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COMMITTEE ON NUCLEAR SCIENCE

The Radiochemistry of Osmium

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

CONTENTS

The Radiochemistry of Osmium

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

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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).

Schoeller, W. R., and Powell, A. R., The Analysis of Minerals and Ores of The Rarer Elements, 3rd Ed., Griffin, London, 1955.

II. RADIOACTIVE NUCLIDES OF OSMIUM

The radionuclides of osmium that are of interest to the radiochemist are given in Table I. The information tabulated is similar to that appearing in compilations 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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III. THE CHEMISTRY OF OSMIUM AND ITS APPLICATION TO THE RADIOCHEMISTRY
      OF THE OSMIUM RADIONUCLIDES.

Radiochemistry is probably best described as being an analysis technique
used primarily (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 ele-
ment concentration in a particular sample material. In order to be an aid in

TABLE I

THE RADIOACTIVE NUCLIDES OF OSMIUM

Radio-Nuclide	Half-Life	Mode of Decay	Energy of Radiation	Produced By
Os^{182}	24.0 h	EC	γ 0.510	Re-p-4n
Os^{183}	12.0 h	EC	γ 0.3, 1.6	Re-p-3n
Os^{185}	97 d	EC	γ 0.648, 0.878	Re-d-2n, Re-p-n Os-n-γ
Os^{186m}	8×10^{-10} s	IT	γ 0.137	Daughter Re^{186}
Os^{190m}	6 h	IT	γ 0.03	Daughter 12 d Ir^{189}
Os^{190m}	9.5 m	IT	γ 0.039, 0.187, 0.359, 0.508, 0.614	Daughter 3 h Ir^{190}
Os^{191m}	14 h	IT	γ 0.074	Os-n-γ
Os^{191}	16 d	β^-	β^- 0.143 γ 0.171, 0.129	Os-n-γ, Os-d-p, Os-γ-n
Os^{193}	31 h	β^-	β^- 1.1 γ 0.066	Os-n-γ, Os-d-p, Ir-d-2p

accomplishing any one 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

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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 osmium and its compounds and their potential usefulness in devising radiochemical analysis methods for the osmium radionuclides. 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 Osmium

Osmium, like all the other platinum metals, occurs in extremely small amounts in nature. It is estimated that the earth's crust contains only $1 \times 10^{-7}\%$ osmium. It is usually associated as free metal with the other platinum metals and is commonly found with ores of such metals as copper,

silver, gold, iron, and nickel. It is usually obtained from these base
materials by a reduction process.

1. Metallic Osmium

Metallic osmium is a gray, brittle metal possessing a considerable hard-
ness. It has a density of 22.7 and a melting point of $2700°$ C. In a compact
form, it is insoluble in acids; however, when finely divided, it is soluble
in fuming HNO_3 forming osmium tetroxide, OsO_4, which is highly volatile.

2. The Compounds of Osmium

Osmium can form compounds having oxidation states of +2, +3, +4, +6,
and +8.[3] The Os^{+2} ions are unstable in acid. Such groups as Cl^-, Br^-, NO_2^-,
$C_2O_4^-$, NO^-, and NH_3^- form complex ions with Os^{+3} and Os^{+4}. Ions of Os^{+8},
such as perperosmic acid, H_2OsO_5, can exist in hydrochloric acid. In
alkaline solutions, Os^{+3} and Os^{+4} can form oxide or hydrated oxide com-
pounds. Many osmates are known, although the trioxide of Os^{+6} has not
been isolated. Osmyl compounds are also known; however, they readily de-
compose in acid solution. These compounds can be described in the following
manner:

a. The Oxide Compounds of Osmium. Os^{+4} is the most stable oxidation
state of osmium. Its binary compounds include osmium (IV) oxide, OsO_2.
It is usually obtained as a black or brown powder from a chemical reaction
between osmium metal and osmium tetroxide, OsO_4. It is inert towards water
and acids and hydrogen will easily reduce it to the metal. When heated in
air, it is converted to the tetroxide. A hydrate form, $OsO_2 \cdot 2H_2O$, can be
produced if a solution of the tetroxide is reduced.

Osmium tetroxide, OsO_4, is usually produced by heating powdered osmium
metal in air to about $200°$ or by oxidizing osmium metal or its compounds with
hot concentrated HNO_3 or H_2SO_4. It is colorless, volatile, and poisonous.
It is only slightly soluble in water but extremely soluble in nonassociated
organic solvents such as chloroform. It is a strong oxidizing agent and is
frequently used in specific organic oxidations.

b. The Halide Compounds of Osmium. Os^{+4} forms binary compounds with
fluorine, chlorine, and iodine. An incomplete fluorination of powdered

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osmium metal will form the tetrafluoride, OsF_4, and the hexafluoride, OsF_6.
Osmium tetrachloride, $OsCl_4$, is obtained by uniting chlorine and osmium metal
at temperatures of 650-700°. It is a black volatile material which will
slowly dissolve in water to produce a yellow solution and deposit OsO_2. Osmium
iodide, OsI_4, is formed by evaporating a solution of the hydrated dioxide
with hydriodic acid.

Osmium dichloride, $OsCl_2$, is formed by heating the trichloride, $OsCl_3$,
in a vacuum to 500°. It is insoluble in water and does not react with HCl
and H_2SO_4. Osmium trichloride, $OsCl_3$, is formed by the chlorination of
osmium metal at temperatures above 700°. It is hygroscopic and dissolves
readily in water to yield weakly acidic solutions.

c. Miscellaneous Compounds of Osmium. Os^{+2} can combine directly at
high temperatures with sulfur, selenium, and tellurium to form the sulfide,
selenide, and telluride compounds. They are inert to alkalies and to most
acids but can be converted to the tetroxide by hot concentrated HNO_3. Os^{+6}
forms a binary compound, OsP_2, when elemental osmium and phosphorus are com-
bined at temperatures above 500°. Osmium phosphide is a non-volatile grayish
substance that does not react with acids or alkalis. Other compounds of the
Os^{+4}, Os^{+3}, and Os^{+8} states are usually complex.

d. The Complex Compounds of Osmium. Os^{+4} forms many complex compounds,
most of which are anionic. Many of these complexes contain sulfito, halogen,
or halogen-sulfito groups. Typical of the sulfito and the mixed compounds
are the types, $M_8Os(SO_3)_6$ and $M_8OsCl_4(SO_3)_4$. The sulfito group compounds
result from the reaction of sodium bisulfate on $Na_6\left[OsO_2(SO_3)_4\right] \cdot 5H_2O$. The
reactions of sulfites and bisulfites upon hexachloroosmate (IV) compounds pro-
duce the mixed chlorosulfito complexes. The halo complexes usually have the
form $M_2\left[OsCl_6\right]$. Mixed hexa-halo compounds of such types as $M_2\left[OsCl_5Br\right]$ and
$M_2\left[OsCl_3Br_3\right]$ are usually formed by the reduction of aqueous solutions of
osmium tetroxide, containing the appropriate alkali metal salt, with ethanol.

Os^{+6} forms numerous complexes. These include the osmates, M_2OsO_4;
the osmyl derivatives, $M_2\left[OsO_2X_4\right]$; the oxy-osmyl salts, $M_2\left[OsO_3X_2\right]$ and the
nitrilohalides, $M\left[OsNX_4\right]$ or $M_2\left[OsNX_5\right]$. The osmate compounds are usually
obtained either by fusing metallic osmium with mixtures of alkali metal

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hydroxide and nitrates or by the reduction of osmium tetroxide in alkaline
solution with ethanol. The osmyl complexes - containing Cl, CN, NO_2, SO_3,
or C_2O_4 groups - are prepared by reacting the tetroxide with materials con-
taining these groups. The cyano complexes are inert to acids; the other
complexes are rapidly decomposed by water. Chloro, nitro, bromo, and
oxalato groups are usually contained in the oxy-osmyl complexes. The nitro
complexes are the most stable and can be formed in the treatment of aqueous
osmium tetroxide with alkali metal nitrites. The nitrilohalides can be
produced by reacting hydrohalic acids with the Os^{+8} complexes known as the
osmiamates, $M[OsO_3N]$. The osmiamates are formed by reacting concentrated
NH_4OH with warm, strongly alkaline solutions of the tetroxide. The nitrilo-
halides dissolve and rapidly decompose in water.

Fluoro complexes of the composition $M_2[OsO_4F_2]$ have been formed by
reacting saturated solutions of alkali metal fluoride with osmium (VIII)
tetroxide. These complexes readily dissolve in water and decompose in air.
Hydroxo complexes, such as $K_2[OsO_4(OH)_2]$ are formed by adding saturated solu-
tions of alkali to aqueous solutions of the tetroxide.

Os^{+2} forms hexocyano complexes of the composition $M_4[Os(CN)_6]$ by adding
alkali cyanides to a solution of osmium tetroxide. Nitrosyl derivatives,
$M_2[Os(NO)X_5]$, and sulfito compounds, such as $M_4[Os(SO)_3]$ are also known. In
the nitroso compounds, Cl^-, Br^-, or I^- groups complete the complex.

Hexahalo complexes of Os^{+3} are known; however, the purity of such com-
pounds has not been well established. Ammine complexes are known for Os^{+4},
Os^{+3}, and Os^{+2}. These compounds are usually formed by the reaction of other
complex compounds with ammonia.

B. The Analytical Chemistry of Osmium

Osmium, like all of the other platinum metals, is usually determined
gravimetrically as the metal.[4,5] Formic acid, sodium formate and hydrogen
will reduce it to the metallic state, and it can be displaced from solution
with zinc, aluminum, or magnesium metal powders. Other organic reagents, such
as thionalde, strychnine sulfate, thiourea, or thiazole, can be used to
precipitate osmium metal.[6,7]

Gilchrist[8] and Beamish[9] have reviewed many of the methods that can be used to isolate and separate osmium and the other platinum metals from other elements and from each other. Many of these methods can be used by a radiochemist in his work with the osmium radionuclides.

1. Separation By Precipitation

Osmium, like all of the other platinum metals, can be separated from most of the other chemical elements by saturating an acid solution with hydrogen sulfide.[4, 10] Elements such as silver, copper, cadmium, mercury, indium, germanium, tin, lead, arsenic, antimony, bismuth, molybdenum, selenium, tellurium, and rhenium can interfere in this separation. Aqua regia will readily dissolve osmium sulfide.[4] Taimini and Salaria[11] report that the solubility of osmium sulfide in alkaline solution is adequate enough to separate osmium from many other elements.

Osmium (as well as the other platinum metals) can be separated from such base metals as gold, copper, and zinc by digesting any of its chloro compounds in a solution of sodium nitrite in order to convert the osmium to a soluble nitrite complex.[12] The base metals can then be removed from the mixture by being precipitated as oxides or hydrated oxides. Os^{+4} and the other platinum metals can also be separated from gold by precipitating gold from an acid solution with such reagents as ferrous sulfate,[13] sulfur dioxide,[4] oxalic acid,[4] hydroquinone,[14] tetraethylammonium chloride,[15] and sodium nitrite.[16]

2. Separation By Volatilization

Osmium can be readily oxidized to Os^{+8} and the formation of the volatile octavalent oxide has been used most frequently to separate osmium from all of the other platinum metals (except ruthenium) and other chemical elements. • Tennant[17] first used an oxidizing fusion and a distillation process involving nitric acid. Gilchrist[18] later showed that osmium could be rapidly distilled from a hexabromosmate solution by the use of a 10% HNO_3 solution. However, in the same investigation, it was shown that the distillation of hexachlorosmate solutions with nitric acid took a much longer time to complete than distillation with H_2SO_4. Various modifications of this distillation technique exist.[19-23]

The volatile osmium tetroxide can be collected and absorbed in receiving liquids such as hydrochloric acid-sulfur dioxide solution,[18] 6 $\underline{N}$ HCl-Thiourea solution,[20,25] 30% hydrogen peroxide,[24] or 6 $\underline{N}$ sodium hydroxide.[26,27]

Osmium (as well as ruthenium) can be separated from other elements by a perchloric acid distillation of the chlorosalts.[24] Westland and Beamish[13] have also used a method in which osmium was removed from a chloride solution by a distillation at 115° with a H_2O_2 - H_2SO_4 mixture. The tetroxide was absorbed either in a 40% HBr solution or in a 5% solution of thiourea in ethanol-hydrochloric acid (1:1). Separations of osmium from other elements by the use of aqua regia distillations are also recorded.[9]

The separation of osmium from ruthenium usually occurs in most of these distillations. Whenever the oxides of both elements are volatilized, as in the hydrogen peroxide method of Westland and Beamish,[24] the distillate can be treated with H_2SO_4 and boiled to remove osmium. Ruthenium can then be obtained by a distillation from a bromate mixture.[13, 24]

3. Separation By Solvent Extraction

Osmium can not be extracted from a 6.9 $\underline{M}$ HI solution with ethyl ether.[28] This system can be used to separate osmium (and Ir, Pt, Pd, and Ru) from Au^{+3}, Sb^{+3}, Hg^{+2}, Cd^{+2}, and Sn^{+2}. All of these elements are easily extracted from an iodide solution by ethyl ether. Amyl acetate extractions of $HCl-NH_4Cl-SnCl_2$ solutions have been used to extract Ir, Pt, Rh, Au, and Te and separate them from osmium and ruthenium.[29] Only small amounts of palladium will extract in this system.

Osmium can be isolated from ruthenium, following a collective distillation of the volatile tetroxides, by forming its diphenylthiourea complex in 5-7 $\underline{N}$ HCl and extracting the immiscible product from the acid solution with $CHCl_3$.[30] The complex, tetraphenyl-arsonium hexachlorosmate, formed in a 0.1-0.3 $\underline{N}$ HCl solution can also be extracted with $CHCl_3$.[30] Neither ethyl nor amyl acetate will extract the phenylthiourea complex of Os^{+4} from a dilute HCl solution;[31] however, the Pd^{+2} and Cu^{+2} complexes extract completely. The Pt^4 complex is only partially extracted, while the Ir^{+4}, Rh^{+3}, Ru^{+3}, Au^{+3}, Fe^{+3}, Co^{+2}, Ni^{+2}, and Cr^{+6} complexes do not extract.

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.[32] The palladium, iridium, and gold complexes also extract into carbon tetrachloride.

4. Chromatographic Separations

Beamish[9] reports that no successful applications of either cation- or anion-exchange resin separations of osmium (and ruthenium) have been recorded since the ease with which osmium salts can be reduced by organic reagents would preclude such separations. The only known chromatographic separation of osmium from other elements involves the use of cellulose columns. Burstall, et al[33] have used such columns and methyl propyl ketone or methyl ethyl ketone in HCl as solvents to separate gold, osmium, platinum, palladium, rhodium, iridium, and ruthenium in that order from a chloride system.

IV. DISSOLUTION OF SAMPLES CONTAINING OSMIUM

All of the platinum metals except palladium resist attack by single mineral acids.[9] 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,[34] concentrated H_2SO_4 and sulfur,[35] aqua regia,[36,37] sulfide fusions,[38,39] leaching,[40] and amalgamation.[41] Many procedures involving "fire assay" methods of isolating the platinum metals from ores are known.[9] Typical of newer methods of fire assay is that proposed by Plummer, et al.[42,43] 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 is carried out at a temperature of 1450° and, after its preparation, the button is dissolved in HCl and HNO_3. The platinum metals are then extracted from the solution by methods similar to those described elsewhere in this monograph. In a similar method,[44] osmium (and ruthenium) were recovered from the button by a distillation of the volatile oxides.

Any one of these dissolution techniques can be adapted for use in the radiochemistry of the osmium radionuclides. The addition of osmium

carrier to the mixture before dissolution begins will assist in achieving
an exchange of the radioactive and inactive osmium 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[45] is one of several that report on the toxicology of most
inactive elemental compounds. Such a manual as this should be consulted be-
fore any analysis is undertaken.

Safe practices in handling radioactive sample materials are always impor-
tant in radiochemistry. The discharge of radioactivity by explosion or evolu-
tion 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[46] and in the International
Atomic Energy Agency's publication, entitled "Safe-Handling of Radioisotopes."[47]
Many other similar sources of information exist and should be consulted.

VI. COUNTING TECHNIQUES FOR THE RADIOACTIVE OSMIUM ISOTOPES

The analysis of sample materials containing osmium 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 tech-
nique is dependent upon the specific characteristics of the osmium radio-
isotope 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 osmium 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 osmium. The radioactivity of these can be

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measured by either standard Geiger-Mueller, gamma scintillation, or proportional counting techniques.[48-51]

VII. RADIOCHEMICAL PROCEDURES FOR THE OSMIUM RADIONUCLIDES

Although no specific carrier-free separation methods for the osmium radionuclides appear in the current literature, it should be possible to use any of the volatility, solvent extraction, or chromatography methods reported elsewhere in this monograph to serve as a means of obtaining essentially carrier-free osmium radionuclides. The carrier radiochemical procedures that now exist for the osmium radionuclides have originated from investigations concerned either with the preparation of radioactive osmium tracers,[26] the separation of osmium radionuclides from fission products,[26] or in radioactivation analysis.[52,53] Small amounts of stable osmium have been determined in meteorites[25] and in electrolytic iron[27] by radioactivation analysis methods.

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. Whenever possible, an evaluation of each procedure is made with regard to its use in the decontamination of other radioactive species from the radioactive osmium isotopes.

PROCEDURE 1

Procedure Used In: Preparation of radioactive osmium tracers

Method: Distillation and precipitation

Element Separated: Osmium radionuclides

Type Material Analyzed: Rhenium metal[26]

Type Nuclear Bombardment: 60" cyclotron reactions

Procedure By: Chu (Reported by Meinke[26])

Separation Time: ~ 20 minutes

Chemical Yield of Carrier: ~ 100%

Decontamination: 10^2 from other radioactivities present

Equipment Required: Standard

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PROCEDURE 1 (Continued)

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. Neutralize and then acidify the NaOH soln. with 6 $\underline{N}$ HCl.

7. Add 3 cc 10% sodium thiosulfate and heat in water bath.

8. Filter and count as the brown osmium sulfide.

PROCEDURE 2

Procedure Used In: Preparation of radioactive osmium tracers and separation of osmium radionuclides from fission products.

Method: Distillation and precipitation

Element Separated: Osmium radionuclides

Type Material Analyzed: Uranium metal[26]

Type Nuclear Bombardment: 184" cyclotron (all high energy particles)

Procedure By: Folger and Hicks (Reported by Meinke[26])

Separation Time: ~ 2.5 hours

Chemical Yield of Carrier: ~ 30%

Decontamination: ~ 10^4 - 10^5 from fission products

Equipment Required: Standard

Procedure:

1. Use ~ 20 mg. Os carrier and dissolve target in conc. HCl under reflux. Add ~ 5 mg Ge carrier and boil with conc. HCl ($GeCl_4$ is driven off).

2. Add I^- and IO_3^- (slight x's I.$^-$) and boil to remove I_2.

3. Add conc. HNO_3 (Sol'n. is already ~ 10 $\underline{N}$ in H^+). Add HNO_3 to make it ~ 6 $\underline{N}$ in NO_3^- and distill in an air stream. Catch OsO_4 in 6 $\underline{N}$ NaOH in an ice bath. (Gives orange sol'n.)

4. Pass in H_2S to ppt OsS_2 (black). Acidify with conc. HCl to ~ 1 $\underline{N}$ and centrifuge. Wash (Use Aerosol and heat to aid coagulation. Addition of KNO_3 might help).

5. Dissolve sulfide in conc. HNO_3 and redistill (distillation should proceed from 8-10 $\underline{N}$ HNO_3 in an air stream). Catch OsO_4 in 6 $\underline{N}$ NaOH in an ice bath.

6. Repeat 4. (The wash may be made with ~ 1 $\underline{N}$ HCl if desired.)

7. Dissolve the sulfide in conc. $HClO_4$. Add Mo holdback (~ 5 mg) and 2 cc conc. H_3PO_4 (complexes Mo). Distill in an air steam, catching OsO_4 in 6 $\underline{N}$ NaOH in an ice bath.

8. Repeat 6 and 7.

9. Make slightly acid with HCl. Reduce with Mg metal to some lower oxidation state of Os (to prevent loss of OsO_4). Boil. Add Mg and HCl as needed to completely ppt Os metal. Excess Mg may be removed by washing with warm 2-6 $\underline{N}$ HCl. Weigh as Os metal.

Remarks:

1. CAUTION: OsO_4 is extremely toxic!

2. In step 4 an attempt is made to remove most of the Cl^- from the sulfide so that upon dissolving and distilling $GeCl_4$ will not be carried over. This should no longer be necessary in step 6.

3. Any Ru contaminant remaining after step 5 will likely be carried through the rest of the procedure. For additional purification repeat steps 4 and 5.

4. If iodine is a likely contaminant, repeat step 2.

PROCEDURE 3

Procedure Used In: Radioactivation analysis

Method: Distillation and precipitation

Element Separated: Os^{191} (16 d) and Os^{193} (31 h)

Type Material Analyzed: Iron meteorites[25]

Type Nuclear Bombardment: $Os^{190}(n,\gamma)Os^{191}$
$Os^{192}(n,\gamma)Os^{193}$

Procedure By: Herr, W., et al[25]

Separation Time: Several hours

Chemical Yield of Carrier: 60-70%

Decontamination: Excellent from rhenium

Equipment Required: Standard

Procedure:

1. Irradiate 1-2 grams of the meteorite for at least 3 days in a reactor (Note 1). Prepare and irradiate Os comparator samples (K_2OsCl_6) in the same manner.

2. After the irradiation, transfer the irradiated material to a distillation flask and dissolve in HNO_3-H_2SO_4 acid mixture, then add Os carrier and CrO_2 solution.

3. Heat and distill the osmium from the mixture as OsO_4. Distill into a mixture of 6 $\underline{N}$ HCl and thiourea.

4. Determine the yield of the experiment (Note 2). Then aliquot the solution for counting (Note 3).

5. Comparator sample is treated in the same manner.

Notes:

1. In this instance, the irradiations were made in the BEPO reactor at Harwell; neutron flux = 10^{12} N/cm^2.

2. By measuring color intensity with a MQ-4 spectrophotometer at a wave length of 430 m/μ.

3. By gamma counting.

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PROCEDURE 4

Procedure Used In: Radioactivation Analysis

Method: Distillation and precipitation

Element Separated: Os^{191m} (14 h), Os^{191} (16 d), or Os^{193}(31 h)

Type Material Analyzed: Electrolytic iron[27]

Type Nuclear Bombardment: $Os^{190}(n,\gamma)Os^{191m}$
$$Os^{190}(n,\gamma)Os^{191}$$
$$Os^{192}(n,\gamma)Os^{193}$$

Procedure By: Mahlman, H. A. (Reported by Leddicotte[27])

Separation Time: 2 hours

Chemical Yield of Carrier: 65-70%

Decontamination: $\sim 10^5$ from all elements

Equipment Required: Standard

Procedure:

  A. Irradiation of Sample Material

  1. Irradiate known amounts of test (Note 1) and comparator (Note 2)
samples in a neutron flux of at least 6.5×10^{11} n/sec/cm^2 for 16 hours
(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 aqua regia and dilute to
volume with distilled water. By means of a volumetric pipette, pipet at least
0.5 ml of the dilution to a 125-ml volume distillation flask. Then add 2 ml
of osmium carrier (Note 4) and 10 ml of conc. HCl. Proceed with Step 2 of
Part II below.

    II. The Test Sample

  1. After the irradiation, quantitatively transfer the test sample
(Note 1) to a 125-ml volume distillation flask. Add 2 ml of osmium
carrier and 10 ml of conc. HCl. Heat to boiling under reflux conditions
in order to dissolve test sample.

2. Add an excess of saturated KI solution and boil to remove I_2. Cool.

3. Then add sufficient conc. HNO_3 to make solution 6 $\underline{N}$ in HNO_3. Heat and distill in an air stream. Catch the osmium carrier and the osmium radio-nuclides in 6 $\underline{N}$ NaOH contained in a centrifuge tube immersed in an ice bath (Note 5). Continue distillation until no more carrier is given off.

4. Saturate the 6 $\underline{N}$ NaOH solution with H_2S, then add enough conc. HCl to make the solution ~ 1 $\underline{N}$ in HCl. Heat to coagulate precipitate (Note 6); then centrifuge. Discard supernatant liquid. Wash at least once with 1 $\underline{N}$ HCl.

5. Dissolve OsS_2 in conc. HNO_3 and redistill from a 6 $\underline{N}$ HNO_3 solution. Catch the OsO_4 in 6 $\underline{N}$ NaOH.

6. Make the NaOH solution slightly acid with HCl and then add magnesium metal powder in small amounts. Heat gently while adding metal powder (Note 7) then boil. Add Mg powder and conc. HCl as needed to completely precipitate the osmium carrier and the osmium radionuclide(s) as osmium metal. Wash the metal precipitate with warm 2-6 $\underline{N}$ HCl (Note 8).

7. Filter, weigh as Os metal and then mount for radioactivity measurements.

C. Measurement of the Radioactivity and Calculation of Stable Osmium Content of Test Sample

1. The osmium radioactivity in both the test and comparator samples may be assayed either for beta or gamma radioactivity. Use a Geiger-Mueller counter for beta measurements and a gamma scintillation counter for the gamma measurements (Note 9).

2. Following the radioactivity measurements, correct the observed radioactivity for loss of "carrier" during the experiment, half-life of the osmium isotope, and the sample weights of both the test and comparator samples (Note 10). A simple ratio of these corrected radioactivities be-comes a measure of the amount of stable osmium in the test sample:

% Os in test sample = $\dfrac{\text{Corrected Os radioactivity in test sample}}{\text{Corrected Os radioactivity in comparator sample}}$ X 100.

Notes:

1. Use at least 0.1-0.2 gram portions.

2. Use at least 0.010 gram of osmium metal.

3. The limits of measurement for determining osmium by this procedure is 0.01 microgram.

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

5. Distills as OsO_4 to give an orange-colored solution.

6. Aerosol solution may be used to assist in coagulation.

7. Causes a reduction to some lower oxidation state of Os.

8. Removes excess magnesium metal.

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

10. Decay measurements may be followed, if required.

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