Th.

Time for sep'n: 24 hours

Type of bbdt: protons from 184"

Equipment required: beakers, centrifuge cones, 250 ml separatory funnel, resin column, automatic sampler, pH meter.

Yield: Not known - estimated 75%

Degree of purification: Complete separation from all other elements by factor of at least 10^4.

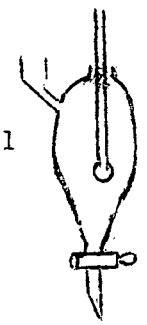
Procedure:

(1) Dissolve thorium in hot conc. HNO_3. Add 1 drop 1 N HF occasionally to catalyze dissolution.

(2) Evaporate solution nearly to crystallization. Cool. Transfer to 250 ml pear-shaped separatory funnel. One which has been modified to provide a side funnel as shown in figure 1 is recommended.

(3) Add 1-2 volumes penta ether (dibutoxytetraethylene glycol)*. Stir. Let settle. Drain aqueous layer into original beaker. Drain pentaether layer into bottle for storage.**

Fig. 1



(4) Return aqueous layer to funnel. Add solid ammonium nitrate with stirring until solution is saturated. Add 2-3 volumes penta ther. Stir. Drain aqueous into 50 ml centrifuge cone. Drain pentaether layer into storage bottle.

(5) Repeat pentaether extraction once again after adding 0.5 ml conc. HNO_3 to replace that extracted by solvent.

(6) Aqueous layer in 50 ml centrifuge cone centrifuged to separate last cc's of pentaether, which are pipetted off.

(7) Add NH_4OH to ppt last amounts of thorium as $Th(OH)_4$. This serves to carry the actinium out of the salted solution. Wash twice with H_2O.

* It is quite important that the solution be cool before the solvent is added as pentaether is rapidly decomposed by hot nitric acid.

** Pentaether is used to extract the bulk of the thorium away. The thorium serves as its own salting agent in the first pass which extracts the bulk of it and reduces the aqueous volume greatly. Subsequent extractions must be aided by NH_4NO_3 salting.

(8) Dissolve mixed hydroxides in minimum amount HCl. Dilute to 5 ml. Adjust pH to 1.5 --- 2.5*** check with Beckman pH meter using 1 drop glass electrode. Add 10 ml 0.15 M TTA in benzene. Stir. Recheck and if necessary readjust pH. Stir well 10-20 minutes.

(9) Centrifuge. Pipet off benzene layer containing thorium.

(10) To aqueous add 10 ml fresh TTA. Stir, check pH. Stir 10-20 minutes. Centrifuge. Pipet off benzene layer.

(11) To aqueous layer containing actinium, rare earth and other activities add NH_4OH to adjust pH to between 5.5-7.0***.

(12) Add 10 ml TTA-benzene. Stir. Recheck pH. Contact 20 minutes.

(13) Pipet benzene layer containing actinium and rare earths into clean 50 ml centrifuge cone. Re-extract activity into 2.5 ml 0.1 N HCl by 2 minutes of stirring.

At this point the only likely impurities are rare-earth fission products. If these do not interfere, this solution may be considered the final solution. If separation from rare earths is desired the following resin separation is recommended.

(14) Add a few mg of ammonium form colloidal dowex 50 resin to the dilute HCl solution. Warm to $\sim 60^{\circ}C$ in water bath for 2-3 minutes. Centrifuge.

(15) If assay of supernate indicates nearly complete adsorption on resin, pipet the resin on to the top of a short resin column. Elute with 5% citrate solution of pH 3.8 - 4.0. Use a mechanical sampler to take samples every 20 minutes.

The rare earth and actinium peaks can not be predicted accurately enough to eliminate the necessity of alpha and beta counts to determine their location. The rare earth fractions come off in the first samples as indicated by the beta counts. The actinium peak is located by the alpha counts of Ac^{225}. The elution of Bi^{213} and its associated Po^{213} daughter alpha activity in the early fractions obscures the location of the actinium peak unless samples are pulse analyzed or unless the 47-minute Bi^{213} is allowed to decay before counting.

My experience with a column 6 cm x 2 mm of colloidal resin eluted with pH 3.9 citrate at a rate of 1 drop per 2.5 minutes was that the rare earth fraction came off within two hours and the actinium fraction, well separated from the rare earths, started to come off after 5 hours and was spread over 2-3 hours. Others (Orth & Street) report much more rapid elution under essentially the same conditions.

*** An equal volume of TTA-benzene will extract thorium essentially completely from an aqueous solution of pH >1. Actinium extraction is 0 at pH 2.5 or less, is 10% at pH 4 and rises sharply to essentially complete extraction at pH 5.5 or greater. See Hagemann AECD 1933.

7/6/49

P-18-46

CHEMICAL SEPARATIONS

Element separated: Actinium

Procedure by: Meinke

Parent material: Tracer Pa^{230}

Time for sep'n: 3-4 hrs.

Milking experiment

Equipment required: Standard, centrifuge

Yield: ~ 40%

Degree of purification: Factor of at least 10^7 from Pa, U and Th.

Advantages: Can separate very small amounts of Ac from large amounts of Pa, U and Th activity. In one experiment separated 500 d/m Ac^{226} from 10^7 total d/m of Pa^{230} and about equivalent amounts of U and 30 minute Th^{226}.

Procedure:

Pa^{230} in 6 N HNO_3 after DIPK extractions (procedure 91-1)

(1) Take 10 cc of Pa soln and add 1/4 mg La^{+++} and 5 mg Ce^{+++} carriers.

(2) Add 10 drops of conc HF to ppt the fluorides. Centrifuge.

(3) Metathesize ppt to La and Ce hydroxides by adding several ml of conc KOH soln. Centrifuge out the hydroxides and wash once with 5 ml alkaline water.

(4) Dissolve ppt in few drops 6 N HCl and dilute to 5 cc.

(5) Add 1/4 mg Zr^{+4} carrier and H_3PO_4 to make 3 N PO_4^{-3}. Discard ppt.

Steps 2 through 5 are repeated alternately or consecutively until the desired degree of purification is obtained. For the purifications noted above, 10 fluoride pptns and 9 phosphate pptns were made. After the 10th fluoride ppt had been metathesized to the hydroxide, the following procedure was used:

(6) Dissolve hydroxide ppt in 10 M HNO_3, make .01 M Fe^{+++} and oxidize Ce^{+++} to Ce^{++++} with solid sodium bismuthate (warm to speed up reaction.) (Ce^{+4} will now carry on the $Zr_3(PO_4)_4$ ppt.)

(7) Repeat step (5).

(8) Repeat (2) and (3).

(9) Dissolve ppt in few drops 6 N HCl, dilute to known volume and plate aliquot for counting.

Remarks:

The fluoride cycles decontaminate primarily from Pa, the phosphate from Th. If further purification is required include more cycles in procedure.

Only one milking can be made from a given batch of Pa by this procedure since it is difficult to again get the Pa into an extractable form once fluoride ion has been added.

It has been found that the $LaCl_3$ solution makes a more adherent and thinner plate than the LaF_3 ppt. The amount of La^{+++} carrier used in step (1) should be determined by the amount of bulk that can be tolerated on the final plate.

CHEMICAL SEPARATIONS

Element separated: Thorium

Procedure by: Meinke

Target material: Tracer Pa separated from 60" bbdt of ionium.

Time for sep'n: Several hours.

Type of bbdt: (Milking expt.)

Equipment required: Stirrers and TTA

Yield: As high as 50% possible.

Degree of purification: Decontaminate from 10^7 c/m Pa, 10^6 c/m U and 10^5 c/m Ac.

Advantages: Gives carrier-free Th, a thin plate for pulse analysis and good purification although not speed.

Procedure:

(1) Nitric acid used throughout. Make sample 6 N acid and TTA extract (with .4M TTA in benzene) 5 times with double volume of TTA -- stirring 5 minutes for each extraction. (Removes Pa into TTA ~ 70% or more per pass).

(2) Evaporate to dryness (wash twice with water and take these washings also to dryness) and take up in acid pH 1.0. TTA extract with equal volume (.25M TTA in benzene) stirring 15 minutes. (Th into TTA but not U or Ac.)

(3) Repeat TTA extn of (2) with fresh TTA and combine the extns.

(4) Wash TTA with equal volume of pH 1.0 soln for 15 min. (U contamination into acid.)

(5) Wash TTA with 6 N acid (equal volume) and stir 15 min. (Th into acid).

(6) Repeat parts (2), (3), and (4). (Repeat wash as in (4) if necessary for further U purification.)

(7) Plate out the .25 M TTA on Pt plates and flame.

Remarks: See curves of Hagemann for % extn into TTA vs pH for Th and Ac. At pH of 1 Th should go into the TTA almost completely but U should only go in less than 10% -- perhaps as little as 2%. Ac will not go into TTA until about pH 3 or so and of course Pa goes in up to about 6 or 8N acid.

pH conditions for separating Th from U by TTA extns are quite critical!

Equivalent and molecular weight of TTA is 222 gms.

8/24/49

P-18-254

CHEMICAL SEPARATIONS

Element separated: UX_1 (Thorium)

Procedure by: D. B. Stewart

Target material: $UO_2(NO_3)_2.6H_2O$ in which UX_1 has come to equilibrium

Time for sep'n: 24 hrs.

Equipment required: 40 ml centrifuge cone

Yield: 50,000 - 10,000 c/m from 20 g UNH.

Degree of purification: factor of $\sim 10^6$ from U.

Advantages: Good yield with small amount of inert carrier (Very voluminous insoluble precipitate) (Uranium does not precipitate at all)

Procedure:

(1) Dissolve 20 g $UO_2(NO_3)_2.6H_2O$ in 20-30 ml 0.01 N HNO_3 in a 40 ml centrifuge cone and warm solution to about 80°C in a hot water bath. Add 0.5 mg - 1 mg Zr carrier as nitrate.

(2) Add 5 ml of a saturated solution of m-nitrobenzoic acid in water and continue warming for about 1 hr. Let stand overnight.

(3) Centrifuge, decant supernatant, and wash $Zr(C_6H_4NO_2COO)_4$ twice with 0.01 N HNO_3 + m-Nitrobenzoic acid.

Remarks:

Saturated solution of m-nitrobenzoic acid made up by dissolving 400 mg. of the material in 100 ml H_2O. Heat to 80°C. Allow to stand several hours & filter to remove excess and impurities.

7/28/49
P-18-'81

CHEMICAL SEPARATIONS

Element separated: Thorium

Procedure by: Meinke

Parent material: Tracer Pa and daughters (both α & K)
Milking experiment

Time for sep'n: ~ 3/4 hr.

Equipment required: standard

Yield: Only ~ 40-50% Th per cycle

Degree of purification: 2-3% Ac carried per cycle - other elements decontaminated by factor of at least 100.

Advantages: Good procedure if Th present in ~ same amount as other activities.

Procedure:

Pa daughters in 6 N HCl after milking from Pa in TTA (91-1).

(1) To ~ 10 cc daughter soln add 1/2-1 mg Zr^{+4} carrier and enough H_3PO_4 to make ~ 4 M in $PO_4^{\equiv}$. Centrifuge ppt (carries Th^{+4}).

(2) Add to the ppt 3 mg La^{+++} carrier and dilute with 1 N HCl. Add HF, digest and centrifuge.

(3) Metathesize the fluoride ppt to hydroxide by adding conc KOH. Centrifuge. Wash once with alkaline water.

(4) Dissolve in HCl and repeat steps 1-3 reducing amount of La carrier.

(5) Plate as the $LaCl_3$ soln, flame and count.

Remarks:

$Zr_3(PO_4)_4$ ppt quite specific for carrying Th^{+4} from other elements in the heavy region. Yield lost in the LaF_3-$La(OH)_3$ pptns.

Do not use this procedure if more purification needed than given by 2 cycles since the Th yield will be very low.

$LaCl_3$ soln when evaporated sticks to Pt plates much better than the ppts encountered in this procedure.

8/12/49
P-18-151

Solution of Thorium Metal and Thorium Dioxide

Thorium metal can be dissolved rapidly in conc HCl but a considerable amount of black insoluble residue is formed in the process. If a few drops of $(NH_4)_2SiF_6$ solution (enough to make $\sim$ 0.1 M) are added to the HCl before solution is started the black residue is dissolved, leaving only a small residue of thorium oxide (<1%) in the clear solution.

Thorium metal can be dissolved in conc. HNO_3 with the addition of $(NH_4)_2SiF_6$ (or HF) to .01 M. The metal becomes passive to the solution from time to time requiring further additions of acid and $SiF_6^{=}$.

If the excess HNO_3 is evaporated off care should be taken not to allow the solution to go completely to dryness or difficultly soluble ThO_2 will be formed.

If it is desired to dissolve ThO_2, the HNO_3-$(NH_4)_2SiF_6$ solution should be used and the mixture heated with stirring for several hours. ThO_2 when first formed is much more soluble than after prolonged heating.

Note: A bombardment of 50 mg 13% ionium (Th^{230}) in thorium (Th^{232}) mixture in the dioxide form should be mentioned here. The hydroxide was pptd and heated in a Pt crucible until only the dioxide remained. This dioxide was then packed into a Pt "boat" 1" x 1/2" x .085" and wet with a few drops of sodium silicate soln. The mixture was then dried under a heat lamp, more silicate added and again dried. The boat was then flamed over a Fisher burner.

It was found that a target prepared this way could withstand considerable mechanical shock and also the high target temperature produced by the 60" cyclotron deuteron beam without breaking the silica crust.

It was also found that the target material could be rather easily scraped out of the boat and mostly dissolved in 5 or 6 hours -- after several additions of HNO_3^- $SiF_6^{=}$ soln.

Newton, Hyde, Meinke

8/15/49

P-18-202

CHEMICAL SEPARATIONS

Element separated: Protactinium

Procedure by: Meinke

Target material: ~ 10 gms Th metal

Time for sep'n: 1 1/2-2 hrs.

Time of bbdt: 60" D^+ bbdt and 184" bbdt all particles

Equipment required: Centrifuge Kjeldahl flasks, dry ice and stirrers.

Yield: Roughly 10% through entire chemistry

Degree of purification: Separate from all elements by a factor of at least 10^3. For further purification from Cb and Zr do more DIPK washes.

Advantages: Gives carrier-free Pa on weightless plates for pulse analysis and counting. Purification can be made more extensive by repeating individual steps.

Procedure:

(1) Nitric acid used except where indicated otherwise. Dissolve Th metal in conc. HNO_3 ~ .01 M in $(NH_4)_2SiF_5$ soln (25 cc acid and 3 or 4 drops of 1/5 M SiF_6 soln usually sufficient to dissolve 10 gms Th.)

(2) Dilute to ~ 4 N acid and Th^{+4} ccn. less than 0.65 M (Greater ccn. of Th salt interfers with pptn.)

(3) Add to 40 cc $Th(NO_3)_4$ soln in 4 N HNO_3 an excess of $Mn(NO_3)_2$. (1/2 cc of 50% soln sufficient.)

(4) Add 1.5 cc $KMnO_4$ soln (40 mg/cc). (Pa carried quantitatively on 1.5 gm/liter MnO_2 ppt.)

(5) Digest over water bath, centrifuge and pour off supn.

(6) To ppt. add few drops of 4 N acid and dissolve in a few drops of sat. soln of $NH_2OH \cdot HCl$.

(7) Dilute to required volume and repeat pptns. three times, reducing volume each time. Final volume is a few cc's.

(8) Make soln 6 N HNO_3 or HCl. Extract with 2-3 times volume of diisopropyl ketone (DIPK) shaking together for 1/2 min. in Kjeldahl flasks and separating phases by freezing aqueous layer with dry ice - acetone mixture. (Pa into DIPK ~ 60% yield/pass).

(9) Wash DIPK layer with 3 washs of an equal volume of soln 1 N HNO_3 and 3 N NH_4NO_3 in successive flasks.

(10) Pa then washed into 2 successive portions of .1 N HNO_3.

(11) DIPK extn repeated once and .1 N solns combined and made 6 N HNO_3.

(12) Equal volume of TTA (.4 M in benzene) stirred for 5 min. with the 6 N acid - (Pa into TTA.)

(13) Organic layer washed once with equal volume 6 N HNO_3.

(14) The Benzene-TTA plated out on platinum.

Remarks: The am't of F^- introduced by the .01 M $(NH_4)_2SiF_6$ is not enough to complex an appreciable amount of the Pa. Traces of Pa coppt with good yield from 1 - 5 N HNO_3 soln less than .65 M Th^{+4} on 1.5 gm/liter MnO_2 with good separation from macro am't of Th. A concentration factor of at least 10 can be obtained by these pptn cycles.

Any Th and fission product that extract into DIPK are washed out in the acid-salt washes. 0.1 N HNO_3 used to wash Pa out of DIPK keeps Pa from hydrolyzing to the colloid state.

The Pa must never get very near a neutral pH or it will go into the non-extractable colloid.

TTA separates Pa from all elements formed in bbdt except Zr, Cb, and Hf. DIPK extracts only Pa and U at these cons. MnO_2 carries Pa, Zr, Cb and maybe some others, but does eliminate things like I which might solvent extract through the other chemical procedures.

8/24/49

P-18-258

CHEMICAL SEPARATIONS

Element separated: Protactinium

Procedure by: Meinke

Target material: $Th(NO_3)_4$ or thorium metal

Time for sep'n: 2 minute minimum, average 15 min. with metal

Type of bbdt: 60" & 184" - all particles

Equipment required: stirrer

Yield: 40-80%

Degree of purification: Factor of at least 100 from all elements present except Zr, Cb, Hf.

Advantages: Fast, weightless plate & Pa, good for alpha pulse analysis. Zr & Cb fission products coming through procedure make Geiger counting of Pa impossible without more chemistry.

Procedure:

(1) Dissolve Th metal in conc. HNO_3 ~.01 M in $(NH_4)_2SiF_6$ soln. (25 cc. acid and 3 or 4 drops of 1/5 M $SiF_6^=$ sol'n sufficient to dissolve 10 gms Th.) $Th(NO_3)_4$ can be dissolved directly in 4 N HNO_3.

(2) Dilute to ~ 4 N acid.

(3) Add equal volume of TTA (.4 M in benzene) and stir for 5 minutes. (Pa, Zr, Cb into organic layer).

(4) If want somewhat better purification wash TTA layer with equal volume of 4 N HNO_3. (May lose up to half Pa yield in this wash.)

(5) Plate out benzene-TTA layer on platinum.

Remarks: TTA separates Pa from all elements formed in bbdt except Zr, Cb, & Hf.

This method used for excitation function work where as many as 16 foils are worked up simultaneously. Identical amounts of reagents are added and each sample subjected to the same procedure, giving approximately equal chemical yields for each foil (to within 5 or 10%).

6/22/49

P-18-5

CHEMICAL SEPARATIONS

Element separated: Protactinium (~ 2 mg)

Procedure by: Crane

Removal of macro amounts of Pa from rare earths, Mn, Zr, iron

Time for sep'n: Several days

Yield: ~ 80%

Equipment required: anion exchange resin, beakers, hot plate, centrifuge

Advantages: Takes Pa out of colloidal state

Procedure:

(1) Add ten times as much Zr^{+4} as you have Pa (~ 20 mg of Zr^{+4}) make 3 M in HF and allow to stand for several hours. Then add excess Ba^{+2} ion; Pa carries on the $BaZrF_6$ ppt.

(2) Check floride solution for Pa activity. If carrying not complete add 10 mg Zr^{+4} and digest at low temperature for a few hours.

(3) Combine $BaZrF_6$ + Pa ppts and dissolve in conc. HNO_3 + boric acid.

(4) Dilute and precipitate Zr + Pa as hydroxide with KOH.

(5) Redissolve ppt in conc. HCl. Boil this solution for a few hours then make HCl 8 M and absorb on anion exchange resin (Dow A-1 used in 20 cm x 1 cm^2 column; flow rate ~ 1 drop/min). Wash resin with 8 M HCl.

(6) Elute with 4 M HCl. Pa will come off in ~ 15 column volumns. (Uranium requires ~ 45 column volumns).

Alternate step for (1): If desired and solution of Pa does not contain too much Zr^{+4} and other floride complex ions the Pa solution may be absorbed directly on the resin from a 3 M HF soln, washed with conc HCl and eluted with 4 M HCl.

(7) Final solutions of HCl are then concentrated, made 6 M HCl and Pa extracted into equal volume diisopropyl ketone.

(8) The Pa is taken back into .1 volume 0.1 M HNO_3 solution and made 4 M in HCl to keep Pa from forming colloid.

8/17/49

P-18-242

CHEMICAL SEPARATIONS

Element separated: Uranium

Procedure by: Crane

Target material: ~20 gm of Th metal

Time for sep'n: Several hrs.

Type of bbdt: 184" bbdt

Equipment required: Centrifuge, Kjeldahl flasks, dry ice and stirrers.

Yield: ~ 90%

Degree of purification: Separate all elements in Th fission by factor greater than 10^6.

Advantages: Gives carrier free Uranium.

Procedure:

(1) Nitric acid used except where indicated otherwise. Dissolve Th metal in conc. HNO_3 & ~ .01 M in $(NH_4)_2SiF_6$ (50 cc acid and ~6 drops 1/5 M $SiF_6^=$ — Solution usually sufficient to dissolve 20 gram Th metal).

(2) Evaporate to near dryness & redissolve in 1 M HNO_3 and saturate with NH_4NO_3.

(3) Ether extract uranium using 3 separate portions of ether and combining; wash twice with .1 M HNO_3 + 10 M NH_4NO_3.

(4) Extract uranium back into water solution. Add La^{+++} carrier ~ 1 mg/cc solution

(5) ppt hydroxide with NH_4OH. (carries uranium)

(6) Dissolve in 6 M HNO_3 and add Zr^{+4} scavenger (~ 1 mg/cc), dilute to 3 N acid.

(7) Add iodic acid to ppt $ZrO(IO_3)_2$ to scavenge solution.

(8) Remove supernatent and ppt La^{+3} as hydroxide.

(9) Dissolve in 1 M HNO_3. Saturate with NH_4NO_3 and ether extract using 3 separate portions of ether and combining.

(10) Wash twice with .1 M HNO_3 + 10 M NH_4NO_3 and re-extract uranium into water.

Remarks: Use one part ether, two parts salt solution in extraction. Wash with equal volume salt solution. Re-extract into half volume water.

In step 7 do not add excess iodic acid or La will also be pptd. Add just enough to ppt the Zr as $ZrO(IO_3)_2$, otherwise much yield will be lost. For ether extraction of uranium see: A. S. Newton, Phys. Rev. 75 209 (1949).

6/16/49

CHEMICAL SEPARATIONS

Determination: Acid equivalent, i.e., H^+ & carboxyl

Procedure by: Newton & McDonell

Target material: Alcohols (ethanol)

Time: 10 min.

Type of bbdt: 10 Mev p

Equipment required: burette glassware

Yield: quantitative

Degree of precision: $\pm$ 1%

Procedure:

(1) Dilute 5 cc of irradiated sample to 20 cc with water or neutral ethanol.

(2) Add 3 drops 1% phenolphthalein indicator solution.

(3) Titrate with 0.1 N NaOH to sharp phenolphthalein end point.

(4) Acid equivalents = vol. of alkali x normality.

Remarks:

A blank should be run on the ethanol to insure neutrality. Other substances besides free H^+ and carboxyl that titrate fast with NaOH include several phenols, lactones (inner esters), and some esters. These must be determined by further analysis.

References: Standard Organic Analyses Texts

8/12/49
P-18-157

CHEMICAL SEPARATIONS

Substance determined: Carbonyl

Procedure by: Newton & McDonell

Target material: Alcohols (ethanol)

Time for sep'n: one day

Type of bbdt: p (~10 Mev)

Equipment required:
Pyrex test tubes
burettes, pipettes
steam bath

Yield: Quantitative precise to ± 1%

Procedure:

(1) To 5 cc[1] (pipette accuracy) of irradiated alcohol add 3 cc hydroxylamine reagent[2] (pipette accuracy) and 5 cc of buffered indicator reagent[3] (graduated cylinder). Treat a blank of 5 cc absolute alcohol identically in all steps. Seal in a glass bomb tube.

(2) Heat in steam bath 2 hours[4]. Allow stand to cool overnight.

(3) Break the bomb tube, rinse quantitatively into a flask with measured portions of 95% ethanol. Treat blank identically.

(4) Titrate sample to the greenish blue end point color of the blank (or titrate both sample and blank to same end point color) with alcoholic 0.5 N NaOH soln.[5][6][7]

(5) Calc. equivalent wt. of acetaldehyde from the difference in titres of blank and sample, assuming the titration is a hydrogen determination by the reaction:

$$H_3C-C(=O)-H + H_3N^+OH \longrightarrow H_3C-C(H)=NOH + H^+ + H_2O$$

$$H^+ + OH^- \longrightarrow H_2O \quad (8)(9)$$

Remarks:

(1) About 0.001 moles of carbonyl is maximum sample size for the specified reagent quantities.

(2) Prepare 0.5 M hydroxylamine solution by dissolving 35 g of hydroxylamine hydrochloride in 160 cc of dist water and diluting to 1 liter with 95% ethanol.

(3) Prepare buffered indicator soln, 20 cc C.P. pyridine to 1.0 cc of 1 percent alcoholic brom phenol blue indicator and diluting to 500 cc with 95% ethanol.

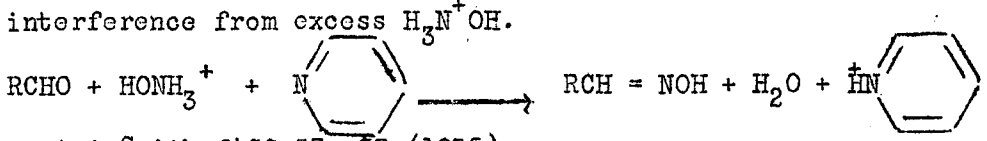
(4) Excessive heating (>5 hrs.) causes a breakdown of the hydroxylamine salt with inaccurate results.

(5) Alcoholic 0.5 N NaOH is prepared with 90% methanol rather than ethanol, since the latter oxidizes in air, producing an aldehyde which resinifies in base, coloring the soln. Standardize vs standard HCl.

(6) The water content must be nearly identical in blank & sample, since it affects indicator color and buffer action of pyridine.

(7) The end point colors may be matched to an accuracy within a fraction of a drop, i.e. ± 0.02 ml.

(8) The pyridine buffer allows effective titration of liberated H^+ without interference from excess H_3N^+OH.



(9) Ref. Bryant & Smith JACS 57, 57 (1935).

8/11/49
P-18-168

CHEMICAL SEPARATIONS

Determination: Saponification Equivalent (esters)

Procedure by: Newton & McDonell

Target material: alcohols (ethanol)

Time for sep'n: 1 day

Type of bbdt: p (10 Mev)

Equipment required:
glassware
steam bath

Yield: Qualitative only

Procedure:

(1) Seal 5 cc irradiated sample + 2 cc NaOH soln[1] in Pyrex glass test tube.

(2) Heat for 2 hrs. with occasional agitation in a steam bath. Treat a blank ethanol sample identically.

(3) Cool tubes, break and rinse into beaker. Add excess standard acid. Titrate with standard NaOH to phenolphthalein end point[2][3].

(4) Difference in quantity NaOH between blank and sample as determined in the titrations is cited as equivalent to maximum possible ester.[3][4]

Remarks:

(1) NaOH solution made by diluting 20 N aq. NaOH to 1 N with absolute ethanol.

(2) Presence of aldehydes causes brown discoloration (condensation resins) of irradiated samples and yellow in the blank. Considerable dilution is necessary to enable an accurate visual end point determination.

(3) Alkali consuming interferences include Cannizzaro reaction on aldehydes. Poly functional compounds such as β-diketones and β-keto esters undergo cleavage, etc.

(4) It is emphasized that this procedure comprises merely a qualitative test for the easily saponifiable esters (ethyl acetate, ethyl formate, methyl acetate, etc.) expected in ethanol bombardments. For accurate determination in the presence of aldehydes, or for difficulty saponifiable esters, considerable refinement in procedure is necessary. Ref. Shriner and Fuson "Systematic Ident. of Org. Cpds."John Wiley & Sons, New York, 1948. p. 128 and other standard organic analysis texts.

8/12/49
P-18-155