NAS-NS 3045

THE RADIOCHEMISTRY OF IRIDIUM

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October 1961
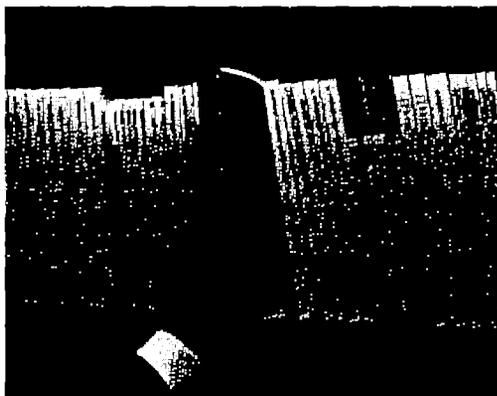
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The Radiochemistry
of Iridium

U.S.
Atomic
Energy
Commission

COMMITTEE ON NUCLEAR SCIENCE

The Radiochemistry of Iridium

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Oak Ridge, Tennessee

October 1961

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 iridium 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 iridium which might be included in a revised version of the monograph.

CONTENTS

The Radiochemistry of Iridium

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

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II. RADIOACTIVE NUCLIDES OF IRIDIUM

The radionuclides of iridium that are of interest in the radiochemistry of iridium 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]

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

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TABLE I

THE RADIOACTIVE NUCLIDES OF IRIDIUM

Radio-nuclide	Half-life	Mode of Decay	Energy of Radiation	Produced By
Ir^{187}	11.8 h	EC, β^+	β^+ 2.2 ~1.3 abs	Re-α-2n, Re^{185}-α-2n, Os-d-3n
Ir^{188}	41.5 h	EC, β^+	β^+ 2.0 ~1.8 abs	Re-α-n, Re-α-3n, Re^{187}-α-3n, Os-d-2n
Ir^{190}	3.2 h	β, EC	β^+ 1.7	Re-α-n, Re^{187}-α-n, Os-d-n, Os-d-2n
Ir^{192m}	1.42 m	IT	0.057 Spect Conv.	Ir-n-γ
Ir^{192}	74.37 d	EC,β^-	β^- 0.67 γ 0.136, 0.201, 0.206, 0.296, 0.870	Os-d-2n, Ir-n-γ, Ir-n-2n, Ir-d-p, Pt-d-α, Pt-γ-pn
Ir^{193m}	5.7×10^{-9} s	IT	γ 0.065	Daughter Os^{193}
Ir^{194}	19.0 h	β^-	β^- 2.18, 1.98, others γ 0.290, 0.326, others	Ir-n-γ, Ir-d-p, Pt-γ-p
Ir^{195}	140 m	β^-	β^- 1.8 abs γ 0.49, 0.84	Pt-γ-p, Pt-n-p
Ir^{196}	9 d	β^-	β 0.08 abs	Pt-n-p
Ir^{197}	7 m	β^-	β^- 1.65, 0.6 abs	Pt-γ-p, Pt-n-pn
Ir^{198}	45 s	β^-	β^- 3.6 abs γ 0.78	Pt-n-p

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

Radiochemistry is probably best described as being an analysis 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 deter-
mine 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

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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 amounts 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 behavior of iridium and its compounds that might be useful in devising radiochemical analysis methods for the radionuclides of iridium. More detailed information can be obtained from the references cited in this monograph.

A. The General Chemistry of Iridium

Iridium usually occurs as the native metal in combination with platinum, osmium, and gold. It is also present in meteoritic iron and in all of the platinum ores. It is obtained from these base materials by refining processes.

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1. Metallic Iridium

Iridium, as a metal, is silver white and brittle with a distinct crystal structure. It is very hard and is not very ductile. It has a density of 22.65 and a melting point of 2454°. When heated in air at a bright red heat, iridium will volatilize. Molten iridium will dissolve carbon but will not combine with it. When the melt is cooled, the carbon separates out as graphite. Iridium can absorb hydrogen only when it is electrolytically charged with the gas and in a finely divided state.

In its chemical behavior, iridium metal is not attacked by any acid; however, it can be attacked by hydrochloric acid in the presence of air and when heated under pressure at 125°. It can be converted to iridium dioxide, IrO_2, by heating to a dull red heat in an air or oxygen atmosphere. IrO_2 will decompose again at higher temperatures. It can be attacked by chlorine gas when heated at red heat and a double chloride salt is produced if it is mixed with sodium chloride and heated.

2. The Compounds of Iridium

Iridium exhibits oxidation states of 0, +1, +2, +3, +4, and +6.[3] The trivalent (+3) and the tetravalent (+4) states are the most important. Many ions of these species exist in solution with the +4 compounds being the most stable. The +6 oxide and its salts are known only in alkaline solutions.

Both the simple and complex trivalent compounds are very similar to those of rhodium (III). The chief compounds of iridium (III) are the oxides, the halides, and many complex compounds. The Ir (IV) compounds are mostly anionic in species. The oxide, the halides, and a number of complex salts have been established as iridium (IV) compounds. Sulfide and carbonyl compounds also exist for iridium (IV). Table II shows the solubilities of some of the iridium compounds.

a. The Oxide Compounds. The simple tripositive iridium oxide compound, anhydrous black iridium (III) oxide, Ir_2O_3, can be formed by heating potassium hexachloroiridate (IV), $K_2[IrCl_6]$ in the presence of sodium carbonate. The hydrated sesquioxide, $Ir_2O_3 \cdot XH_2O$, formed by adding dilute alkali

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Table II. Solubility of Iridium Compounds

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Bromides	$IrBr_3 \cdot 4H_2O$	Very Soluble		Insoluble in alcohol
	$IrBr_4$	Soluble; decomposes		Soluble in alcohol
Chlorides	$IrCl_2$	Soluble		Insoluble in acids and alkali
	$IrCl_3$	Insoluble		Insoluble in acids and alkali
	$IrCl_4$	Soluble	Decomposes	Soluble in alcohol and dilute HCl
Fluorides	IrF_6	Decomposes	Decomposes	
Iodides	IrI_3	Slightly soluble	Soluble	Slightly soluble in alcohol
	IrI_4	Insoluble	Insoluble	Soluble in KI; insoluble in alcohol
Oxides	Ir_2O_3	Insoluble		Soluble in H_2SO_4 and hot HCl; insoluble in alkali
	$Ir_2O_3 \cdot XH_2O$	Insoluble		Soluble in acid and alkali
	IrO_2	Insoluble	Insoluble	Insoluble in acid and alkali
	$IrO_2 \cdot 2H_2O$ or $Ir(OH)_4$	Insoluble	Insoluble	Soluble in HCl
Sulfate	$Ir_2(SO_4)_3 \cdot XH_2O$	Soluble		
Sulfides	IrS	Insoluble		Soluble in K_2S; insoluble in acid
	Ir_2S_3	Slightly soluble		Soluble in HNO_3 and K_2S
	IrS_2	Insoluble		Soluble in aqua regia; insoluble in acid
	$Ir(HS)_3 \cdot 2H_2O$	Insoluble		Soluble in HNO_3

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to a solution of potassium hexachloroiridate, (III), $K_3[IrCl_6]$, in an atmosphere of carbon dioxide, can be oxidized by air to the dioxide. When heated, Ir_2O_3 will decompose to iridium metal and IrO_2.

Iridium dioxide, IrO_2, can be produced by heating (at about 1070°) powdered iridium metal in air or oxygen. Dissociation will occur at higher temperatures and results in the formation of metallic iridium. Remy[3] notes that is has been assumed that iridium dioxide could form well defined compounds with strong basic oxides; however, later studies show these are only adsorption products.

A hydrate form of iridium dioxide, $IrO_2 \cdot 2H_2O$ or $Ir(OH)_4$, can be prepared by heating a solution of sodium chloroiridate (III), $Na_3[IrCl_6]$, with potassium hydroxide. The hydrate is very insoluble in alkali solutions, but readily soluble in acids. The anhydrous form is insoluble in HNO_3 and H_2SO_4; it can be dissolved in HCl to form the complex acid, $H_2[IrCl_6]$.

No iridium oxide compounds of the oxidation states of 0, +1, +2, and +6 are known.

b. The Halide Compounds. Chloride, bromide, and iodide compounds of Ir (III) are known; the fluoride compound has not been prepared. Anhydrous iridium chloride, $IrCl_3$, has been produced by a direct union of chlorine with iridium metal heated to about 600°. Hydrated chlorides, bromides, and iodides, such as $IrCl_3 \cdot 3H_2O$, $IrBr_3 \cdot 4H_2O$, and $IrI_3 \cdot 3H_2O$, are obtained by mixing solutions of the hydrated sesquioxide, Ir_2O_3, with halogen acids. The hydrated chlorides will dissolve in water to produce dark green acidic solutions indicating anionic complexes of chlorine and iridium. All of the iridium (III) halides will decompose at elevated temperatures to form the lower halides. Continued heating will produce the free metal.

Of the Ir (IV) compounds, iridium tetrafluoride and iridium tetrachloride are the only halide compounds that have been characterized. IrF_4 is produced when the hexafluoride, IrF_6, is reduced with powdered metal at a temperature of about 150°. $IrCl_4$ is formed by the action of aqua regia on ammonium hexachloroiridate (IV). Both of these halide compounds are unstable. IrF_4, a yellow nonvolatile oil, can be decomposed by strong heating to give lower fluorides. In water, it will decompose rapidly to the hydrated dioxide. $IrCl_4$ loses water and chlorine when gently heated.

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The iridium (VI) halide compound, IrF_6, is obtained as volatile yellow solid by a reaction of the elements at temperatures of 200°. It can be decomposed by water to evolve oxygen and ozone and to form the dioxide hydrate and HF. When treated with chlorine, IrF_4 and chlorine monofluoride are formed. Reactions with hydrogen gas will produce iridium metal.

Iridium (I) is known only in the form of the halides IrCl (red), IrBr (brown), and IrI (black). They are the products of the thermal decomposition of the trihalides and they are very insoluble in acids.

c. The Sulfide, Sulfate, and Carbonyl Compounds. The sulfide compounds, IrS, Ir_2S_3, and IrS_2, are formed by the direct union of the elements. The sulfate and carbonyl compounds, such as $K_4[Ir(CN)_6]$ and $Na_6[Ir(SO_3)_4]\cdot 10H_2O$, are complex iridium compounds.

d. The Complex Compounds. Iridium (III) produces numerous complex compounds. All exhibit a coordination number of 6. All of the iridium (III) complexes, except those for the halides, are inert to substitution and form compounds closely resembling the rhodium (III) complexes. The chloro complexes, $M_3[IrCl_6]$ and $M_2[IrCl_5(H_2O)]$, are usually obtained by a reduction of the corresponding iridium (IV) compounds. The bromo and iodo forms are also obtained in the same manner.

The main class of the Ir (IV) complexes are the halogen compounds. The chloro complexes are produced either by the reaction of chlorine on a heated mixture of iridium metal and alkali metal chloride or by the addition of an alkali metal chloride to a solution of hydrated iridium dioxide in HCl. Ir (IV) bromo complexes are usually prepared by adding the alkali metal bromide to the HCl solution of IrO_2. Fluoro compounds, such as $K_2[IrF_6]$ and $Pb[IrF_6]$, are usually produced by heating a mixture of iridium metal and K_3HPbF_8. No iodine complexes are known. Complex ammines and oxalates have been identified but not characterized.

B. The Analytical Chemistry of Iridium

Following its isolation and separation from other elements, iridium, like all of the other platinum metals, is usually determined gravimetrically as the metal.[4,5] Formic acid or sodium formate will reduce it to the

metallic state. Powdered zinc, aluminum, or magnesium can also be used to displace it from solution.

The reviews by Gilchrist[6] and Beamish[7] afford excellent summaries on many of the methods that can be used to isolate and separate iridium and the other platinum metals from other elements and from each other. Many of these methods are suitable for use by a radiochemist in his separations of the iridium radionuclides and most of them are considered in the general information that follows:

1. Separation By Precipitation

Precipitations with hydrogen sulfide from an acid solution[4, 8] will separate the platinum metals from most of the other chemical elements. 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 sulfides are readily soluble in aqua regia; however, the compounds that result can contain closely bound sulfate groups which may affect any further reactions of the platinum metals with other reagents. Taimini and Salaria[9] have used the solubility of iridium sulfide (and the other platinum metal sulfides) in alkaline solution to separate them from many other chemical elements.

In a very early investigation by Leidie[10] it was shown 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 such base metals as gold, copper, zinc, etc., could be removed from the mixture by being precipitated as oxides or hydrated oxides. In later studies[11,12] on this method, it was found that rhodium, iridium, platinum, ruthenium, and palladium could be isolated by reconverting the nitrite compounds to the chloro forms before being precipitated with such reagents as ammonium chloride.[10]

Blackmore, et al[13] and Gilchrist[14] have shown that Ir^{+4} (as well as Os^{+4}, Ru^{+4}, and Pt^4) can be separated from many other elements as ammonium chloroiridate. This compound can be calcined to produce iridium metal. Gold can be separated from iridium and the other platinum metals by precipitation methods using such reagents as ferrous sulfate,[15] sulfur dioxide,[4]

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oxalic acid,[4] hydroquinone,[16] tetraethylammonium chloride,[17] and sodium nitrite.[18] Usually the choice of reagent is dependent upon the separation procedure to be followed in the subsequent assay of the solution for iridium.

Beamish[7] reports that iridium (and palladium and rhodium) can be separated from platinum by a controlled hydrolysis of their chloro complexes in the presence of bromate. Gilchrist,[19,20] after removing osmium and ruthenium by distillation, oxidized Ir, Rh, Pd, and Pt to their higher valence states and hydrolyzed the solution with sodium hydrogen carbonate to pH 6-8 to precipitate Ir, Rh, and Pd and separate them from Pt^{+4}. Ryan[21] also separated platinum from iridium (and Au, Pd, and Rh) by a hydrolytic separation. Lloyd and Morris,[22] using radioactive Ir^{192} tracer and the techniques developed by Pierson[23] and Powell[24,25] concerned with the separation of Pt, Rh, Ir, and Pd with calomel and hypophosphorus acid, showed rhodium could be separated from iridium if bromide was present. When iodide was present, the calomel salts and acid slurry quantitatively separated the iridium.

Iridium (as well as Pt and Rh) can be quantitatively separated from palladium by precipitating palladium either with dimethylglyoxime,[20,26-30] or with α-nitroso-β-naphthol,[31] or by treating an acid solution of the metal with sodium dimethylglyoximate.[32] Gold has also been separated from iridium by precipitating it with either dimethylglyoxime,[33] α-nitroso-β-naphthol,[31] or hydroquinone.[29] It has also been reported that dimethylglyoxime precipitations will separate platinum almost quantitatively from iridium and the other non-volatile platinum metals.[33,34] Westland and Beamish[15] in their studies on the isolation of microgram amounts of platinum and palladium by reduction with tellurium metal powder showed that iridium would also precipitate if an excess of palladium was present.

According to Beamish,[7] iridium and rhodium usually appear together after the separation of gold, osmium, ruthenium, palladium, and platinum. In combination as the insoluble residues from fire-assay extractions, they are resistant to acid dissolution. The residues have been put into solution by such techniques as chlorination in the presence of sodium chloride,[35] or by a sodium peroxide fusion.[36]

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The separation of the two metals by precipitation techniques is some-
times difficult.[7]   Selective extractions with fused sodium bisulfate,[37]
reductions of the hexachloro salts with mercury,[38] chloride salt reductions
at 90-95° with mercurous chloride[39] and a fusion in lead at 1300°[40] have
been used as methods to separate rhodium and iridium. Generally, these
methods are not capable of achieving complete separations. Gilchrist[41]
has shown that a quantitative separation of iridium from rhodium could be
obtained by converting the metals to sulfate salts and then reducing rhodium
with $TiCl_3$. The excess titanium was removed by precipitating it with
cupferron. Pollard[42] has used $TiCl_3$ and mercaptobenzothiazole to reduce
rhodium and separate it from iridium.

Rhodium can also be separated from iridium by a reduction and precipita-
tion from hexanitrite solution by sodium sulfide.[43] Methods involved with
the reduction of rhodium by chromous chloride,[43] by boiling it with anti-
mony metal dust in H_2SO_4[15,44] and by copper powder from HCl solutions[45,46]
have also been used to separate it from iridium. Rhodium, after its reduction
with chromium chloride solution, can be quantitatively separated from
iridium by a precipitation with thioacetanilde;[47] iridium being
recovered from the filtrate as the sulfide.

2. Separation By Volatility

Iridium, like platinum, palladium, and rhodium, is non-volatile and
osmium and ruthenium can be separated from it by use of distillation
methods.[7] 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. The undistilled mixture then can be
processed for iridium and the other platinum metals by any of the methods
cited in this monograph.

3. Separation By Electrolysis

Rhodium can be separated and deposited on a platinum cathode by
electrolyzing a solution of the two metals for 90 minutes at a gradually
lowered cathode potential (from -0.25 V to -0.40 V).[48] Codeposition of
iridium was observed by the authors. However, it was shown that the addi-

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tion of 3.5 $\underline{M}$ ammonium chloride to the solution before electrolysis resulted in a deposition of rhodium free from iridium.

4. Separation By Solvent Extraction

Some of the solvent extraction methods described by Morrison and Friesen[49] can be considered for use in the radiochemistry of the iridium radionuclides.

a. <u>Ion Association Systems</u>. Ethyl ether will not extract iridium (or Pt, Pd, Os, and Ru) from a 6.9 $\underline{M}$ HI solution[50] and this system can be used to separate it from Au^{+3}, Sb^{+3}, Hg^{+2}, Cd^{+2}, and Sn^{+2}. Gold has also been isolated and completely separated from iridium (Pd, Pt, Rh, and Ru) by extracting it into isopropyl ether from a 2.5-3.0 $\underline{M}$ HBr solution.[51] Iridium (as well as Pt, Rh, Au, Te, and small amounts of Pd) can be separated from osmium and ruthenium solutions contained in $HCl\text{-}NH_4Cl\text{-}SnCl_2$ by an extraction with amyl acetate.[52]

b. <u>Chelate Complex Systems</u>. Sandell[53] reports that iridium and the other platinum metals in the quadrivalent or trivalent states will not produce dithizonates in weakly acid solution so that they can be separated from the dithizonates of other elements by extracting the latter into chloroform. The phenylthiourea complexes of Ir^{+4}, Rh^{+3}, Ru^{+3}, Os^{+4}, Au^{+3}, Fe^{+3}, Co^{+2}, Ni^{+2}, and Cr^{+6} can not be extracted from a dilute HCl solution with either ethyl or amyl acetate.[54] The Pd^{+2} and Cu^{+2} complexes completely extract under these conditions, while the Pt^{+4} complex is only partially extracted. Iridium (as well as Pd, Au, and Os^{+8}) forms a colored complex with ephedrine hydrochloride and can be separated from platinum and rhodium by extracting it from a slightly acid solution into carbon tetrachloride.[55]

5. Chromatography Separations

a. <u>With Inorganic Adsorbents</u>. Alumina columns and various reagents, such as benzidine, have been used to separate the platinum metals in aqueous solutions from Pb, Cu, Zn, and Ni.[56] Selective separations of each of the platinum metals from each other have also been accomplished under the same or similar conditions.[57]

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b. <u>With Ion Exchange Resins</u>. Iridium, as Ir^{+3}, can be separated from Pt^{+4} by first adsorbing them from a dilute chloride solution on to the anion exchange resin, Dowex-1, and then using 10 $\underline{N}$ HCl as a column eluant.[58] Ir^{+3} will desorb from the column while Pt^{+4} (and/or Pd^{+2}) remains on the column. Iridium (and rhodium) can also be separated from platinum by use of the anion exchange resin Permutit E. S. in the hydroxide form and 1 $\underline{N}$ NaOH as the eluant.[59] In this separation, sodium oxalate was used to reduce the Ir and Rh to the tetravalent state, after which they were adsorbed upon the resin; following the removal of Ir and Rh by the sodium hydroxide elution, the Pt was eluted from the column with HNO_3.

The chloro complexes of Ir, Pd, Pt, and Rh have been adsorbed and selectively separated by NH_4OH-NH_4Cl elutions on a Dowex-2 resin column.[60] Iridium has also been separated from platinum, rhodium, and palladium by use of Amberlite IRA-400 resin and elutions with HCl.[61]

Iridium has been separated from platinum, rhodium, and palladium by use of a Dowex-50 cation resin column.[62] The chloride solutions of the metals were first converted to the perchlorate form and passed through the Dowex-50 column. Ir, Pd, and Rh adsorbed upon the column, while Pt passed through. They were subsequently separated from each other by eluting with HCl solutions of varied molarity. Ammonical solutions and Amberlite IR-100 resin columns have also been used to separate Ir (Pd and Rh) from platinum.[60,63,64] The cation resin, Espatite-K-V-1, in either the H^+ or Na^+ form, has been used to separate the chloride complexes of Ir (Pt, Pd, and Rh) from those of copper, nickel, iron, and lead.[65]

c. <u>By Paper Chromatography</u>. Kember and Wells[66] describe separations of iridium, platinum, rhodium, and palladium in microgram amounts by use of paper-strip chromatography and various solvents. Using hexone-pentanol-HCl mixtures, separations of iridium, palladium, and platinum, in that order, were achieved. When Ir, Pt, Pd, and 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 copper, iron, and nickel could be separated from the platinum metals by use of n-butanol saturated with 3 $\underline{N}$ HCl. Burstall, et al [67] used cellulose columns and methyl propyl

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ketone or methyl ethyl ketone-HCl mixtures as solvents to separate gold, osmium, platinum, palladium, rhodium, iridium, and ruthenium in that order from a chloride system. Stannous chloride was then used to separate Pt, Pd, Au, and Rh and acetone-HCl was used to separate Ir. Lederer[26] and Payne[69] also separated gold, iridium, platinum, palladium, rhodium, and ruthenium, in that order, by a similar system. Cellulose columns pretreated with such solvents as hexone-3% HCl have been used to separate milli-gram amounts of Pt, Pd, Rh, and Ir from each other and from iron, copper, zinc, nickel, and mercury.[70] Pt and Ir were separated together from the mixture and from each other by use of reducing conditions in order to decrease the mobility of iridium on the column.

d. By Electro-Chromatographic Methods. Majumdar and Chakrabartty[71] report that the platinum metals can be separated from each other by a electro-chromatography technique using a potential of 150 volts and different electrolytes. Descending chromatography and horizontal electro-chromatography have been used to separate Pt, Pd, Ir, and Rh.[72]

IV. DISSOLUTION OF SAMPLES CONTAINING IRIDIUM

All of the platinum metals except palladium resist attack by single mineral acids.[7] Selective dissolution methods to separate base metals from materials containing the platinum metals have involved collective precipitation by zinc or iron and subsequent attack with HNO_3 and HCl,[73] concentrated H_2SO_4 and sulfur,[74] aqua regia,[39,75] sulfide fusions,[76,77] leaching[78] and amalgamation.[79] Many procedures involving "fire assay" methods of isolating the platinum metals from ores are known.[7] Typical of newer methods of fire assay is that proposed by Plummer, et al.[80,81] In general, it consists of preparing a base metal alloy button by reduc-tion 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 after which the platinum metals were extracted 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 iridium radionuclides. The addition of iridium

carrier to the mixture before dissolution begins will assist in achieving

an exchange of the radioactive and inactive iridium atoms.

V. SAFETY PRACTICES

Adequate safety precautions should be followed in dissolving any sample

material whether it is radioactive or non-radioactive. The manual by Pieters

and Creyghton[82] 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 impor-

tant 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[83] and in the

International Atomic Energy Agency's publication, entitled "Safe-Handling

of Radioisotopes."[84] Many other similar sources of information exist

and should be consulted.

VI. COUNTING TECHNIQUES FOR THE RADIOACTIVE IRIDIUM ISOTOPES

The analysis of sample materials containing iridium radionuclides may

be completed either by a direct (non-destructive) measurement of the radio-

nuclides in the irradiated sample or by obtaining the radionuclides in some

form by radiochemically processing the irradiated sample. The use of either

technique is dependent upon the specific characteristics of the iridium

radioisotope being measured, i.e., its half-life, the type radiations it

emits as it decays and the energy of these radiations. The ease with which

a non-destructive analysis method can be applied is most frequently influenced

by the radioactivity of the sample matrix containing the iridium radionuclide.

If this presents a considerable interference, then the sample must be pro-

cessed radiochemically.

Table I of this monograph shows the nuclear characteristics of each of

the known radioactive isotopes of iridium. The radioactivity of these can

be measured by either standard Geiger-Mueller, gamma scintillation or proportional counting techniques.[85-88] The gamma radiations from Ir^{192} and Ir^{194} have been used in a non-destructive radioactivation analysis method to determine the iridium content of aluminum foils,[89] gold,[89] platinum,[91] and rhodium.[92]

VII. RADIOCHEMICAL PROCEDURES FOR THE IRIDIUM RADIONUCLIDES

Although no specific carrier-free separations of the iridium radionuclides appear in the current literature, it should be possible to use any of the solvent extraction or chromatography methods reported elsewhere in this monograph to serve as a means of obtaining essentially carrier-free radioactive iridium. Most of the carrier radiochemical procedures have originated from investigations concerned either with the preparation of radioactive iridium tracers,[93, 94] separation of iridium radionuclides from the fission products,[93] or the determination of small amounts of iridium by radioactivation analysis.[95, 96] Platinum,[97] rhodium chloride,[98] palladium,[98] deep sea sediments,[98] and paper ash[98] have been analyzed for trace iridium by radioactivation analysis methods.

In the procedures that follow, information is given about the specific use of the procedure, the type of material analyzed, type nuclear bombardment, etc. Whenever possible, a statement is made about the decontamination levels achieved by the particular procedure cited.

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Procedure Used In: Preparation of radioactive iridium tracers

Method: Solvent extraction

Element Separated: Iridium radionuclides

Type Material Analyzed: Iridium Foil

Type Nuclear Bombardment: 104" cyclotron (any energy protons)

Procedure By: Thompson and Rasmussen (Reported by Meinke[93])

Separation Time: 1 hour

Chemical Yield of Carrier: ~50%

Decontamination: 10^2

Equipment Required: Standard

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 an equal volume of 3 $\underline{N}$ 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 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.)

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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.

PROCEDURE 2

Procedure Used In: Preparation of radioactive iridium tracer and separation of radioactive iridium from fission products

Method: Distillation, solvent extraction, and precipitation

Element Separated: Iridium radionuclides

Type Material Analyzed: Uranium metal

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

Procedure By: Wolfe (Reported by Meinke[93])

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

Chemical Yield of Carrier: 3-5%

Decontamination: 10^4 (except from Rh)

Equipment Required: Standard

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 $\underline{N}$ 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 $\underline{N}$ and extract twice with equal volume butyl acetate to decontaminate from Hg and from Au.

8. Dilute the solution to ~ 0.5 $\underline{N}$ 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 $\underline{N}$. 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 $\underline{N}$ and add 20 ml pyridine.

13. Boil the solution for five minutes, place in a separatory funnel, and add 19 $\underline{N}$ 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

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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 bromcresol 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.

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.

PROCEDURE 3

Procedure Used In: Preparation of radioactive iridium tracers

Method: Distillation and precipitation

Element Separated: Iridium radionuclides

Type Material Analyzed: Rhenium metal

Type Nuclear Bombardment: 60" cyclotron (37-Mev alphas, 9.5-Mev protons, or 19-Mev deuterons)

Procedure By: Chu (Reported by Meinke[93])

Separation Time: 1 hour

Chemical Yield of Carrier: 70%

Decontamination: 10^2

Equipment Required: Standard

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 $\underline{N}$ 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.

PROCEDURE 4

Procedure Used In: Preparation of radioactive iridium tracers

Method: Solvent extraction and precipitation

Element Separated: Iridium radionuclides

Type Material Analyzed: Platinum

Type Nuclear Bombardment: Cyclotron

Procedure By: Gardner, D. G.[94]

Separation Time: Several hours

Chemical Yield of Carrier: ~70%

Decontamination: ~10^6

Equipment Required: Standard

Procedure:

1. The Pt target was dissolved in boiling aqua regia and 3 mg Ir carrier and 10 mg each of the following carriers added: Cu, Ni, Zn, and Au.

2. The solution was evaporated to incipient dryness, diluted to 10 ml with water and 10 drops conc. HCl added.

3. Au was extracted 6-8 times with ethyl acetate. See Note 1.

4. The aqueous phase (yellow-brown) was treated with 1-2 drops H_2N NH_2 to destroy NO_3. (Solution turns pale.) See Note 2.

5. Pt was reduced with $SnCl_2$ (solution turns deep red) and extracted 6-8 times with ethyl acetate. See Note 3.

6. The aqueous phase was evaporated to dryness with 2-3 ml aqua regia and 5 mg Pt carrier added. The NO_3 was removed by addition of 20 drops conc. HCl and evaporation to dryness.

7. The residue was dissolved in 2 ml H_2O and 4 drops 6 $\underline{N}$ HCl.

8. The solution was saturated with solid NH_4Cl, warmed to dissolve any excess and cooled in ice for 0.5 hr. The red precipitate of Pt and Ir was washed several times with saturated NH_4Cl solution.

9. The precipitate was dissolved in hot water, and NH_4^+ removed by evaporation to dryness with 2-3 ml aqua regia.

10. The residue was dissolved in 2-3 ml H_2O plus 2-5 drops conc. HCl and evaporated to dryness again.

11. The residue was dissolved in 6-8 ml H_2O and made basic to litmus with a few drops of saturated Na_2CO_3 solution (solution turns from brown to yellow).

12. The solution was heated to boiling, 4-6 ml NaOBr solution (0.5 ml 1 $\underline{M}$ $NHCO_3$/1 ml saturated Br_2 solution) added and heating continued until the solution turns greenish-blue. See Note 4.

13. 1-2 drops 6 $\underline{N}$ HCl was added to the still warm solution and the solution digested until the IrO_2 coagulated.

14. The precipitate was washed several times with H_2O, dissolved in conc. HBr and evaporated to dryness. The residue was dissolved in H_2O and mounted for counting.

Notes:

1. For both the Au and Pt extractions, $\dfrac{\text{aqueous phase}}{\text{organic phase}} = 2\text{-}4$.

   New glassware was used for the last extraction in each case.

2. Metallic Pt may precipitate from hot solution.

3. If a red precipitate forms, conc. HCl is added until it dissolves. In the presence of a large amount of Pt a series of partial reductions and extractions to remove all the Pt is preferred.

4. The addition of a drop of 1 $\underline{M}$ Na_2CO_3 solution and/or saturated Br_2 solution may expedite the formation of the blue-green color.

Procedure Used In: Radioactivation analysis

Method: Solvent extraction and precipitation

Element Separated: Ir^{192} (74 d)

Type Material Analyzed: Platinum[97]

Type Nuclear Bombardment: $Ir^{191}(n,\gamma)Ir^{192}$

Procedure By: Jowanovitz, L. S., et al[97]

Separation Time: Several hours

Chemical Yield of Carrier: Quantitative

Decontamination: Excellent from Pt^{195} and Au^{199}

Equipment Required: Standard

Procedure:

1. Seal powdered Pt metal and hydrous iridium oxide comparator samples (Note 2) in a quartz tube for the irradiation.

2. Irradiate for 12-24 hours in a reactor (Note 2).

3. After irradiation, dissolve platinum sample in aqua regia. Then boil, or evaporate, repeatedly with HCl. Transfer to separatory funnel.

4. Adjust solution to 6 $\underline{N}$ HCl, then add 30-50 mg of Ir as $IrCl_6^{-2}$ carrier and an equal volume of ethyl acetate (Note 3) to the funnel. Shake; separate layers; discard organic layer (Note 4). Repeat ethyl acetate extraction at least twice.

5. Transfer final aqueous solution to a suitable container; add brom-cresol purple indicator, then add sufficient sodium bicarbonate solution until end-point of brom-cresol purple is obtained.

6. Add 20 ml of 10% sodium bromate solution, then heat to boiling for 20-25 minutes. Add additional sodium bromate if necessary (Note 5).

7. Cool solution, then filter through a 19-mm. diameter S and S Red Ribbon filter paper by suction filtration. Wash precipitate and paper several times with 1% ammonium chloride solution. Dry, mount for counting (Note 6).

8. Process the irradiated hydrous iridium oxide comparator sample in the following manner:

a. Dissolve in hot HBr and pipet a measured aliquot of the solution to a 19-mm filter paper. Allow the solution to evaporate.

b. Then mount in the same manner as the unknown for counting (Note 6).

Notes:

1. 0.10 gram of Pt metal and 0.5-10 milligrams of comparator.

2. Irradiation made in CP-5 at Argonne; 168 hours irradiation in ORNL Graphite Reactor also used.

3. Saturated with HCl.

4. Contains Au^{199} radioactivity.

5. Solution should be dark green or until precipitation of iridium hydroxide begins.

6. A gamma scintillation counter was used for the measurement of Ir^{192}.

PROCEDURE 6

Procedure Used In: Radioactivation Analysis

Method: Precipitation

Element Separated: Ir^{192} (74 d)

Type Material Analyzed: Rhodium chloride, palladium, paper ash, and deep sea sediments.[98]

Type Nuclear Bombardment: $Ir^{191}(n,\gamma)Ir^{192}$

Procedure By: Emery and Mahlman (Reported by Leddicotte[98])

Separation Time: 2-3 hours

Chemical Yield of Carrier: 60%

Decontamination: 10^5 from Pd

Equipment Required: Standard

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 1) and comparator (Note 2)

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samples in a neutron flux of at least 6.5×10^{11} n/sec/cm^2 for 62 hours or longer (Note 3). Prepare the test and comparator samples for the irradiation either by wrapping each specimen in aluminum foil or placing it in a quartz ampoule.

B. Preparation of Irradiated Materials for Analysis

I. The Comparator Sample

1. After the irradiation, quantitatively transfer the comparator sample (Note 2) to a 100-ml volumetric flask. Dissolve in HCl and dilute to volume with distilled water. Shake vigorously to mix solution.

2. By means of a 1-ml volumetric pipette, transfer an aliquot to a second 100-ml volumetric flask, dilute to volume with 1 N HCl. Mix well by shaking.

3. By means of a volumetric pipette, pipet at least 1.0 ml from this dilution into a 125-ml volume distillation flask. Then, add 2 ml of standardized iridium carrier (Note 4) plus 1 ml each of Os, Pt, Au, Ru, Rh, and Pd carriers (Note 5) to the flask. Then continue with Step 1 of Part III below.

II. The Test Samples

1. After quantitatively transferring the irradiated samples to a 125-ml distillation flask, process the irradiated test samples in the following manner:

    a. <u>Rhodium chloride</u>: Dissolve in a minimum amount of water.

    b. <u>Palladium metal</u>: Dissolve in aqua regia. Heat to dissolve.

    c. <u>Paper ash and deep sea sediments</u>: Add 5 ml conc. HNO$_3$ and 1 ml HClO$_4$; heat to boiling; add additional conc. HNO$_3$ if necessary until sample is completely dissolved.

2. Cool the solution, if necessary, then add 2 ml of standardized iridium carrier (Note 4) plus 1 ml each of Os, Pt, Au, Ru, Rh, and Pd carriers (Note 5) to the flask. Then continue with Step 1 of Part III below.

III. Radiochemical Separation

1. To the flask (Note 6) add 10 ml of conc. HNO_3 and distill OsO_4 into 6 $\underline{N}$ NaOH contained in a tube held in an ice bath.

2. Repeat Os carrier addition and distillation.

3. Transfer the residue from the distillation flask to a beaker, add 10 ml of 70% $HClO_4$ and boil to fumes of $HClO_4$ (Note 7).

4. Repeat Ru carrier addition and $HClO_4$ fuming.

5. Cool the solution, transfer to a separatory funnel, and add enough conc. HCl to make the solution 4 $\underline{N}$ in HCl. Add an equal volume of butyl acetate and extract (Note 8) by shaking. Repeat butyl acetate addition and extraction. Discard the organic phases.

6. Dilute the aqueous phase with water to make the solution 0.5 $\underline{N}$ in HCl, then add 5 ml of 1% alcoholic solution of dimethylglyoxime. Digest the mixture for 10 minutes, then filter. Discard the palladium precipitate.

7. To the filtrate, add sufficient conc. HCl to make the solution 5 $\underline{N}$ in HCl. Then, add 10% $SnCl_2$ solution dropwise until Pt^{+4} is reduced to Pt^{+2} (Note 9).

8. Extract Pt^{+2} from the solution by adding an equal volume of butyl acetate and shaking the mixture. Repeat the butyl acetate addition and extraction at least once more. Separate the phases; discard the organic phase(s).

9. Make the aqueous phase alkaline with 6 $\underline{N}$ NaOH, boil the solution, and saturate the solution with H_2S. Acidify the solution by adding conc. HCl dropwise to it during the sulfide saturation. Filter.

10. Dissolve sulfide precipitate in aqua regia, add 2 ml of conc. H_2SO_4 and boil to fumes of H_2SO_4 (Note 10). Cool, repeat H_2SO_4 addition and fuming.

11. Cool the solution, dilute to double volume (Note 11) with water, then boil and precipitate rhodium metal by adding $TiCl_3$ solution dropwise until a slight excess is present. Filter.

12. Add sufficient conc. HCl to the filtrate to make the solution 0.5 $\underline{N}$

in HCl. Cool in an ice bath and add sufficient cupferron solution to precipitate titanium cupferrate. Filter.

13. Heat the filtrate to boiling; cool, then neutralize to a bromcresol purple end-point by adding saturated $NaHCO_3$ solution dropwise. Then, add small portions of solid sodium bromate to the solution until no further IrO_2 is precipitated.

14. Dissolve the IrO_2 in 1-2 ml conc. HCl (Note 12). Precipitate metallic Ir from the solution by adding powdered zinc metal (Note 13).

15. Weigh the Ir to determine chemical yield. Mount for counting.

IV. Measurement of the Radioactivity and
    Calculation of Stable Iridium Content
    of Test Sample

1. The Ir^{192} or Ir^{194} radioactivity in both the test and comparator samples may be assayed either by beta or gamma counting. Use a Geiger-Mueller counter for beta measurements and a gamma scintillation counter for the gamma measurements (Note 14).

2. Following the radioactivity measurements, correct the observed radioactivity for "loss" of carrier during the experiment, half-life of the iridium isotope and the sample weights of both the test and comparator samples (Note 15). A simple ratio of these corrected radioactivities becomes a measure of the amount of stable iridium in the test sample:

$$\% \text{ Ir in Test Sample} = \frac{\text{Corrected } Ir^{192} \text{ (or } Ir^{194}) \text{ radioactivity in test sample.}}{\text{Corrected } Ir^{192} \text{ (or } Ir^{194}) \text{ radioactivity in comparator}}$$

Notes:

1. Use at least 0.1-0.2 gram portions.

2. Use at least 5-10 milligrams of hydrated iridium oxide or $Na_2IrCl_6 \cdot 6H_2O$.

3. The limits of measurement for determining iridium by this procedure is about 0.005 micrograms.

4. Standardized to contain at least 10 milligrams of iridium per milliliter.

5. These are holdbacks, or scavenging carriers, made up to contain 5-10 milligrams of element per milliliter. Depending upon type of sample material, some of these carriers will not be required; other elemental carriers may be added.

6. Flask equipped with air entry.

7. Ru carrier expelled here.

8. Gold carrier extracted here.

9. Solution will become red in color.

10. Sulfides must be completely converted to the sulfate complex.

11. Additional water may be added.

12. Additional rhodium carrier may be added here and steps 11 and 12 repeated.

13. Powdered magnesium or aluminum may be used instead.

14. Gamma-ray energy discrimination may be used here.

15. Decay measurements may be followed, if required.

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