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The Radiochemistry of Rhenium

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The Radiochemistry of Rhenium

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

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I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF RHENIUM

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Rodden, C. J., ed., Analytical Chemistry of the Manhattan Project, Book 8, Part I, p. 442-443, National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, 1950.

II. RADIOACTIVE NUCLIDES OF RHENIUM

The radioactive nuclides of rhenium that are of interest in the radiochemistry of rhenium are given in Table I. This table has been compiled from information appearing in "Table of Isotopes" by D. Strominger, J. M. Hollander, and G. T. Seaborg, Reviews of Modern Physics 30, 585-904 (1958).

Table I

Radioactive Nuclides of Rhenium

Radionuclide	Half-life	Mode of Decay	Energy of Radiations, Mev	Produced By
Re^{178}	15 m	β^+	β^+: 3.1	
Re^{180}	2.4 m	β^+, EC	β^+: 1.1 γ: 0.11, 0.88	
Re^{180}	18 m	EC	γ: 0.227, 0.282	
Re^{180}	20 h	β^+	β^+: 1.9	
Re^{181}	20 h	EC	γ: Many	
Re^{182}	12.7 h	EC	γ: Many	Daughter of Os^{182}(21.9 h)
Re^{183}	71 d	EC	γ: Many	Daughter of Os^{183}(13.5 h)
Re^{184}	50 d	EC	γ: Many	
Re^{184}	2.2 d	EC or IT	γ: 0.043, 0.159	
Re^{186}	88.9 h	β^-, γ	β^-: 0.934, 1.072 γ: 0.1372, 0.627, 0.764	$Re^{185}(n,\gamma)Re^{186}$ $Os^{186}(n,p)Re^{186}$
Re^{188m}	18.7 m	IT	γ: 0.0635, 0.105	$Re^{187}(n,\gamma)Re^{188m}$
Re^{188}	16.7 h	β^-, γ	β^-: 1.96, 2.12 γ: 0.1551	$Re^{187}(n,\gamma)Re^{188}$[a]
Re^{189}	150 d	β^-, γ	β^-: 0.2 γ: 1.0	
Re^{190}	2.8 m	β^-, γ	β^-: 1.7 γ: 0.191, 0.392, 0.57, 0.83	

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[a] Also produced by $Os^{188}(n,p)Re^{188}$, $Ir^{191}(n,\alpha)Re^{188}$, and $W^{186}(n,\gamma)W^{187}\ W^{187} \xrightarrow[24\ h]{\beta^-} Re^{187}(n,\gamma)Re^{188}$.

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

Radiochemistry is probably best described as being an analysis technique used primarily either (1) to assist in obtaining a pure radionuclide in some 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 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. In "carrier-free" separations, i.e. radiochemical techniques used mostly for absolute radioactivity measurements (see (1) above), it is required that the radioelement be isolated in a manner able to give either no amount or a minimal amount of stable element 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 the radioelement's radioactivity. One major difference exists between "carrier" radiochemistry and more conventional analysis techniques in that it is never always necessary to recover completely the added amount of "carrier" element, since a 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. Appendix A lists some of the more recent references cited for the determination of rhenium by these analysis techniques.

The following information is intended to give some general idea of the behavior of rhenium and its compounds and how this behavior can be used in devising radiochemical analysis methods for the radionuclides of rhenium. More detailed information can be obtained either from the references given in this section or from the general references given in Section I.

A. The General Chemistry of Rhenium

Rhenium is an extremely rare element. It is distributed widely in nature, yet it can only be found on the earth's surface in parts per billion. It has no characteristic mineral, and it occurs in the highest concentration in molybdenite and in some platinum ores. It is chiefly produced by oxidizing smelter residues obtained in the processing of molybdenite. ReO_4^- ions are formed during the oxidation process and finally separated as potassium perrhenate, $KReO_4$, by adding potassium chloride to a solution of the rhenium ions. Metallic rhenium can be produced by heating the $KReO_4$ in a hydrogen atmosphere.

1. Metallic Rhenium

Rhenium metal is usually obtained as a dark-gray powder. When fabricated into metal sheet, it resembles platinum in appearance, and it is soft and malleable when it is pure. Rhenium metal melts at 3150°, and it has a density in the compact state of 20.9.

At ordinary temperatures, it is resistant to air oxidation; at temperatures in excess of 1000°C it is attacked by oxygen. Powdered rhenium metal is slowly volatilized when heated gently in an oxygen atmosphere and will form rhenium heptoxide, Re_2O_7. Conditions involving moist air and ordinary temperatures will bring about a gradual oxidation and the formation of strong perrhenic acid, $HReO_4$.

Rhenium metal does not form hydrides or nitrides. It will combine with phosphorus, arsenic, silicon and tungsten to form compounds; it will form mixed crystals only with chromium.

Hydrochloric and hydrofluoric acids do not dissolve rhenium metal, but it will dissolve rapidly in nitric acid to form perrhenic acid, $HReO_4$. It will dissolve slowly in sulfuric acid to give $HReO_4$ also. Perrhenic acid salts can be formed by fusing rhenium metal with alkali hydroxide.

2. Compounds of Rhenium

Rhenium can form compounds corresponding to all of the oxidation states from -1 to +7. According to Latimer(1) the potentials in acid solution are

$$\overbrace{Re^- \text{ --- } Re \text{ --- } Re^+(?) \text{ --- } Re^{+++} \text{ --- } ReO_2 \text{ --- } ReO_4}^{0.363}$$

and rhenium in all lower oxidation states is readily oxidized by oxygen to the perrhenates. Compounds of the heptapositive state, +7, are the most prominent. The +4 state is also favored by rhenium in some of its compounds. Compounds for the +3, +5, and +6 valence states also exist. Rhenium also exhibits a mononegative valence, -1. Rhenide, Re^-, has been prepared in solution by reducing perrhenate with zinc in dilute sulfuric acid.(2)

The most important compounds formed by rhenium include oxides, oxysalts, sulfides, fluorides, chlorides, chloro-salts, carbonyl compounds, and rhenides. Table II lists the more important of these compounds and gives information about their solubilities.

a. The Oxide Compounds

Rhenium metal will burn in oxygen to form rhenium heptoxide, Re_2O_7. The yellow Re_2O_7 crystals melt at 220° and dissolve very readily in water to form perrhenic acid, $HReO_4$. Rhenium heptoxide, although very soluble in alcohol, is not very soluble in ether. A white oxide of unknown composition can be formed by gently heating the yellow heptoxide crystals in air during the combustion of the rhenium metal. It is believed that this oxide is a modified Re_2O_7 compound or the peroxide, Re_2O_8.

Table II

The Solubility of Rhenium Compounds[a]

Compound	Formula	Solubility In Cold Water	 In Hot Water	 For Other Reagents
Chlorides:	$ReCl_3$	Soluble	Soluble	Soluble in acids and alkalis
	$ReCl_4$	Soluble; decomposes	Soluble; decomposes	Soluble in HCl
	$ReCl_5$	Decomposes	Decomposes	Soluble in HCl and alkalis
	$ReCl_6$	Soluble; decomposes	Soluble decomposes	Soluble in HCl
Fluorides:	ReF_4	Decomposes	Decomposes	Soluble in 40% HF
	ReF_6	Soluble; decomposes	Soluble; decomposes	
Oxides:	Re_2O_3	Insoluble	Insoluble	Soluble in HNO_3; insoluble in HCl
	ReO_2	Insoluble	Insoluble	Soluble in conc. HNO_3 and H_2O_2
	ReO_3	Insoluble	Insoluble	Soluble in alkalis, H_2O_2 and HNO_3
	Re_2O_7	Very soluble	Very soluble	Very soluble in alcohol, acids and alkalis
Oxy-Salts:	ReO_3Br			
	$ReOCl_4$	Decomposes	Decomposes	
	ReO_3Cl	Decomposes	Decomposes	
	$ReOF_4$			
	ReO_2F_2			
Sulfides:	ReS_2	Insoluble	Insoluble	Soluble in HNO_3; insoluble in alcohol and alkalis
	Re_2S_7	Insoluble	Insoluble	Soluble in HNO_3, alcohols, and H_2O_2
Carbonyls:	$Re(CO)_5Cl$	Insoluble	Insoluble	Insoluble in organic solvents
	$Re(CO)_5Br$	Insoluble	Insoluble	Insoluble in organic solvents
	$Re(CO)_5I$	Insoluble	Insoluble	Insoluble in organic solvents
Metal-Organic:	$(C_6H_5)_4AsReO_4$	Insoluble	Insoluble	Insoluble in alcohol; soluble in other organic solvents
	$C_{20}H_{16}N_4 \cdot HReO_4$	Soluble	Soluble	

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[a] Additional information appears in "Handbook of Chemistry and Physics, 42nd Ed., 1960-61," Chemical Rubber Publishing Company, Cleveland (1960).

Red rhenium trioxide, ReO_3, is formed when Re_2O_7 mixed with rhenium metal is heated to 300° in a sealed capillary tube.

Rhenium dioxide, ReO_2, a brown-black powder can be obtained by heating rhenium heptoxide in a hydrogen atmosphere at 300°. When ReO_2 is heated in oxygen, it burns to rhenium heptoxide; it can be reduced to the metal when heated in a hydrogen atmosphere. Hydrochloric acid will dissolve ReO_2 to form green-colored $H_2(ReCl_6)$ salts. These salts have a tendency to hydrolyze and produce a brown-black rhenium dioxide hydrate, $ReO_2 \cdot x\ H_2O$.

Rhenium sesquioxide, Re_2O_3, is known only in the hydrated form of $Re_2O_3 \cdot x\ H_2O$. It is produced by adding alkali hydroxide to a solution of Re_2Cl_6. This hydrated oxide form is unstable, and it will gradually decompose water to form hydrogen.

b. The Oxy-salt Compounds

Perrhenates (Re^{+7}), rhenates (Re^{+6}), hyporhenates (Re^{+5}), metahyporhenates (Re^{+5}), pyrohyporhenates (Re^{+5}), orthohyporhenates (Re^{+5}), and rhenites (Re^{+4}) as oxy-salt compounds of rhenium are known.

The perrhenates, $M^1(ReO_4)$, are the most stable of these compounds and result from the neutralization of perrhenic acid, $HReO_4$, with alkali hydroxides. They usually are formed as anhydrous crystals and will be colorless unless colored cations are present. They are generally soluble in water and can be melted without decomposition. Almost all other rhenium compounds are prepared from potassium perrhenate, $KReO_4$. Potassium perrhenate is more stable, even in strong alkaline solutions, than potassium permanganate. Perrhenates may also be formed directly by fusing rhenium metal powder in the presence of oxygen with alkali hydroxides.

The rhenates, $M_2^1(ReO_4)$, and the hyporhenates and their derivatives, $M^1(ReO_3)$, $M_4^1(Re_2O_7)$, and $M_3^1(ReO_4)$, are not easily prepared. Usually they are present in melts, and, since temperature-dependent equilibra exist between the various oxidation states, these oxy-salts are difficult to isolate because of the changes in temperature and oxygen content.

The rhenites, $M_2^1(ReO_3)$, are obtained by fusing ReO_2 with alkali hydroxides. They are usually brown in color and are insoluble in water and caustic alkalis.

c. The Sulfur Compounds

Rhenium does not form a monosulfide compound. The disulfide, ReS_2, and the heptasulfide, Re_2S_7, are the chief sulfide compounds of rhenium.

Rhenium disulfide can be prepared either by a direct combination of the components or by treating Re_2S_7 in nitrogen. It occurs usually as black, trigonal leaflets which are insoluble in hydrochloric acid and in alkali sulfide solutions. When strongly heated, it will decompose into Re and S_2. Since ReS_2 can take up excess sulfur in solid solution, its composition does not correspond exactly to the formula ReS_2.

Rhenium heptasulfide, Re_2S_7, is produced by saturating strongly acid solutions of the perrhenates with hydrogen sulfide. However, it will be dispersed as a colloid if the acid concentration is not at an optimum condition. Remy(3) reports that these conditions are 12 g of HCl per 100 ml of solution. Re_2S_7 is insoluble in hydrochloric acid and in alkali sulfide solutions. When it is dissolved in nitric acid, it will form perrhenic acid, $HReO_4$. An irreversible reaction will occur and the disulfide, ReS_2, will be formed when the heptasulfide is heated.

Monothioperrhenate ions, $(ReO_3S)^-$, are formed when neutral perrhenate solutions or dilute perrhenic acid of a cation are saturated with H_2S. The alkali monothioperrhenates are very soluble in water; whereas, such compounds as thallium(I) thioperrhenate, $Tl(ReO_3S)$, is only slightly soluble. The monothioperrhenates will gradually decompose in solution to form compounds with a higher sulfur content. Tetrathioperrhenate compounds are also known to exist.

d. The Halogen Compounds

The halogen compounds of rhenium generally form stable acid-complexes. Fluoride, chloride, bromide, and iodide compounds of rhenium are known. The bromide and the iodide compounds do not exist in the free state; however, their acido-salts correspond to the chloro-salt compounds.

Rhenium hexafluoride, ReF_6, is formed as a colorless gas when rhenium powder is reacted with fluorine at 125°. When the gas condenses, a yellow crystalline mass is formed. When ReF_6 gas mixed with hydrogen is passed through a tube at 200°, rhenium tetrafluoride, ReF_4, is deposited on the walls of the tube as a greenish black mass. ReF_4 will decompose in water. It dissolves completely in 40% HF. If this solution is treated with KF, potassium hexafluororhenate(IV), $K_2(ReF_6)$, will be produced. $K_2(ReF_6)$ can also be produced by reducing $KReO_4$ in a hydrofluoric acid solution with KI. Oxyfluorides, $ReOF_4$ and ReO_2F_2, can also be prepared.

Rhenium pentachloride, $ReCl_5$, is formed when rhenium is combined with chlorine at a temperature of 125°. $ReCl_3$ and Re_2Cl_6 are also formed in this process; however, $ReCl_5$ can be separated by sublimation in a high vacuum. $ReCl_5$ is deep brown-black in color, and when it is heated in nitrogen, it will form Re_2Cl_6. The oxychlorides, $ReOCl_4$ and ReO_3Cl, are formed when $ReCl_5$ is heated in oxygen. When it is treated with dilute hydrochloric acid, $ReCl_5$ will dissolve and will form the acid, $H_2(ReOCl_5)$, as well as perrhenic acid, $HReO_4$, and chlororhenic acid, $H_2(ReCl_6)$. Chlororhenic acid, $H_2(ReCl_6)$, and free chlorine are produced when $ReCl_5$ is treated with concentrated HCl.

Chlororhenic acid, $H_2(ReCl_6)$, can also be prepared by dissolving ReO_2 in hydrochloric acid or by reducing perrhenate compounds with HI in concentrated hydrochloric acid solution. $H_2(ReCl_6)$ is very similar to chloroplatinic acid, $H_2(PtCl_6)$, in its reactions. For example, potassium hexachlororhenate, $K_2(ReCl_6)$, obtained by warming a mixture of potassium perrhenate and potassium iodide with concentrated HCl, is very insoluble in hydrochloric acid. $K_2(ReCl_6)$ is hydrolytically decomposed in water.

When $ReCl_5$ is thermally decomposed, rhenium trichloride, $ReCl_3$ or Re_2Cl_6, is formed. $ReCl_3$ is soluble in water and is rapidly hydrolyzed in pure aqueous solution to form $Re_2O_3 \cdot x\, H_2O$. It is stable in HCl solution, and at ordinary temperatures, it will not react with permanganate or chlorine water. It exists in hydrochloric acid solution as $H(ReCl_4)$, and when alkali chlorides are added to this solution, chlororhenate(III) salts, $M^1(ReCl_4)$, will crystallize out. Upon heating, the chlororhenate salts will decompose to produce chlororhenate(IV) salts, rhenium and Re_2Cl_6.

Rhenium trioxychloride, ReO_3Cl, can be obtained either by reacting metallic rhenium with a mixture of chlorine and oxygen, or by heating $ReCl_5$ or Re_2Cl_6 in oxygen, or by treating Re_2O_7 with $ReCl_5$. If an excess of $ReCl_5$ is used, rhenium oxytetrachloride, $ReOCl_4$, will be formed. ReO_3Cl can be hydrolyzed in water to produce $HReO_4$ and HCl, whereas, in the hydrolysis of $ReOCl_4$, $HReO_4$ and HCl are produced and the black oxide, ReO_2, is deposited upon the walls of the vessel. When $ReOCl_4$ is dissolved in hydrochloric acid, a complex acid, $H_2(ReOCl_6)$, is formed. The salts of this acid are very unstable. $ReOCl_4$ will react with ammonia to form $ReO(NH_2)_2Cl$. This oxydiamidodichloride compound will decompose at temperatures above 400° to form Re and ReO_2. Diamidorhenic acid, $H_2\{ReO_3(NH_2)_2\}$ will be formed if $ReO(NH_2)_2Cl$ is reacted with ice water and can be transformed to $Re(NH_2)_2O_2$, diamidorhenium dioxide, if heated in a vacuum at 100°.

e. The Carbonyl Compounds

Rhenium pentacarbonyl, $[Re(CO)_5]_2$ can be produced by heating rhenium heptoxide, Re_2O_7, at 250° with carbon monoxide at a pressure of 300 to 400 atmospheres. Colorless crystals are produced by this reaction. The pentacarbonyl is slightly volatile. It is not very soluble in organic solvents. It is stable at ordinary temperatures, but will decompose at temperatures higher than 250°.

If $ReCl_5$ is heated with CO and Cu, or if $KReO_4$ is heated with CO and CCl_4, rhenium chloropentacarbonyl, $Re(CO)_5Cl$, can be formed. The corresponding bromo- or iodo-pentacarbonyl compounds can be obtained if $K_2(ReBr_6)$ or $K_2(ReI_6)$ are used instead of $ReCl_5$. The rhenium pentacarbonyl halides are colorless crystals. They are not very soluble in organic solvents and are quite stable at ordinary temperatures.

Some of the carbon monoxide in the rhenium pentacarbonyl and in the pentacarbonyl halides, when these compounds are reacted with pyridine or orthophenanthroline, can be replaced by these nitrogen compounds to form organic pyr or o-phen compounds.

f. The Rhenide Compounds

The ability of rhenium to exist in the mononegative valence (-1) state gives rise to certain rhenide compounds. Mononegative rhenium was first observed following the reduction of dilute, acidified solutions of potassium perrhenate in a Jones reductor. In studies with alkali perrhenates, it was possible to isolate such compounds as potassium rhenide tetrahydrate, $KRe \cdot 4H_2O$, by an extraction of the potassium hydroxide formed in a reaction involving the reduction of potassium perrhenate in ethylenediamine-water solutions by means of potassium metal.(4) Unfortunately, limited information exists on the properties of this and corresponding rhenides.

B. The Analytical Chemistry of Rhenium

As pointed out elsewhere in this monograph, the use of a known amount of inactive rhenium carrier in a separation method almost always makes it practical to obtain the rhenium carrier in a weighable form in the final stage of the separation procedure used. Two things are achieved if this is done. The radionuclide is concentrated into a small mass for the radioactivity measurements, and the carrier is obtained as a weighable compound which can be used to determine any loss of the "carrier" during the analysis. Three weighable forms, i.e. (1) the metal,(5) (2) tetraphenylarsonium perrhenate,(6) and (3) nitron perrhenate,(7,8) are considered to be acceptable gravimetric forms for determining rhenium. Duval(9) in his pyrolysis studies of various rhenium compounds, suggests certain criteria for obtaining both the tetraphenylarsonium perrhenate and nitron perrhenate in a desirable weighing form. One prerequisite in obtaining any of these weighing forms is that the rhenium be separated from other elements (in radiochemistry, these could be either stable or radioactive) before the final precipitation of the rhenium or one of its compounds is made.

Hillebrand, et al,(5) point out that in the method involving the weighing of rhenium as the metal that the rhenium must be separated from other nonvolatile elements before its conversion. A precipitation of rhenium as rhenium heptoxide, Re_2O_7, can be used to bring about this separation. Rhenium metal can then be produced by igniting the Re_2S_7 at 900°C in a hydrogen atmosphere.

When a precipitate of tetraphenylarsonium perrhenate, $(C_6H_5)_4AsReO_4$, is desired, the rhenium in the form of perrhenate can be precipitated from solutions varying from strong ammonical (6 M) to moderately acidic (5 M HCl) by treating the solution with an excess of 1% solution of tetraphenylarsonium chloride.(6) Permanganate, perchlorate, periodate, iodide, bromide, fluoride, nitrate, thiocyanate, mercury, bismuth, lead, tin, silver, and vanadyl ions will interfere in this precipitation of rhenium as tetraphenylarsonium perrhenate. Tungstate and metavanadate ions will not interfere under these conditions. If the precipitation is made in either a 6 M ammonium hydroxide or a 0.6 M tartaric acid solution, molybdenium will not interfere.

Tungsten, molybdenum, palladium, platinum, gold, and germanium will interfere in the precipitation of rhenium with diphenylendanilodihydrotriazole, nitron.(10) Also, nitrates, chromates and the higher valence states of manganese must be removed before the precipitation or high results will occur. In order to minimize these interferences, the rhenium can be first separated as Re_2S_7 and then dissolved in a sodium hydroxide solution containing H_2O_2 in order to prevent greater than theoretical yields. The rhenium in this solution is in the perrhenate form and can be precipitated from a 0.04 N sulfuric acid solution with an excess of a 5% solution of nitron acetate (5 grams of nitron in 3 ml of acetic acid and dissolved in 100 ml of water). The composition of the nitron perrhenate formed is $C_{20}H_{16}N_4 \cdot HReO_4$.

The metal or either of the above rhenium compounds can be conveniently used to obtain the rhenium "carrier" and the rhenium radionuclides in a form suitable for a radioactivity measurement after they have been isolated from a stable and/or radioactive nuclide mixture. Of course, the following information on current ideas in isolating and determining inactive rhenium do not preclude that it is always necessary in a radiochemical separation to obtain the carrier and the radioelement as a precipitate before the radioactivity measurement. Sometimes it would be sufficient to accept and use, for example, one of the phases obtained in solvent extraction, or an aliquot from the eluate obtained from an ion-exchange separation column, or a portion of a paper chromatogram, in the radioactivity measurement.

1. Separation By Precipitation

Rhenium can be separated from many other elements by precipitating it as Re_2S_7 from a strongly acid or alkaline solution.(5) Nonsulfide-forming elements are separated by saturating either a 4 N hydrochloric acid or a 6 N sulfuric acid solution with hydrogen sulfide. Since Re_2S_7 is insoluble in alkaline sulfide solution, the solubility of molybdenum sulfide in a similar solution can be used in separating rhenium and molybdenum.(5) Technetium (as a radioactive species) in a lower oxidation state (reduced from Tc^{+7} to Tc^{+4}) will not precipitate in a strong acid solution so rhenium may be separated as Re_2S_7 from it by a hydrogen sulfide precipitation at 9-10 N HCl.(11,12,13)

Gerlit(14) has reported that rhenium can be separated from technetium by reducing Tc^{+7} to Tc^{+4} and carrying the Tc^{+4} from the solution on an iron hydroxide precipitate.

Jasim, et al.,(15) reports on the determination of rhenium and its separation from manganese, technetium, ruthenium and molybdenum on an ultramicroscale.

Rhenium is not precipitated in either acid or alkaline solution by such organic reagents as dimethylglyoxime, α-nitroso-β-naphthol, cupferron, α-benzoinoxime, or by 8-hydroxyquinoline. Benzoinoxime(16) and 8-hydroxyquinoline in acetic acid(17) have been used to quantitatively separate it from molybdenum; after filtering, rhenium was determined in the filtrate as nitron perrhenate.(10) However, Hurd(18) points out that small amounts of rhenium cannot be determined in the presence of large amounts of molybdenum, because perrhenic acid can be adsorbed very readily upon the molybdenum-hydroxyquinolate complex.

Rhenium (as well as tellurium,selenium, molybdenum, mercury, gold and platinum) can be separated from either aluminum or uranium by precipitating aluminum and uranium from solution with 2 N sodium sulfide.(19) Subsequent separations of the rhenium from any of the other elements would have to be made before the final precipitation of rhenium.

Tribalat(20) and Tribalat and Beydon(21) have used tetraphenylarsonium chloride to separate rhenium from molybdenum. Tetraphenylphosphonium chloride and tetraphenylstibonium chloride also form insoluble crystalline salts with perrhenate.(22) Tetraphenylphosphonium perrhenate is sufficiently insoluble to be determined gravimetrically.

A water insoluble yellow crystalline hydride sublimate, biscyclopentadienylrhenium, $(C_5H_5)_2ReH$, can be formed by the interaction of rhenium, as rhenium pentachloride, with cyclopentadienylsodium in tetrahydrofuran.(23) It is readily oxidized in air but can react as a base with other salt compounds to form more complex rhenium compounds. Bankovski, et al.,(24) have shown that the thioxinates of elements which form sulfides are not hydrolyzed by water and are more stable than the oxinates. This analytical study with thioxine (8-mercaptoquinoline) and its use with certain masking agents, such as thiourea and KCN, appears to have applications for separating rhenium from such elements as gold, platinum, cerium, tungsten, indium, and cobalt.

2. Separations by Volatility

Rhenium can be separated from molybdenum by volatilizing rhenium heptoxide, Re_2O_7, from a hot acid solution.(25) Hoffman and Lundell(26) have used the dropwise addition of nitric acid, hydrochloric acid and hydrobromic acid to a hot (200-220°C) sulfuric acid solution to volatilize rhenium. Germanium, arsenic, selenium, tin and antimony will also be volatilized under these conditions. Small amounts of rhenium in molybdenite ores can also be volatilized from a sulfuric acid solution of the one by heating (at temperatures of 260-278°C) the solution in the presence of steam and air.(27) Small amounts of molybdenium and selenium will also volatilize from the mixture. Gile, et al.,(28,29) have used CO_2 gas to distill Re_2O_7 from conc. H_2SO_4-

9<u>N</u> HBr solutions. Rhenium, as Re_2O_7, can also be distilled from a mixture containing technetium(30) by distilling with HCl gas from 80% sulfuric acid at 200°.

The dropwise addition of hydrochloric acid or hydrobromic acid to a hot (200-220°C) perchloric acid solution containing rhenium can also be used to volatilize rhenium, as Re_2O_7.(26) Antimony, arsenic, chromium, germanium, osmium, ruthenium, and tin are also volatile under these same conditions. Glendenin(31) and Parker, et al.,(32) have shown that rhenium can be partially separated from technetium, ruthenium and molybdenum, because it is nonvolatile in a perchloric acid solution. Although it has been suggested(33) that the interference of molybdenum in a volatilization system can be inhibited by adding H_3PO_4 or SiO_2 to the solution, it is not practical to add H_3PO_4 or SiO_2 to the perchloric acid system, since molybdenum will be retained with the rhenium. Edwards and Pool(34) have used repeated evaporations of solutions containing rhenium and technetium alternately with hydrochloric and nitric acids. Rhenium will volatilize under these conditions, and this property suggests a method of separation. The volatilization of rhenium sulfide heated to 100°C in a chlorine stream(12) also suggests a possible separation method for the rhenium radionuclides.

If any of these volatilization methods are used in the radiochemistry of rhenium, it must be recognized that the radionuclides of any other volatile element, either wholly or partially volatile under the same conditions represent potential interferences and must be removed. A technique such as the nonvolatility of rhenium in an HCl distillation(35) appears practical; for instance, arsenic, tin and antimony will distil under these conditions.

3. Separations by Electrolytic Methods

Hillebrand, et al.,(36) indicate that electrolytic methods are not very satisfactory. A number of elements interfere, and only small amounts of rhenium (less than 15 milligrams) can be handled. Usually the deposition is incomplete, and the deposited rhenium is contaminated with oxygen. The best results are obtained when a stationary cathode of sand-blasted platinum gauze and a spiral anode enclosed in an unglazed millite thimble are used. The electrolyte should be dilute sulfuric acid (5 + 95) and the electrolysis should occur overnight at a current density of 0.25 ampere per dm^2 and 2.34 volts between the electrodes. Although deposits of this type can be weighed, it is probably best to convert the deposit to perrhenic acid, $HReO_4$, by exposure to moist oxygen or air, and then determining the rhenium by some gravimetric method. Rogers(37) has shown that rhenium (and molybdenum) can be partially separated from technetium by depositing technetium as the dioxide from a 2 M NaOH solution. A saturated calomel electrode at a controlled cathode potential of -1.1 volts was used to electrodeposit technetium in concentrations of 10^{-4} M or greater.

4. Separation by Solvent Extraction

Solvent extraction methods used as separation methods for other analysis techniques can often be adapted for use in radiochemistry and can be quite useful in separating a radioelement either in a "carrier-free" state or in combination with milligram amounts of "carrier." Morrison and Freiser(38) have recently reviewed the applications of ion association and chelate complex systems to the determination of most of the elements. Some of these methods, particularly those concerned with organic soluble chelates are applicable for use as separation processes in the radiochemistry of rhenium.

a. Ion Association Systems

At least 61% of Re^{+7} (as well as Nb^{+5}, Ta^{+5}, Sn^{+2}, or Sn^{+4}) can be extracted from a 20 M HF solution by ethyl ether.(39) Rhenium can also be separated from molybdenum either by an ethyl ether extraction from a KSCN-$HgNO_3$(40) system or by a butyl alcohol extraction from a KSCN-HCl-$SnCl_2$ system.(41) Rhenium cannot be extracted by ethyl ether from a dilute (1 + 1) hydrochloric acid solution;(42) likewise, rhenium as either Re^{+4} or Re^{+7} is not easily extracted from an aqueous HBr-ethyl ether system.(43) Other systems, involving thiocyanate-ethyl ether,(44) heteropoly acids,(45) alkyl phosphoric acids,(46) and trialkyl phosphine oxides,(47) offer some possibilities of separating rhenium from other elements, particularly molybdenum.

Rhenium, as ReO_4^-, can be separated from molybdenum and many other elements, but not technetium, by extractions with hexone, butex, and other solvents.(30,48) Gerlit(14) has shown that rhenium, as ReO_4^-, could be separated from ruthenium and molybdenum (but not technetium) by extracting it either from an acid solution with alcohols, ketones, or tributyl phosphate or from a basic solution with ketones or cyclic amines. Re^{+7} has been extracted from a 3 $\underline{M}$ K_2CO_3 solution of chromium and niobium with methyl ethyl ketone;(49) a similar separation was also effected by use of 50% or 70% tributyl phosphate in benzene extraction of a hydrochloric acid solution.(49) It is also possible to consider the work of Boyd and Larsen(50) in their studies with technetium. In this investigation, extractions with tertiary amines, as well as quaternary ammonium salts, give an excellent separation of technetium from other elements. Such techniques could also be used for separating rhenium from other elements.

Rhenium tetraphenylarsonium chloride salts have been found to be extractable into chloroform and have provided a basis for separating rhenium from molybdenum(21,51,52) and from tungsten.(52) Chloroform extractable salts have also been observed with tetraphenylphosphonium chloride,(53) triphenylbenzylphosphonium chloride,(54) and 2,4-diphenylthiosemicarbazide chloride.(55) Mixtures of chloroform-2-isobutanol have also been used to extract rhenium 4-hydroxy-3-mercaptotoluene chloride complex from a solution containing molybdenum and rhenium salts.(56) Rhenium has also been separated from technetium by forming a copper-phthalocyanin complex to carry the technetium in a solvent extraction process.(57) Hiskey and Meloche(27) also report on the extraction of ReO_4^- thiocyanate with amyl alcohol.

b. Chelate Complex Systems

Although a limited number of literature references exist for the determination of rhenium by chelate compounds, it is recognized that many of the systems described in Morrison and Freiser(38) could be used to assist in separating radiorhenium from other radioactive or stable elements. In particular, the fact that rhenium is not precipitated (as pointed out elsewhere in this report) from either acid or alkaline solutions of dimethylglyoxime, α-nitroso-β-naphthol, cupferron, α-benzoinoxime, or by 8-hydroxyquinoline offers a potential method for its separation from other elements. However, in the use of dimethylglyoxime, it has been found that Re^{+7} ions can be partially reduced with $SnCl_2$ to give a yellow dimethylglyoxime complex in acid solution that can be extracted with benzyl alcohol.(58) Alpha-benzildioxime will also form a complex with partially reduced Re^{+7} ions and the complex can be extracted from a 9 M H_2SO_4 solution with benzyl alcohol. Oi(58) has used this method to separate a few micrograms of rhenium from milligram amounts of molybdenum.

Molybdenum and tungsten can be specifically separated from rhenium (and all other elements) by a benzoinoxime precipitation in an acid solution followed by a chloroform extraction of their complexes.(59) Rhenium can be extracted from a concentrated HCl solution of 2% sodium diethyldithiocarbamate by ethyl acetate.(60) Some interferences from molybdenum and other elements were experienced. Goishi and Libby(61) report on a pyridine method of separating rhenium. In this method, pyridine is added to a solution of perrhenate and the mixture shaken with 4 N NaOH. The layers are separated by centrifugation; Mn^{+6} and Tc^{+7} also extract under these conditions. A similar system has been used to determine Re^{+7} in chromite and columbite ores.(49)

5. Separations by Ion Exchange Resins

Rhenium's anionic behavior has made it possible to develop anionic-exchange resin techniques capable of separating rhenium from other elements. Conversely, although very little information is available, it should be possible to use cationic-exchange resins to separate rhenium from cationic species by taking advantage of the fact rhenium will not be adsorbed to any great extent by the cation resin.

Perrhenate ion, Re^{+7}, has a very high affinity for strong-base anion exchangers.(30,62-64) It is strongly adsorbed from 0.1 M HCl solution by the anion exchanger, Amberlite IR-4.(65) Anion exchange reactions in phosphate systems have been used to separate rhenium from tungsten,(63,66-70) and from vanadium(67) and from molybdenum.(68,69)

ReO_4^- has been separated from TcO_4^- on Dowex-2 resin in the sulfate form by use of a 0.1 M ammonium sulfate-thiocyanate solution at pH 8.3-8.5.(70) ReO_4^- can also be separated from TcO_4^- by elution of the anions from Dowex-1 (8% crosslinkage) resin with 0.2 M $HClO_4$,(71) or 0.25 M potassium perchlorate.(72) Kraus and Nelson's(63) investigations of anion exchange studies of metal complexes in hydrochloric acid and other chloride solutions have brought about several useful techniques for separating rhenium from many elements. Hicks, et al.,(73) have shown that Re^{+7} is not easily eluted from a Dowex-2 anion exchange resin column when it is complexed with 12 M HCl. Fisher and Meloche(74) and Meloche and Preuss(75) have shown that similar ion exchange systems can be used to separate Re^{+7} from Mo^{+6}.

6. Separations by Paper Chromatography and Electrophoresis

The separation of ReO_4^- from TcO_4^- by paper chromatography has been studied by Lederer,(76) Lederer and Ward,(77) and de Carvalho.(78) Paper electrophoresis has also been used by de Carvalho(48) to separate Tc^{+4} from Re^{+4}. A 1% solution of $SnCl_2 \cdot 2H_2O$ in molar hydrochloric acid as the electrolytes and a current of 150 volts were used. Rhenium, in this instance, remained at the origin as ReO_2 and anionic chlorocomplexes of Re^{+4}. In each of these methods, technetium must be first reduced by such agents as hydrazine,(48) hydrobromic acid,(48) hydroiodic acid,(48) or hydrochloric acid.(79)

IV. DISSOLUTION OF SAMPLES CONTAINING RHENIUM

When dissolving rhenium-containing samples, it is necessary to use techniques that will minimize the loss of rhenium by volatilization.(80) If sulfuric or perchloric acid solutions are fumed, with or without hydrochloric acid or nitric acid, serious loss of rhenium can occur. No losses of rhenium occur when hydrochloric, nitric, or hydrochloric-nitric acid solutions are boiled. Such solutions should not be evaporated to dryness or the residue ignited. Minerals containing rhenium can be dissolved in nitric acid or in mixtures of nitric-hydrochloric acid. Acid-insoluble samples can be fused with either sodium carbonate or sodium carbonate-sodium nitrate, or sodium peroxide-sodium hydroxide.

Any one of these techniques can be adapted for use in the radiochemistry of the rhenium radionuclides. However, it is considered most practical to add the inactive rhenium carrier to the mixture before dissolution begins. This assists in achieving an exchange of the carrier with the radionuclide. In particular, it is to be recommended that the dissolution of rhenium-containing materials should be carried out under strongly oxidizing conditions in order to ensure the conversion of all lower states of rhenium to Re^{+7}. The use of such conditions will also aid in bringing about a proper exchange between the inactive and radioactive rhenium ions.

V. SAFETY PRACTICES

No matter what method is used for decomposing a sample, adequate safety precautions should be used. The toxicology of most elemental compounds have been reported by Pieters and Creyghton,(81) and it should be consulted for information on handling rhenium-containing materials safely.

Safety practices in handling radioactive sample materials is always important in radiochemistry. The discharge of radioactivity by explosion or evolution into a laboratory area can be hazardous and can result in widespread contamination. Thus, some source of information on safe handling practices in processing radioactive samples should be consulted before a radiochemical analysis is undertaken. One such source is that which is given in the Oak Ridge National Laboratory's Master Analytical Manual.(82) Many other similar sources of information exist and should be consulted.

VI. COUNTING TECHNIQUES FOR RADIOACTIVE RHENIUM ISOTOPES

The analysis of sample materials containing radionuclides of rhenium may be completed either by a direct (nondestructive) measurement of the radioactivity of the particular radionuclide or by obtaining the particular radionuclide in some form by radiochemically processing the radioactive sample. The use of either technique is dependent upon the radioactivity of the rhenium radionuclide being measured and such characteristics as the radionuclide's half-life, the type of radiations it emits as it decays and the energy of its radiations must be considered in selecting the analysis technique to be followed.

Table I of this monograph shows the nuclear characteristics of each of the known radioactive isotopes of rhenium. The chief radioisotopes of rhenium usually encountered by the radiochemist are Re^{186} (88.9 h), Re^{188m} (18.7 m), and Re^{188} (16.7 h). These isotopes are produced as a result of a number of nuclear reactions on stable isotopes of rhenium or on the stable isotopes of other elements. The radioactivity of any of these rhenium radionuclides can be analyzed and measured by standard Geiger-Mueller, gamma scintillation and proportional counting techniques.(83-86)

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR RHENIUM

Very few radiochemical procedures exist for the determination of the rhenium radionuclides. Each of the procedures have evolved from each investigator's choice of ideas and techniques similar to those expressed in Section III of this monograph. In almost all of the procedures to be cited, a <u>carrier</u> technique has been used to separate the radionuclides from the radioactive mixtures. <u>Carrier-free</u> separations involving distillation and the carrying of the rhenium radioactivity upon copper sulfide(28,29) and the anion exchange of ReO_4^- from TcO_4^- and molybdenum(70) have been described. It would appear that any volatility, solvent extraction, or chromatography separation procedure could be used to serve in the <u>carrier-free</u> separation of the rhenium radionuclides.

The <u>carrier</u> radiochemical procedures that follow have originated from analysts engaged either in work on the preparation and use of radioactive tracers,(61,87) or fission product analysis,(31) or in the use of radioactivation analysis.(88,89) In particular, it has been necessary to consider the use of radiochemical separations (see Procedures 1 to 5) for the rhenium isotopes in radioactivation analysis concerned with the determination of rhenium in enzyme solutions,(90) meteorites,(91-93) ores,(49) minerals and rocks,(94) and marine biological ash.(95) A detailed procedure of the use of radioactivation analysis and the radiochemical separation method followed in the determination of trace rhenium in enzyme solutions(90) and ores(49) appears in the ORNL Master Analytical Manual.(96,97)

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., appear 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 rhenium isotope.

PROCEDURE 1

Procedure Used In: Radioactivation analysis

Type of Material Analyzed: Chromite, columbite and titanite ores(49)

Type of Nuclear Bombardment: $Re^{185}(n,\gamma)Re^{186}$ (Re^{186}: 88.9 h)
$Re^{187}(n,\gamma)Re^{188}$ (Re^{188}: 16.7 h)

Procedure By: Leddicotte, G. W. and Grimanis, A. P. (Reported by Leddicotte(96))

Chemical Yield of Carrier: ~70%

Separation Time: 2-3 hours

Decontamination: See Note 1

Equipment Needed: Neutron source and standard laboratory equipment

Procedure

A. Irradiation of Sample Material

1. Irradiate known amounts of test (see Note 2) and comparator (0.025 to 0.030 g. of rhenium metal to nearest 0.1 mg.) samples in a neutron flux of at least 5×10^{11} n/cm^2/sec for 16 hours (see Note 3). Use small quartz tubes or aluminum foil to contain the samples.

B. Preparation of Irradiated Test Portions for Analysis

I. Comparator Samples

1. After the irradiation, quantitatively transfer the comparator sample to a 50 ml volumetric flask, then dissolve it in a small measured volume of conc. HNO_3, then dilute to 50 ml with water. Mix well; using safe-handling practices for radioactive materials.

2. Pipet a 1.00 ml aliquot of this solution into a second 50 ml volumetric flask; dilute to volume with water. Mix well.

3. Pipet a 1.00 ml aliquot of this solution into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same tube 2.00 ml of a standard carrier solution of known rhenium concentration (Note 4). Dilute the solution to 10 ml with water. Continue with Part C below.

II. Test Sample(s)

1. Quantitatively transfer all of the irradiated test portion from the quartz tube or aluminum wrap to a nickel crucible. Add 0.5 g. of NaOH (as pellets) to each crucible. Place the crucible into a muffle furnace preheated to 325-350°C. Heat for 5 minutes. Remove from the furnace, then add ~ 0.8 gram of Na_2O_2 in two portions (~ 0.4 g. each time). Slowly swirl the crucible after each addition (Note 5).

2. Return the crucible to the muffle furnace (Note 6). Heat at a temperature of 650-680°C. for at least 10 minutes. The crucible should be swirled several times during this heating period.

3. Cool the crucible; then add 10 ml of water. Stir the mixture with a stirring rod. Transfer the slurried solution to a 50-ml glass centrifuge tube. Add 8 ml of 3 M HCl and 5 ml of 6 N HNO_3 to the solution. If the solution is not acidic, add additional 6 N HCl dropwise to the mixture. Then, by means of a volumetric pipet, add to the same centrifuge tube 2.00 ml of a standard carrier solution of known rhenium concentration. Stir the solution (Notes 7 and 8). Continue with Part C.

C. Radiochemical Separation of Rhenium

1. Cool the solution (Note 9); then add 1 or 2 NaOH pellets to the tube (Note 10). A precipitate results, remove by centrifugation. After centrifuging, transfer the supernatant liquid to a new centrifuge tube. Save for further processing.

2. Dissolve the precipitate by adding dropwise 6 N HCl. Stir while adding acid and only add enough acid to dissolve the precipitate. Adjust volume to 10 ml with water; then add 1 or 2 NaOH pellets to the tube (Note 10). Centrifuge; combine this supernatant liquid with supernatant liquid obtained in C-1 above.

3. Add sufficient solid K_2CO_3 to make the solution 3 M in K_2CO_3 (Note 11). Stir the mixture until all of the K_2CO_3 is dissolved.

4. Transfer the solution to a 125-ml separatory flask; add an equal volume (Note 12) of equilibrated methyl ethyl ketone (Note 13). Shake the mixture for 2 minutes. Allow the phases to separate, then discard the aqueous (lower) phase.

5. Wash the organic phase by adding an equal volume of 3 M K_2CO_3 solution and shaking the mixture for 2 minutes. Allow the phases to separate; then discard the aqueous phase.

6. Transfer the organic phase to a 100-ml beaker; add 2 drops of 30% H_2O_2 and then slowly evaporate (on a steam bath or on a low-heat hot plate) the mixture to near dryness. Cool, then add 15 ml of H_2O and 0.4 g. of NaCl. Heat the solution to boiling and add 5-6 ml of 1% tetraphenylarsonium chloride solution to it. Digest the mixture for one hour on a steam bath.

7. Filter off the $(C_6H_5)_4AsReO_4$ precipitate through a tared filter paper (Munktells No. 00) that is held in a Hirsch funnel; wash the precipitate three times with 10 ml portions each of ice water and alcohol. Dry the precipitate for 15 minutes in a drying oven at 110°C. Weigh the $(C_6H_5)_4AsReO_4$ precipitate (Note 14) and filter paper on an analytical balance. Then mount

the precipitate and filter paper for the radioactivity measurements. (See Part D below.)

D. Measurement of the Radioactivity from Re^{186} (and/or Re^{188}) and Calculation of Inactive Rhenium Content of the Original Sample

1. This analysis may be completed by either beta or gamma counting. Re^{186} (88.9 h) decays with negatron beta radiations (0.934 and 1.072 Mev), orbital electron capture (x-ray emission observed) and gamma ray (0.1372, 0.627, and 0.764 Mev) emission. Re^{188} (16.7 h) decays with negatron beta radiations (1.9, 1.96, and 2.12 Mev) and gamma radiations (many; chief of which are those having energies of 0.1550, 0.623, 0.828, and 1.610 Mev). These respective measurements may be made by counting with a Geiger-Mueller counter, a gamma scintillation counter, or a gamma scintillation spectrometer. In the use of the latter instrument, the photopeaks of the major gamma radiations are measured.

2. Following the radioactivity measurements, the observed radioactivity is corrected for loss of "carriers" during the experiment, half-life of the rhenium radioactive isotope measured, and the sample weights of either the test or comparator sample. A comparison of these corrected radioactivities becomes a measure of the stable rhenium content of the test sample:

$$\text{Percent stable Re in Test Sample} = \frac{\text{Corrected Radioactivity of Re in Test Sample}}{\text{Corrected Radioactivity of Re in Comparator Sample}} \times 100.$$

NOTES:

1. In this instance, at least 10^6 from Cr^{51} (27 d) and Nb^{95} (35 d); no other contaminants found.

2. At least 0.10 gram portions should be used. Duplicate portions of test and comparator samples should be analyzed.

3. The Oak Ridge National Laboratory Graphite Reactor was used for the irradiations. The sensitivity of the method is such that 1×10^{-9} gram of

rhenium can be determined. The sensitivity can be improved by use of higher neutron fluxes.

4. As perrhenic acid, $HReO_4$, solution; Re^{+7} concentration equals 10 milligrams per milliliter.

5. The Na_2O_2 should be added at 5 minute intervals. Swirling the crucible stirs up all unreacted particles.

6. Temperature of furnace should be changed to 650-680°C.

7. The solution of the chromite ore must be clear. If not heat the solution until it becomes clear.

8. A white precipitate of Nb_2O_5 should occur at this point during the treatment of the columbite ore. If the precipitate is black, heat the mixture to boiling until a white precipitate is obtained. Remove the Nb_2O_5 by filtering or by centrifuging the mixture.

9. If a chromite ore is being processed, add 1 ml of tartaric acid solution.

10. This should be sufficient NaOH to make the solution basic. If not, add additional NaOH pellets to neutralize solution.

11. If total supernatant liquid volume is 40 milliliters, 16.6 grams of solid K_2CO_3 will be required to make solution 3 $\underline{M}$ in K_2CO_3.

12. Volume should be approximately 50 ml.

13. The methyl ethyl ketone is equilibrated by stirring or shaking a volume of it with 3 $\underline{M}$ K_2CO_3 solution.

14. By comparing the final weight of the $(C_6H_5)_4AsReO_4$ precipitate obtained here with the theoretical yield expected for the amount of rhenium carrier added, it is possible to determine the chemical yield of the experiment. The chemical yield correction is then used to determine the amount of Re^{186} (and/or Re^{188}) recovered during the separation process.

PROCEDURE 2

Procedure Used In: Radioactivation analysis

Type Material Analyzed: Enzymes(90)

Type of Nuclear Bombardment: $Re^{185}(n,\gamma)Re^{186}$ (Re^{186}, 88.9 h)
$Re^{187}(n,\gamma)Re^{188}$ (Re^{188}, 16.7 h)

Procedure By: Brooksbank, W. A. and Leddicotte, G. W. (Reported by Leddicotte(97))

Chemical Yield of Carrier: ~ 70%

Separation Time: 2-3 hours

Decontamination: 10^5

Equipment Needed: Neutron source and standard laboratory equipment

Procedure

A. Irradiation of Sample Materials

1. Irradiate known volumes of test (see Note 1) and comparator (0.025 to 0.030 g. of rhenium metal to nearest 0.1 mg) samples in a neutron flux of at least 5×10^{11} n/cm^{-2}/sec^{-1} for 16 hours. (See Note 2)

B. Preradiochemical Processing

I. Comparator Samples

1. Quantitatively transfer the comparator sample to a 50 ml volumetric flask, dissolve in a small measured volume of conc. HNO_3, dilute to 100 ml with water. Mix well; using safe-handling practices for radioactive materials.

2. Pipet a 1.00 ml aliquot of this solution into a second 50 ml volumetric flask, dilute to volume with water. Mix well.

3. Pipet a 1.00 ml aliquot of this solution into a 125-ml distillation flask. Add to the same flask, by means of a volumetric pipet, 2.00 ml of standard rhenium carrier solution (see Note 3). Also, add 1 ml each of the recommended holdback carriers (see Note 4). Dilute to 20 ml with water, mix well, and add 10 ml of conc. H_2SO_4. Proceed with step 1 of Part C below.

II. Test Samples

1. Transfer all of the solution to a 125-ml distillation flask. Add to the same flask, by means of a volumetric pipet, 2.00 ml of standard rhenium carrier solution (see Note 3). Also, add 1 ml each of the recom-

mended holdback carriers (see Note 4). Add an equal volume of water and 10 ml of HNO_3-H_2SO_4 mixture ($2HNO_3:3H_2SO_4$). Proceed with step 1 of Part C below.

C. Radiochemical Separation

1. Place the distillation head on the flask (see Figure 1) and distil in a current of air until H_2SO_4 fumes are evolved. Collect the distillate in 20 ml of 6 N NaOH contained in a 50-ml centrifuge tube held in an ice bath.

2. After the distillation has been stopped, heat the distillate to near boiling and then saturate the solution with H_2S until the coagulation of Re_2S_7 is complete. Centrifuge and discard the supernatant liquid. Wash the Re_2S_7 with 10 ml of hot water.

3. Dissolve the Re_2S_7 in 1 ml of conc. HNO_3; add 5 ml of conc. HBr and evaporate to dryness. Dissolve the residue in 15 ml of H_2O.

4. Add 1 ml of iron holdback carrier (5 mg of Fe^{+3}/ml) to the solution; then add conc. NH_4OH dropwise until the precipitation of $Fe(OH)_3$ is complete. Heat to coagulate precipitate. Centrifuge; discard the precipitate.

5. Repeat $Fe(OH)_3$ scavenging at least two more times. After final scavenging, transfer supernatant liquid to another 50-ml centrifuge tube.

6. Add 0.4 g. of solid NaCl to the solution, then heat the solution to boiling and add 5 ml of 1% tetraphenylarsonium chloride solution to it. Digest the mixture for one hour on a steam bath.

7. Filter off the $(C_6H_5)_4AsReO_4$ precipitate through a tared filter paper (Munktells No. 00) that is held in a Hirsch funnel; wash the precipitate three times with 10 ml portions each of ice water and alcohol. Dry the precipitate for 15 minutes in a drying oven at 110°C. Weigh the $(C_6H_5)_4AsReO_4$ precipitate (Note 5) and filter paper on an analytical balance. Then mount the precipitate and filter paper for the radioactivity measurements (see Part D).

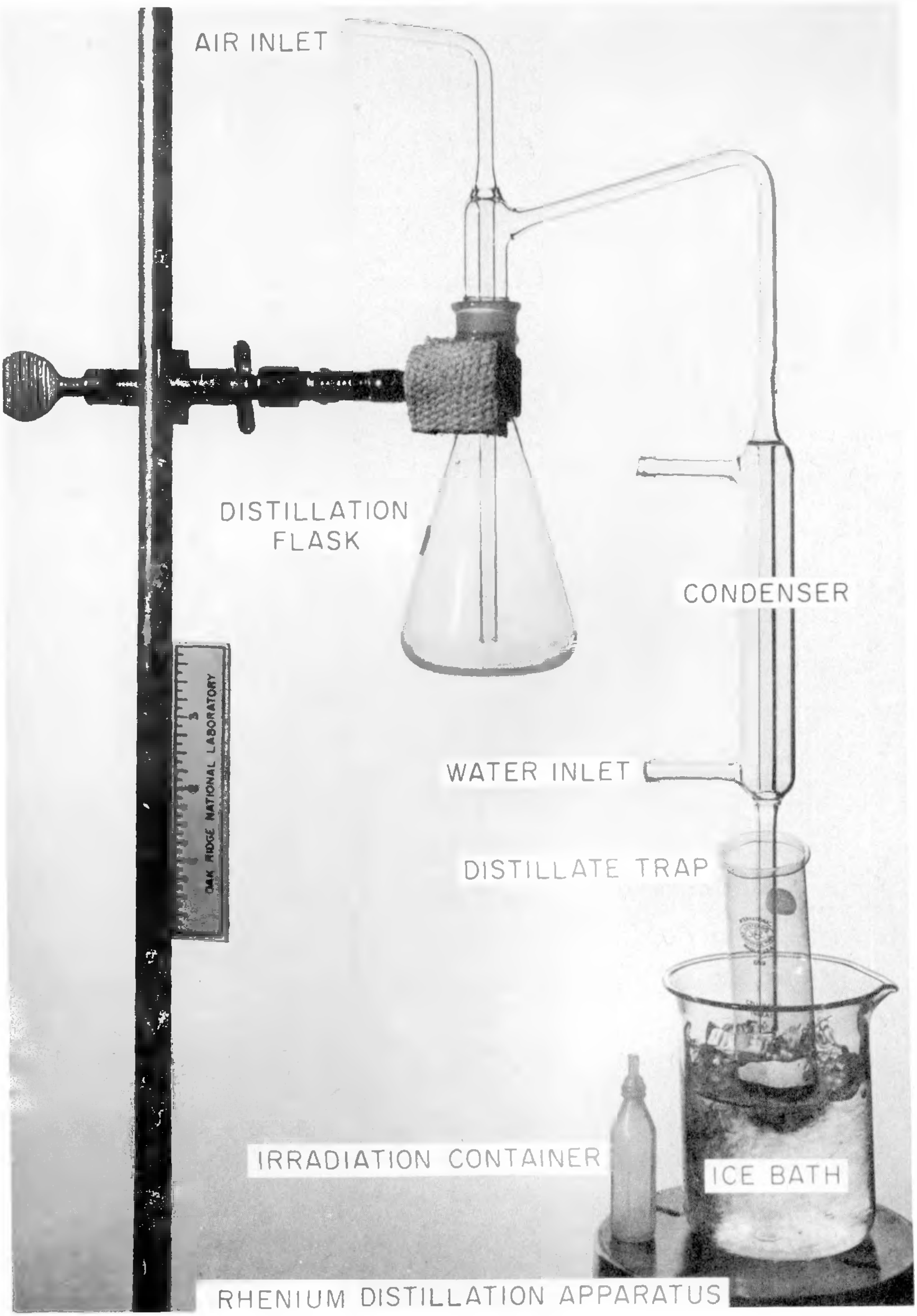
AIR INLET
DISTILLATION FLASK
CONDENSER
OAK RIDGE NATIONAL LABORATORY
WATER INLET
DISTILLATE TRAP
IRRADIATION CONTAINER
ICE BATH
RHENIUM DISTILLATION APPARATUS

Fig. 1

D. Measurement of the Radioactivity from Re^{186} (and/or Re^{188}) and Calculation of Inactive Rhenium Content of the Original Sample

1. This analysis may be completed by either beta or gamma counting. Re^{186} (88.9 h) decays with negatron beta radiations (0.934 and 1.072 Mev), orbital electron capture (x-ray emission observed) and gamma radiations (0.1372, 0.627, and 0.764 Mev). Re^{188} (16.7 h) decays with negatron beta radiations (1.9, 1.96, and 2.12 Mev) and gamma radiations (many; chief of which are those having energies of 0.1550, 0.623, 0.828 and 1.610 Mev). These respective measurements may be made by counting with a Geiger-Mueller counter, a gamma scintillation counter, or a gamma scintillation spectrometer. In the use of the latter instruments, the photopeaks of the major gamma radiations are measured.

2. Following the radioactivity measurements, the observed radioactivity is corrected for loss of "carrier" during the experiment, half-life of the rhenium radioactive isotope measured, and the sample weights of either the test or comparator sample. A comparison of these corrected radioactivities becomes a measure of the stable rhenium content of the test sample:

$$\text{Percent Stable Re in Test Sample} = \frac{\text{Corrected Radioactivity of Re in Test Sample}}{\text{Corrected Radioactivity of Re in Comparator Sample}} \times 100.$$

NOTES:

1. In this instance, 1 milliliter of solution was placed in a polyethylene bottle; comparator samples placed in small quartz tubes and attached to sides of bottle with Scotch tape.

2. The Oak Ridge National Laboratory Graphite Reactor was used for the irradiations. The sensitivity of this method is such that 1×10^{-9} gram of rhenium can be determined. The sensitivity can be improved by use of higher neutron fluxes.

3. The standard rhenium solution recommended has a concentration of 10 milligrams of Re^{+7} per milliliter.

4. Holdback carriers recommended are: copper, cobalt, iron, manganese, sodium, strontium, and zinc.

5. By comparing the final weight of the $(C_6H_5)_4AsReO_4$ precipitate obtained here with the theoretical yield expected for the amount of the carrier added, it is possible to determine the chemical yield of the experiment. The chemical yield correction is then used to determine the amount of Re^{186} (and/or Re^{188}) recovered during the separation process.

PROCEDURE 3

Procedure Used In: Radioactivation analysis

Type of Material Analyzed: Iron Meteorites(88,89)

Type of Nuclear Bombardment: $Re^{185}(n,\gamma)Re^{186}$ (Re^{186} 88.9 h)
$Re^{187}(n,\gamma)Re^{188}$ (Re^{188} 16.7 h)

Procedure By: Brown and Goldberg

Chemical Yield: 60-90%

Decontamination: Adequate from arsenic, selenium, germanium and other volatile halides.

Equipment Needed: As indicated in procedure.

Procedure

1. Dissolve 0.3 to 0.5 gr. of irradiated meteorite in 20 ml. of concentrated HBr. Add 10-15 mg. of Re in the form of standardized potassium perrhenate carrier. Evaporate to dryness. Add 10 ml. more of HBr and repeat evaporation.

2. Take up the residue in 10 ml. of water. Add 10 ml. of concentrated sulfuric acid and distill in a current of air until 2 or 3 ml. of sulfuric acid remain in the flask. Collect the distillate in 20 ml. of water in a 50 ml. centrifuge tube kept in an ice bath.

3. Place the centrifuge tube in a steam bath and pass in H_2S until

the coagulation of Re_2S_7 is complete. Centrifuge and discard the supernate. Wash the Re_2S_7 with 10 ml. H_2O.

4. Dissolve the Re_2S_7 in 1 ml. of HNO_3; add 5 ml. of conc. HBr and evaporate to dryness. Take up residue in 20 ml. of H_2O.

5. Add 5 mg. of ferric iron in the form of ferric chloride. Add NH_4OH drop by drop till precipitation of ferric hydroxide occurs. Heat on steam bath. Centrifuge, and discard the precipitate. Repeat $Fe(OH)_3$ scavenging at least two more times.

6. Add 5 ml. of a 1% aqueous solution of tetraphenylarsonium chloride. Let the precipitate of tetraphenylarsonium perrhenate stand for 20 minutes. Filter, wash with two 25 ml. portions of hot water and 25 ml. of alcohol. Weigh, dry 15 minutes at 110° and mount for counting.

7. Ten to fifteen mg. of irradiated rhenium metal was dissolved in 10 ml. of nitric acid and diluted to 1000 ml. A 1 ml. aliquot of this solution was added to the carrier aliquot. The combined solution was diluted to 50 ml. The standard was then treated as in paragraph 6.

NOTE

The 90 hr. rhenium-186 was used as a basis for counting. The meteoritic rhenium gave the reported 90 hr. half-life and an absorption curve that was identical with that of the standard rhenium sample.

PROCEDURE 4

Procedure Used In: Radioactivation analysis

Type Material Analyzed: Marine Biological Ash(95)

Type of Nuclear Bombardment: $Re^{185}(n,\gamma)Re^{186}$, ($Re^{186}$, 88.9 h)

Procedure By: Fukai and Meinke(95)

Chemical Yield of Carrier: (Unknown)

Separation Time: (Unknown)

Decontamination: (Unknown)

Equipment Needed: (Unknown)

Procedure

NOTE: The authors(95) point out that the specimens were irradiated for 10 hours, then processed radiochemically. Re^{186} removed from mixture by $(C_6H_5)_4AsCl$ precipitation followed by chloroform extraction. Re^{186} radioactivity measured by means of gamma spectrometry.

PROCEDURE 5

Procedure Used In: Radioactivation analysis

Type Material Analyzed: Meteorites,(93) Minerals and Rocks(94)

Type of Nuclear Bombardment: $Re^{185}(n,\gamma)Re^{186}$ (Re^{186}, 88.9 h)

Procedure By: Herr(57)

Chemical Yield of Carrier: (Unknown)

Separation Time: (Unknown)

Decontamination: Adequate decontamination from osmium

Equipment: As indicated in procedure

Procedure

NOTE: No specific information has been given on this procedure.

PROCEDURE 6

Procedure Used In: Preparation of radioactive tracers

Type Material Bombarded: Tantalum, Tungsten

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

Procedure By: Hicks, Wilkinson (reported by Meinke(87))

Separation Time: 30 minutes

Chemical Yield of Carrier: ~ 100%

Decontamination: Good

Equipment Needed: As indicated in procedure

Procedure

1. Dissolve W and Ta in HF with a minimum of HNO_3 in platinum disk, and Re carrier added.

2. H_2S is passed into the boiling solution for 15 minutes precipitating black Re_2S_7. Centrifuge and wash in a lusteroid test tube.

3. Dissolve Re_2S_7 in 3 cc 1 <u>M</u> NaOH and 1 drop 30% H_2O_2 and transfer to glass centrifuge cone.

4. Scavenge twice or three times with $Fe(OH)_3$ (~ 1 mg Fe^{+++}).

5. Reprecipitate Re_2S_7 from strong HCl solution (add 10 cc conc. HCl), centrifuge and wash.

6. This procedure gives excellent purity, but for additional purity, the sulfide can be transferred to a still with H_2SO_4 and the volatile oxide distilled in a current of air and catching the distillate in concentrated NaOH.

PROCEDURE 7

Procedure Used In: Carrier-free separation of Re from irradiated targets

Type of Material Analyzed: Tantalum

Type of Nuclear Bombardment: Cyclotron particles

Procedure By: Gile, et al.(28,29)

Chemical Yield of Carrier: A carrier-free separation; no carrier added

Separation Time: Several hours

Decontamination: 10^2-10^3

Equipment Needed: Standard

Procedure

1. Dissolve tantalum target in mineral acid solution; then, evaporate solution to precipitate Ta_2O_5. Centrifuge. Transfer supernatant liquid to distillation flask.

2. Add 36 N H_2SO_4 and 9 N HBr to the distillation flask; distill Re_2O_7 with CO_2 into conc. HNO_3.

3. Evaporate the nitric acid solution; dilute to 3 N H_2SO_4 and add copper carrier. Saturate with H_2S, carrying the Re_2O_7. Centrifuge; discard the supernatant liquid.

4. Dissolve the CuS precipitate in dilute HNO_3. Evaporate the solution to dryness. Take up the residue in water, then neutralize with NaOH to precipitate the copper. Centrifuge; discard the supernatant liquid.

5. Transfer precipitate to a watch glass. Dry by evaporation. Mount for counting.

PROCEDURE 8

Procedure Used In: Radioactive tracer applications of technetium

Type of Material Analyzed: Irradiated silver (NOTE 1)

Type of Nuclear Bombardment: Mesons (NOTE 1)

Procedure By: Goishi and Libby(61)

Chemical Yield: ~ 100% of Re^{+7} carrier added

Decontamination: None from Tc or Mn

Equipment Needed: Standard

Procedure

1. Make solution 4 M in NaOH; add Re carrier.

2. Add pyridine and extract Re. (NOTE 2).

3. Add 4 M HCl to the pyridine extracts; saturate with H_2S to precipitate Re_2S_7. Centrifuge; discard supernatant liquid.

4. Dissolve Re_2S_7 precipitate in dilute NaOH and 30 H_2O_2. Add 0.05 M $(C_6H_5)_4AsCl$ to precipitate $(C_6H_5)_4AsReO_4$.

5. Filter off $(C_6H_5)_4AsReO_4$; mount for radioactivity measurement.

NOTES

1. Procedure studied for use in isolating technetium radioactivity from meson-irradiated silver. Can be used also in determination of trace rhenium.

2. Pyridine equilibrated by saturating with 4 N NaOH.

PROCEDURE 9

Procedure Used In: Studies on separating Re from Mo target (and Tc)(70)

Type of Material Analyzed: Molybdenum

Type of Nuclear Bombardment:

Procedure By: Atteberry and Boyd(70)

Chemical Yield of Carrier: ~ 100%

Separation Time: Several hours

Decontamination: Completely from Tc

Equipment: Standard plus anion exchange resin column.

Procedure

1. Add concentrated H_2SO_4 to solution of target. Distill Re_2O_7 and Tc_2O_7 into water.

2. Add Re carrier and saturate water solution with H_2S to precipitate Re_2S_7. (NOTE 1)

3. Dissolve Re_2S_7 in H_2O_2 and NH_4OH. Place on Dowex-2 anion exchange resin column. Elute ReO_4^- with 0.1 $\underline{M}$ $(NH_4)_2SO_4$ and NH_4SCN solution adjusted to pH 8.3-8.55 with NaOH.

4. Continue elution until all Re radioactivity is removed (NOTE 2). Then evaporate to small volume for counting.

NOTES

1. Tc radioactivity will also carry.

2. Tc radioactivity remains on column.

PROCEDURE 10

Procedure Used In: Separation of rhenium from fission products

Type of Material Analyzed: Fission product mixture

Type of Nuclear Bombardment: Neutrons

Procedure By: Glendenin(31)

Chemical Yield of Carrier: ~ 100%

Separation Time: Several hours

Decontamination: None from Tc

Equipment Needed: Standard

Procedure

1. Add conc. HBr to fission product solution; evaporate off I_2 and Br_2.

2. Add H_2SO_4 and distill Re_2O_7 into water.

3. Add Re carrier to distillate; saturate with H_2S to precipitate Re_2S_7. Centrifuge; discard supernatant liquid.

4. Dissolve Re_2S_7 in conc. HNO_3; add Fe^{+3} carrier and NH_4OH to precipitate $Fe(OH)_3$. Remove scavenger precipitation by centrifuging or filtering.

5. Add 0.05 M $(C_6H_5)_4AsCl$ to the filtrate to precipitate $(C_6H_5)_4AsReO_4$. Mount and count.

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APPENDIX A

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