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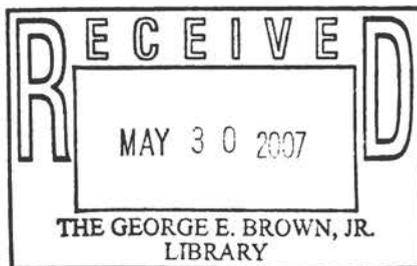


The Radiochemistry of Tungsten

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

The Radiochemistry of Tungsten

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

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II. THE RADIOACTIVE NUCLIDES OF TUNGSTEN

The radioactive nuclides of tungsten that are of interest in the radiochemistry of tungsten are given in Table I. This table has been compiled from information appearing in reports by Strominger, et al.,⁽¹⁾ and by Hughes and Harvey.⁽²⁾

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

Table 1: The Radioactive Nuclides of Tungsten

<u>Radio-nuclide</u>	<u>Half-life</u>	<u>Mode of Decay</u>	<u>Energy of Radiations, Mev</u>	<u>Produced by</u>
W ¹⁷⁶	80 m	EC (99%) β ⁺ (~0.5%)	β ⁺ : ~2.0 γ: ~1.3	W-dp-4n
W ¹⁷⁷	130 m	EC	γ: ~0.5; 1.2	W-dp-4n
W ¹⁷⁸	21.5 d	EC	γ: ~0.3 (weak)	W-γ-2n, W-n-3n, W-dp-3n
W ¹⁷⁹	30 m	EC	γ: 0.030	W-γ-n, W-n-2n, W-d-t, W-dp-2n
W ¹⁷⁹	5.2 m	EC or IT	γ: 0.22	W-α-cn, W-p-pn
W ¹⁸¹	145 d	EC	γ: 0.136; 0.152	W ¹⁸⁰ (n,γ)W ¹⁸¹
W ^{183m}	5.5 s	IT	γ: 0.105; 0.155	W ¹⁸² (n,γ)W ^{183m}
W ^{185m}	1.62 m	IT	γ: 0.130; 0.165	W ¹⁸⁴ (n,γ)W ^{185m} Re ¹⁸⁵ (n,p)W ^{185m} a Os ¹⁸⁸ (n,α)W ^{185m} a
W ¹⁸⁵	73.8 d	β ⁻	β ⁻ : 0.430 γ: None	W ¹⁸⁴ (n,γ)W ¹⁸⁵ Re ¹⁸⁵ (n,p)W ¹⁸⁵ a Os ¹⁸⁸ (n,α)W ¹⁸⁵ a
W ¹⁸⁷	24.0 h	β ⁻	β ⁻ : 1.33; 0.63; 0.34 γ: 0.0721; 0.1062; 0.1138; 0.1343	W ¹⁸⁶ (n,γ)W ¹⁸⁷ Os ¹⁸⁹ (n,α)W ¹⁸⁷ a Re ¹⁸⁷ (n,p)W ¹⁸⁷ a
W ¹⁸⁸	69.5 d	β ⁻ (?)	β ⁻ : ? γ: ?	W ¹⁸⁷ (n,γ)W ¹⁸⁸ b

^a If element is a major constituent of the sample matrix, it can undergo a fast neutron reaction to produce element of interest.

^b A second-order neutron reaction.

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

Radiochemistry is probably best described as being primarily an analysis technique used 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, the "carrier" separations 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, techniques used mostly for absolute radioactivity measurements, 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 radiochemistry and more conventional analysis techniques in that it is not 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 similar analysis techniques are seldom used in radiochemistry, because they do not separate the desired radionuclides from contaminants (either radioactive or stable) in the mixtures being analyzed. However, some of the developments used in these analyses techniques may be useful for consideration in radiochemistry.

The following information is intended to give some general idea of the behavior of tungsten and its compounds and how this behavior can be used in devising radiochemical analysis methods for the radionuclides of tungsten. 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 Tungsten

Tungsten is one of the four transition elements (Cr, Mo, W, and U) that constitutes Group VI B of the periodic system and is considered to be mainly an acid-forming element. The elements of Group VI B have two incomplete electron shells - the outermost and the one next to it; therefore, irregular oxidation states exist and do not change rapidly in chemical behavior. Tungsten exists in the same positive oxidation states as molybdenum. Tungsten forms compounds having valence states of from 2 to 6. Most tungsten compounds contain tungsten in the oxidation state of +6. It will form stable hexachlorides, hexafluorides and unstable hexabromides. The tungstates, tungstic acid (from which the tungstates are derived), and the anhydride of tungstic acid, tungsten trioxide, are the most important compounds of tungsten. Table II lists the more important of these compounds and gives information about their solubilities.

1. Compounds of Tungsten

a. The Hexavalent Tungsten Compounds

Tungsten trioxide, WO_3 , occurs in nature and is formed by heating the acid. The acidification of a cold solution of a tungstate with hydrochloric acid brings about the formation of α -tungstic acid, $H_2WO_4 \cdot H_2O$; a hot solution will form β -tungstic acid, H_2WO_4 . $H_2WO_4 \cdot H_2O$ is soluble to some degree in water; whereas, H_2WO_4 is insoluble in water and all acids, except hydrofluoric. Tungstic acid forms complex tungstate compounds. Complex alkali metal compounds of the type $(Na_2O)_m(WO_3)_n$ in which $m = 1$ and n varies from 1 to 6 are known. Many more complexes in which m or n is unity can also be formed.^(3,4) Normal or simple tungstates, such as $M_2O \cdot WO_3$ forms, can result from the fusing of WO_3 with sodium carbonate or potassium carbonate. Meta-tungstates, which contain $4WO_3$ radicals per M_2O molecule, are known. The paratungstates generally contain 12 WO_3 radicals for every 5 M_2O molecules and can be made commercially. For example, $Na_{10}W_{12}O_{41} \cdot 28H_2O$ is formed by heating wolframite with soda ash and extracting the fused mass with water. Upon neutralization with hydrochloric acid, the sodium paratungstate salt separates as large triclinic crystals.

The addition of strong acids to hot solutions of most tungstates will precipitate yellow tungstic acid, which is practically insoluble in water and in most acids. Metatungstates are usually soluble forms of tungstic acid salts and will give no precipitate with acids. The treatment of tungstic acid, tungsten trioxide, or alkali and alkaline earth tungstates with reducing agents at high temperatures can usually bring about the production of a variety of colored compounds. The most frequent colored product produced is usually an intense blue in color. These compounds generally have compositions which correspond to the presence of tungsten in a mean oxidation state lower than 6, but higher than 5. Exposure to sunlight will cause tungsten trioxide to take on a bluish tint even when kept under water. Nascent hydrogen ($Zn + HCl$) will precipitate from a tungstate solution a blue precipitate that is stable in air. The blue precipitate that forms when $SnCl_2$ and HCl are used to react with a tungstate solution will gradually discolor on standing in air and will be finally transformed into yellow tungstic acid, H_2WO_4 .⁽⁴⁾

When hydrogen peroxide solutions at a temperature of 100° are used to dissolve either tungstic acid or tungsten trioxide, a peroxy-acid, H_2WO_5 , or tungsten oxide-peroxyhydrate, $WO_3 \cdot H_2O_2$, is formed. Peroxytungstates result when tungstates are treated with hydrogen peroxide.

Silicotungstate compounds are formed when silicic acid is made soluble in hot solutions of acid alkali tungstates. These salts contain a large number of WO_3 radicals for each SiO_2 , in addition to alkali oxide and water. Remy⁽⁴⁾ points out that, although these salts are generally called silicotungstates, the name polytungstosilicates is more correct since they are derived from silicic acid or its salts by the addition of tungstic acid radicals (tungstate groups).

The tungstosilicates are readily decomposed when treated with alkalis. Tungstic acid also forms compounds exactly analogous to the silicotungstates when boric acid (tungstoborates), phosphoric acid (tungstophosphates) and arsenic acid (tungstoarsenates) are treated with hot solutions of acid alkali tungstates. In each instance, the compounds will contain a large number of WO_3 radicals. The upper limit is 12 WO_3 radicals for each

Table II: Solubility of Tungsten Compounds

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Arsenide	WAs ₂	Insoluble	Insoluble	Decomposes in hot HNO ₃ and hot H ₂ SO ₄
Boride	W ₂ B	Insoluble	Insoluble	
	WB	Insoluble	Insoluble	
	WB ₂	Insoluble	Insoluble	Soluble aqua regia
Bromide	WBr ₂	Decomposes		
	WBr ₅	Decomposes		Soluble alkali, absolute alcohol, chloroform, ether
	WBr ₆	Insoluble	Decomposes	Soluble NH ₄ OH
Carbide	WC	Insoluble		Soluble HNO ₃ -HF, aqua regia
	W ₂ C	Insoluble		Soluble HNO ₃ -HCl
Carbonyl	W(CO) ₆	Decomposes		Decomposes in fuming HNO ₃
Chloride	WCl ₂	Decomposes		
	WCl ₄	Decomposes		
	WCl ₅	Decomposes		Very slightly soluble in CS ₂
	WCl ₆		Decomposes	Very soluble in CS ₂ ; soluble in alcohol, ether & benzene
Fluoride	WF ₆	Decomposes	Decomposes	Soluble alkali
Iodide	WI ₂	Insoluble	Decomposes	Soluble in KOH & alkali; insoluble in CS ₂ and alcohol
	WI ₄	Insoluble	Decomposes	Soluble in absolute alcohol; insoluble in ether, chloroform & turpentine

Oxide	WO_2	Insoluble	Insoluble	Soluble in acid and KOH
	WO_3	Insoluble	Insoluble	Soluble in hot alkali and HF; insoluble in other acids
Oxy-Salts	WOb_r_4	Decomposes	Decomposes	
	WO_2Br_2			
	$WOCl_4$	Decomposes	Decomposes	Soluble in CS_2 , benzene
	WO_2Cl_2	Soluble	Decomposes	Soluble in alkali, NH_4OH ; insoluble in alcohol
Phosphide	WOF_4	Decomposes		Slightly soluble in CS_2 ; insoluble in CCl_4
	W_2P			Soluble in fused $NaCO_3+NaNO_3$; insoluble in acids; aqua regia
	WP	Insoluble		Soluble in HNO_3+HF ; insoluble in alkali and HCl
	WP_2	Insoluble	Insoluble	Soluble in HNO_3+HF , aqua regia; insoluble in alcohol, ether
Sulfide	WS_2	Insoluble		Soluble in HNO_3+HF , fused alkali; insoluble in alcohol
	WS_3	Slightly soluble	Soluble	Soluble in alkali

molecule of the other acid; this limit is never exceeded. The characteristic property of these compounds, i.e., the heteropolyacids, is that they contain at least two different acid radicals, one of which is usually in large numbers.

Remy⁽⁴⁾ notes that the introduction of one or more WO_4 radicals into H_2WO_4 can produce a series of isopolyacid compounds capable of reacting to form polytungstate salts. However, it has not been possible to distinguish these reactions by analytical data.

Tungsten trioxide, WO_3 , results from the oxidation of tungsten or its compounds by heating in air. The dioxide, WO_2 , is formed from this by treating it with reducing agents. WO_3 is a soft lemon yellow powder that will turn orange when heated. When ignited at high temperatures, or if fused with borax, it becomes crystalline. WO_3 melts at 1473° and will volatilize above 1750° ; however, it can be completely volatilized as an oxychloride at 500° if the volatilization occurs in a stream of hydrogen chloride gas. Tungsten trioxide is insoluble in water. Caustic alkalis will dissolve it to form tungstates, the salts of tungstic acid. Although WO_3 can be formed by igniting tungstic acid, it cannot be reconverted to the acid form by adding water to the ignited salt. Tungsten trioxide does not appear to yield a true salt in which the metal is a part of the cation. Intermediate oxides, such as $W_{10}O_{29}$ and W_4O_{11} , are formed in the reduction of tungsten trioxide to the metal.

Hexahalides are formed by the reduction of tungsten in a hydrogen atmosphere. In combination with chlorine and by heating, these reactions can produce tungsten hexachloride, WCl_6 . The hexachloride is insoluble in cold water; it will decompose in warm water. It is soluble in alcohol, ether and other organic solvents. Oxyhalides, such as $WOCl_4$ and WO_2Cl_2 are known. The WO_2Cl_2 is volatile when heated. The hexabromide, WBr_6 , is similar to WCl_6 but it is more readily decomposed. A complex gaseous hexafluoride, WO_2F_4 , can result from the action of hydrofluoric acid on tungstate compounds. The hexahalides and the oxyhalides are quickly hydrolyzed by water to tungstic acid and the corresponding hydrogen halide.

The treatment of a tungstate solution with hydrogen sulfide brings

about at first a partial replacement of the oxygen of the tungstic acid with sulfur to form an oxothiotungstate. Ultimately, the oxygen is completely replaced by the sulfur to form a thiotungstate, $M_2(WS_4)$. The addition of acids to a solution of a thiotungstate will produce tungsten trisulfide, WS_3 , a chocolate brown precipitate.

Hexavalent tungsten can react with acid anions to form a few complex acido-salt compounds such as the halogeno- and oxohalogeno-compounds. For example, tungstates dissolved in aqueous hydrofluoric acid will produce colorless crystals of oxofluorotungstate salts, such as $Cu(WO_2F_4) \cdot 4H_2O$ and $(NH_4)_3(WO_3F_3)$. Double salts of WO_2Cl_2 are also known.

b. The Pentavalent Tungsten Compounds

The pentahalides of tungsten are formed by the thermal decomposition of the hexahalides in a distillation with hydrogen. The pentachloride, WCl_5 , forms brilliant black-green needles and when burned in oxygen will form $WOCl_4$. WCl_5 dissolves in water with a partial decomposition to form green solutions containing WO^{+3} and WO_2^+ . (These ions are also formed by reducing a solution of tungstic acid in hydrochloric acid with tin.) WO^{+3} can be changed to $(WOCl_5)^{\ominus}$ or $(WOCl_4)^{\ominus}$ in the presence of excess chloride ion. Treatment of a solution of WO^{+3} ions with ammonium hydroxide will give a precipitate of $W(OH)_5$. The pentabromide compounds behave similarly.

Alkali tungstates dissolved in a concentrated acid alkali oxalate solution and reduced with tin foil can produce red oxalato salts of pentatungsten having the general formula $M_3[WO_2(C_2O_4)_2]$. When dissolved in concentrated hydrochloric acid, these compounds will produce a solution of a deep blue color. Green, $M_2(WOCl_5)$, bright blue, $M(WOCl_4 \cdot H_2O)$, and brownish yellow, $M(WOCl_4)$, salts can be formed by saturating the solution with hydrogenchloride gas. The corresponding bromo- and complex thiocyanato-salts of pentavalent tungsten are also known.

c. The Tetravalent Tungsten Compounds

The most representative compound of tetravalent tungsten is tungstenite mineral, WS_2 . This compound is not soluble in water or in dilute acids. When WO_3 is reduced with hydrogen at low temperatures, the oxide, WO_2 , can be formed. In the distillation of tungsten hexachloride, WCl_6 , at a high

temperature with hydrogen, the tungsten tetrachloride, WCl_4 , is formed. WCl_4 is a grey-brown hygroscopic compound which is easily hydrolyzed in water. Tungsten tetraiodide, WI_4 , produced by heating WCl_6 in the presence of liquid HI in a sealed tube, also has similar properties. Many acid-anionic salts of tetravalent tungsten are known. Known as the octacyano-tungstate(IV) salts, they have the form $M_4[W(CN)_8]$, and can be prepared by a number of methods. The salts are crystalline and yellow in color and are stable in air. They are readily soluble in water, and the aqueous solutions are neutral.

d. The Trivalent Tungsten Compounds

Simple compounds of trivalent tungsten are unknown. The reduction of tungstates with tin and hydrochloric acid in the presence of an alkali chloride or ammonium chloride can result in such compounds as $K_3W_2Cl_9$.

e. The Divalent Tungsten Compounds

In the reduction of WCl_6 with hydrogen and by the thermal dissociation of the tetrachloride, WCl_2 can be formed. It reacts with water to bring about a slow evolution of hydrogen and the precipitation of WO_2 . The dibromide, WBr_2 , can be formed in a similar manner, and it will react in the same way as WCl_2 does. The tungsten diiodide, WI_2 , produced by passing iodine vapor over freshly reduced metallic tungsten, is insoluble in cold water. It can be decomposed by hot water to be hydrolyzed and oxidized in a series of simultaneous reactions.

Additional information about the compounds of tungsten has been presented by Li and Wang.⁽⁵⁾ This source is significant in its presentation of detailed information on the preparation of the many and varied compounds of tungsten.

B. The Analytical Chemistry of Tungsten

As it has already been pointed out in this monograph, the use of a known amount of inactive tungsten carrier in a radiochemical separation method almost always makes it practical to obtain the tungsten carrier in a weighable form in the final stage of the separation procedure used. If this is done, the tungsten radionuclide(s) can be concentrated into a small mass for the radioactivity measurements, and any loss of the tungsten

carrier during the analysis can be easily accounted for.

Tungsten can be qualitatively detected or quantitatively determined as tungsten trioxide, WO_3 , after it has been separated as tungstic acid by digesting with hydrochloric or nitric acid and precipitated with cinchonine.⁽⁶⁾ The alkaloid tungstate is then ignited to WO_3 . In addition to the cinchonine method, Duval,⁽⁷⁾ in his thermogravimetric studies, has investigated at least 20 other methods of obtaining a WO_3 precipitate. In addition, he has evaluated metal tungstate precipitates, such as $CaWO_4$, $BaWO_4$, $CdWO_4$, and $PbWO_4$. Of this latter group, the $PbWO_4$ precipitate appeared to be a satisfactory weighing form.

The cinchonine and the lead tungstate methods are probably the best methods that can be used to obtain the tungsten carrier and the tungsten radionuclide(s) in a form suitable for a radioactivity measurement after they have been isolated from a stable and/or radioactive nuclide mixture. If it is not desirable to radiochemically separate the tungsten radionuclide in a precipitable form before the radioactivity measurements, then it is 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 measurements.

1. Separation by Precipitation

The chief method for the separation of tungsten from a solution of a metal, an ore concentrate, and any other type of sample material depends on its precipitation as tungstic acid, H_2WO_4 , by digestion with strong mineral acids. Usually the H_2WO_4 can be dissolved in ammonium hydroxide for further purification from contaminants. (In a radiochemical analysis, contaminants could be either inert species or radioactive species originating from stable elements in the sample matrix.) The tungsten is finally precipitated as an alkaloid tungstate by cinchonine hydrochloride⁽⁶⁾ in a slightly acid solution, and the trioxide is obtained upon ignition of the precipitate at temperatures of from 750° to $850^\circ C$.

Sodium, potassium, ammonium salts, phosphorus, molybdenum, arsenic and fluorine can interfere in the precipitation of tungsten by an acid

digestion and can retard the cinchonine precipitation. If citrates, tartrates, or phosphates are present in the solution, H_2WO_4 will form soluble complex salts with these acids and cannot be precipitated. Silicon, tin, niobium and tantalum can be precipitated with the tungstic acid and phosphorus, molybdenum, iron, vanadium and chromium are carried down with the tungstic acid.

Silica can be separated from tungstic acid by volatilization with either hydrofluoric acid or sulfuric acid-hydrofluoric acid mixture. (8) If the volatilization is made at temperatures above $850^{\circ}C$, some WO_3 will be given off. Tungsten can be separated from a number of elements by a precipitation by α -benzoinoxime in dilute acid. (9) Molybdenum precipitates as well as tungsten and can be separated from it by volatilizing the molybdenum as $MoO_3 \cdot 2HCl$, (10) or by utilizing the insolubility of tungstic acid in 50% sulfuric acid. (11) Small amounts of arsenic can be removed from tungsten by adding sulfurous or hydrobromic acid to reduce the arsenic, and then adding hydrochloric acid in excess and boiling to a small volume. (12) Small amounts of iron and titanium can be separated from tungsten by a NaOH precipitation. (13) Niobium, tin and tantalum can be separated by digesting the fresh precipitate of tungstic acid with concentrated ammonium hydroxide and filtering. (13) If iron is present, some loss of tungsten will be experienced by its absorption on the ferric hydroxide precipitate.

Tungsten can also be precipitated from a mixture by mercurous nitrate (14) and such organic reagents as benzidine, (15) rhodamine B, (16) tannic acid, antipyrine, (17) anti-1, 5-di(p-methoxy-phenyl)-1 hydroxylamino-3 oximino-4-pentene, (18) 4-amino-4'-chlorodiphenyl, (19) and 8-mercaptoquinoline. (20) All of these yield the trioxide on ignition. The complex pentene reagent (18) has provided determinations of tungsten equivalent to the standard cinchonine method. The determination can be carried out in 0.2 N HCl solution and is selective for the separation of tungsten from at least 65 other elements.

With regard to specific separations, tungsten, as W^{+6} , has been separated from Mo^{+6} , Nb^{+5} , Ta^{+5} , U^{+6} , Cr^{+6} , V^{+5} , and Pd^{+2} in an acid solution by a precipitation with a 2% alcoholic α -benzoinoxime solution. (9,21)

Tungsten has been separated from Fe^{+3} , Al^{+3} , Be^{+2} , Zn^{+2} , Ni^{+2} , Co^{+2} , Mn^{+2} , Pb^{+2} , Cd^{+2} , Bi^{+3} , Cu^{+2} , and Hg^{+2} by precipitation as the W^{+6} oxinate with β -hydroxyquinoline solution from an acetate buffered solution in the presence of EDTA. ⁽²²⁾ Mo^{+6} , Tl^{+4} , V^{+5} , and U^{+6} also separate. W^{+6} has been separated from Mo^{+6} by precipitating it as a tungstate from a mineral acid solution with cinchonine. ⁽²³⁾ Silicon, arsenate and phosphate ions are the only interfering ions. Gelatin ⁽²⁴⁾ and various alkaloids ⁽²⁵⁾ can also be used in the same separation.

Lambie ⁽²⁶⁾ and Simpson, et al., ⁽²⁷⁾ report on the use of the insolubility of WO_3 in mineral acid solution as a means to determine tungsten in steels. Silicon and phosphorus interfere in this method.

A carbonate fusion will separate W^{+6} from Fe^{+3} and Tl^{+4} . W^{+6} (and Mo^{+6} , Cr^{+6} , V^{+5} , and P^{+5}) are soluble in the acid leach of the carbonate melt. Cu^{+2} can be used to collect small amounts of Mo^{+3} and precipitated with H_2S in order to separate molybdenum and tungsten. ⁽²⁴⁾ W^{+6} remains in solution. Rhenium can be separated from tungsten by carrying it on a precipitate of CdS from an H_2S -saturated oxalic acid or tartaric acid solution. ⁽²⁹⁾ Hydrogen sulfide precipitations from mineral acid produce very little precipitate of tungsten sulfide; however, appreciable amounts of tungsten may be carried down by molybdenum or other sulfides. ⁽³⁰⁾ Reed ⁽²⁹⁾ also briefly describes the precipitation techniques used by other investigators to separate other elements, such as molybdenum, vanadium, arsenic, antimony, thorium, aluminum, silicon, tin, chromium and carbon, from tungsten. Hillebrand, et al., ⁽³¹⁾ also briefly report on precipitation methods used by other investigators to separate tungsten from tin, columbium, tantalum, iron, titanium, arsenic, phosphorus and antimony. For example, tungsten can be separated from small amounts of tin, columbium, and tantalum by digesting the freshly precipitated tungstic acid with an excess of ammonium hydroxide; a sodium hydroxide precipitation from an acid solution will separate small amounts of iron and titanium from tungsten.

2. Separation by Volatilization

Perillon ⁽³²⁾ reports that tungsten can be volatilized when the tri-

oxide or its alkali salts are heated to red heat in a current of dry hydrochloric acid gas. Brophy and Van Brunt⁽³³⁾ recommend that tungsten, as tungstic oxide, is best separated from thoria by volatilization in a current of equal parts of dry hydrochloric acid gas and oxygen at 700°C. Jannasch⁽³⁴⁾ used an atmosphere of $\text{CCl}_4\text{-CO}_2$ for a similar separation.

3. Separation by Solvent Extraction

Solvent extraction methods used as separation methods for other analysis techniques⁽³⁵⁾ can often be adapted for use in radiochemistry. Some of these methods, particularly those concerned with organic soluble compounds, are applicable for use as separation processes in the radiochemistry of the tungsten radionuclides.

a. Ion Association Systems

Milner, et al.,⁽³⁶⁾ in studies concerned with tantalum and niobium have shown that W^{+6} (and Mo^{+6}) can be partially extracted from 10 M $\text{HF-6MH}_2\text{SO}_4\text{-2.2M NH}_4\text{F}$ solutions with methyl isobutyl ketone. Ti, U, Zr, Fe, Al, Mn, Sn and Ga do not extract at all; whereas, Ta and Nb are completely extracted. Ethyl ether will extract less than 0.5% W^{+6} from a 20 M HF solution, while Nb^{+5} , Ta^{+5} and Re^{+7} are extracted in concentrations greater than 50%.⁽³⁷⁾

W^{+6} (as well as Mo^{+6} , Fe^{+2} , and Al^{+3}) will only partially extract (1% or less) into ethyl ether from a 1.5 M KI-1.5 N H_2SO_4 solution.⁽³⁸⁾ Cd, In, and Sn are completely extracted under these conditions, while Bi, Cu, Zn, Hg, and Sb show varied degrees of extraction.

Heteropoly acids of W (and Mo, As, P, V, and Si) are characteristically soluble in organic solvents, and it is possible to use these ion association systems in separating these elements from other elements or each other. Tungstophosphoric acid can be extracted completely from 6 N H_2SO_4 with 1-pentanol.^(39,40) Under these conditions, Mo is also quantitatively extracted; As, Fe, Cr and Cu are only slightly extracted. Various esters, ketones, aldehydes and ethers are also good solvents.⁽⁴¹⁾

Tungsten has been separated from molybdenum by extracting it from a KSCN-NaF-SnCl_2 solution with butyl acetate⁽⁴²⁾ and from a $\text{HCl-H}_3\text{PO}_4$ system with ethyl ether.⁽⁴³⁾ Tungsten has also been separated from rhenium by

extracting it from a KSCN-HgNO_3 solution with ethyl ether. (44)

b. Chelate Complex Systems

W^{+6} can be separated from many elements by extracting an aqueous oxine solution of the ions with chloroform. (45) The presence of EDTA inhibits most of these ions when an extraction is made from a solution at a pH of from 2.4 to 4.3. Tungsten (and Mo) can be separated from all other common metal ions in an acid solution by using chloroform to extract their α -benzoinoxime complexes. (46) W^{+6} (as well as Sn, Ti, Zr, V^{+5} , and Mo^{+6}) forms an insoluble complex with N-benzoylphenylhydroxylamine that can be extracted with chloroform from an acid solution at pH 4. (47,48)

Tungsten cupferrate is only partially extracted from a (1 + 9) HCl solution with ethyl acetate. (49) V^{+5} , Ti^{+2} , Sn^{+4} , Th and Mo^{+6} quantitatively extract under these conditions. Tungsten does not form a complex with 3-hydroxyl-1,-3-diphenyltriazine in acid solutions below pH 3; however, Mo^{+6} , V^{+3} , V^{+5} , and Ti^{+4} do and can be extracted and separated from tungsten with organic solvents. (50) Tungsten salts of sodium diethyl-dithiocarbamate can be extracted from an acid solution (pH 1-1.5) with ethyl acetate. (51)

W (as well as Mo and V) form heteropolyacids with phosphates in acidic solutions, and these complexes can be readily extracted into a number of organic solvents. (52) For instance, complexes of W, Mo, V, As, Sb, Zr, and Mo can be extracted from a concentrated H_2SO_4 solution with ethyl ether.

Thiocyanate in the presence of SnCl_2 and in an HCl solution will form a yellow-colored complex of W^{+6} that can be extracted into either ethyl ether, ethyl acetate, isopropyl ether, or an isoamylalcohol-chloroform mixture. (53) Fe, Ti, etc., must be removed by a NaOH precipitation and Mo by H_2S before the extraction is made.

Bagshawe and Truman (54) have used a 10% hydroxylamine sulfate and a 1% toluene-3, 4-dithiol to form a complex of W (and Mo) that can be extracted from a HCl solution with amyl acetate. The Mo is removed by shaking and separating the layers; Mo will extract into the amyl acetate. After the removal of Mo and a reduction of the aqueous solution with SnCl_2 ,

additional toluene-dithiolis added and the W extracted. In other studies, Humence⁽⁵⁵⁾ and Miller⁽⁵⁶⁾ found that the tungsten dithiol complex could also be extracted with amyl acetate from a hot concentrated hydrochloric acid solution containing stannous chloride. These same studies also showed that the complex could be extracted from a hydrochloric acid solution into either isoamyl acetate or n-butyl acetate. Similar systems were used by Greenberg⁽⁵⁷⁾ to separate tungsten from Ta, Ti, and Zr and by Machlan and Hague⁽⁵⁸⁾ and Stonhill⁽⁵⁹⁾ to separate W from Mo.

The $(C_6H_5)_4As^+$ salts of tungsten cannot be extracted into chloroform from an acid solution. This system has been used to separate W (and Mo) from rhenium.⁽⁶⁰⁾ The morin complex of W has been used to separate W from Mo by extracting it into chloroform from an HCl-NaF solution.⁽⁶¹⁾

4. Separation by Chromatography

a. By Organic Adsorbents (other than ion exchange resins)

Tungsten, as $WO_4^{=}$, has been separated from other metal ions by use of chromatographic columns containing 8-hydroxyquinoline as the support.⁽⁶²⁾ Robinson^(63,64) has also shown that $WO_4^{=}$ could be separated from the constituents of copper alloys and alloy steels by use of an 8-hydroxyquinoline column. $WO_4^{=}$ exhibits a yellow color under the conditions used. Ag^{+1} , Bi^{+3} , Ni^{+2} , MoO_4^{-2} , Zn^{+2} and UO_2^{+2} can interfere since they also form adjacent yellow or orange bands.

b. By Ion Exchange Resins

Kraus, et al.,⁽⁶⁵⁾ and Kraus and Nelson⁽⁶⁶⁾ report on the use of an anion exchange resin (Dowex-1, X-10) in studies concerned with distribution coefficients for W^{+6} in HCl and HCl-HF systems. In one of these,⁽⁶⁵⁾ it was possible to quantitatively separate U^{+6} , W^{+6} and Mo^{+6} by use of 0.5 M HCl-1 M HF and 7 M HCl-1 M HF mixtures as the eluting agents. Hicks, et al.,⁽⁶⁷⁾ studied the behavior of anionic species of a number of metal ions on the anion exchange resin, Dowex-2. Each metal segregated into groups according to their elution behavior with various concentrations (12 M to 0.1 M) of hydrochloric acid, 3 M $HClO_4$, 1 M NH_4OH and 1 M NaOH. This study showed that molybdenum and many other elements could be sep-

arated from tungsten (and Ru, Rh, Re, Os, Ir, Pt⁺⁴, Au⁺³ and Te⁺³) by elutions with HCl, HClO₄ and NH₄OH. Tungsten was then separated from Ru, Rh, Re, Os, Ir, Pt⁺⁴, Au⁺³ and Tl⁺³ by elution with 1 M NaOH as the reagent. The rest of these elements were retained upon the ion exchange resin.

Samsahl (68) has shown that tungsten (and molybdenum) can be separated from cobalt, zinc, iron nickel, manganese and chromium by the use of short anion exchange resin (Dowex-2, 200-400 mesh) columns coupled in series and saturated with chloride, citrate and hydroxide ions. These studies were made in order to separate radioactive elements present as impurities in a water cooled reactor. Tungsten (and Mo) are quantitatively retained on the resin in chloride form; the other elements pass through to the citrate resin, where iron, cobalt, zinc and nickel are adsorbed as complex ions. Manganese and chromium pass through and are finally precipitated on the hydroxide form.

Tungsten has been separated from titanium by the use of SBS cation exchange resin in the hydrogen form. (69) Tungsten, as pertungstate ions, was removed from the resin column by eluting the column with an acid solution (at pH 5) and a 10% H₂O₂ solution. Titanium was changed to a stable complex per-acid cation and was retained by the column.

c. By Paper Chromatography

Tungsten, as WO₄^m, can be separated from other ions by paper chromatography uses of butanol-HBr mixtures (70) and ketone-HCl mixtures (71) as solvents. DeCarvalho (72) has shown that W⁺⁶ can also be separated from other elements by using butanol-HCl mixtures as solvents. N-butanol-H₂O₂-HNO₃ mixtures have been used (73) to separate the per-acids of tungsten, molybdenum and vanadium. Pluchet and Lederer (74) also report on the use of acetate buffered solutions and various solvents to separate tungsten from vanadium.

IV. DECOMPOSITION OF MATERIALS CONTAINING TUNGSTEN

Most tungsten-bearing materials can be decomposed either by HCl-HNO₃ mixtures (75) or by mineral acid mixtures containing small amounts of hydro-

fluoric acid.⁽⁷⁶⁾ If strong HF solutions are used, tungsten can be lost as WF_6 since it boils at $19^\circ C$.⁽⁷⁷⁾ Although rocks and stony meteoritic materials can be sintered in sodium peroxide at elevated temperatures,⁽⁷⁸⁾ fusions with alkali salts can prevent complete precipitation of tungsten by digestion with acids or retard its precipitation by cinchonine.⁽⁷⁵⁾ If a treatment of a tungsten-bearing material in its oxide or alkali salt form is made at red heat and in a current of hydrochloric acid gas, tungsten will volatilize.⁽³²⁾

Such dissolution methods as these can be adapted for use in the radiochemistry of the tungsten radionuclides. The addition of tungsten carrier to the mixture before dissolution begins will assist in achieving an exchange of the radioactive and inactive tungsten atoms.

V. SAFETY PRACTICES

Adequate safety precautions should be followed in dissolving any inactive or radioactive sample material. The manual by Pieters and Creighton⁽⁷⁹⁾ gives an excellent report on the toxicology of most inactive elemental compounds. Such a manual as this should be consulted before any analysis is undertaken.

Safe practices in handling radioactive sample materials are always important in radiochemistry. The discharge of radioactivity by explosion or evolution into a laboratory area can be hazardous and can result in wide-spread contamination. Thus, some information on safe-handling practices in processing radioactive materials should be consulted before a radiochemical analysis is undertaken. Safe-handling practices, such as those which appear in the Oak Ridge National Laboratory's Master Analytical Manual⁽⁸⁰⁾ and the International Atomic Energy Agency's publication,⁽⁸¹⁾ should be followed in processing any radioactive material. Many other similar sources of information exist and should be consulted.

VI. COUNTING TECHNIQUES FOR THE RADIOACTIVE TUNGSTEN ISOTOPES

The analysis of sample materials containing tungsten radionuclides may be completed either by a direct (nondestructive) measurement of the radioactivity of the particular radionuclide or by obtaining the radio-

nuclide in some form by radiochemically processing the radioactive sample. The use of either technique is dependent upon the specific characteristics of the tungsten radioisotope being measured, i.e., its half-life, 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 tungsten radionuclide. If this presents a considerable interference, the sample must be processed radiochemically.

Table I of this monograph shows the nuclear characteristics of each of the known radioactive isotopes of tungsten. The most frequently determined of the tungsten radioisotopes are W^{185} (73.8 d) and W^{187} (24 h). The radioactivity of these, as well as any other tungsten radionuclide, can be measured by either standard Geiger-Mueller, gamma scintillation and proportional counting techniques.⁽⁸²⁻⁸⁵⁾ For example, Morrison⁽⁸⁶⁾ and Morrison and Cosgrove⁽⁸⁷⁾ have determined W^{187} (24 h) by a non-destructive gamma spectrometric method in a radioactivation analysis of silicon for microgram amounts of stable tungsten. Similar techniques were used by Leliaret, et al.,^(88,89) in the determination of trace tungsten in steel.

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR THE TUNGSTEN RADIONUCLIDES

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

Gile, et al.,⁽⁹⁰⁾ report on the use of an iron hydroxide precipitation and an HCl-ethyl ether extraction for the Fe^{+3} as a means of obtaining carrier-free radioactive tungsten tracer from an irradiated tantalum target. Although no other specific carrier-free methods for the tungsten radionuclides appear in the current literature, it should be possible to use any solvent extraction or chromatography methods reported elsewhere in this monograph to serve as carrier-free methods.

The carrier radiochemical procedures that now exist for the tungsten

radionuclides have originated from investigations concerned with either the preparation of radioactive tracers,⁽⁷⁷⁾ the separation of radioactive tungsten isotopes from fission product mixtures⁽⁹¹⁾ or in radioactivation analysis.^(92,93) With regard to radioactivation analysis, trace amounts of tungsten in titanium,⁽⁹⁴⁾ silicon,⁽⁹⁵⁾ high alloy steels,^(68,88,89) metals and alloys,⁽⁹⁶⁾ aluminum,⁽⁹⁷⁻⁹⁹⁾ ores,⁽⁹⁶⁾ rocks,⁽¹⁰⁰⁾ meteorites,⁽¹⁰⁰⁾ and biological materials⁽¹⁰¹⁾ have been determined by carrier radiochemical methods.

In each of the radiochemical methods 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 usefulness in the decontamination of other radioactive species from the radioactive tungsten isotopes.

PROCEDURE 1

Procedure Used In: Preparation of radioactive tungsten tracer (carrier-free)

Method: Precipitation and solvent extraction

Element Separated: Radioactive tungsten isotopes

Type of Material Analyzed: Irradiated tantalum target

Type of Nuclear Bombardment: Cyclotron

Procedure By: Gile, et al⁽⁸⁶⁾

Chemical Yield: Carrier-free (98%)

Time of Separation: Short

Degree of Purification: Excellent

Equipment required: Standard

Procedure:

1. Boil solution with conc. H_2SO_4 to destroy HF.
2. Add 20% NaOH to precipitate Ta_2O_5 scavenger. Filter.
3. Acidify filtrate with HCl; add Fe^{+3} carrier and NaOH (to pH4) to precipitate $Fe(OH)_3$, carrying radioactive tungsten.

PROCEDURE 1 (Continued)

4. Dissolve $\text{Fe}(\text{OH})_3$ in 6 M HCl, add equal volume of ethyl ether to extract Fe^{+3} .

5. Separate phases; discard organic. Aliquot aqueous for radioactivity measurements by some type of counter.

PROCEDURE 2

Procedure Used In: Preparation of radioactive tungsten tracers

Method: Solvent extractions and precipitation

Element Separated: Radioactive tungsten

Type Material Bombarded: Tantalum

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 and Williamson (Reported by Meinke⁽⁷⁷⁾)

Separation Time: 30 minutes

Chemical Yield of Carrier: ~ 100%

Decontamination: Separate 10^5 counts per minute from Ta and spallation products

Equipment Needed: As indicated in Procedure.

Procedure:

1. Dissolve Ta in HF and minimum of HNO_3 . Add 20-30 mg W carrier (No less).
2. Destroy all HNO_3 with hydroxylamine or hydrazine. Make about 2 N in HCl, add 0.1 gm solid SnCl_2 , 0.5 gm NH_4SCN , and H_3BO_3 to complex all HF as HBF_4 in that order.
3. Heat until a bright apple green complex appears, transfer to a sep. funnel, and extract twice with at least equal volume ethyl acetate.
4. Wash organic layer twice with equal volume 2 N HCl, and evaporate organic layer to dryness.
5. Take up the blue residue with 6 N HCl and 1 drop 30% H_2O_2 (or conc HNO_3) and 1 drop aerosol. Bright yellow WO_3 precipitates after digestion on a hot water bath.

PROCEDURE 2 (Continued)

6. Centrifuge and wash WO_3 with 6 N acid. Then dissolve in 1 cc 6 N NH_4OH , centrifuge and discard any ppt. Ferric hydroxide scavenges (with 1/2-1 mg Fe^{+++}) any now be used for further purity but usually are not necessary.

7. Add 5 cc conc. HNO_3 and 1 drop of aerosol, digest on a hot water bath, centrifuge and wash WO_3 formed with 6 N acid.

Remarks: WF_6 boils at $19^\circ C$ so don't boil target sol'n any more than necessary.

PROCEDURE 3

Procedure Used In: Separation of tungsten radioactivity from fission product mixtures.

Method: Solvent extraction and precipitation

Element Separated: W^{185} (73.8 d) and W^{187} (24 h)

Type of Material Analyzed: Fission Product Solution

Type of Nuclear Bombardment: $W^{184}(n,\gamma)W^{185}$ and $W^{186}(n,\gamma)W^{187}$

Procedure By: Prestwood (reported by Kleinberg⁽⁸⁷⁾)

Chemical Yield of Carrier: Quantitative

Time of Separation: Several hours

Degree of Purification: Good from fission products

Equipment Required: Standard

Procedure:

1. To a 40-ml conical centrifuge tube add 2.0 ml. of standard W carrier and an aliquot of the sample. Then add 10 ml. of conc. HNO_3 and digest on a steam bath for 10 minutes. Remove, centrifuge, and discard the supernate.

2. To the $WO_3 \cdot xH_2O$ residue add 6 drops of conc. NH_4OH and dilute to 15 ml. with H_2O . Add, with swirling, 2 drops of Fe carrier solution (Note 1) and 2 drops of aerosol solution. Centrifuge and decant the supernate into a clean centrifuge tube.

3. To the solution add 10 drops of saturated tartaric acid solution, and 10 drops of conc. H_2SO_4 , 5 drops each of Bi and Mo carriers. Place on steam bath and pump in H_2S rather vigorously for at least 2 minutes. (Note 2) (Some

PROCEDURE 3 (Continued)

time is required for MoS_3 to coagulate. Coagulation is aided by the precipitation of Bi_2S_3 .) Filter the hot mixture containing the sulfide precipitates through No. 40 Whatman (9 cm.) filter paper in a 2", 60° funnel (Note 3) and collect the filtrate in a clean centrifuge tube. Wash the centrifuge tube and the precipitate with 2-3 ml. of water and pour the washings through the filter funnel. To the filtrate add 10 ml of conc. HNO_3 and digest on a steam for 10 minutes. Remove, centrifuge, and discard the supernate.

4. Repeat Steps 2 and 3.

5. Dissolve the $\text{WO}_3 \cdot \text{xH}_2\text{O}$ precipitate in 6 drops of conc. NH_4OH and add 15 drops of saturated tartaric acid solution. With 10 ml. of H_2O transfer the solution to a 60 ml. separatory funnel. Add 10 drops of conc. HCl , 1 ml. of Nb carrier, and 10 ml. of chloroform. Shake briefly and add 5 ml. of 6% cupferron reagent. Shake for 30 sec. and allow to stand for 1-2 minutes. Drain off chloroform layer and discard. Extract again with 5 ml. of chloroform. Drain water layer into clean 40-ml. of centrifuge tube.

6. Repeat Step 3 for the addition of the tartaric acid solution. (Cau-
tion: when the mixture is heated on a steam bath, there is a vigorous, evolution of oxides of nitrogen from reaction between tartaric acid present in solution and the nitric acid added.)

7. To the $\text{WO}_3 \cdot \text{xH}_2\text{O}$ precipitate obtained in Step 6 add 6 drops of conc. NH_4OH . Transfer the resulting solution to a 125-ml. Erlenmeyer flask with the aid of H_2O from a wash bottle. The volume of solution should be about 15 ml. Add 6 drops of glacial $\text{HC}_2\text{H}_3\text{O}_2$ and 10 ml. of the buffer solution. Heat to boiling and add 1 ml. of 5% 8-hydroxyquinoline reagent dropwise. Boil for about 30 seconds, let stand for a few minutes, and filter through a tared No. 42 Whatman filter, 7/8" diameter, using a ground-off Hirsch funnel and a filter chimney. (No. 50 Whatman paper is also suitable, but the filtration process is slower.) Dry at 120° for 10 minutes. Allow to stand for 20 minutes and weigh. Mount on two-sided Scotch tape on an Al plate and cover with Nylon film. β -count immediately (Note 4).

PROCEDURE 3 (Continued)

Notes:

1. The percentage loss of W in this step is almost exactly equal to the number of drops of Fe carrier added.
2. It is necessary at this stage to keep the solution hot in order to keep the formation of sulfur to a minimum in the step where HNO_3 is added to destroy tartrate.
3. Filtration is superior to centrifugation at this stage. "Floaters" are invariably present after centrifugation.
4. 24 h W^{187} and 73 d W^{185} are the isotopes counted.

PROCEDURE 4

Procedure Used In: Radioactivation analysis

Method: Precipitation

Element Separated: W^{187} (24 h)

Type of Material Analyzed: Titanium,⁽⁹⁴⁾ Zirconium and other metals and alloys;⁽⁹⁶⁾ ores⁽⁹⁶⁾

Type of Nuclear Bombardment: $\text{W}^{186}(\text{n},\gamma)\text{W}^{187}$

Procedure By: Mullins, Brooksbank, and Leddicotte (Reported by Mullins and Leddicotte⁽¹⁰²⁾)

Chemical Yield of Carrier: 65-75%

Separation Time: 4 hours

Degree of Purification: Complete decontamination of zirconium, niobium, and tantalum is made.

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 1) and comparator (Note 2) samples in a neutron flux of 5×10^{11} n/sec/cm² for 16 hours or longer (Note 3). Comparator sample is irradiated in a small quartz vial. The test sample may be irradiated in aluminum foil, plastic vials, quartz vials or any way that may be convenient for the analyst and compatible with the irradiation facility.

PROCEDURE 4 (Continued)

B. Preparation of Irradiated Test Portion and Analysis

The Comparator Sample

1. After the irradiation, quantitatively transfer the comparator sample (Note 2) to a 100-ml volumetric flask, and dissolve it in 25 ml of 19 M NaOH, and dilute to volume with water. Mix well, using safe handling practices for radioactive materials.
2. Pipet a 1.0 ml aliquot of this solution into a 100-ml volumetric flask; dilute to volume with water and mix well.
3. Pipet a 1.0 ml aliquot of this solution into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same tube 1 ml of standard tungsten carrier of known concentration (Note 4). Mix well and continue with step 8 in The Test Sample.

The Test Sample

1. After irradiation the sample is placed in a 50-ml lusteriod tube for dissolution. Add 1 ml of H₂O and 1 ml of 16 M HNO₃ (Note 5) and 27 M HF dropwise until dissolution is complete. Add a total of 1.5 ml of 27 M HF and digest at room temperature for 10 minutes (Note 6).
2. Pipet 1.0 ml of standardized tungsten carrier and mix well. Add 10 ml of 16 M HNO₃. Slowly, add saturated Al(NO₃)₃ with stirring until tungstic acid begins to precipitate. Transfer the sample to a 50-ml glass centrifuge tube and heat to boiling for 15 seconds. Centrifuge and discard the supernate. Wash the precipitate twice with 30 ml of hot 0.5 M HCl.
3. Dissolve the tungstic acid with 1 ml of 6 M NH₄OH by gently heating over a flame (Note 7). Add 20 ml of basic wash solution (Note 8) and add 5 mgs each of Nb and Fe holdback carrier. Heat to boiling for 15 seconds and centrifuge. Transfer the supernate to a 50-ml glass centrifuge tube and repeat addition of Nb and Fe holdback carriers and centrifuge.
4. Filter the supernate through No. 00 Munktell filter paper into a 50-ml glass centrifuge tube (Note 9). If no other contaminants from the original sample are known to be present except Ta and Nb, then continue with step 5. If the acid and basic sulfide groups are present, then continue with step 6.

PROCEDURE 4 (Continued)

5. Add 10 ml of 12.5% cinchonine solution in 6 M HCl and heat at 60° to 70° C to precipitate tungstic acid. Centrifuge and discard supernate. Add 25 ml of 6 M HCl and boil for 1 minute (white tungsten cinchonine precipitate is converted to yellow H_2WO_4). Centrifuge and wash H_2WO_4 in 30 ml of hot 0.5 M HCl. Centrifuge and filter with 15 ml of hot 0.5 M HCl on to No. 00 Munktell filter paper. Ignite to WO_3 in a muffle furnace at 700° C for 30 minutes. Weigh the amount of WO_3 recovered and prepare sample for radioactivity measurement (Note 10).

6. Add 1 ml of 15 M NH_4OH and 1 ml of 50% tartaric acid. Mix well and check with pH paper to make sure the solution is basic (Note 11). Add 10 mgs of cobalt holdback carrier and saturate with H_2S . Heat to aid coagulation. Centrifuge and decant the supernate into 50 ml glass centrifuge tube.

7. Cautiously (in a well ventilated hood, neutralize with 6 M HCl and then make the solution 0.2 M in HCl (Note 12). Boil for 30 seconds to drive off excess H_2S and add 10 mgs of Cu holdback carrier and saturate with H_2S . Centrifuge and decant supernate into a 50-ml glass centrifuge tube. Boil for 30 seconds to drive off excess H_2S .

8. Precipitate H_2WO_4 with the addition of 10 ml of 18 M H_2SO_4 by boiling over a flame. Digest for 5 minutes. Centrifuge and wash H_2WO_4 with 35 ml of hot 0.5 M HCl. Filter, ignite and weigh as in step 5.

C. Measurement of Radioactivity and Calculation of Inactive Tungsten Content of the Original Sample

1. The measurement of tungsten-187 may be completed by gamma counting on a gamma scintillation spectrometer. Either the 0.48 or the 0.68 Mev gamma radiations may be measured. If one so desires, a gross gamma measurement may be made on a gamma scintillation counter.

2. Following the radioactivity measurements, the observed W^{187} radioactivity is corrected for loss of "carrier" during the experiment, decay, and sample weights of both the test and comparator sample. A comparison of these corrected radioactivities becomes a measure of the stable tungsten content of the test sample:

PROCEDURE 4 (Continued)

$$\text{Percent stable tungsten in test sample} = \frac{\text{Corrected radioactivity of tungsten in test sample}}{\text{Corrected radioactivity of tungsten in comparator sample}} \times 100$$

Notes:

1. At least 0.10 gram portion of solid samples should be used.
2. Use tungstic acid, H_2WO_4 , for tungsten comparator; approximately 25 mgs.
3. The ORNL Graphite Reactor was used for this irradiation. The sensitivity of the method is such that 1×10^{-9} grams of tungsten can be determined. The sensitivity can be improved by use of higher neutron fluxes.
4. As tungstic acid, H_2WO_4 , standardized to 10 mg per milliliter.
5. HNO_3 is used in the dissolution because tungsten is not soluble in HF alone.
6. The sample is digested for 10 minutes because tungsten is slow to dissolve at this concentration of HF and HNO_3 . The extra HF is added to keep the tungsten carrier in solution, since the HNO_3 would precipitate it as H_2WO_4 .
7. Cloudiness may be due to an excess of Al or Zr that was not washed out.
8. Basic wash solution is prepared by mixing 3 ml of 6 M NH_4OH with 1 ml of 6 M HNO_3 and 5 ml of H_2O .
9. Filtering in a medium of NH_4NO_3 solution gives a decontamination factor of Ta ranging from 250 to 500. If high concentrations of Ta are known to be present, this step should be repeated.
10. By comparing the final weight of the WO_3 precipitate obtained here, with the theoretical yield expected from the amount of tungsten 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 W^{187} recovered during the separation process.
11. The tartaric acid prevents the precipitation of cobalt holdback carrier before saturation with H_2S as well as to prevent tungsten from precipitating during the acid sulfide step.
12. Ignore any precipitate that may form here.

PROCEDURE 5

Procedure Used In: Radioactivation analysis

Method of Separation: Precipitation

Element Separated: W^{187} (24.1 h)

Type of Material Analyzed: Silicon⁽⁹⁵⁾

Type of Nuclear Bombardment: $W^{186}(n,\gamma)W^{187}$

Procedure By: James and Richards⁽⁹⁵⁾

Chemical Yield of Carrier: Quantitative

Time of Separation: Several hours

Degree of Purification: Good from radionuclides of Cu, Sb, Ta, Au, Bi, Co, Zn, Fe, Mn, Mo, K and Na

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

NOTE: Authors⁽⁹⁵⁾ indicate that samples were irradiated in the BEPO reactor at Harwell after which they were etched in a HF-HNO₃ mixture to remove surface contamination and then dissolved by fusing in caustic soda. The added tungsten carrier was removed from the solution of the irradiated samples by precipitation. The final separated tungsten precipitate was ignited to WO₃, cooled, weighed and then the W^{187} radioactivity measured by gamma spectrometry. It was possible to determine at least 8×10^{-11} gram of tungsten by this method.

PROCEDURE 6

Procedure Used In: Radioactivation Analysis

Method of Separation: Precipitation

Element Separated: W^{187} (24.1 h)

Type of Material Analyzed: High alloy steels^(88,89)

Type of Nuclear Bombardment: $W^{186}(n,\gamma)W^{187}$

Procedure By: Leliaert, et al^(88,89)

Chemical Yield of Carrier: 99.8%

Time of Separation: A few hours

PROCEDURE 6 (Continued)

Degree of Purification: Excellent separation from the radionuclides of Cu, Co, Mo, Mn, Cr, As, Fe, and Ta

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

1. Dissolve the irradiated samples (Notes 1 and 2) in 6 N HCl. After the reaction subsides, add concentrated HNO_3 dropwise and precipitate the added tungsten carrier as yellow tungstic acid by heating on a hot plate until the HCl and HNO_3 are completely removed.

2. Cool the solution and dilute with 50 ml of water; then add 2-5 ml of 30% H_2O_2 (Note 3) and 5 ml of 1% Na_2VO_4 solution (Note 4).

3. Heat the solution on a hot plate until the peroxy acid is completely decomposed to tungstic acid (Note 5). Continue heating for an additional 15 minutes. Cool the mixture.

4. Filter the solution through a fine grained filter-paper; then wash with 3% HNO_3 .

5. Mount the filter-paper and the precipitate and measure its radioactivity (Note 6).

6. Calculate the amount of stable tungsten in the test samples (Note 7).

Notes:

1. Samples were irradiated in a neutron flux of 10^7 n/cm² produced by a cyclotron deuteron (11.5 Mev) bombardment on a beryllium target and in the BRI reactor at a flux of 10^{11} n/cm²/sec. The sample size was adjusted so as to obtain a constant self-shielding effect.

2. Samples sometimes processed by a non-destructive methods; see authors' reports. (88,89)

3. To solubilize the tungstic acid as peroxytungstate.

4. The vanadate ions reduce molybdate adsorption on the tungstic acid precipitate.

5. Disappearance of the wire red color of the peroxyvanadic acid serves as an indicator.

6. Gamma counting by means of a Tracerlab Superscaler.

PROCEDURE 6 (Continued)

7. Comparator or standard samples were irradiated and processed in the same manner. A comparison of the radioactivity of the test sample with the radioactivity of the comparator sample gave the quantity of stable tungsten in the test sample.

PROCEDURE 7

Procedure Used In: Radioactivation Analysis

Method of Separation: Precipitation

Element Separated: W^{187} (24.1 h)

Type of Material Analyzed: Aluminum⁽⁹⁷⁻⁹⁹⁾

Type of Nuclear Bombardment: $W^{186}(n,\gamma)W^{187}$

Procedure By: Albert, et al⁽⁹⁷⁻⁹⁹⁾

Chemical Yield of Carrier: Good

Time of Separation: Several hours

Degree of Purification: Excellent from all elements except molybdenum

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

1. Dissolve irradiated aluminum (Note 1) in HCl in the presence of tungsten carrier and carriers of other elements (Note 2).
2. Adjust the solution to a molarity of from 4-6 N in HCl and saturate with H_2S . Filter the mixture (Note 3).
3. Dissolve the H_2S precipitate in mineral acid, add HBr and distil. Collect the distillate (Note 4).
4. Adjust the molarity of the distillate fraction to a pH of 5 and treat with oxine solution. Filter the mixture. The insoluble fraction can be processed (Note 5).
5. Add salicylaldehyde solution to the filtrate; digest the mixture, then filter (Note 6).
6. Add α -benzoinoxime solution to the filtrate. Digest the mixture, then filter (Note 7).

PROCEDURE 7 (Continued)

7. Mount the W (and Mo) precipitate for counting (Note 8).

Notes:

1. Irradiated in the Saclay reactor at neutron flux of 10^{12} n/cm²/sec.
2. Standardized carriers of Cu, Pd, Mo, Bi, Se, Hg, As, Sb, Ag, Te, Fe, Ga, Rare Earths, Sc, Zr, Hf, Cr, Mn, Ni, Co, Zn, Sr, Ca, Na, Rb, Cs, and K.
3. The filtrate can be processed for such elements as Fe, Ga, Rare Earths, Sc, Zr, Hf, Cr, Mn, Ni, Co, Zn, Sr, Ca, Na, Rb, Cs, and K.
4. Se, Hg, As, and Sb separated here.
5. Contains Ag and Te.
6. Precipitate contains Cu and Pd.
7. The precipitate contains W and Mo; the filtrate may be processed for Bi.
8. Standard counting methods employed here.

PROCEDURE 8

Procedure Used In: Radioactivation analysis

Method: Ion exchange with carriers

Element Separated: W^{187} (24 h)

Type of Material Analyzed: Stainless steel, its corrosion products, and other elements, present as impurities in a water-cooled nuclear reactor.⁽⁶⁸⁾

Type of Nuclear Bombardment: $W^{186}(n,\gamma)W^{187}$

Procedure By: Samsahl⁽⁶⁸⁾

Chemical Yield of Carrier: Quantitative

Degree of Purification: Excellent

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

The information given by Samsahl⁽⁶⁸⁾ in the section of his report entitled "Experimental" is considered to be rather concise and informative for use as the detailed Procedure for this radiochemical separation method. It reads as follows:

Experimental

The experiments were performed with irradiated (Note 1) metallic chromium, molybdenum and tungsten and salts of the cations, Na^{+1} , Mn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , Cu^{+1} , Zn^{+2} , and Sr^{+2} . The samples were individually brought into solution with hot 1:1 HCl containing a few drops of H_2O_2 and taken to dryness on a water bath. Subsequently, the residues were dissolved in water and diluted to a suitable strength of gamma activity. Carriers were added in amounts of about 5 mg of appropriate cation per 100 ml of solution. No carriers were added to the solutions of tungsten and molybdenum. Then 20 ml portions of a single gamma emitter solution were added to four ion exchange columns consisting of Dowex-2 (200-400 mesh) resin in the citrate, chloride and hydroxide forms, and Dowex-50 (200-400 mesh) in the hydrogen form. Each column consisted of 10 ml of water-sedimented resin contained in a 2.5 cm diameter glass filter crucible (Note 2). The active solutions were sucked through at a rate of about 4 milliliters per minute and the columns washed with two 5-ml portions of water and drained by suction. Finally, the crucibles were placed directly at a definite geometry on the top of a gamma scintillation detector and the radioactivity assayed with a single channel pulse analyzer.

The activity of the Dowex-50 resin was measured and used as a standard for the estimation of the percent absorption on the other resins. The eluate was controlled for possible gamma activity.

Notes:

1. Irradiated in the Swedish R-1 reactor. Samples of irradiated steel and D_2O were also processed by this method.
2. Samsahl's report⁽⁸⁶⁾ should be consulted for a description of the ion exchange column and other information.

PROCEDURE 9

Procedure Used In: Radioactivation analysis

Method of Separation: Precipitation

Element Separated: W^{187} (24.1 h)

Type of Material Analyzed: Rocks and Meteorites⁽¹⁰⁰⁾

Type of Nuclear Bombardment: $W^{186}(n,\gamma)W^{187}$

Procedure By: Atkins and Smales⁽¹⁰⁰⁾

Chemical Yield of Carrier: 40-60%

Time of Separation: Several hours

Degree of Purification: Good from Ta^{182} and other radioelements

Equipment Required: Neutron source and standard laboratory

Procedure:

1. Irradiate test samples and comparator samples for 36 hours in a neutron flux (NOTE 1). Sealed dry silica ampoules should be used to contain the samples (NOTE 2).

2. Dissolve the irradiated samples (NOTE 3) in the following manner:

a) Rocks and stony meteorites: Sinter with sodium peroxide for 10 min at $480^{\circ}C$ in a 5-ml nickel crucible. Transfer the cake to a 250-ml beaker; then proceed with Step 3 below.

b) Iron meteorites and iron and steel samples: Dissolve in a minimum amount of a mineral acid mixture containing hydrofluoric acid. Proceed with Step 3 below.

3. Add 10 ml of 20% tartaric acid and 70 ml of distilled water containing 5 g of ammonium chloride. Acidify the solution with 10% v/v H_2SO_4 .

4. Boil the solution and add NH_4OH dropwise until it is just alkaline; then add 50% HCl until the solution is acid and then two drops in excess. Next add 50 ml of hot 2% tannin solution slowly and with constant stirring. Boil gently to coagulate the precipitate; then add 10 ml of 5% cinchonine in 25% hydrochloric acid to the hot solution slowly and with constant stirring. Digest the mixture for 30 minutes.

5. Filter through an 11-cm Whatman No. 541 filter paper. Wash the precipitate with hot 2% ammonium chloride solution. Discard the washings.

6. Transfer the tannin-cinchonine precipitate of tantalum and tung-

PROCEDURE 9 (Continued)

sten to a 250-ml beaker and add 20 ml of concentrated HNO_3 and 5 ml of concentrated H_2SO_4 . Heat on a hot-plate until all of the organic material is destroyed, adding more HNO_3 when necessary. Fume to remove excess HNO_3 .

7. Cool the solution and then precipitate the hydrated oxides of tantalum and tungsten by the addition of 50 ml of demineralized water. Add 5 ml of conc. HCl ; boil, then centrifuge. Discard the supernate.

8. Dissolve the precipitate in a 10 ml volume of 0.4 M HF -6 M H_2SO_4 mixture (NOTE 4). Transfer the acid solution to a 100-ml separatory funnel.

9. Add 10 ml of DIPK (or hexone) to the solution (NOTE 5). Shake for 2 minutes. Remove the aqueous phase and extract with an additional 10 ml of the conditioned organic solvent. Separate the phases and retain each.

10. Combine the organic phases and shake briefly with 10 ml of the mixed acid solution. Separate the phases; combine the aqueous phase with the aqueous phase obtained above (NOTE 6).

11. Transfer the aqueous phase to a 150-ml beaker, add 15 ml of conc. HNO_3 and digest on a hot-plate. After cooling, centrifuge the mixture. Discard the supernatant liquid.

12. Wash the tungsten oxide precipitate with hot conc. HNO_3 ; discard the washings.

13. Dissolve the oxide in 0.88 M ammonia solution; dilute to 15 ml with water and centrifuge. Discard the residue if any.

14. Digest the solution on a water bath with conc. HNO_3 to precipitate tungsten oxide. Centrifuge; wash the precipitate with hot conc. HNO_3 .

15. Repeat Steps 13 and 14 at least once more (NOTE 7).

16. Dissolve the tungsten oxide in a minimum volume of 0.88 M ammonia solution. Heat the solution to boiling, then slowly add 1 ml of 5% 8-hydroxyquinoline solution in 2 N acetic acid to precipitate tungsten oxinate. Acidify the solution with acetic acid and then centrifuge the mixture. Discard the supernatant liquid.

PROCEDURE 9 (Continued)

17. Wash the precipitate with water and finally alcohol. Then slurry the precipitate onto a weighed counting tray with a little alcohol. Dry under an infra-red heating lamp; weigh for chemical yield determination and count. (NOTE 8)

18. Count the samples and standards and correct the measured W^{187} radioactivity for background and decay. The amount of tungsten present in the test sample X, is given by the relation:

$$\frac{\text{Mass of W in test}}{\text{Mass of W in std.}} = \frac{\text{Radioactivity of } W^{187} \text{ in sample corrected for 100\% chemical yield}}{\text{Radioactivity of } W^{187} \text{ in standard corrected for 100\% chemical yield}}$$

NOTES

1. In this work, the "self-serve" position of the BEPO reactor was used for the irradiation.
2. In these experiments, the rock samples and stony meteorites were ground to pass a 100-mesh B.S. sieve and the iron meteorites, and standard iron and steel samples were irradiated as turnings or single pieces of the metal.
3. Standard tungsten and tantalum carriers should be present during the dissolution; a simultaneous determination of tungsten and tantalum was made.
4. If an insoluble residue forms, filter or centrifuge the solution to remove it.
5. DIFK (or hexone) previously conditioned with 0.4 N HF-12 N H_2SO_4 mixture.
6. The tungsten is contained in the combined aqueous phases; tantalum is in the organic solvent.
7. The tungsten oxide-ammonium tungstate cycle may be repeated if this should be necessary to achieve radiochemical purity.
8. Count may be made by beta or gamma counting. Radiochemical purity confirmed by half-life determinations, beta absorption curves and gamma spectra.

PROCEDURE 10

Procedure Used In: Radioactivation analysis

Method: Publication⁽¹⁰¹⁾ should be consulted

Element Separated: W^{187} (24.1 h)

Type of Material Analyzed: Biological Materials⁽¹⁰¹⁾

Type of Nuclear Bombardment: $W^{186}(n,\gamma)W^{187}$

Procedure By: Fukai and Meinke⁽¹⁰¹⁾

Chemical Yield of Carrier: Unknown

Time of Separation: Unknown

Degree of Purification: Adequate from other radionuclides

Equipment Required: Standard

Procedure:

NOTE: No specific information has been presented by the authors on the radiochemical separation method used. Their publication⁽¹⁰¹⁾ should be consulted.

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