NAS-NS
3044

National
Academy
of
Sciences

National Research Council

NUCLEAR SCIENCE SERIES

The Radiochemistry of Platinum

U.S.
Atomic
Energy
Commission

COMMITTEE ON NUCLEAR SCIENCE

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

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

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

C. J. BORKOWSKI
Oak Ridge National Laboratory

ROBERT G. COCHRAN
Texas Agricultural and Mechanical College

SAMUEL EPSTEIN
California Institute of Technology

U. FANO
National Bureau of Standards

HERBERT GOLDSTEIN
Nuclear Development Corporation of America

J. W. IRVINE, JR.
Massachusetts Institute of Technology

E. D. KLEMA
Northwestern University

W. WAYNE MEINKE
University of Michigan

J. J. NICKSON
Memorial Hospital, New York

ROBERT L. PLATZMAN
Laboratoire de Chimie Physique

D. M. VAN PATTER
Bartol Research Foundation

LIAISON MEMBERS

PAUL C. AEBERSOLD
Atomic Energy Commission

J. HOWARD McMILLEN
National Science Foundation

CHARLES K. REED
U. S. Air Force

WILLIAM E. WRIGHT
Office of Naval Research

SUBCOMMITTEE ON RADIOCHEMISTRY

W. WAYNE MEINKE, *Chairman*
University of Michigan

NATHAN BALLOU
Naval Radiological Defense Laboratory

GREGORY R. CHOPPIN
Florida State University

GEORGE A. COWAN
Los Alamos Scientific Laboratory

ARTHUR W. FAIRHALL
University of Washington

JEROME HUDIS
Brookhaven National Laboratory

EARL HYDE
University of California (Berkeley)

JULIAN NIELSEN
Hanford Laboratories

G. DAVID O'KELLEY
Oak Ridge National Laboratory

ELLIS P. STEINBERG
Argonne National Laboratory

PETER C. STEVENSON
University of California (Livermore)

DUANE N. SUNDERMAN
Battelle Memorial Institute

CONSULTANTS

HERBERT M. CLARK
Rensselaer Polytechnic Institute

JOHN W. WINCHESTER
Massachusetts Institute of Technology

The Radiochemistry of Platinum

G. W. LEDDICOTTE
Oak Ridge National Laboratory
Oak Ridge, Tennessee

October 1961

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

Printed in USA. Price $0.50. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

FOREWORD

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

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

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

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

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

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

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

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

CONTENTS

The Radiochemistry of Platinum

G. W. LEDDICOTTE*
Oak Ridge National Laboratory
Oak Ridge, Tennessee

I. GENERAL REFERENCES ON THE INORGANIC AND ANALYTICAL CHEMISTRY OF PLATINUM

Sidgwick, N. V., The Chemical Elements and Their Compounds, pp. 1454-1628, Oxford University Press, London, 1950.

Kleinberg, J., Argersinger, W. J., Jr., and Griswold, E., Inorganic Chemistry, pp. 581-588, Heath, Burton (1960).

Remy, H., Treatise on Inorganic Chemistry, Volume I, pp. 342-351, Elsevier, Amsterdam (1956).

Beamish, F. E., "A Critical Review of Methods For Isolating and Separating The Six Platinum Metals," Talanta 5, p. 1-35 (1960).

Scott, W. W., Standard Methods of Chemical Analysis, Volume 1, pp. 712-728, Van Nostrand, New York, 1939.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., Applied Inorganic Analysis, John Wiley, New York, 1953.

Rodden, C. J., Analytical Chemistry of the Manhattan Project, pp. 3-159, 483 and 491-493, McGraw-Hill, New York (1950).

II. THE RADIOACTIVE NUCLIDES OF PLATINUM

The radionuclides of platinum that are of interest in the radiochemistry of platinum are given in Table I. This table has been completed from information appearing in reports by Strominger, et al[1] and by Hughes and Harvey.[2]

*Operated for U. S. Atomic Energy Commission by Union Carbide Corporation

Table I

THE RADIOACTIVE NUCLIDES OF PLATINUM

Radio-Nuclide	Half-Life	Mode of Decay	Energy of Radiation	Produced By
Pt^{191}	3.0 d	EC	γ 0.083, 0.096, 0.173, 0.6, 1.5	Ir-d-2n, Pt-n-2n
Pt^{193m}	4.3 d	IT,EC	γ 0.135 γ 0.2, 1.5	Ir-d-2n, Pt-n-γ, Pt-d-2n, Pt-d-p, Pt-γ-n
Pt^{195m}	3.8 d	IT	γ 0.029, 0.097, 0.126, 0.255	Pt-n-γ, Pt-d-p, Pt-γ-n
Pt^{197m}	80 m	IT	γ 0.337	Pt-d-p, Pt-n-2n, Pt-γ-n Hg-n-α, Au-n-p
Pt^{197}	18 h	β^-	β^- 0.67 γ 0.077, 0.191	Pt-n-γ, Pt-d-p, Pt-γ-n Pt-n-2n, Hg-n-α
Pt^{199}	31 m	β^-	β^- 1.8 γ 0.074, 0.197, others	Pt-n-γ, Pt-d-p, Hg-n-α
Pt	82 d	β^-	β^- 0.5 γ 0.6	Pt-n-γ

III. THE CHEMISTRY OF PLATINUM AND ITS APPLICATION TO THE RADIOCHEMISTRY OF THE PLATINUM RADIONUCLIDES

Radiochemistry is probably best described as being an anlysis technique used primarily either (1) to assist in obtaining a pure radionuclide of some specific element in a suitable form so that an absolute measurement of its radioactivity, radiation energies, and half-life can be made, or (2) to determine the amount of radioactivity of a particular radioelement in a radionuclide mixture, or (3) to complete a radioactivation analysis being used to determine the stable element concentration in a particular sample material. In order to be an aid in accomplishing anyone of the above interests, radiochemistry usually considers the isolation of the desired radionuclide by either carrier or carrier-free separation methods.

Generally, "carrier" methods are used most frequently in radiochemistry. They involve the addition of a small amount of inactive stable element to a solution of the irradiated material to serve as a carrier of the radionuclide of that element through the separation method. "Carrier-free" separations connote that no carrier is added. These radiochemical techniques are used mostly to obtain radionuclides for absolute radioactivity measurements, and it is required that the desired radioelement be isolated in a manner able to

give either no amount or a minimal amount of stable element (either isotopic or non-isotopic with it) in the final form to be used in the radioactivity measurements.

In most instances, radiochemistry is dependent upon more conventional ideas in analytical chemistry involving separations by such methods as precipitation, solvent extraction, chromatography, volatilization, and/or electrolysis and the subsequent presentation of the isolated radioelement in a form suitable for a measurement of its radioactivity. When "carrier" techniques are employed, one major difference exists between radiochemistry and more conventional analysis techniques in that it is never always necessary to recover completely the added amount of "carrier" element. Each radiochemical analysis is designed to assure that the atoms of a radioactive element achieve an isotopic state with the atoms of the inactive element and any loss of the radioactive species is proportional to the loss of "carrier" during the separation process.

Colorimetric, polarographic and volumetric analysis techniques are seldom used in radiochemistry because they do not separate the desired radionuclide from contaminants (either radioactive or stable) in the mixture being analyzed. However, some of the developments used in these analysis techniques may be useful for consideration in radiochemistry.

The following information is intended to give some general idea of the behaviour of platinum and its compounds and their potential usefulness in devising radiochemical analysis methods for the radionuclides of platinum. More detailed information can be obtained either from the references given in this section or from the general references given in Section I of this monograph.

A. The General Chemistry of Platinum

Platinum is most often found in alluvial deposits as native metal and can be found in these deposits in combination with the other platinum group metals and gold, silver, copper, nickel, iron and lead. Platinum can also occur as a mineral in ultrabasic rocks, e.g. cooperite, PtS, and sperrylite, $PtAs_2$. The chief present-day source of platinum is the Sudbury (Canada) ore, a nickeliferrous pyrrhotite ore. Metallic platinum (as well as other metals of the platinum group) is recovered from the residues obtained in the refinement processes used to heat this nickel-bearing ore.

1. Metallic Platinum

Platinum metal is obtained as a gray-white, lustrous, metal. It is a soft, ductile metal that has a density of 21.45. It has a melting point of 1774°.

Metallic platinum can absorb both oxygen and hydrogen. In a finely divided state, it can absorb up to 100 times its own volume of each of these elements. Platinum can also absorb small amounts of helium.

Platinum (like the other noble metals) will not be attacked by strong acids. Aqua regia must be used to dissolve it; hexachloroplatinic acid, $H_2(PtCl_6)$, is formed by this reaction. Metallic platinum can react with hot alkali peroxides to become brittle and to decompose. It will unite with chlorine gas at temperatures above 250° C to form platinum dichloride, $PtCl_2$; at a dull red heat, it will combine with fluorine to produce platinum tetrafluoride, PtF_4, and platinum difluoride, PtF_2. Sulfur, selenium, and tellurium can readily attack platinum if proper conditions exist. It will form fusible alloys with phosphorus and can be alloyed with arsenic, antimony, bismuth, lead, silver, and tin. Cobalt, copper, gold, iron, and nickel all form mixed crystals with platinum. Although it is at the end of the electrochemical series, platinum will also form many complex ions.

2. The Compounds of Platinum

Platinum (like palladium) forms both divalent (+2) and tetravalent (+4) compounds. The most common or simple dipositive compounds are the oxides, sulfides, and the halides. Tetrapositive compounds of platinum include binary compounds of oxides, sulfides, selenides, and tellurides. In addition, platinum forms tetrahalides and, unlike palladium, forms many other complex cationic compounds. Platinum is the only one of the platinum metals (ruthenium, osmium, rhodium, iridium, palladium, platinum) to form alkyl compounds. Table II lists some of the platinum compounds and gives information about their solubilities.

a. The Oxide and Hydroxide Compounds of Platinum. Although platinum can combine directly with oxygen at a moderate temperature to form an oxide, these compounds are usually impure. Most frequently pure oxides and their hydrates are formed by indirect means. Platinum monoxide, PtO, the lowest oxide of platinum, does not exist in a pure state but in combination with metallic platinum or

platinum dioxide, PtO_2. Its corresponding hydroxide, $Pt(OH)_2$, a black powder, is obtained by heating potassium chloroplatinite, K_2PtCl_4, with alkali hydroxides. $Pt(OH)_2$ will oxidize readily and when strongly heated it will decompose to give platinum metal and PtO_2.

Tetravalent platinum oxide, PtO_2, is the most stable oxide compound of platinum. It is usually obtained as a reddish-brown hydrate precipitate by boiling $PtCl_4$ with alkalis. PtO_2 is soluble in acids; however, when heated for a long time at a temperature of 200° C, it becomes insoluble. Continued heating above 200° C transforms it either to platinum monoxide or to metallic platinum and oxygen. PtO_2, when freshly precipitated, is also soluble in concentrated alkali solutions.

Platinum sesquioxide, Pt_2O_3, can be obtained only in the hydrous state and is produced by the action of NaOH on disulfatoplatinum (III) acid, $H\left[Pt(SO_4)_2\right]$.(3) Pt_2O_3 is oxidized by warming with oxygen and will give up water in this process.

A hexavalent oxygen compound of platinum, i.e., platinum (VI) oxide, PtO_3, appears to have been characterized.(3) Obtained by the anodic oxidation of PtO_2 in potash at temperatures below 0° C, it is a very unstable compound. It will slowly decompose at ordinary temperaturesand will lose oxygen when suspended in water. If it is gently heated, it will lose oxygen rapidly. Dilute hydrochloric acid treatment of PtO_3 will produce free chlorine.

b. The Halide Compounds of Platinum. Platinum dichloride, $PtCl_2$, and platinum dibromide, $PtBr_2$, are most frequently obtained by the thermal decomposition of the tetrahalide compounds. $PtCl_2$ can also be obtained from the thermal decomposition of chloroplatinic acid, $H_2\left[PtCl_6\right]$. The dihalide compounds are only sparingly soluble in water. $PtCl_2$, a greenish-grey or brownish powder, will dissolve in strong HCl to form the complex acid, tetrachloroplatinum (II) acid, $H_2\left[PtCl_4\right]$. This acid forms tetrachloroplatinite salts, e.g. $K_2\left[PtCl_4\right]$, when treated with reagents containing the corresponding alkali.

Of the tetrapositive halide compounds, only platinum tetrafluoride, PtF_4, a yellowish-red solid, is made by a direct combination of the elements. Extreme (red) heat must be used to effect this combination. Platinum tetrachloride, $PtCl_4$, a reddish-brown, hygroscopic mass, is produced by thermally decomposing (at 300° C) chloroplatinic acid in a chlorine atmosphere. Platinum tetrabromide,

Table II

SOLUBILITY OF PLATINUM COMPOUNDS

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Arsenide	$PtAs_2$	Insoluble		Insoluble
Bromides	$PtBr_2$	Very slightly soluble	Insoluble	Soluble in HBr and KBr
	$PtBr_4$	Slightly soluble	Slightly soluble	Very soluble in alcohol, ether, and HBr.
Chlorides	$PtCl_2$	Very slightly soluble	Insoluble	Soluble in HCl and NH_4OH. Slightly soluble in NH_3. Insoluble in alcohol and ether.
	$PtCl_3$	Slightly soluble	Soluble	Very slightly soluble in conc. HCl. Soluble in hot HCl.
	$PtCl_4$	Very soluble	Very soluble	Soluble in acetone. Slightly soluble in alcohol and NH_3. Insoluble in ether.
	$PtCl_4 \cdot 5H_2O$	Very soluble	Very soluble	Soluble in alcohol and ether.
Cyanide	$Pt(CN)_2$	Insoluble	Insoluble	Soluble in KCN. Insoluble in acids, alkalis, and alcohol.
Fluorides	PtF_2	Insoluble	Insoluble	
	PtF_4	Soluble; decomposes	Very soluble	Soluble in acids and alkalis.
Hydroxides	$Pt(OH)_2$	Insoluble	Insoluble	Soluble in HCl, HBr, alkalis. Insoluble in H_2SO_4 and dilute HNO_3.
	$Pt(OH)_2 \cdot 2H_2O$	Insoluble	Insoluble	Soluble in conc. acids
Iodides	PtI_2	Insoluble	Insoluble	Soluble in HI. Slightly soluble in Na_2SO_3. Insoluble in acids.

	PtI_4	Soluble; decomposes		Soluble in alcohol, alkalis, acetone, HI, KI, and NH_3.
Oxides	PtO	Insoluble	Insoluble	Soluble in HCl, H_2SO_3. Insoluble in acids and aqua regia.
	$PtO \cdot 2H_2O$	Insoluble	Insoluble	Soluble in conc. HCl, H_2SO_4 and HNO_3.
	Pt_3O_4	Insoluble	Insoluble	Insoluble in acids and aqua regia.
	$Pt_2O_3 \cdot XH_2O$	Insoluble	Insoluble	Soluble in conc. H_2SO_4 and caustic alkalis.
	PtO_2	Insoluble	Insoluble	Insoluble in acids and aqua regia.
	$PtO_2 \cdot H_2O$	Insoluble	Insoluble	Slightly soluble in NaOH. Insoluble in acetic acid, aqua regia, and HCl.
	$PtO_2 \cdot 2H_2O$	Insoluble	Insoluble	Soluble in HCl, aqua regia, and KOH.
	$PtO_2 \cdot 3H_2O$	Insoluble	Insoluble	Insoluble in HCl and aqua regia.
	$PtO_2 \cdot 4H_2O$	Insoluble	Insoluble	Soluble in acids and dilute caustic alkalis.
	PtO_3	Insoluble	Insoluble	Soluble in HCl and H_2SO_3. Slightly soluble in HNO_3 and H_2SO_4.
Phosphide	PtP_2O_7	Very slightly soluble		
Sulfate	$Pt(SO_4)_2 \cdot 4H_2O$	Soluble	Decomposes	Soluble in acid, alcohol, and ether.
Sulfides	PtS	Insoluble	Insoluble	Soluble in $(NH_4)_2S$. Insoluble in acids and alkalis.
	Pt_2S_3	Insoluble	Insoluble	Slowly soluble in aqua regia. Insoluble in acids.
	PtS_2	Insoluble	Insoluble	Soluble in HCl and HNO_3. Insoluble in $(NH_4)_2S$.

$PtBr_4$, is formed by dissolving platinum metal in a hydrobromic acid-bromine mixture, then removing the solvent and drying the residue. The addition of a hot aqueous solution of KI to a concentrated $H_2[PtCl_6]$ acid solution will produce platinum iodide, PtI_4.

Platinum tetrafluoride, PtF_4, decomposes very vigorously in water; platinum tetrachloride, $PtCl_6$, is very soluble in water and depending upon the temperature can be recovered from the resulting solution in hydrate forms with varied amounts of water of crystallization. It is present in the aqueous solution as the complex acid, dihydroxotetrachloroplatinum (IV) acid, $H_2[PtCl_4(OH_2)]$, which can be isolated by heating the hydrated compounds to 100° C. $PtBr_4$ and PtI_4 are not very soluble in water. $PtCl_4$, $PtBr_4$, and PtI_4 will decompose when heated to form the free halogen and the corresponding dihalide.

A hexavalent platinum fluoride, PtF_6, has been isolated by reacting a platinum filament with fluorine at 300 mm pressure.(4) This compound is formed as a red-black material and appears to be the most unstable and most reactive of the known hexafluorides.

One of the most important platinum compounds, chloroplatinic acid, $H_2[PtCl_6]$, is formed by treating platinum sponge with hydrochloric acid containing chlorine. It can be crystallized from its solutions as brownish-red delequiscent prisms. It is soluble in water, alcohol, and ether. It forms hexachloroplatinate salts, $M_2[PtCl_6]$, when alkali salts are added to its solutions. Ammonium chloroplatinate, $(NH_4)_2[PtCl_6]$ is the best known of these. It is not very soluble in water or alcohol, and it will decompose completely when heated and leave a residue of platinum sponge. The potassium salt, $K_2[PtCl_6]$ is also insoluble in water and alcohol; however, sodium chloroplatinate is very soluble in both water and alcohol. Insoluble silver chloroplatinate, $Ag_2[PtCl_6]$ can be precipitated if silver nitrate solution is added to a solution of a chloroplatinate.

c. Sulfide, Selenide, and Telluride Compounds of Platinum. Platinum monosulfide, PtS, can be formed either by heating a mixture of finely divided platinum and powdered sulfur or by saturating a chloroplatinate (II) salt or tetrachloroplatinum (II) acid with hydrogen sulfide. The grayish-black needle-like precipitate produced will not react with either acids or alkalis and is

insoluble in aqua regia. Platinum disulfide, PtS_2, is produced by saturating a boiling solution of a chloroplatinate (IV) salt or hexachloroplatinic acid, $H_2[PtCl_6]$, with hydrogen sulfide. The black precipitate is very insoluble in acids dissolving slowly in concentrated nitric acid and in aqua regia. It is also insoluble in alkali solutions and can only be put into solution if it is mixed with other soluble sulfides. It will dissolve in polysulfide solutions and can be much more rapidly solubilized if arsenic, tin, antimony, or gold sulfides are present.

Double compounds, or thiosalts, of the platinum sulfides have been obtained by heating finely divided platinum metal with alkali carbonate and sulfur.(5) The general compositions of this thiosalts are $M_4Pt_3S_6$ and $M_1Pt_4S_6$, and they can form diplatinum trisulfide, Pt_2S_3, when oxidized in air.

Selenium and tellurium form binary compounds with platinum. The compounds, platinum selenide, $PtSe_2$, and platinum telluride, $PtTe_2$, are very resistant to acids.

d. Cyano Compounds of Platinum. Tetracyanoplatinum (II) acid, $H_2[Pt(CN)_4]$, can be formed by saturating its silver or copper salts with hydrogen sulfide. It is a strong, dibasic acid, and its alkali and alkaline earth salts are very soluble in water. The best known of these compounds are potassium tetracyanoplatinate, $K_2[Pt(CN)_4]\cdot 3H_2O$ and barium tetracyanoplatinate (II), $Ba[Pt(CN)_4]\cdot 4H_2O$.

e. Complex Platinum Compounds. Many coordination compounds of platinum are known. It can form acido compounds in both the +2 and +4 states and will unite with ammonia and nitrogen bases to form platinum ammines. The hexachloroplatinates (IV), $M_2[PtCl_6]$ are the best known of the acido compounds. When these salts are heated with alkali solutions, hexahydroxoplatinates (IV), $M_2[Pt(OH)_6]$, are formed. If acid is added to solutions of these salts, a white precipitate of hexahydroxoplatinic acid, $H_2[Pt(OH)_6]$, will be produced.

The tetrachloroplatinates (II) are the chief acido compounds of divalent platinum and they have as their antecedent the corresponding acid, H_2PtCl_4. Tetrachloroplatinum (II) acid, $H_2[PtCl_4]$ cannot be isolated, but exists only as a dark red solution and as its salts. The cyanoplatinates mentioned earlier are also acido compounds of divalent platinum.

The platinum ammines exist in very large numbers. No attempt will be made

to characterize these compounds, since more specific information is given elsewhere[7,8]. In addition to the ammines, many complex platinum compounds containing organic sulfides, R_2S, tertiary phosphines, R_3P, and tertiary arsines, R_3As, etc. are known.[8] Each of these compounds closely resemble the ammines.

f. The Alkyl Compounds of Platinum. Platinum is the only one of the platinum metal group that will form alkyl compounds.[9] The triaklyl platinum halide, trimethylplatinum iodide, $(CH_3)_3PtI$, is characteristic of this group of compounds. It can be produced by the action of Grignard reagent on $PtCl_4$. Its crystals are orange in color; they will not dissolve in water but can be put into solution with organic solvents. Tetramethyl platinum, $(CH_3)_4Pt$, is formed by the action of sodium methyl on $(CH_3)_3PtI$. It is stable in air and is soluble only in organic solvents.

B. The Analytical Chemistry of Platinum

Platinum, after its isolation and separation from other elements, is usually determined gravimetrically as the metal.[10,11] Reducing agents such as formic acid or sodium formate, or its displacement with powdered zinc, aluminum, or magnesium metal, are most frequently used to precipitate platinum as the metal.

The reviews by Gilchrist[12] and Beamish[13] report on many of the methods used to isolate and separate platinum and the other platinum group metals from other elements and from each other. Some of these methods have been or can be considered by radiochemists in their work with the platinum radionuclides and the information presented below is intended to provide ideas for possible use in other radiochemical separation methods for the platinum radioisotopes.

1. Separation By Precipitation

The platinum metals can be separated from most of the other chemical elements by a precipitation with hydrogen sulfide in an acid solution.[14,15] Silver, copper, cadmium, mercury, indium, germanium, tin, lead, arsenic, antimony, bismuth, molybdenum, selenium, tellurium, and rhenium can interfere in this separation. All of the platinum metal sulfides are readily soluble in aqua regia and the compounds that result can contain closely bound sulfate groups which may affect any subsequent reactions of these compounds with

other reagents. Taimini and Salaria[16] have used the solubility of the metal sulfides in alkaline solutions to separate platinum, as well as the other platinum metals, from many of the other chemical elements. Richmond, et al[17] have also used hydrogen sulfide separations in their work on binary alloys of platinum and uranium.

As early as 1900, Leidie[18] showed that a digestion of the chloro compounds of the platinum metals with sodium nitrite would convert these compounds into soluble stable nitrite complexes so that base metals could be readily separated from the platinum metal by precipitating them from the solution as oxides or as hydrated oxides. Such a method has been used to separate gold and base metals from rhodium, iridium, ruthenium, platinum, and palladium. For example, after a conversion of the nitrite solutions, platinum (and iridium) were isolated with ammonium chloride.[19] Gilchrist and Wichers[20] have also used this approach to isolate the platinum metals. In each of these applications, it was shown that it was necessary to reconvert the nitrite compounds to the chloro compounds before they could be further processed.[18]

Blackmore, et al[21] and Gilchrist[22] have precipitated platinum as ammonium chloroplatinate. This separates it from many other elements. Os^{+4}, Ru^{+4}, and Ir^{+4} also precipitate. The ammonium chloroplatinate can be calcined to produce platinum metal. Sodium formate[10,11,21,23] and zinc metal[10,11,21] have also been used to precipitate platinum metal. Hagen[24] has shown that small amounts of platinum metal could be reduced and collected by coprecipitation upon macro amounts of tellurium metal from a hot acid solution reduced with a 20% stannous chloride solution. Westland and Beamish[25] have used a similar method to isolate platinum and palladium.

Gold can be separated from the platinum metals by precipitation methods using such reagents as ferrous sulfate[25], sulfur dioxide[10], oxalic acid[10], hydroquinone[26], tetraethylammonium chloride[27]; and sodium nitrite.[23] The choice of reagent depends upon the separation procedure to be followed in analyzing the solution for platinum.[10]

Beamish[13] reports that in practically all of the acceptable analytical schemes for separating the platinum metals, osmium is removed first by a distillation as OsO_4 from a nitric acid solution. Ruthenium is then removed as

RuO_4 from a dilute H_2SO_4 solution containing bromate. Palladium, rhodium, and iridium are separated, either singly or collectively, from platinum by controlled hydrolysis of their chloro complexes in the presence of bromate. The precipitate(s) are readily filterable and contain very little platinum.

Sometimes platinum and palladium are isolated together. A number of precipitation methods exist to separate them. Besides the hydrolysis of the chloro complex,[13] platinum can be separated from palladium by a precipitation as ammonium chloroplatinate,[21,22] the hexachloride,[28] and a reduction with acetylene.[29] Hydrolytic separations involving zinc oxide,[30] lime water,[31] and sodium hydrogen carbonate[32-34] have been used also to effect a separation of platinum and palladium. The precipitation of palladium quantitatively from a chloride solution by the addition of a soluble iodide also has been used to separate palladium and platinum.[35] Mercuric cyanide solutions[36] and ethylene[37] can also be used to precipitate palladium salts and separate them from platinum.

2. Separation By Volatility or Electrolysis

Although platinum is considered to be one of the nonvolatile members of the platinum group (the others are Pd, Ir, and Rh) volatile platinous chloride, $PtCl_2$, can be formed and lost if ammonium chloroplatinate is ignited in a reducing atmosphere[10]; however, no separational methods for platinum by such a volatilization technique have been recorded. Likewise, Beamish[13] reports that there are no recorded electrolytic separation methods for platinum.

3. Separation By Solvent Extraction

Morrison and Freiser[38] present information on the applications of solvent extraction in the analytical chemistry of platinum. Some of these methods can be used in the radiochemistry of the platinum radionuclides.

a. Ion Association Systems. Meinke,[39] reporting on the preparation of radioactive tracers, describes a radiochemical procedure in which greater than 95% Pt^{+2} could be extracted from a 3 M HCl - 10% $SnCl_2$ solution into ethyl ether. Radioactive platinum has also been isolated from a radioactive osmium target by extracting a 3 M HCl solution with ethyl ether.[40] An

ethyl ether extraction from a 6.9 M HI solution has been used[41] to quantitatively extract Au^{+3}, Sb^{+3}, Hg^{+2}, Cd^{+2}, and Sn^{+2} from iodide solutions containing Pt (as well as Pd, Ir, Os, and Ru). The platinum metals do not extract under these conditions. Methyl isopropyl ketone will partially extract platinum (and Ru and Rh) from iodide - 5% HCl solutions.[42]

McBryde and Yoe[43] have isolated and completely separated Au^{+3} from Pt (Pd, Rh, Ir, and Ru) by extracting the gold from a 2.5-3.0 M HBr solution into isopropyl ether. Amyl acetate will extract and separate platinum from osmium and ruthenium contained in $HCl-NH_4Cl-SnCl_2$ solutions.[44] Rh, Ir, Au, Te, and small amounts of Pd also extract in this system. Pt^{+2} will only partially extract from a 1 M HCl solution into tri-n-octylphosphine oxide.[45] Cr^{+6}, Au^{+1}, Hf^{+4}, Fe^{+3}, Mo^{+6}, Sn^{+4}, U^{+6}, and Zr^{+4} quantitatively extract in this system.

b. Chelate Complex Systems. Pt (as well as Bi, Cd, Cu, Pd, Sn^{+2}, U^{+6}, Hg, Th, Co, Pb, Fe^{+2}, Ni, Zn, La, Ce^{+4}, In, Sc, and Eu) forms a water insoluble complex with 1-(2-pyridylazo)-2-naphthol.[46] These complexes are soluble in amyl alcohol. Sandell[47] reports that Pt^{+2} dithizonate forms a collodial solution when a chloroform extraction of a weakly acid solution is made. The dithizonates of Pt^{+4} and the other platinum metals in the quadrivalent or trivalent states do not react under these conditions.

Thiosemicarbizide forms a colored compound with Pt^{+4} in a weakly basic solution that can be extracted into either ethyl or amyl acetate.[48] The phenylthiourea complex of Pt^{+4} is partially extracted (40%) from a dilute HCl solution with either ethyl or amyl acetate.[49] Under these conditions, the Pd^{+2} complex extracts quantitatively and the Cu^{+2} complex extracts to about 16%. Less than 1% of the Ir^{+4}, Rh^{+3}, Ru^{+3}, Os^{+4}, Au^{+3}, Fe^{+3}, Co^{+2}, Ni^{+2}, and Cr^{+6} complexes will extract in these systems.

Coburn, et al,[50] following a cation ion exchange resin method of separating platinum (and palladium) from copper, iron and nickel, converted the Pt and Pd chlorides to diethyldithiocarbamates and extracted them with chloroform. Palladium was then extracted with p-nitroso-dimethylamine and determined by dimethylglyoxime; platinum was determined by thiophenol.

Neither platinum nor rhodium produce a carbon tetrachloride extractable colored-complex with ephedrine hydrochloride.[51] Pd, Au, Ir, and Os^{+8} do and are extractable. Microgram amounts of Pt^{+2} and Pt^{+4} form colored-complexes with thiosalicylideneethylenediimine that are extractable into chloroform.[51] These complexes (as well as those of Ni^{+1}, In^{+2}, Te^{+4}, Sn^{+2}, Sb^{+3}, Cd^{+2}, Pb^{+2}, and Au^{+3}) are stable in HCl.

4. Chromatography Separations

a. By Organic and Inorganic Adsorbents. Although Beamish[13] in his review reports that one of the first chromatographic methods for the platinum metals involved the use of a column of powdered carbon, the use of carbon as an adsorbent has not been seriously considered in separations of the platinum metals. Dubrisy[53] has shown that when dilute solutions of a platinum metal were passed through a column of finely divided carbon, the metals collected in the upper part of the tube and could be subsequently extracted with suitable solvents. Bauer and Nagel[54] used a similar method to separate gold, silver, and platinum from sea water.

Platinum can be separated from iridium, ruthenium, palladium, and rhodium by adsorption from an aqueous solution upon an alumina column and eluting with various reagents.[55] Pb, Cu, Zn, and Ni, but not Fe^{+3}, can be separated from the platinum metals in this system. Venturello and Saini[56] have also used an alumina column to separate the platinum metals from other elements. After their adsorption on the column, benzidine was used as the eluant reagent to effect the separation.

b. With Ion Exchange Resins. Kraus and Nelson,[57] and Kraus, et al[58] have shown that Pt^{+4} could be separated from Ir^{+3} by adsorption upon an anion exchange resin, Dowex 1, in the chloride form. Ir^{+3} was eluted with 10 N HCl; Pt^{+4} (and/or Pd^{+2}) remained on the ion exchange column in this system. Blasius and Wachtel[59] have used an anion exchange resin (Permutit E. S.) in the hydroxide form to separate Pd-Pt, Rh-Pt, and Ir-Pt. After adsorption upon the column from NaOH solutions, Pd was separated from Pt by elution with NaOH; Pt was removed from the column by elution with HNO_3. In the separations of Rh and Ir, sodium oxalate was used to reduce both Rh and Ir to

the tetravalent state and after adsorption separated from Pt by elution with 1 N NaOH; Pt remained on the column and was removed from the column with a HNO_3 elution.

The anion-exchange resin, Dowex-2, has been used to adsorb and separate the chloro complexes of Pd, Pt, Rh, and Ir,[60] Elutions with ammonium hydroxide-ammonium chloride were used to effect the separations. Amberlite IRA-400 resin has been used in studies concerned with the anion exchange separations of Pt from Rh, Pd, and Ir.[61] Distribution coefficients for the chlorides of these metals were obtained; however, the recovery of platinum was incomplete since Pt^{+4} was reduced to Pt^{+2} during the reduction of iridium by hydroxylamine. As part of this investigation, the authors[61] showed that the separation of Pt from Rh, Ir, and Pd was best obtained by a hydrolytic precipitation of Rh, Ir, and Pd. Following this precipitation, these three metals were separated from each other by dissolving the oxides in HCl and then adsorbing the solution upon the Amberlite IRA-400 resin column and eluting with HCl.

Stevenson, et al[62] have used the cation resin, Dowex-50, to separate Pt from Pd, Rh, and Ir. Chloride solutions of the metals were converted to the perchlorate form and passed through the Dowex-50 column. Palladium, rhodium, and iridium were adsorbed on the column, while platinum passed through. Pd, Rh, and Ir were subsequently separated from each other by elutions with various molarities of HCl. MacNevin and Crummett[60,63] and MacNevin and McKay[64] report on the use of the cation resin, Amberlite IR-100, and elutions with ammoniacal solutions to separate Pt from Rh, Ir, and Pd.

Milligram amounts of Pt (and Pd, Ir, and Rh) as the chloride complexes have been separated from copper, nickel, iron, and lead by use of the cation resin, Espatite-K-V-1, in either the H^+ or Na^+ form.[65] The acid form of 8% cross-linked Dowex-50 resin has been used to separate iron, copper, and nickel from platinum and palladium.[50] Hydrochloric acid solutions (at pH 1.5) of the metallic mixtures were passed through the column. Copper, iron, and nickel were retained on the column while Pt and Pd passed on through. Pt was then separated from Pd by converting the chloride solution to diethyldithiocarbamates and extracting with chloroform.

c. By Paper Chromatography. Pt^{+4} has been separated from other cations by use of paper chromatography and solvent systems such as butanol-HCl[66], alcohol-HCl[67,68], binary alcohol mixtures containing HCl[69], ketone-HCl[70], and butanol-HBr.[71] Platinum (and Pd^{+2}) have been separated completely from mixtures containing copper and silver using paper chromatography and HCl-saturated butanol.[72,73] If gold is present in the mixture, it will extract with the butanol phase which travels ahead of the aqueous front. Kember and Wells[74] describe separations of platinum, rhodium, palladium, and iridium in microgram amounts by use of paper-strip chromatography and various solvents. Using hexone-pentanol-HCl mixtures, separations of rhodium, palladium, and platinum, and of iridium, palladium, and platinum, in that order, were achieved. When Ir-Pt-Pd-Rh were mixed and separated, the iridium was reduced by the solvent mixture and it separated with rhodium. Other tests in the same study showed that associated base metals, copper, iron, nickel, etc., could be separated from the platinum metals by use of n-butanol saturated with 3 N HCl.

Burstall, et al[75] have shown that methyl propyl ketone or methyl ethyl ketone-HCl mixtures will separate gold, osmium, platinum, palladium, rhodium, iridium, and ruthenium in that order from a chloride system on a cellulose column. Stannous chloride was found to be a suitable reagent for separating Pt, Pd, Au, and Rh. Acetone-HCl was used to extract Ir^{+4}. Lederer[73] has also noted a similar behavior with gold, iridium, platinum, palladium, rhodium, and ruthenium. Rees-Evans, et al[76] have used 15-30 cm cellulose columns pretreated with such solvents as hexone-3% HCl to separate milligram amounts of Pt, Pd, Rh, and Ir from each other and from iron, copper, zinc, nickel, and mercury. Pt and Ir were separated together from the mixture and then from each other by use of reducing conditions in order to decrease the mobility of the iridium on the column.

d. By Electro-Chromatographic Methods. Platinum, palladium, and gold have been separated from milligram amounts of copper by separating the copper by applying a current of 200 milliamperes across a paper strip immersed in hydrochloric acid and potassium chloride.[77] A potential of 12 volts was maintained between the carbon electrodes. Ethyl ether-HCl mixtures were used as solvents to

further separate the Pt, Pd, and Au; gold separated first with the ethyl ether front.

Majumdar and Chakrabartty[78] report on electro-chromatography techniques using a potential of 150 volts and different electrolytes to separate the platinum metals. MacNevin and Dunton[79] used descending chromatography and horizontal electro-chromotography to show that milligram amounts of mixtures of 2 or 3 of the platinum metals (Pt, Pd, Ir, and Rh) could be separated. Lederer[80] showed that rhodium could be separated chromatographically from Pt^{4} and Pd^{+2} by paper electrophoresis. Cetini[81] used a similar technique to separate Pt^{+2}, Au^{+3}, WO_4, and Co^{+2}.

IV. DISSOLUTION OF SAMPLES CONTAINING PLATINUM

All of the platinum metals except palladium resist attack by single mineral acids.[13] Selective dissolution methods to separate base metals from materials containing the platinum metals have involved collective precipitations by zinc or iron and subsequent attack with HNO_3 and HCl,[82] concentrated H_2SO_4 and sulfur,[83] aqua regia,[84,85] sulfide fusions,[86,87] leaching[88] and amalgamation.[89] Many procedures involving "fire assay" methods of isolating the platinum metals from ores are known.[13] Typical of newer methods of fire assay is that proposed by Plummer, et al.[90,91] In general, it consists of preparing a base metal alloy button by reduction with mechanically mixed carbon, sodium carbonate, borax, and ore; base metal oxides are added, if required. The reduction was carried out at a temperature of 1450° and, after its preparation, the button was dissolved in HCl and HNO_3. The platinum metals were then extracted from the solution by methods similar to those described elsewhere in this monograph.

Any one of these dissolution techniques can be adapted for use in the radiochemistry of the platinum radionuclides. The addition of platinum carrier to the mixture before dissolution begins will assist in achieving an exchange of the radioactive and inactive platinum atoms.

V. SAFETY PRACTICES

Adequate safety precautions should be followed in dissolving any sample material whether it is radioactive or nonradioactive. The manual by Pieters and

Creyghton[92] is one of several that report on the toxicology of most inactive elemental compounds. Such a manual as this should be consulted before any analysis is undertaken.

Safe practices in handling radioactive sample materials are always important in radiochemistry. The discharge of radioactivity by explosion or evolution into a laboratory area can be hazardous and can result in wide-spread contamination. Thus, some source of information on safe-handling practices for processing radioactive materials should be consulted before a radiochemical analysis is begun. Information on such practices appears in the Oak Ridge National Laboratory's Master Analytical Manual[93] and in the International Atomic Energy Agency's publication, entitled "Safe-Handling of Radioisotopes."[94] Many other similar sources of information exist and should be consulted.

VI. COUNTING TECHNIQUES FOR THE RADIOACTIVE PLATINUM ISOTOPES

The analysis of sample materials containing platinum radionuclides may be completed either by a direct (nondestructive) measurement of the radionuclide in the irradiated sample or by obtaining the radionuclide in some form by radiochemically processing the irradiated sample. The use of either technique is dependent upon the specific characteristics of the platinum radioisotope being measured, i.e., its half-life, the type radiations it emits as it decays and the energy of those radiations. The ease with which a nondestructive analysis method can be applied is most frequently influenced by the radioactivity of the sample matrix containing the platinum radionuclide. If this presents a considerable interference, then the sample must be processed radiochemically.

Table I of this Monograph shows the nuclear characteristics of each of the known radioactive isotopes of platinum. The radioactivity of these can be measured by either standard Geiger-Mueller, gamma scintillation, or proportional counting techniques.[95-98] One of these, gamma scintillation spectrometry,[98] has been used by Miller[99] in determining the stable platinum content of platinum-rhodium alloys. A nondestructive analysis of the irradiated materials by using the 0.070-and 0.179-Mev gamma radiation from the 31-minute Pt^{199} isotope was made.

VII. RADIOCHEMICAL PROCEDURES FOR THE PLATINUM RADIONUCLIDES

Both carrier-free and carrier radiochemical analysis procedures exist for the platinum radionuclides. Such procedures as these have evolved from each investigator's choice of ideas and techniques similar to those reported in Section III of this monograph.

Typical of the carrier-free techniques originated to prepare radioactive platinum tracers is that by Gile, et al.[40] The carrier radiochemical procedures that now exist for the platinum radionuclides have originated from investigations concerned with either the separation of radioactive tracers,[39] the separation of radioactive platinum isotopes from fission products,[39] or in radioactivation analysis.[100,101] With regard to radioactivation analysis, this unique technique has been applied to the determination of trace stable platinum in marine organisms,[102] in refined silver and nickel cathodes,[103] and metals.[104]

In the radiochemical procedures that follow, special information, regarding the procedure's use, the type of nuclear bombardment, the type of material analyzed, separation time, etc., appears as part of each procedure. When ever possible, an evaluation of each procedure is made with regard to its use in the contamination of other radioactive species from the radioactive platinum isotopes.

PROCEDURE 1

Procedure Used In: Preparation of Radioactive Platinum Tracer

Method: Solvent extraction (carrier-free)

Element Separated: Radioactive platinum tracer

Type Material Analyzed: Osmium target

Type Nuclear Bombardment: Cyclotron

Procedure By: Gile, J. D., et al[40]

Separation Time: A few minutes

Chemical Yield of Carrier: Carrier-free procedure

Decontamination: Excellent from osmium

Equipment Required: Standard

Procedure:

1. Dissolve osmium target in aqua regia. Add additional HNO_3 and evaporate solution to near dryness to volatilize OsO_4. Repeat HNO_3 addition and evaporation.

2. Take up residue in HCl; add enough water to make the solution 3 M in HCl. Then add 10% $SnCl_2$ solution to reduce platinum and an equal volume of ethyl ether.

3. Extract H_2PtCl_4 into the ethyl ether by shaking mixture for several minutes. Separate phases, save the organic phase. Repeat extraction if required.

4. Evaporate organic phase to dryness; take up residue in dilute acid. Aliquot for radioactivity measurements.

PROCEDURE 2

Procedure Used In: Preparation of Radioactive Platinum Tracers

Method: Precipitation

Element Separated: Radioactive platinum tracer

Type Material Analyzed: Platinum, iridium, gold, or mercury

Type of Nuclear Bombardment: a. 60" cyclotron (37-Mev alphas, 9.5-Mev protons, 19-Mev deuterons)
b. 184" cyclotron (388-Mev alphas, 348-Mev protons, 194-Mev deuterons)

Procedure By: Wilkinson and Hicks (Reported by Meinke[39])

Separation Time: 1-4 hours

Chemical Yield of Carrier: ~100%

Decontamination: Decontaminates well from Au, Ir, and Hg

Equipment Required: Standard

Procedure:

1. Dissolve targets (except Ir) in HCl with minimum of HNO_3.

2. Add Au, Hg, Pt, and Ir carriers as needed. Extract the solution twice with equal volumes of ethyl acetate to get rid of Au (chloride concentration need only be above 1 N), with gold added for the second extraction.

PROCEDURE 2 (Continued)

3. Destroy all nitrates 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 an equal volume of 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 it forms a slow dissolving sponge.)

PROCEDURE 3

Procedure Used In: Preparation of radioactive platinum tracers

Method: Precipitation and solvent extractions

Element Separated: Radioactive platinum tracer

Type Material Analyzed: Iridium

Type of Nuclear Bombardment: 184" cyclotron (any energy protons)

Procedure By: Thompson and Rasmussen (Reported by Meinke[39])

Separation Time: 30 minutes

Chemical Yield of Carrier: ~70%

Decontamination: 10^2

Equipment Required: Standard

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 amounts. (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 3 N HCl.

7. Plate organic layer and 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.

PROCEDURE 4

Procedure Used In: Preparation of Radioactive Platinum Tracer; separation from fission products

Method: Distillation, solvent extraction, and precipitation

Type Material Analyzed: Uranium metal

Type of Nuclear Bombardment: 184" cyclotron (388-Mev alphas)

Procedure By: Wolfe (Reported by Meinke[39])

Separation Time: 30 hours (when separated with Ir and Rh)

Chemical Yield of Carrier: ~5%

Decontamination: 10^4

Equipment Required: Standard

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 an equal volume of 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 cherry-red color of Pt^{+2} 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.

PROCEDURE 5

Procedure Used In: Radioactivation analysis

Method: Precipitation

Element Separated: Pt^{197} (18 h)

Type Material Analyzed: Marine Organisms[102]

Type Nuclear Bombardment: $Pt^{196}(n,\gamma)Pt^{197}$

Procedure By: Fukai and Meinke[102]

Separation Time: (unknown)

Chemical Yield of Carrier: (unknown)

Decontamination: (unknown)

Equipment Required: (unknown)

Procedure:

Note: The authors[102] point out that the specimens were irradiated for a few hours, then processed radiochemically. Pt^{197} radioactivity was measured by gamma spectrometry.

PROCEDURE 6

Procedure Used In: Radioactivation Analysis

Type Material Analyzed: Refined silver and nickel cathodes[103]

Type Nuclear Bombardment: Neutron

Procedure By: Zvyagintsev, O. E., and Kulak, A. I.[103]

Separation Time: (unknown)

Decontamination: Radioactive gold also determined in this work. No information available on decontamination.

Equipment Required: (unknown)

Procedure:

Note: Specific information on this procedure not available. Publication should be consulted.

PROCEDURE 7

Procedure Used In: Radioactivation Analysis

Method: Precipitation

Element Separated: Pt^{197} (18 h)

Type Material Analyzed: Metals[104]

Type Nuclear Bombardment: $Pt^{196}(n,\gamma)Pt^{197}$

Procedure By: Mahlman, H. A. (Reported by Leddicotte[104])

Separation Time: 3.0 hours

Chemical Yield of Carriers: 65-70%

Decontamination: $>10^4$

Equipment Required: Standard

Procedure:

1. Dissolve the irradiated sample (Note 1) in HCl plus a few drops of HNO_3 and add standardized Pt carrier. Add the following holdback carriers: Cu, Fe, Co, Sr, Na, Au, Hg, and Ir. Evaporate to dryness.

2. Take up residue in 20 ml of 1 N HCl and extract the solution twice with equal volumes of ethyl acetate (Note 2). Discard organic layers.

3. To the aqueous layer, add hydroxylamine hydrochloride dropwise to

destroy any nitrates in the solution. Add 0.1 gram of $SnCl_2$. Centrifuge and discard ppt.

4. The red color ($PtCl_4$) is extracted from the supernate by shaking with an equal volume of ethyl acetate (Note 3). Wash the organic layer twice with equal volumes of 6 N HCl and then evaporate to dryness.

5. The residue is taken up in 2 N HCl and Pt metal is precipitated with magnesium metal powder. Centrifuge and discard supernate. Wash ppt with two 10 ml portions of 2 N HCl. Centrifuge and discard washes.

6. Filter the Pt through a tared filter paper. Wash with three 10-ml portions of hot H_2O and two ml portions of alcohol. Dry for 15 minutes at 110° C. Weigh as platinum metal. Mount and count (Note 4).

Notes:

1. Samples irradiated in the ORNL Graphite Reactor at a flux of about 6.5×10^{11} $n/cm^2/sec.$ for 16 hours. Limits of measurement about 1.0 microgram.

2. Additional gold holdback carrier may be added before the second extraction.

3. If aqueous phase is still red in color repeat extraction with an equal volume of ethyl acetate. Combine extracts.

4. May be completed either by Geiger-Mueller or gamma scintillation counting.

REFERENCES

1. Strominger, D., Hollander, J. M., and Seaborg, G. T., "Table of Isotopes," Rev. Mod. Phys. 30 (2), p. 585-904 (1958).

2. Hughes, D. J., and Harvey, J. A., "Neutron Cross Sections," Brookhaven National Laboratory, Upton, New York, Report No. BNL-325, 1958.

3. Remy, H., Treatise on Inorganic Chemistry, Volume I, p. 346, Elsevier, Amsterdam, 1956.

4. Weinstock, B., Claassen, H. H., and Malm, J. F., J. Am. Chem. Soc. 79, 5832 (1957).

5. Remy, H., op. cit., p. 347.

6. Remy, H., op. cit., p. 348.

7. Munzer, G., Das Platin, Leipzig (1929).

8. Remy, H., op. cit., p. 348-349.

9. Remy, H., op. cit., p. 345.

10. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. E., Applied Inorganic Analysis, pp. 339-383, John Wiley and Sons, New York, 1953.

11. Charlot, G., and Bezier, D., Quantitative Inorganic Analysis, pp. 538-539, John Wiley and Sons, New York, 1957.

12. Gilchrist, R., Chem. Rev. 32, 277 (1943).

13. Beamish, F. E., Talanta 5, 1-35 (1960).

14. Lundell, W. F., et al, op. cit., pp. 358-359.

15. Rodden, C. J., Analytical Chemistry of the Manhattan Project, pp. 491-493, McGraw-Hill, New York, 1950.

16. Taimini, I. K., and Salaria, G. B. S., Anal. Chim. Acta. 11, 329 (1954).

17. Richmond, M. S., Baldwin, J. R., and Maienthal, E. J., "Chemical Analysis of Binary Alloys of Platinum and Uranium," USAEC Report, NBS-4555 (1956).

18. Leidie, E., Bull. Soc. Chim. France 10, 253 (1901).

19. Ann. Inst. Platine (Russia) 4, 347 (1926).

20. Gilchrist, R., and Wichers, E., J. Amer. Chem. Soc. 57, 2565 (1935).

21. Blackmore, A. P., Marks, M. A., Barefoot, R. R., and Beamish, F. E., Anal. Chem. 24, 1815 (1952).

22. Gilchrist, R., Anal. Chem. 25, 1617 (1953).

23. Gilchrist, R., J. Res. Nat. Bur. Standards 20, 745 (1938).

24. Hagen, S. K., Microchemie 20, 180 (1936).

25. Westland, A. D., and Beamish, F. E., Mikrochim. Acta 1957, p. 625.

26. Beamish, F. E., Russell, J. J., and Seath, J., Ind. Eng. Chem., Anal. Ed. 9, 174 (1937).

27. Maynard, J. L., ibid., 8, 368 (1938).

28. Pshenitsyn, N. K., and Gladyshevskaya, K. A., Inst. Obschei i Neorg. Khim., Akad. Nauk, S. S. S. R. 22, 60 (1948).

29. Pshenitsyn, N. K., Ginsburg, S. E., and Salskaya, L. G., ibid., 64.

30. Pshenitsyn, N. K., and Ginsburg, S. E., ibid., 24, 251 (1835).

31. Dobereiner, F., Liebig's Ann. 14, 251 (1835).

32. Gilchrist, R., J. Res. Nat. Bur. Standards 6, 421 (1931).

33. Gilchrist, R., J. Res. Nat. Bur. Standards 12, 291 (1934).

34. Ryan, D. E., Analyst 76, 310 (1951).

35. Beamish, F. E., and Dale, J., Ing. Eng. Chem., Anal. Ed. 10, 697 (1938).

36. Lundell, W. F., et al, op. cit., p. 357.

37. Ogburn, S. C., and Brastow, W. C., J. Amer. Chem. Soc., 55, 1307 (1933).

38. Morrison, G. H., and Freiser, H., Solvent Extraction In Analytical Chemistry, John Wiley and Sons, New York, 1957.

39. Meinke, W. W., Chemical Procedures Used In Bombardment Work at Berkeley, USAEC Report, AECD-2738 (1949).

40. Gile, J. D., Harrison, W. H., and Hamilton, J. G., J. Chem. Phys. 19, 1426 (1951).

41. Kitahara, S., Bull. Inst. Phys. Chem. Research (Tokyo) 24, 454 (1948).

42. West P. W., Serrise, P., and Carlton, J. K., Anal. Chim. Acta 6, 488 (1952).

43. McBryde, W. A. E., and Yoe, J. H., Anal. Chem. 20, 1094 (1948).

44. Ayres, G. H., and Meyer, A. S., Anal. Chem. 23, 299 (1951).

45. White, J. C., "Extraction of the Elements With Tri-2-Ethylhexyl-and Trihexylphosphine Oxides from Acidic Solutions," CF-57-1-5, Oak Ridge National Laboratory, January 2, 1957.

46. Cheng, K. L., and Bray, R. H., Anal. Chem. 27, 782 (1955).

47. Sandell, E. B., Colorimetric Determination of Traces of Metals, 2nd ed., Interscience, New York, 1950.

48. Arreguine, V., Rev. Asso. bioquim. Argentina 14, 196 (1947).

49. Ayres, G. H., and Tuffly, B. L., Anal. Chem. 24, 949 (1952).

50. Coburn, H. G., Beamish, F. E., and Lewis, C. L., Anal. Chem. 28, 1297 (1956).

51. Thompson, S. O., Beamish, F. E., and Scott, M., Ind. Eng. Chem. Anal. Ed. 9, 420 (1937).

52. Beck, G., Mikrochemie ver. Mikrochim. Acta 33, 188 (1947).

53. Dubrisay, R., Compt. rend. 225, 300 (1947).

54. Bauer, E., and Nagel, O., Chem. Abs. 9, 289 (1915).

55. Schwab, G. M., and Ghosh, A. N., Z. Anorg. Chem. 258, 323 (1949).

56. Venturello, G., and Saini, G., Ann. Chem. Appl. 39, 375 (1949).

57. Kraus, K. A., and Nelson, F., J. Am. Chem. Soc. 76, 984 (1954).

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

59. Blasius, E., and Wachtel, U., Z. fur. Anal. Chemie, 142, 341 (1954).

60. MacNevin, W. M., and Crummett, W. B., Anal. Chem. 25, 1628 (1953).

61. Berman, S. S., and McBryde, W. A. E., Can. J. Chem. 36, 835 (1958).

62. Stevenson, P. C., Franke, A. A., Borg, R., and Nervik, W., J. Am. Chem. Soc. 75, 4876 (1953).

63. MacNevin, W. M., and Crummett, W. B., Anal. Chim. Acta 10, 323 (1954).

64. MacNevin, W. M., and McKay, E. A., Anal. Chem. 29, 1220 (1957).

65. Pshenitsyn, N. K., Gladyshevskaya, K. A., and Ryakhova, L. M., Zhur. Neorg. Khim. 2, 1057 (1957).

66. Lederer, M., Anal. Chim. Acta 7, 458 (1952).

67. Lederer, M., Anal. Chim. Acta 5, 185 (1951).

68. DeCarvalho, R. G., Paper, Inter. Conf. of Analytical Chemistry, Lisbon, 1956.

69. Walker, W. R., and Lederer, M., Anal. Chim. Acta 5, 191 (1951).

70. Carleson, G., Anal. Chem. Scand. 8, 1673 (1954).

71. Kertes, S., and Lederer, M., Anal. Chim. Acta 15, 543 (1956).

72. Bouissieres, C., and Lederer, M., Bull. Soc. Chim. France 1952, 904-910.

73. Lederer, M., Nature 162, 776 (1948).

74. Kember N. F., and Wells, R. A., Analyst 80, 735 (1955).

75. Burstall, F. H., Davies, G. R., Linstead, R. P., and Wells, R. A., J. Chem. Soc. 1950, 516.

76. Rees-Evans, D. B., Ryan, W., and Wells, R. A., Analyst 83, 356 (1958).

77. Anderson, F. R. A., and Lederer, M., Anal. Chim. Acta. 5, 321 (1951).

78. Majumdar, A. K., and Chakrabartty, M. M., Naturwiss. 44, 9 (1957).

79. MacNevin, W. M., and Dunton, M. L., Anal. Chem. 29, 1806 (1957).

80. Lederer, M., J. Chromatog. 1, 279 (1958).

81. Cetini, G., Atti. Accad. Sci. Torino, 91 (1956-57).

82. Wilm, T., J. Chem. Soc. 40, 514 (1881).

83. Seliverstov, N. S., Inst. Obshchei i Neorg. Khim. Akad. Nauk., SSSR 22, 80 (1948).

84. Karpov, B. G., and Fedorova, A. N., Ann. Inst. Plat. 9, 106 (1932).

85. Zhemchuzhny, S. F., et al, ibid, 4, 339 (1926).

86. Lovely, W. H. C., Chem. Eng. Mining Rev. 33, 199 (1941).

87. Griffth, L., Trans. Canad. Inst. Mining Met. 43, 153 (1940).

88. Hoffman, I., Westland, A. D., Lewis, C. L., and Beamish, F. E., Anal. Chem. 28, 1174 (1956).

89. Plaksin, I. N., and Schtamova, S. M., Ann. Inst. Plat., 11, 141 (1933).

90. Plummer, M. E. C., Lewis, C. L., and Beamish, F. E., Anal. Chem. 31, 254 (1959).

91. Plummer, M. E. V., and Beamish, F. E., Anal. Chem. 31, 1141 (1959).

92. Pieters, H. A. J., and Creyghton, J. W., Safety in the Chemical Laboratory, Academic Press, New York, 1957.

93. Leddicotte, G. W., Reynolds, S. A., Corbin, L. T., Safety, Method No. 50150, ORNL Master Analytical Manual, TID-7015, Section 5.

94. International Atomic Energy Agency, Safety Series No. 1, Safe Handling of Radioisotopes, Vienna, 1958.

95. Reynolds, S. A., Record of Chemical Progress 16, 99 (1955).

96. Price, W. J., Nuclear Radiation Detection, McGraw-Hill, New York, 1958.

97. Siegbahn, K., Beta- and Gamma-Ray Spectroscopy, Interscience, New York, 1955.

98. Crouthamel, C., Applied Gamma-Ray Spectrometry, Pergamon, New York, 1960.

99. Miller, C. E., "Neutron Activation Analysis Methods for the Group VIII Elements," USAEC Report, ORNL-2715 (May, 1959).

100. Boyd, G. E., Anal. Chem. 21, 335 (1949).

101. Leddicotte, G. W., Pure and Applied Chemistry 1, 61-80 (1960).

102. Fukai, R., and Meinke, W. W., Limnology and Oceanog. 4, 398 (1959).

103. Zvyagintsev, O. E., and Kulak, A. I., Zhur. Neorg. Khim. 2, 1687 (1957).

104. Leddicotte, G. W., "Platinum, Neutron Activation Analysis (Isotopic Carrier) Method," Method No. 5 11610, to be issued in the Oak Ridge National Laboratory Master Analytical Manual.

USAEC Division of Technical Information Extension, Oak Ridge, Tennessee