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NUCLEAR SCIENCE SERIES

**The Radiochemistry
of Gold**

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The Radiochemistry of Gold

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

CONTENTS

I. General References on the Inorganic and Analytical Chemistry of Gold	1
II. Radioactive Nuclides of Gold	1
III. The Chemistry of Gold and Its Application to the Radiochemistry of Gold Radionuclides	3
A. Review of the Chemistry of Gold	4
1. Metallic Gold	5
2. The Compounds of Gold	6
a. The Oxide and Oxyacid Compounds of Gold	6
b. The Halide Compounds of Gold	7
c. The Sulfide Compounds of Gold	10
d. The Cyanide and Cyanoaurate Compounds of Gold	11
e. The Organometallic Compounds of Gold	12
B. Analytical Methods for Gold	12
1. Separation by Reduction to Metal	12
2. Volatilization	13
3. Separation by Electrolytic Methods	13
4. Separation by Solvent Extraction	13
a. Ion Association Systems	14
b. Chelate Complex Systems	15
5. Separations by Ion Exchange Resins	15
6. Separations by Paper Chromatography and Electrophoresis	16
IV. Decomposition of Materials Containing Gold	17
V. Safety Practices	17
VI. Counting Techniques for Radioactive Gold Isotopes	17
VII. Collection of Detailed Radiochemical Procedures for Gold	18
References	31
Appendix A	34

The Radiochemistry of Gold

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

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II. RADIOACTIVE NUCLIDES OF GOLD

The radioactive nuclides of gold that are of interest in the radiochemistry of gold are given in Table I. This table has been compiled from

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

information appearing in reports by Strominger, et al., ⁽¹⁾ and by Hughes and Harvey. ⁽²⁾

Table I. Radioactive Nuclides of Gold

<u>Radio-nuclides</u>	<u>Half-life</u>	<u>Mode of Decay</u>	<u>Energies of Radiation</u>	<u>Produced By</u>
Au ¹⁹¹	3.0 h	EC	γ : 0.3;0.14;0.60	Ir(α ,4n)Au ¹⁹¹ Pt(d,3n)Au ¹⁹¹
Au ¹⁹²	4.7 h	EC, β^-	γ : 0.317;0.296	Ir(α ,3n)Au ¹⁹² Pt(d,2n)Au ¹⁹²
Au ^{193m}	3.8 s	IT	γ : 0.257;0.032	Ir(α ,2n)Au ¹⁹³ Pt(d,n)Au ¹⁹³
Au ¹⁹³	16 h	EC	γ : 0.112;0.173;0.186	Pt(d,3n)Au ¹⁹³
Au ¹⁹⁴	39.5 h	EC, β^-	γ : 0.327;0.291;0.64	Ir(α ,3n)Au ¹⁹⁴ Pt(d,2n)Au ¹⁹⁴ Pt(d,3n)Au ¹⁹⁴ Pt(p,n)Au ¹⁹⁴
Au ^{195m}	30 s	IT	γ : 0.261;0.057;0.318	
Au ¹⁹⁵	185 d	EC	γ : 0.031;0.099;0.130	Ir(α ,2n)Au ¹⁹⁵ Pt(d,n)Au ¹⁹⁵ Pt(d,3n)Au ¹⁹⁵ Pt(p,n)Au ¹⁹⁵ Au ¹⁹⁷ (n,2n)Au ¹⁹⁶
Au ^{196m}	14.0 h	EC or IT		
Au ¹⁹⁶	5.60 d	EC, β^-	β^- 0.30 γ : 0.331;0.354	Pt(d,n)Au ¹⁹⁶ Au ¹⁹⁷ (n,2n)Au ¹⁹⁶ Au ¹⁹⁷ (γ ,n)Au ¹⁹⁶
Au ^{197m}	7.4 s	IT	γ : 0.130;0.277;0.407	Au ¹⁹⁷ (γ , γ)Au ^{197m} Au ¹⁹⁷ (n,n)Au ^{197m}
Au ¹⁹⁸	2.70 d	β^-	β^- 0.959;0.28;1.37 γ : 0.41177;0.676;1.089	Au ¹⁹⁷ (n, γ)Au ¹⁹⁸ Hg ¹⁹⁸ (n,p)Au ¹⁹⁸
Au ¹⁹⁹	3.15 d	β^-	β^- 0.30;0.25;0.46 γ : 0.209;0.050	Pt(d,n)Au ¹⁹⁹ Hg ¹⁹⁹ (n,p)Au ¹⁹⁹
Au ²⁰⁰	48 m	β^-	β^- 2.2 γ : 1.13;0.39	Hg ²⁰⁰ (n,p)Au ²⁰⁰
Au ²⁰¹	26 m	β^-	β^- 1.5 γ : 0.55	Hg ²⁰² (γ ,p)Au ²⁰¹ Hg ²⁰¹ (n,p)Au ²⁰¹
Au ²⁰²	25 s	β^- or IT		Hg ²⁰² (n,p)Au ²⁰²
Au ²⁰³	55 s	β^-	β^- 1.9	Hg(n,nn)Au ²⁰³ Hg ²⁰⁴ (γ ,p)Au ²⁰³

III. THE CHEMISTRY OF GOLD AND ITS APPLICATION TO THE RADIOCHEMISTRY OF GOLD 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 concentration of a specific stable element 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., those radiochemical techniques used mostly for absolute radioactivity measurements, it is required that the radioelement be isolated in a manner capable of giving either no amount or a minimal amount of stable element in the final form to be used in the radioactivity measurements.

In most instances, analytical radiochemistry is dependent upon more conventional ideas in analytical chemistry involving separations by such methods as precipitation, solvent extraction, chromatography, volatilization, and/or electroanalysis 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 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 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 in radiochemistry. Appendix A lists some of the more recent references cited for the determination of gold by such analysis techniques.

The general information that follows describes the behavior of gold and its compounds and how this behavior can be used in developing radiochemical analysis methods for the gold radionuclides. More detailed information can be obtained either from the specific references given in this section or from the general references given in Section I of this monograph.

A. Review of the Chemistry of Gold

Gold is generally found in the native form as very fine metallic particles dispersed through quartz. It is also found associated with sulfide ores such as pyrite, chalcopyrite, arsenopyrite, and stibnite. Gold also appears as finely dispersed particles in telluride ore compounds, such as nagyagite (a mixture of lead, gold, copper and silver sulfides and tellurides), calaverite, AuTe_2 , sylvanite, AgAuTe_4 , and in some compounds of selenium. Most of these compounds and ores are found as original ore deposits. In some instances, it is possible to obtain gold in its native state from secondary, or alluvial, deposits. Here the gold, as the free metal or as a gold-containing compound, has been removed from the place of original deposit by erosion and laid down again in a secondary deposit, where it is usually found in the form of fine or very fine grains.

Gold can be recovered from the sediments obtained by washing these deposits. The washing technique is often combined with an amalgamation process in which the gold in a sediment is dissolved in mercury to form

an amalgam. The gold is recovered from the amalgam by distilling off the mercury. The most important process for extracting gold from its ores is the cyanide process. Here the finely ground ore is leached with potassium or sodium cyanide solution. The gold is converted to a soluble complex cyanide and is recovered from the solution either by a reduction to the metal with zinc or by electrolysis.

1. Metallic Gold

Metallic gold is yellow in color and has a bright luster. It is stable in air and is very ductile. It crystallizes from solution in the cubic system, and it will form mixed crystals with platinum, palladium, silver and copper. It can unite with hydrogen to form a colorless, solid, unstable hydride, but it will not react in air or with water. It will not react with the halogens in the dry, gaseous state; at ordinary temperatures, no direct reactions occur with the halogens, and it is only possible for gold to combine with fluorine at temperatures above 300° . However, gold will dissolve very rapidly in an aqueous solution of chlorine at ordinary temperatures to form complex ions, e.g., tetrachloroaurate and trichlorooxoaurate ions.

Gold will dissolve in aqua regia and also in concentrated sulfuric acid if strong oxidizing agents, such as iodic acid, nitric acid, manganese dioxide, or selenic acid, are present. It will not react directly with molten caustic alkalis or with sulfuric, hydrochloric, phosphoric or arsenic acids. It stands far below hydrogen in the electrochemical series; therefore, it is not able to go into solution by hydrogen displacement, and it cannot be solubilized even under the oxidizing action of atmospheric oxygen.⁽³⁾ By reason of its electrochemical behavior, gold can be displaced from its solutions by almost all other metals unless it is in solution in the form of a very stable complex.

Ions, such as Fe^{+2} , Sn^{+2} , SO_3^{-2} , NO_2^{-1} , Zn, and Hg, can reduce gold and precipitate it from a chloride solution. Organic compounds, such as oxalic acid, formaldehyde, sugar, and tartaric, citric and acetic

acids and their salts, will also reduce gold and precipitate it from a solution as the metal. Acetylene and CO can also be used to precipitate gold from chloride solutions.

2. The Compounds of Gold

Gold (like copper and silver) can exist in its compounds in the valence states of +1 and +3. Although copper and silver also exhibit an oxidation state of +2, no positive evidence exists for Au^{+2} compounds since it appears that such compounds as $AuCl_2$, AuO , $AuSO_4$ are compounded from the combination of Au^{+1} and Au^{+3} salts.⁽⁴⁾ Gold is most stable in the +3 state and salts derived from Au^{+3} are usually complex anionic salts. Monovalent gold, Au^{+1} , also forms complex anion salts. Gold sulfide, Au_2S , and the halides, AuX , are important Au^{+1} compounds. The apparent solubilities⁽⁵⁾ of these and other compounds of gold are tabulated in Table II.

All gold compounds are characterized by their tendency to decompose easily. Reducing agents, frequently at only moderate temperatures, will cause them to dissociate and release free gold.

a. The Oxide and Oxyacid Compounds of Gold

The existence of a monovalent gold oxide, Au_2O , or a hydroxide compound appears to be doubtful,⁽⁶⁾ since the products of a chemical reaction between an Au^{+1} compound and an alkali results in the formation of a mixture of metallic gold and gold oxide, Au_2O_3 . The chief method of preparing trivalent Au_2O_3 is by treating $AuCl_3$ with alkali or alkaline earth hydroxides, or by boiling $AuCl_3$ with alkali carbonates to obtain hydrous gold(III) oxide, $AuO(OH)$, and then dehydrating this compound at a temperature of 140-150°. If heated beyond 160°, the freshly prepared Au_2O_3 will begin losing oxygen. The hydrous gold oxide, or auric acid, is amphoteric and is soluble in concentrated hydrochloric, nitric and sulfuric acids forming complex oxyacid solution compounds, such as $H[AuCl_4]$, $H[Au(NO_3)_4]$, or $H[Au(SO_4)_2]$. When these solutions are diluted, hydrolysis occurs and auric acid is reprecipitated.⁽⁴⁾ If the chloride

and nitrate solutions are evaporated, crystalline hydrates of these acid solutions can be obtained. When an elemental salt compound is added to these oxyacid solutions and the mixture evaporated, solid compounds, such as $K(AuCl_4)$, or $K[Au(SO_4)_2]$, are produced.

Auric acid is the acid anhydride of a series of compounds known as the aurate salts. The evaporation of $AuO(OH)$ in concentrated HNO_3 and in the presence of alkali hydroxides will produce such aurate salts as $KAuO_2 \cdot 3H_2O$ or $NaAuO_2 \cdot H_2O$. Acetatoaurates can be produced by treating the corresponding aurate, $M(AuO_2)$, with glacial acetic acid. Sulfatoaurate salts, e.g., potassium disulfatoaurate(III), $KAu(SO_4)_2$, can also be produced by dissolving $AuO(OH)$ in concentrated sulfuric acid and adding to the mixture a solution of the hydrogen sulfate compound of the element of interest and evaporating the solution to dryness at a temperature of 200° . Alkali thiosulfate compounds when added to a solution of $AuO(OH)$ will produce thiosulfatoaurate(I) salts.

b. The Halide Compounds of Gold

Au^{+1} can form simple halide compounds. Solid gold chloride, $AuCl$, and gold bromide, $AuBr$, are formed by heating (at 185°) anhydrous $AuCl_3$ and $AuBr_3$, respectively. Gold iodide, AuI , is formed by either dissolving Au_2O_3 in hydriodic acid, or by adding iodide ions to Au^{+3} salt solutions.

$AuCl$ is usually obtained as an impure pale yellow powder that will decompose in water to form $AuCl_3$ and elemental gold. When heated, $AuCl$ decomposes to produce elemental gold and Cl_2 . It will dissolve in alkali chloride solutions, to form complex ions, i.e., chloroaurate(I) ions, $(AuCl_2)^-$. $AuCl$ will also form complex compounds with ammonia and can be combined with carbon monoxide to form gold carbonyl chloride, $Au(CO)Cl$. All of these complex compounds decompose in aqueous solutions either to deposit elemental gold or to form other complex gold ions.

$AuBr$, is much more easily decomposed than $AuCl$. It dissolves in alkali bromide solution to form bromoaurate(I) ions, $(AuBr_2)^-$. Gold

Table II. Solubility of Gold Compounds

Compounds	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Bromides	AuBr	Insoluble	Insoluble	Decomposes in acid
	AuBr ₃	Slightly soluble		Soluble in ether
Chlorides	AuCl	Decomposes very slightly	Decomposes	Soluble in HCl and HBr
	AuCl ₃	Very soluble	Very soluble	Soluble in alcohol and ether. Slightly soluble in NH ₃ . Insoluble in CS ₂
Cyanides	AuCN	Very slightly soluble		Soluble in KCN and NH ₄ OH. Insoluble in alcohol and ether
	Au(CN) ₃ ·3H ₂ O	Very soluble	Decomposes very soluble	Soluble in alcohol and ether
Iodides	AuI	Very slightly soluble	Slightly soluble Decomposes	Soluble in KI
	AuI ₃	Insoluble	Decomposes	Soluble in iodides
Nitrate	AuH(NO ₃) ₄ ·3H ₂ O	Soluble decomposes		Soluble in HNO ₃
Oxides	Au ₂ O	Insoluble	Insoluble	Soluble in HCl. Slightly soluble in KOH. In soluble in H ₂ SO ₄ , HNO ₃ and alcohol
	Au ₂ O·XH ₂ O	Soluble		Soluble decomposes in alkali
	Au ₂ O ₃	Insoluble	Insoluble	Soluble in HCl
	Au ₂ O ₃ ·XH ₂ O	Insoluble		Soluble in HCl, NaCN and Conc. HNO ₃
Phosphide	Au ₂ P ₃			Insoluble in HCl and dilute HNO ₃

Selenide	Au_2Se_3			
Sulfides	Au_2S	Insoluble; fresh solution	Precipitate colloidal	Insoluble in acid. Soluble in KCN and aqua regia
	Au_2S_3	Insoluble		Soluble in Na_2S . Insoluble in acid and ether
Telluride	Au_2Te			
	AuTe_2	Insoluble	Insoluble	
Di Alkyls	R_2^+AuX^*	Insoluble	Insoluble	Soluble in benzene and CHCl_3
	R_2AuCN	Insoluble	Insoluble	Soluble in benzene and CHCl_3
	$(\text{R}_2\text{Au})_2\text{SO}_4$	Insoluble	Insoluble	Soluble in ether, benzene and CHCl_3

* X = Cl, Br, I.

*R = Methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, iso-amyl, benzyl, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2$, $(\text{CH}_2)_5$ and $(\text{CH}_2)_{10}$.

iodide, AuI, a lemon yellow powder, is more unstable when heated than are AuCl and AuBr. It is less soluble in water, and it is not as easily decomposed as are AuCl and AuBr. Chloroform and carbon disulfide will cause it to decompose. It will dissolve in KI solution to form an iodoaurate(I) ion, $(\text{AuI}_2)^-$.

The trivalent halogen compounds of gold, AuCl_3 and AuBr_3 , are produced by a direct union of the elements by heating above ordinary temperatures. AuI_3 is formed only by adding a potassium carbonate neutralized solution of chloroauric acid, $\text{H}(\text{AuCl}_4)$, to a KI solution. Complex ions, $(\text{AuI}_4)^-$, are first formed; the addition of more $(\text{AuCl}_4)^-$ produces AuI_3 . AuCl_3 , a red needle-like compound, dissolves in water to form trichloro-oxogold(III) acid, $\text{H}_2(\text{AuCl}_3\text{O})$. This complex acid can react with metal salts to produce insoluble salts, e.g., $\text{Ag}_2(\text{AuCl}_3\text{O})$. When concentrated hydrochloric acid is added to $\text{H}_2(\text{AuCl}_3\text{O})$, chloroauric acid, $\text{H}(\text{AuCl}_4)$, is formed. Chloroauric acid can also be produced by dissolving gold in aqua regia and then removing the nitric acid by evaporating with hydrochloric acid. The end product of this process has the composition $\text{H}(\text{AuCl}_4) \cdot 4\text{H}_2\text{O}$ and is formed as long, bright yellow, needle-like crystals. Chloroauric acid is soluble in alcohol and ether. Numerous chloroaurate salts, e.g., $\text{Na}(\text{AuCl}_4) \cdot 2\text{H}_2\text{O}$ and $\text{K}(\text{AuCl}_4) \cdot 2\text{H}_2\text{O}$, are derivatives of chloroauric acid. Most chloroaurates are soluble in water or ether and are formed as crystals composed of either large rhombic prisms or plates. Gold(III) bromide, Au_2Br_6 and its salts, the tetrabromoaurates, have properties similar to the chloro compounds. Complex compounds, i.e., tetraiodogold(III) acid, $\text{H}(\text{AuI}_4)$ and its salts, the tetraiodoaurates(III), $\text{M}(\text{AuI}_4)$, also resemble the chloro compounds.

c. The Sulfide Compounds of Gold

Gold sulfide Au_2S , a brownish-black solid, is obtained chiefly by saturating potassium dicyanoaurate(I), $\text{KAu}(\text{CN})_2$, with hydrogen sulfide and treating the mixture with HCl. The saturation of a cold solution of AuCl_3 , will not produce a true Au_2S , but one which has the apparent com-

position of AuS, apparently a double compound of Au_2S and Au_2S_3 . The saturation of a hot $AuCl_3$ solution with hydrogen sulfide results only in the deposition of metallic gold. Gold sulfide is insoluble in water and dilute acids and forms colloidal dispersions in the presence of H_2S . It can be decomposed and dissolved by strong oxidizing agents, e.g., aqua regia and chlorine. It forms cyanoaurate(I) compounds when dissolved in alkali cyanide solutions, and, when dissolved in alkali sulfide solutions, it will form either thioaurate(I), monothioaurate, $M(AuS)$, or dithioaurate, $M_3^{+1}(AuS_2)$, salts. All of the gold sulfide compounds when treated with excess alkali sulfide solutions will give up sulfur to form polysulfides. Gold(I) sulfide can be reprecipitated if the thioaurate compounds are decomposed by acids.

Gold(III) sulfide, Au_2S_3 , cannot be formed by a direct combination of the elements. It is obtained by saturating a dilute solution of either chloroauric acid, $H(AuCl_4)$, or gold chloride, $AuCl_3$, or by treating a dry alkali salt like $Li(AuCl_4)$, with H_2S . Au_2S_3 is produced as a black powder and will decompose at temperatures above 200° into the elemental constituents. Thioaurate(III) compounds can be formed by treating Au_2S_3 with cold solutions of alkali sulfide; however, they decompose rapidly to form the corresponding thioaurate(I) compounds.

d. The Cyanide and Cyanoaurate Compounds of Gold

Gold(I) cyanide, $AuCN$, is produced by evaporating a $KCN-AuCl_3$ solution to form a colorless compound, potassium tetracyanoaurate(III), which when heated to temperatures above 200° loses cyanogen to yield potassium dicyanoaurate(I), $KAu(CN)_2$. The complex $KAu(CN)_2$ compound can be decomposed in warm (50°) hydrochloric acid to produce $AuCN$, KCl and HCN . Gold cyanide is insoluble in water, dilute acids and hydrogen sulfide solutions; however, it will dissolve in other alkali cyanides (to form other cyanoaurate(I) salts), sodium thiosulfate, ammonium sulfide and ammonia solutions.

No true compound of gold(III) cyanide exists. KCN will not produce

it by action upon a AuCl_3 solution, but will produce potassium tetracyanoaurate(III) which when treated with strong acids and subsequent evaporation with H_2SO_4 will form the trihydrate of gold(III) cyanide, $\text{Au}(\text{CN})_3 \cdot 3\text{H}_2\text{O}$. Potassium tetracyanoaurate will dissolve in alkali cyanides to form cyanoaurate(I) salts and in alkali sulfides to produce monothioaurates, $\text{M}(\text{AuS})$ and dithioaurates, $\text{M}_3(\text{AuS}_2)$. The thioaurates can be decomposed by acids to reproduce Au_2S .

e. The Organometallic Compounds of Gold

Gold(I) can form unstable alkyl compounds by the action of Grignard reagent on $\text{AuCl} \cdot \text{CO}$. Trivalent gold organometallic compounds are more stable than the univalent gold compounds and several series of organogold(III) derivatives are known, e.g., trialkyl, R_3Au , and dialkyl gold halides, R_2AuX . Anhydrous gold(III) can react directly with aromatic hydrocarbons to produce a series of monoaryl gold(III) compounds. Additional information on the formation of gold organometallic compounds has been given by Remy.⁽⁴⁾

B. Analytical Methods for Gold

As pointed out elsewhere in this monograph, the use of a known amount of inactive gold carrier in a separation method almost always makes it practical to obtain the gold carrier in a weighable form in the final step of 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 in a gravimetric form which can be used to determine any loss of the carrier during the analysis.

Gold is always separated and determined in its ores by the fire assay method.⁽⁷⁾

1. Separation by Reduction to Metal

Gold in solution can be separated by reducing it to the metal with such reducing agents as ferrous sulfate, sulfur dioxide, oxalic acid, hydroquinone, magnesium and zinc. Sometimes metal reductants and their compounds mix with the precipitated metallic gold. Sulfur dioxide also

partially precipitates some of the Group VIII elements, and a reduction with oxalic acid is very slow. Hydroquinone is considered to be the best reducing agent for gold; it gives a sharp separation of gold from copper, nickel, and zinc.⁽⁸⁾ Gold, occurring in the form of tellurides, may also be separated by hydroquinone.⁽⁹⁾ Gold cyanide solutions can be precipitated as colloidal gold by adding sulfuric acid and heating.⁽¹⁰⁾ The addition of a trace of silver to the mixture assists in coagulating the colloidal gold.

2. Volatilization

Hillebrand, et al.,⁽¹¹⁾ report that gold is lost by volatilization if aqua-regia solutions are rapidly evaporated to dryness or if sulfuric acid is added to such solutions and evaporated until H_2SO_4 fumes appear. For example, solutions containing 0.1 gm gold lost about 1-3% upon evaporation. However, volatilization does not occur if 70% perchloric acid is used in the evaporation process.

3. Separation by Electrolytic Methods

Gold may be electrodeposited from alkali cyanides in milligram quantities.⁽¹²⁾ Sand⁽¹³⁾ reports satisfactory deposition of gold from chloride, cyanide, and thioaurate solutions using current densities of 2 to 3 amperes. Perkin and Prebble⁽¹⁴⁾ suggests the use of a dilute solution of potassium cyanide, to which some hydrogen peroxide has been added, to remove gold deposited on a platinum cathode.

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⁽¹⁵⁾ 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 compounds, are applicable for use as separation processes in the radiochemistry of gold.

a. Ion Association Systems

Lenher⁽¹⁶⁾ has extracted Au^{+3} completely from a 10% HCl solution using ethyl acetate. Ethyl ether has been used to separate at least 95% of Au^{+3} from a 6 M HCl solution.⁽¹⁷⁾

Gold can be completely separated from Pd, Pt, Rh, Ir, Ru, but not from Os^{+4} , by extracting 3 M HBr solutions of the metals with isopropyl ether.⁽¹⁸⁾

West, et al.,⁽¹⁹⁾ have shown that Au^{+3} can be partially extracted from an iodide system into methyl isobutyl ketone, methyl isopropyl ketone, ethyl acetate and other solvents. Au^{+3} , Sb^{+3} , Hg^{+2} , Cd^{+2} , and Sn^{+2} are completely extracted from 6.9 M HI solutions into diethyl ether (4:1 volume ratio).⁽²⁰⁾ As^{+3} , Bi^{+3} , Cu^{+2} , Mo^{+6} , Te^{+4} , and Zn^{+2} partially extract under the same conditions, whereas, K, Cs, Ba, Ca, Fe^{+2} , Ni, Cr, Co, Mn, Ti, Zn, Pb, Th, Al, Ga, Be, U, V, Pt, Pd, Ir, Os, and Ru do not extract.

Bock and Bock⁽²¹⁾ have shown that Au^{+3} can be quantitatively extracted into diethyl ether from 8 M HNO_3 . U^{+6} , Zr^{+4} , Th^{+4} , Tl^{+3} , Hg^{+2} , Cr^{+6} , Ce^{+4} , Bi^{+3} , As^{+3} and P^{+5} show varied degrees of extractability under the same conditions.

White,⁽²²⁾ in his use of alkyl phosphine oxides has shown that tri-n-octylphosphine oxide in cyclohexane will completely extract Au^{+1} (as well as Cr^{+6} , Hf^{+4} , Fe^{+3} , Mo^{+6} , Sn^{+4} , U^{+6} , and Zr^{+4}) from 1 M HCl. Sb^{+3} , Bi^{+3} , Cd^{+2} , In^{+3} , Hg^{+2} , Pt^{+2} , and Zn^{+2} partially extract in this system. In a separate study, White⁽²²⁾ has also shown that Au^{+1} (and Sn^{+4} and U^{+6}) can be completely extracted from a 1M HCl solution with tris-2-ethyl-n-hexylphosphine oxide in cyclohexane; however, Au^{+1} will not extract from a 7 M HCl solution using the same reagent. Sn^{+4} , U^{+6} , Ga^{+3} , Hg^{+4} , Fe^{+3} , Mo^{+6} and Zr^{+4} completely extract under these latter conditions.

b. Chelate Complex Systems

Gold (as well as Co, Bi, Cd, Cu, Pb, Hg, Ni, Tl and Zn) forms a water insoluble compound with 2-mercaptobenzothiazole that can be extracted into alcohol or ether. (23) Beck (24) reports that Au^{+3} will form a complex of thiosalicylideneethylenediimine that is extractable into chloroform. This Au^{+3} complex (as well as those for Ni^{+2} , In^{+3} , Te^{+4} , Sn^{+2} , Sb^{+3} , Cd^{+2} , Pb^{+2} , Pt^{+2} , and Pt^{+4}) is stable in HCl.

The Au^{+3} complex of phenylthioaurea (like those of Ir^{+4} , Rh^{+3} , Ru^{+3} , Os^{+4} , Fe^{+3} , Co^{+3} , Ni^{+2} , and Cr^{+6}) will only partially extract (1%) into ethyl or amyl acetate from a dilute HCl solution. (25) Under these same conditions, Pd^{+2} completely extracts; large amounts of Pt^{+4} (40%) and Cu^{+2} (16%) also can be extracted in the same system.

Gold, following its interaction with Rhodamine B, a xanthone dye, can be extracted into either isopropyl ether (26) or benzene. (27) Antimony and thallium also react with Rhodamine B and will extract into benzene. (27)

Gold forms a faint yellow complex with ephidrine hydrochloride that can be extracted into CCl_4 . (28) Os^{+8} , Pd, and Ir also form colored complexes in this system while Pt and Rh do not.

Poluektov (29) has used a 0.03% solution of ethanolic p-dimethylamino-benzalrhodanine to produce a pink-violet gold complex that can be extracted from an acid solution with a benzene-chloroform mixture. Silver will not interfere if it is first separated as the chloride.

Sandell (30) reports that gold dithizonate can be extracted from a dilute mineral acid solution with chloroform. If carbon tetrachloride is used, a floc will appear, and it is postulated that Au^{+3} is probably reduced to Au^{+1} by the CCl_4 .

5. Separations by Ion Exchange Resins

Burstall, et al., (31) have shown that quaternary ammonium strong-base anion exchange resins will absorb the gold cyanide complex, $Au[(CN)_2]^{-2}$. Ni, Co and Cu also form cyanide complexes that absorb upon the resin under the same conditions. These can be selectively eluted from the resin with dilute

HCl and NaCN solutions. Following the elution of these anions, more than 95% of the gold complex can be removed with an acetone-HCl solution.

Kraus and Nelson⁽³²⁾ report that at least 99.9% of the gold content of a 0.0014 M solution of Au(III) in 1 M HCl could be separated rapidly (in 5 minutes) from many other elements by the use of an ion exchange column containing 0.10 gram of Dowex 1 resin. Gibbons⁽³³⁾ also confirmed this effect by use of Deacidite FF ion exchange resin.

6. Separations by Paper Chromatography and Electrophoresis

Au^{+3} can be separated by paper chromatography techniques using either butanol-1 N HCl,⁽³⁴⁾ alcohol-HCl mixtures,^(35,36) binary alcohol mixtures containing HCl,⁽³⁷⁾ ketone-HCl mixtures,⁽³⁸⁾ butanol-HBr mixtures,⁽³⁹⁾ and phenol⁽⁴⁰⁾ as solvents. Small amounts of gold (1 ppm) in chloride solutions of the platinum metals have been determined by paper chromatography using either an ethyl ether-HCl-methyl alcohol mixture⁽⁴¹⁾ or butanol-HCl- HNO_3 mixture⁽⁴²⁾ as a solvent. Gold can also be separated from almost all of the other metals using an ethyl acetate-water- HNO_3 mixture as a solvent.⁽⁴³⁾ It has also been separated from Pt and Pd by use of ethyl ether-HCl mixture as a solvent.⁽⁴⁴⁾ Gold has also been separated from copper, silver, platinum and palladium by butanol-HCl mixture⁽⁴⁵⁾ and from indium, platinum, palladium, rhodium and ruthenium with butanol-HCl- HNO_3 mixtures⁽⁴⁶⁾ as solvents. Methyl ethyl ketone-HCl and methyl propyl ketone-HCl solutions have also been used to separate it from osmium, platinum, palladium, rhodium, iridium and ruthenium.⁽⁴⁷⁾ In all of these separations, gold is extracted with the organic phase which travels ahead of the aqueous front.

Au^{+3} may be separated from Hg^{+2} and Pd^{+2} , but not from Ir^{+4} , Bi^{+3} and Tl^{+3} , with a voltage of 3.6 volts/cm applied to a chromatographic paper immersed in 0.5 N HCl.⁽⁴⁸⁾ The above ions are present as anions. Isoelectric Cd^{+2} and the cationic species of Mo^{+6} , Zr^{+4} , Rh^{+3} , As^{+3} , Sn^{+2} , Sb^{+3} , Pb^{+2} , Cr^{+3} , UO_2^{+2} , Ti^{+4} , Be^{+2} , Fe^{+3} , Co^{+2} , Ni^{+2} , Al^{+3} , Cu^{+2} , Zn^{+2} , Sr^{+2} , and Ba^{+2} were also separated under these conditions.

IV. DECOMPOSITION OF MATERIALS CONTAINING GOLD

Most gold-containing samples can be dissolved in aqua regia. (11,30,49)

Acid insoluble materials can be fused with either sodium carbonate or sodium carbonate-sodium nitrate, or sodium peroxide-sodium hydroxide. (11,50-57)

Biological materials are best dissolved by wet ashing, i.e., digestion with $H_2SO_4-HClO_4-HNO_3$ mixtures while being heated. (33,58-63) Similar techniques can be used to dissolve petrochemicals. (64)

V. SAFETY PRACTICES

Safety practices in handling radioactive materials are always important in radiochemistry. The discharge of radioactivity by explosion or evolution into a laboratory area can be hazardous and can result in wide-spread contamination. Thus, some source of information on safe handling practices 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. (65)

VI. COUNTING TECHNIQUES FOR RADIOACTIVE GOLD ISOTOPES

The analysis of sample materials containing radionuclides of gold 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 gold 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.

Table I of this monograph shows the nuclear characteristics of each of the known radioactive isotopes of gold. The radioactive isotope usually encountered by the radiochemist is Au^{198} , 2.70 d. This isotope is produced by a number of nuclear reactions on the stable isotopes of gold and mercury. Its radioactivity (as well as the radioactivity of any of the radioisotopes listed in Table I) can be measured by standard Geiger-

Mueller, gamma scintillation and proportional counting methods. (66-69)

Although this monograph is concerned with measurements of the gold radionuclides after a radiochemical separation, it should be noted that some of these counting methods have been employed in the direct (or non-destructive) analysis of neutron-irradiated diamonds, (70) semiconductor materials, (71,72) petrochemicals, (73) and metals and alloys. (73)

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR GOLD

The radiochemical procedures that now exist for the determination of the gold radionuclides have evolved from ideas and techniques similar to those reported in Section III of this monograph and reflect on the requirements of each investigation that has been undertaken. Both carrier-free and carrier separation techniques have been employed.

The carrier-free methods have been employed in the preparation of radioactive gold tracers. (74-76) The other solvent extraction separations, as well as the chromatography methods, reported in Section III above, suggest possible carrier-free separations for the radioactive gold isotopes.

Carrier methods have been used in the preparation of radioactive gold tracers (76) and separating gold from fission products. (77) In addition, carrier methods of radiochemical analysis have been used to determine gold by radioactivation analysis. (78,79) The procedures that have been used in the radioactivation analysis determination of trace gold in biological materials, (33,58-63) meteorites, (50-53,56) rocks and minerals, (53-56) semiconductor materials, (71) petrochemicals (64) and sea water (80) are included as part of this collection of radiochemical procedures. However, it should be noted that the procedures developed by Tobias and Dunn (58) and by Gibbons (33) for the analysis of gold in biological materials are usually followed by most investigators. Similarly, the procedures proposed by Brown and Goldberg (50) and by Smales (53) for the analysis of meteoritic materials are used frequently by other investigators.

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

PROCEDURE 1

Procedure Used in: Preparation of radioactive tracers

Method: Solvent extraction

Element Separated: Carrier-free gold radioactivity

Type Material Bombarded: Platinum, iridium (Note 1), mercury, or gold (Note 2)

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

Procedure by: Wilkinson and Hicks (Reported by Meinke⁽⁷⁶⁾)

Separation Time: 30 minutes to 4.0 hours

Yield of Gold Radioactivity: ~100%

Decontamination: Decontaminates well from Pt, Ir and Hg radioactivities

Equipment Required: Standard

PROCEDURE

1. Dissolve Pt, Au, or Hg in aqua regia. (AuCl_3 carrier may be added here)
2. Chloride ion must be greater than 6 N (Hg extracts), and the solution shaken with an equal volume of ethyl acetate (gold in organic layer) and layers separated.

Notes:

1. See Wickers, E., Schlect, W. G., and Gordon, C. L., J. Nat. Bur. Stand. Research 33, 363 (1944) for method of dissolving iridium.
2. This procedure can be used as a carrier method also.

PROCEDURE 1 (Continued)

3. Wash ethyl acetate layer twice with equal volume 6 N HCl.
4. Evaporate ethyl acetate layer to dryness and take up residue in 1 N HCl.
5. Bubble in SO₂ to reduce Au⁺³ to Au in the hot solution.

PROCEDURE 2

Procedure Used In: Preparation of radioactive tracers

Method: Solvent extraction

Element Separated: Carrier-free gold radioactivity

Type Material Analyzed: Tracer mercury

Type of Analysis: Milking experiment

Procedure by: R. W. Fink (Reported by Meinke⁽⁷⁶⁾)

Separation Time: ~10 minutes

Yield of Gold Radioactivity: Quantitative

Decontamination: 10³ from any Hg radioactivity present

Equipment Required: Standard

PROCEDURE

1. Take Hg tracer in 4 ml of ~3 N HCl and extract with 500 μ l of isoamyl acetate. (The presence of at least 0.1 N Cl⁻ is required for a sepn. from Hg.) - Au into the organic layer.
2. Wash the organic layer with equal volume sat. NH₄Cl soln. to insure sepn. from Hg.
3. Plate organic layer for Au sample.

Note: Tl, if present, will follow Au in the solvent extraction.

PROCEDURE 3

Procedure Used in: Preparation of radioactive tracers

Method: Solvent extraction

Element Separated: Gold carrier and gold radioactivity

Type Material Bombarded: Gold leaf

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

Procedure by: Thompson and Rasmussen (Reported by Meinke⁽⁷⁶⁾)

Separation Time: 4-10 minutes

Chemical Yield of Carrier: ~100%

Decontamination: Factor of 50 from Hg and spallation products

Equipment Required: Standard

PROCEDURE

1. Dissolve Au in warm 6 N aqua regia (2 N HNO₃, 4 N HCl) in centrifuge tube. Work in small volume (1-2 ml.).
2. Add hold-back carriers for Hg, Pt, Ir, and Os (~1 mg each).
3. Add (1 to 1/2 ml.) ethyl acetate. Agitate, mixing phases with transfer pipette. (Yellow color of gold quantitatively extracts into organic phase.)
4. Wash the separated ethyl acetate phase once or twice with 6 N HCl. (Any wash of high chloride concentration serves to remove Hg, although Tl if present may not be entirely washed out.)
5. The solution of Au in ethyl acetate may now be rapidly evaporated on the plate for counting or subjected to further specific gold chemistry.

PROCEDURE 4

Procedure Used in: Preparation of radioactive tracers

Method: Fusion and solvent extraction

Element Separated: Gold carrier and gold radioactivity

Type Material Bombarded: Iridium foil

Type of Nuclear Bombardment: 184" cyclotron (388 Mev alphas, 348 Mev protons, 194 Mev deuterons)

Procedure by: Thompson and Rasmussen (Reported by Meinke⁽⁷⁶⁾)

Separation Time: 20-30 minutes

Chemical Yield of Carrier: ~70%

Decontamination: 10^2

Equipment Required: Standard

PROCEDURE

1. Make a melt of KOH and KNO_3 (~50-50, not critical) in a small porcelain crucible, heating strongly over a Fisher burner.
2. To this hot flux add the target Ir metal, continuing to heat (and adding KOH if volume of flux gets too small) until the metal is completely dissolved. (For a small strip of 1 mil foil, this should take no longer than 5-10 min.)
3. Allow flux to cool, then leach for ~5 min. with conc. HCl, adding Au and Pt carriers in small amount. (Ir gives strong blue colored soln.)
4. Extract twice with ethyl acetate to remove Au.
5. Combine organic layers and wash twice with equal volume 3 N HCl.
6. Plate organic layer and flame.

PROCEDURE 5

Type of Analysis: Separation of gold from fission products

Procedure by: G. A. Cowan in report compiled by Kleinberg⁽⁷⁷⁾

PROCEDURE

1. To the sample contained in 20 ml of 1 M HCl in a 40-ml conical centrifuge tube, add 2 ml of 5% sulfosalicylic acid solution, 2.00 ml of Au carrier, 1 drop of Te^{+6} holdback carrier, and 1.5 ml of conc. HI. Heat on a steam bath for 10 to 15 min. Centrifuge and discard the supernate.
2. Wash out chloride ion by filling the centrifuge tube with H_2O and decanting. Repeat. Digest the Au precipitate with 1 ml of conc. HNO_3 , boiling for 1 min in the hood. Centrifuge and discard the supernate.
3. Fill the tube with H_2O and decant. Dissolve the precipitate in 2 ml of conc. HCl and 3 to 4 drops of conc. HNO_3 . Boil off all the HNO_3 .
4. Dilute to 20 ml with 1 M HCl and repeat Steps 1-3 two additional times.
5. Dilute the solution to 20 ml with 1 M HCl and add 3 drops of Ag carrier. Centrifuge and transfer the supernate to another 40-ml centrifuge tube, discarding the AgCl precipitate.
6. Add 4 drops of Fe carrier, and then a slight excess of conc. NaOH. Without delay, centrifuge and transfer the supernate to a clean 40-ml centrifuge tube, discarding the $\text{Fe}(\text{OH})_3$ precipitate. Immediately reacidify the supernate with conc. HCl.
7. Add 1.5 ml of conc. HI and reprecipitate metallic Au as before (Step 1). Dissolve the precipitate in a minimum amount of aqua regia.
8. Wash the solution into a 125-ml separatory funnel with about 40 ml of 1 M HCl. Extract with 25 ml of ethyl acetate. Wash the ethyl acetate layer twice with 5-ml portions of 2 M HCl.
9. Transfer the ethyl acetate extract to a 125-ml Erlenmeyer flask and remove the ethyl acetate on a steam bath. Add 25 ml of 1 M HCl and 1.5 ml of conc. HI. Heat on steam bath for 10 to 15 min to precipitate metallic Au.
10. Filter the Au on a weighed No. 41 H Whatman filter circle, $7/8$ " diameter, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with 1 M HCl, and then with acetone. Dry for 15 min at 110° . Cool, weigh, and mount.

PROCEDURE 6

Procedure Used in: Radioactivation analysis

Method: Fusion, solvent extraction, and precipitation

Element Separated: Gold carrier and Au¹⁹⁸ radioactivity

Type of Material Analyzed: Igneous rocks,⁽⁵³⁾ minerals,^(54,55,57) stoney meteorites⁽⁵⁵⁾

Type of Nuclear Bombardment: Au¹⁹⁷(n, γ)Au¹⁹⁸

Procedure by: Smales, A. A.,⁽⁵³⁾ Vincent, E. A. and Smales, A. A.⁽⁵⁴⁾

Chemical Yield of Carrier: 80%

Separation Time: Not stated

Decontamination Factor: Adequate from other radioactivities

Equipment Required: Standard

PROCEDURE

1. Mix the irradiated sample (powder) with about 0.5 gm Na₂O₂ in a silica crucible and heat at 480-500°C in the muffle for ten minutes. Transfer the cooled sintered cake to a small beaker, moisten with water and add 30 mg Au foil (these carrier foils are conveniently weighed out in advance). Add aqua regia to the crucible and loosen any adhering material with a glass rod. Digest on the hot plate for a few minutes and transfer the acid to the beaker containing the sintered cake and carrier. Repeat the acid digestion of the crucible contents; finally rinsing into the beaker with a little water.
2. Cover the beaker and evaporate the contents to dryness on a hot plate; cool, add fresh aqua regia, and repeat the evaporation. Take up the residue in 1 ml HCl and 20 ml of H₂O, and transfer to a centrifuge tube.
3. Centrifuge off the silica and transfer the supernatant to a fresh tube. Wash the silica twice with hot, dilute HCl adding the washings to the main solution. Discard the silica to active waste.
4. To the main solution, add 10 mg as cations of holdback carriers Na, K, and Cu and 5 mg of holdback carrier Co, Zn and Mn, followed by sufficient magnesium powder to precipitate the Au metal, and leave a slight excess. Warm to expel hydrogen.
5. Centrifuge and decant the supernatant to active waste, and wash the precipitated metal twice with hot water.
6. Dissolve the precipitated metal in a few drops of aqua regia and evaporate nearly to dryness. Dissolve residue in 15 ml of 10% HCl and transfer to a separating funnel. Extract with 30 ml of ethyl acetate, discard the aqueous layer to active waste.
7. Wash the ethyl acetate solution containing the gold twice with 20 ml of 10% HCl. Run the ethyl acetate layer into a beaker and evaporate

PROCEDURE 6 (Continued)

to dryness on a hot plate and dissolve the residue in a few drops of aqua regia. Transfer the solution with water to a centrifuge tube.

8. Add 2 ml of HCl and holdback "carriers" of Na, K, Co, Cu, Zn, and Mn. Heat nearly to boiling and add about 0.5 gm hydroquinone. After standing for a few minutes separate the gold metal by centrifuging. Wash the gold twice with hot water, redissolve in a few drops of aqua regia.
9. Repeat step 8 three more times. Finally wash the gold metal twice with water and then with alcohol. Transfer to a weighed counting tray, dry under a infra-red lamp and weigh to establish the chemical yield.

PROCEDURE 7

Procedure Used in: Radioactivation analysis

Method: Fusion, solvent extraction and precipitation

Element Separated: Gold carrier and Au¹⁹⁸ radioactivity

Type of Material Bombarded: Iron meteorites⁽⁵⁰⁻⁵²⁾ and sea water⁽⁸⁰⁾
(see Note)

Type of Nuclear Bombardment: Au¹⁹⁷(n, γ)Au¹⁹⁸

Procedure by: Goldberg, E. D. and Brown, H.⁽⁵⁰⁾

Chemical Yield of Carrier: 75%

Equipment Required: Standard

PROCEDURE

1. Dissolve 0.3 to 0.5 g of irradiated meteorite in 20 ml of aqua regia. Add 30 mg of Au carrier. Evaporate to dryness.
2. Take up residue in 30 ml of 10% HCl. Extract with 30 ml of ethyl acetate. Wash the ethyl acetate layer twice with 20 ml of 10% HCl.
3. Evaporate the ethyl acetate layer to dryness on a steam bath. Take up the residue with 15 ml H₂O, 5 ml conc. HCl. Bring the solution to a boil and add 10 ml of a 5% aqueous solution of hydroquinone. Continue boiling for 20 minutes or until the gold metal coagulates into lumps.
4. Filter the gold metal on 1-cm paper circles. Wash with 25 ml portions of hot water and one 25 ml portion of ethyl alcohol. Dry for 15 minutes at 110°C and determine the weight of precipitated gold.

Note: Hummel⁽⁸⁰⁾ in his paper on the determination of gold in sea water indicates that the procedure of Goldberg and Brown was followed.

PROCEDURE 8

Procedure Used in: Radioactivation analysis
Type of Material Analyzed: Silicon
Type of Nuclear Bombardment: $\text{Au}^{197}(\text{n},\gamma)\text{Au}^{198}$
Procedure by: James, J. A. and Richards, D. H. (71)
Chemical Yield of Carrier: Unknown
Separation Time: Unknown
Decontamination Factor: Adequate from other radionuclides
Equipment Required: Standard

PROCEDURE

Note: No specific information has been given on this procedure.
Publication should be consulted.

PROCEDURE 9

Procedure Used in: Radioactivation analysis
Method: Solvent extraction and precipitation
Element Separated: Gold carrier and Au^{198} radioactivity
Type of Material Analyzed: Petrochemicals (64)
Type of Nuclear Bombardment: $\text{Au}^{197}(\text{n},\gamma)\text{Au}^{198}$
Procedure by: Mahlman, H. A. (Reported by Leddicotte (64))
Chemical Yield of Carrier: At least 75%
Separation Time: 2 hours
Degree of Purification: Decontamination for all other radioelements
better than 10^5
Equipment Required: Neutron source and standard laboratory equipment

PROCEDURE

A. Irradiation of Sample Materials

1. Irradiate known amounts of test and comparator (0.025 to 0.030 g of gold metal to nearest 0.1 mg) samples in a neutron flux of at least

PROCEDURE 9 (Continued)

5×10^{11} n/cm²/sec for 16 hours (Note 1). Use small quartz tubes, polyethylene bottles or aluminum foil to contain the samples.

B. Preparation of Irradiated Samples for Analysis

1. The Gold Comparator Sample

- a. Quantitatively transfer the irradiated test portion of the gold comparator sample from the quartz tube or aluminum wrap to a 100-ml volumetric flask. Dissolve the test portion in a small, measured volume of aqua regia (4 ml HCl to 1 ml HNO₃); then dilute the solution to 100 ml with water. Mix the solution well by shaking it carefully. Observe the rules for the safe handling of radioactive materials that are outlined in Method No. 5 0050, "Safety."
- b. By means of a volumetric pipet, pipet a 0.100 ml aliquot of this solution into a second 100-ml volumetric flask; then dilute the aliquot to 100 ml with water.
- c. Shake the solution thoroughly; then pipet a 1.00-ml aliquot of it into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same centrifuge tube 2.00 ml of a standard carrier solution of known gold concentration. Also add 1 ml each of holdback carriers of cadmium, cobalt, copper, iron, manganese, phosphorus, sodium, and strontium. (Note 2) Continue with Part C below.

2. Solid Petrochemical Test Samples

- a. If the sample is a solid, or semi-solid, petrochemical, quantitatively transfer the irradiated test portion from the quartz tube or aluminum wrap to a 150-ml glass Erlenmeyer flask, and then add, by means of a volumetric pipet, to the same flask 2.00 ml of a standard carrier solution of known gold concentration. Also add 1 ml each of holdback carriers of cadmium, cobalt, copper, iron, manganese, phosphorus, sodium and strontium (Note 2). To this mixture, add 15 ml of HNO₃-H₂SO₄ mixture (2 volumes of 69% HNO₃ to one volume of conc. H₂SO₄). Also, put 2 or 3 glass beads into the flask, then digest the solution at a moderate temperature (60°C) until all of the petrochemical is destroyed (Note 3). Continue heating until all of the HNO₃ is removed from the solution. Cool; transfer the solution into a 50-ml centrifuge tube and then continue with Part C below.

3. Liquid Petrochemical Test Samples

- a. If the sample is a liquid petrochemical, pipet an aliquot of the irradiated portion into a 125-ml glass Erlenmeyer flask, and then add, by means of a volumetric pipet, to the same flask 2.00 ml of a standard carrier solution of known gold concentration. Also add 1 ml each of holdback carriers of cadmium, cobalt, copper, iron, manganese, phosphorus, sodium and strontium (Note 2). To this mixture, add 15 ml of HNO₃-H₂SO₄ mixture (2 volumes of 69% HNO₃ to one volume of conc. H₂SO₄). Also, put 2 or 3 glass beads into the flask, then digest the solution at a moderate temperature (60°C) until all of the petrochemical is destroyed (Note 3).

PROCEDURE 9 (Continued)

Continue heating until all of the HNO_3 is removed from the solution. Cool; transfer the solution into a 50-ml centrifuge tube and then continue with Part C below.

C. Radiochemical Separation of Gold

1. Concentrate the solution to a volume of 2 or 3 ml. (Note 4)
2. To the hot solution, add small amounts of zinc metal powder (20 mesh) until no further precipitation takes place and an excess of zinc metal powder exists. Centrifuge; discard the supernatant liquid.
3. To the precipitate add 1-2 ml of conc. HCl to dissolve the excess zinc metal. Then, add enough distilled water to make a volume of 20 ml. Stir the mixture thoroughly. Centrifuge; discard the supernatant liquid. Wash the precipitate with 10 ml of hot water; stir while adding water. Centrifuge; discard the water wash.
4. Dissolve the precipitate in 0.25 ml HNO_3 and 1.0 ml of HCl. Heat to complete dissolution. Transfer to a 50-ml separatory funnel. Wash the centrifuge tube with 4 ml of 3 N HCl; add the washes to the separatory funnel.
5. Add 10 ml of ethyl acetate to the separatory funnel. Extract the gold ions from the aqueous solution by shaking the mixture thoroughly. Allow the phases to separate; remove and discard the aqueous phase. Wash the organic layer by adding 10 ml of 3 N HCl to the separatory flask and shaking the mixture. Allow the phases to separate; remove and discard the aqueous phase.
6. Transfer the organic phase to a 50-ml centrifuge tube. Add 2 ml of 0.1 N HCl and remove the ethyl acetate by slowly heating the mixture (Note 5) in a water bath. When all of the ethyl acetate has been removed, transfer the solution to a new 50-ml centrifuge tube. Rinse tube with 2 or 3 ml of 0.1 N HCl and transfer rinses to the new centrifuge tube (Note 6).
7. Heat the solution to boiling. Then add solid sodium bisulfite, NaHSO_3 , to reduce the carrier and precipitate elemental gold. Digest the mixture for 10 minutes by heating in a water bath. Stir the mixture frequently during the digestion process. (Note 7)
8. Filter off the gold through a tared filter paper (Munktells No. 00) that is held in a Hirsch funnel; wash the precipitate three times with 5-ml portions each of H_2O and hot HNO_3 . Then, repeat water washes. Weigh the gold precipitate and filter paper on an analytical balance. Mount the precipitate and count its radioactivity as instructed in Part D below.

D. Measurement of the Radioactivity From Au^{198} and Calculation of Inactive Gold Content of the Original Sample

1. Counting of Beta Radioactivity
 - a. If the beta radioactivity from Au^{198} in the gold precipitate is to be counted, transfer the precipitate and filter paper to a watch glass. Mount the watch glass and its contents on a cardboard mount

PROCEDURE 9 (Continued)

- b. By means of a Geiger-Mueller counter and for the comparator sample, determine the background beta radioactivity and the beta radioactivity of the precipitate. Record the time at which the beta radioactivity was measured.
 - c. Also, for the test sample, determine the background beta radioactivity and the beta radioactivity of the precipitate. Record the time at which the beta radioactivity was measured.
 - d. If it is necessary to make a correction for decay, select some reference time from which the decay correction for Au¹⁹⁸ can be calculated. This reference time might possibly be the same time as the counting time for the first sample analyzed or it might be some earlier time.
 - e. If the degree of the radiochemical purity of the precipitate is not known, check it by counting the beta radioactivity at periodic intervals under the same conditions used to determine the initial count or by making a beta absorption study.
2. Counting of Gamma Radioactivity
- a. If the gamma radioactivity from Au¹⁹⁸ in the gold precipitate is to be counted, transfer the precipitate to a pyrex culture tube (10 mm x 75 mm, w/o rim).
 - b. For the comparator sample, determine the background radioactivity and the gamma radioactivity of the precipitate either by means of a gamma scintillation counter, by gamma discriminatory counting, or by gamma scintillation spectrometry. Record the time at which the gamma radioactivity was measured.
 - c. Also for the test sample, determine the background gamma radioactivity and the gamma radioactivity of the precipitate. Record the time at which the gamma radioactivity was measured.
 - d. If it is necessary to make a correction for decay, select some reference time from which the decay correction for Au¹⁹⁸ can be calculated.

A comparison of the corrected radioactivities for the test and comparator samples becomes a measure of the stable gold content of the test sample:

$$\text{Percent Stable Gold in Test Sample} = \frac{\text{Corrected Au}^{198} \text{ Radioactivity in Test Sample}}{\text{Corrected Au}^{198} \text{ Radioactivity in Comparator Sample}} \times 100.$$

PROCEDURE 9 (Continued)

Notes:

1. The Oak Ridge National Laboratory Graphite Reactor was used for the irradiation. The sensitivity of the method is such that 1×10^{-9} gram of gold can be determined. The sensitivity can be enhanced by the use of higher neutron fluxes.
2. Solutions of the ions of other elements may also be added as holdback carriers.
3. From 1 to 2 hours will be required for digestion. Additional HNO_3 will have to be added during the digestion period.
4. Solution should be clear and yellow in color. If not, or a precipitate forms, add conc. HCl and conc. HNO_3 dropwise while heating.
5. Use a well ventilated fume hood for this operation.
6. The ethyl acetate will form a coating on the walls of the centrifuge tube and will absorb enough of the fine gold precipitate obtained in Step 7 to cause low experimental yields.
7. Hydroquinone can be used instead of NaHSO_3 as the reducing agent. The same techniques given in this step should be followed.

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APPENDIX A

SOME REFERENCES ON THE DETERMINATION OF GOLD BY OTHER ANALYSIS METHODS

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