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NUCLEAR SCIENCE SERIES

The Radiochemistry
of Palladium

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The Radiochemistry of Palladium

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Subcommittee on Radiochemistry
National Academy of Sciences — National Research Council

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

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INTRODUCTION

This volume which deals with the radiochemistry of palladium 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 palladium which might be included in a revised version of the monograph.

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

1. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoritical Chemistry", Vol. XV, Longman's Green and Co., London, 1936, pp. 592-685.

2. Remy, H., "Treatise on Inorganic Chemistry", Vol. II, Translated by J. S. Anderson, edited by J. Kleinberg. New York, 1956, p. 340.

3. Sidgwick, N. V., "The Chemical Elements and Their Compounds", Vol. II, Oxford Press, London, 1950, pp. 1553-1577.

4. Friend, J. N., "A Textbook of Inorganic Chemistry", Vol. IX, Pt. I, Charles Griffin and Co., Ltd., London, 1929, pp. 174-207.

5. Hopkins, B. Smith, "Chapters in the Chemistry of the Less Familiar Elements", Vol. II, Chap. 21, Stipes, Champaign, Ill., 1939, pp. 1-10.

6. Partington, J. R., "A Text-Book of Inorganic Chemistry", MacMillan and Co., Ltd., London, 1950, p. 957.

7. Schoeller, W. R., Powell, A. R., "Analysis of Minerals and Ores of the Rarer Elements", Jafner Publishing Co., New York, 1919, Chapter XXIV.

8. Wilson, C. L., Wilson, D. W., "Comprehensive Analytical Chemistry", Vol. 1A, Elsevier Publishing Co., Amsterdam, 1959.

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9. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., Hoffman, J. F., "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, Inc., New York, 1953, pp. 339-385.

10. Sandell, E. B., "Colorimetric Determination of Traces of Metals", Interscience Publishers, 1959, p. 711.

11. Morrison, G. M., Freiser, H., "Solvent Extraction in Analytical Chemistry", Wiley and Sons, New York, 1957.

II. TABLE OF ISOTOPES OF PALLADIUM (1,2)

Isotope	Half Life	% Abundance	Type of Decay	Method of Preparation
Pd^{98}	17.5 m		EC	Ru^{96}(24 Mev α,2n)
Pd^{99}	21.6 m		$β^+$,γ	Ru^{96}(17 Mev α,n)
Pd^{100}	4.1 d		EC,γ	Rh^{103}(50 Mev d,5n)
				Ag(480 Mev p)
				Ag(420 Mev p)
Pd^{101}	8.5 h		EC,$β^+$,γ	Ru^{98}(17 Mev α,n)
				Ru^{99}(40 Mev α,2n)
Pd^{102}	stable	0.96		
Pd^{103}	17.0 d		EC,γ	Rh^{103}(d,2n)
				Rh^{103}(p,n)
				Pd^{102}(n,γ)
Pd^{104}	stable	10.97		
Pd^{105}	stable	22.23		
Pd^{106}	stable	27.33		
Pd^{107m}	21.3 sec		IT	Pd^{106}(thn,γ)
				Pd^{108}(n,2n)
Pd^{107}	7×10^6 y		$β^-$, no γ	U(n,f)
Pd^{108}	stable	26.7		
Pd^{109m}	4.75 m		IT	Ag^{109}(n,p)
				Pd^{108}(thn,γ)
				Pd^{110}(≤25 Mev n,2n)

Isotope	Half Life	% Abundance	Type of Decay	Method of Preparation
Pd^{109}	13.5 h		β^-,γ	$Pd^{108}(thn,\gamma)$
				$Pd^{110}(\leq 20\ Mev\ n,2n)$
				$Ag^{109}(6.5\ Mev\ d,2p)$
				$Pd^{110}(\gamma,n)$
				U (thn,f)
Pd^{110}	stable	11.81		
Pd^{111m}	5.5 h		IT,β^-	$Pd^{110}(20\ Mev\ d,p)$
				$Cd^{114}(14\ Mev\ n,\alpha)$
Pd^{111}	22 m		β^-,γ	$Pd^{110}(thn,\gamma)$
				$Cd^{114}(14\ Mev\ n,\alpha)$
				U(thn,f)
Pd^{112}	21 h		β^-,γ	U(thn,f)
Pd^{113}	1.4 m		β^-, no γ	U(d,f)
				$Cd^{116}(15\ Mev\ n,\alpha)$
Pd^{114}	2.4 m		β^-, no γ	U(d,f)
Pd^{115}	45 sec		$[\beta^-]$, no strong γ	U(d,f)

III. PALLADIUM CHEMISTRY OF INTEREST TO RADIOCHEMISTS

Palladium belongs to Subgroup VII, platinum metals, transition series Ru, Rh, Pd.

Palladium and platinum resemble one another more closely than any other pair in the group of platinum metals. Both elements are normally only divalent and tetravalent; with palladium the tetravalency is much less stable than the divalency, while with platinum both are equally stable. There are some indications that monovalent palladium exists, but no such compound has been isolated. Trivalent palladium compounds do

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exist, and have been isolated, but they are unstable and are
unlikely to be encountered in radiochemical work.

Palladium is the most abundant of the platinum metals in
the earth's crust as a whole, forming about 1 part in 10^8, which
is about twice as much as platinum. The element is found
together with the other platinum metals, as well as in special
minerals such as braggite (a mixture of platinum, palladium and
nickel sulfides), which contains about 20 per cent of palladium,
potarite (PdHg) and stibiopalladinite (Pd_3Sb). The element can
also be recovered from the anode mud of copper and nickel re-
fining plants.

A. Metallic Palladium

Palladium is a silvery-white ductile metal with a melting
point of 1553.6° C (3). Its density is variously given, depend-
ing upon its physical condition, ranging from 11.4 at 22.5° C (4)
to 11.97 at 0° C (5). It is known that absorption of hydrogen
decreases the density (6). The latter reference gives the value
11.96 at 18° C.

The element can be obtained in different physical states,
compact and colloidal metal, palladium sponge and palladium
black. The metal alloys with most metals, is a powerful catalyst
(especially as the palladium black or colloidal metal), and
absorbs many different gases (the most readily absorbed is
hydrogen).

Compact palladium is only slightly attacked by concentrated
hydrochloric acid, but the finely divided metal obtained by
reduction with Zn dissolves easily in hot hydrochloric acid.
Dilute nitric acid has little action on the metal, although it
does dissolve palladium when present in certain alloys, such as
those with silver or copper. Concentrated nitric acid readily
attacks the metal. Palladium is readily dissolved in aqua regia.

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The halogens dissolved in hydrochloric acid also dissolve the metal. Boiling sulfuric acid dissolves the metal, more easily in the presence of an alkali or ammonium sulfate. Palladium is not attacked by hydrofluoric acid. Palladium, like rhodium, but unlike platinum, osmium and indium, dissolves in fused potassium hydrogen sulfate, yielding palladous sulfate. The metal is also dissolved in fused ammonium sulfate or nitrate, forming an amine. Fusion with sodium peroxide or alkali hydroxide converts it into the hydrated palladium monoxide.

By means of its electrochemical behavior, palladium can be precipitated as a metal from its salt solution by many different reagents, unless it is in solution in the form of a very stable complex. Silver does not reduce palladium as a metal from solutions of its salts, but palladium salt solutions are reduced by all metals which reduce silver from solutions of silver salts. Palladium is also reduced out as a metal from solution of palladium dichloride by hydrazine hydrate, potassium nitrite, phosphorus, formic acid, methane, acetylene and sulfurous acid. The reduction by ethylene is recommended as a means of separating palladium from the other platinum metals (7). Sulfur dioxide precipitates the metal from a solution of palladous nitrate and sulfate, but not from a solution of palladium dichloride.

B. Palladium Compounds

Palladium monoxide (or palladous oxide), PdO. The oxide can be prepared by many different methods. For example the oxide can be obtained by heating palladium in oxygen at 830° C, by strongly heating palladium amalgam, by fusing palladium with sodium peroxide or alkali hydroxide, by treating solutions of palladous salt with alkali hydroxide, or hydrolyzing a faintly acidic solution of the nitrate by boiling it with water.

The hydrated oxide prepared by the wet processes contain

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rather more water than corresponds with palladous hydroxide, $Pd(OH)_2$. The precipitated hydroxide separates with varying amounts of combined water, and the color varies in a corresponding manner from yellowish-brown to black. The anhydrous oxide is obtained only by heating the hydrate at 800° to 840° C in oxygen. When precipitated in the cold, the hydrated monoxide is soluble in diluted acids, and in an excess of alkali hydroxide, but when precipitated hot, or boiled in the mother liquor, it is no longer completely soluble, even in boiling, concentrated alkali hydroxide. When dried at 100° C, it is insoluble in acetic acid, and nearly insoluble in sulfuric and nitric acids. The anhydrous oxide is very sparingly soluble in hydrochloric acid, and in aqua regia.

Palladium dioxide, PdO_2. The dioxide can only be made in the wet way, and is only known in the hydrated form. Hydrated dioxide, $PdO_2 \cdot nH_2O$, can be prepared as a dark red precipitate by treating a solution of potassium chloropalladate, K_2PdCl_6, with a slight excess of potassium hydroxide. When the precipitate is washed and dried over concentrated sulfuric acid, a product which approximates $PdO_2 \cdot 2H_2O$, or $Pd(OH)_4$ is obtained.

The hydrated dioxide is unstable, and it decomposes slowly into monoxide and oxygen even in contact with cold water. When freshly precipitated, it is insoluble in a diluted solution of sodium hydroxide.

The hydrated dioxide is a strong oxidizing agent and reduces hydrogen peroxide both in acidic and alkaline solutions.

Palladium difluoride, PdF_2. The compound can be obtained as a brown precipitate when hydrofluoric acid is added to a concentrated solution of palladous nitrate. The product is sparingly soluble in water, but more soluble in hydrofluoric acid. Potassium fluopalladite, K_2PdF_4, is precipitated when

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potassium fluoride is added to a solution of palladous nitrate.

Palladium tetrafluoride. No fluorine compounds of tetra-valent palladium, simple or complex, are known.

Palladium dichloride (or palladous chloride), $PdCl_2$. The salt can be prepared by evaporating to dryness a solution of palladium in aqua regia, and dehydrating the residue by a gentle heat. It is also formed, as a sublimate, by heating spongy palladium or palladium sulfide in chlorine.

The anhydrous dichloride forms red crystals which are very hygroscopic and readily soluble in water, from which they crystallize in hygroscopic crystals of the dihydrate $PdCl_2 \cdot 2H_2O$.

In hydrochloric acid solutions, $PdCl_2$ forms the complex ions $PdCl_4^{2-}$. The dissociation constant of the chloropalladite ion, $(Pd^{2+})(Cl^-)^4/PdCl_4^{2-}$, has been found by emf measurement to be about 6×10^{-14} at $25°$ C (8). The complex forms a series of salts which have the general formula $M_2^I[PdCl_4]$. By evaporating a solution containing palladium dichloride and alkali chlorides, crystals of the alkali-tetrachloropalladate(II) salts (or alkali-chloropalladite) is formed, e.g., $K_2[PdCl_4]$, which is very soluble in water.

Though the different amine complexes of palladium are discussed later, it is important to pay attention to the fact that palladium forms both complex anions and cations. By treating a solution of palladium dichloride with ammonia, a precipitate is first formed, which is redissolved in an excess of ammonia, yielding the tetraamine complex, $Pd(NH_3)_4^{2+}$. By adding hydrochloric acid to this solution, the palladous dichlorodiamine, $[Pd(NH_3)_2Cl_2]$, is precipitated out. The salt is slightly soluble in water, sparingly soluble in hot nitric acid, soluble in potassium and sodium hydroxides and ammonia, and soluble in hot concentrated hydrochloric acid.

Palladous dichloride is very readily reduced in solution to the metal. The different reducing reagents are discussed elsewhere in this document.

Palladium tetrachloride (or palladic chloride), PdCl4. An aqueous solution of the tetrachloride as the complex $PdCl_6^{2-}$ can be obtained by dissolving palladium dichloride in concentrated aqua regia with gentle heating. The dark brown solution contains a mixture of $PdCl_4^{2-}$ and $PdCl_6^{2-}$ and it gives a precipitate of potassium chloropalladate, $K_2[PdCl_6]$, when treated with potassium chloride, while potassium chloropalladite, $K_2[PdCl_4]$, remains in solution. Palladium tetrachloride has not been isolated.

Palladium dibromide (or palladous bromide), PdBr2. The compound is obtained by the action of a mixture of hydrobromic and nitric acids on the metal, and removing the nitrous acids by boiling and evaporation with an excess of hydrobromic acid. The brown, amorphous mass is insoluble in water and in alcohol, but soluble in hydrobromic acid. It is decomposed by water.

Tetrabromopalladate(II) salts (or bromopalladite salts) of the form $M_2^I[PdBr_4]$ have been obtained.

Palladium tetrabromide (or palladic bromide), PdBr4. The compound has not been prepared, only complex salts of the form $M_2^I[PdBr_6]$.

Palladium diiodide (or palladous iodide), PdI2. The diiodide is prepared by the addition of potassium iodide to a solution of a palladous salt in slight excess. When the salt is dried in air, the monohydrate, $PdI_2 \cdot H_2O$, is formed. To obtain the anhydrous diiodide, the precipitate must be dried in vacuo.

The compound is insoluble in water, alcohol, ether, diluted nitric acid, and hydrochloric acid, slightly soluble in hydriodic acid and hot, concentrated nitric acid, soluble in ammonia and methylacetate, and easily soluble in a solution of

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potassium iodide, forming the complex, $PdI_4{}^{2-}$. From a solution containing this complex, complex iodides such as $M_2^I[PdI_4]$ can be obtained.

No _iodine compounds of tetravalent palladium_, simple or complex, are known.

Palladium mono- and disulfides, PdS and PdS$_2$. Palladium monosulfide (or palladous sulfide) can be obtained by the action of hydrogen sulfide on a solution of a palladous salt. The precipitate is insoluble in ammonium sulfide and in hydrochloric acid, but it is soluble in nitric acid and aqua regia.

If the thio salt formed by adding excess of alkali sulfide to a solution of a palladous salt is decomposed with acetic acid in presence of a large quantity of ammonium acetate, the palladium disulfide is precipitated. The precipitate can be filtered very easily, and is in such a condition that it can be weighed directly for the determination of the content of the metal (9).

Palladium monosulfide can also be made by heating metallic palladium with sulfur.

Palladium disulfide is obtained by melting together palladium monosulfide or ammonium chloropalladate with a mixture of equal parts of sulfur and sodium carbonate.

Other palladium salts.

Palladous nitrate, $Pd(NO_3)_2$, can be obtained by dissolving palladium in nitric acid. The compound cannot be perfectly dried. The salt is very soluble in water, yielding a solution which is readily hydrolyzed, forming hydrated palladium monoxide.

Palladous sulfate, $PdSO_4$, can be obtained by dissolving palladium in hot, concentrated sulfuric acid in the presence of an alkali or ammonium sulfate, or by fusing palladium with potassium hydrogen sulfate. Both the dihydrate and the monohydrate are hygroscopic and are easily hydrolyzed by water,

yielding hydrated palladium monoxide and basic sulfates.

Palladous cyanide, $Pd(CN)_2$, is formed when a solution of potassium or mercuric cyanide is added to a solution of palladium in aqua regia. No other platinum metals form cyanides under these conditions (10). Palladous cyanide gives complex salts with alkaline cyanides.

Palladous thiocyanate, $Pd(CNS)_2$, is obtained as a reddish precipitate when a solution of a palladous salt is treated with ammonium thiocyanate. The compound is soluble in an excess of the reagent, forming the complex anion, $Pd(CNS)_4^{2-}$.

Complexes of divalent palladium. Divalent palladium forms fairly stable complexes, in nearly all of which it has a co-ordination number of 4. The stability of the complexes is greater than with nickel, but less than with platinum. The 4-covalent complexes are nearly all of four types (11): i) $[PdAm_4]Cl_2$; ii) $[PdAm_2Cl_2]$; iii) $[(PdAmCl_2)_2]$; and iv) $(NH_4)_2$ $[PdCl_4^-]$, in which Am represents ammonia, an amine, or half a diamine, and the chlorine atoms can be replaced by other acidic groups. The NH_3 can also be replaced by the sulfur or selenium of the thio- or seleno-ethers, or by oxygen.

This is not the place to describe the numerous different complexes of palladium which have been isolated. Only a few complexes will be mentioned briefly, to give an idea of the different types of complexes which can be formed.

The simple palladous tetraaminochloride, $[Pd(NH_3)_4]Cl_2$, can be formed by the action of dry ammonia on dry palladous chloride. It is very soluble in water, forming the complex cation $Pd(NH_3)_4^{2+}$. A series of tetraamine salts has been made, with ammonia, pyridine, ethylene diamine, etc. (12).

The diamines, $[PdAm_2Cl_2]$, which are not ionized, have been made in great variety. One method to obtain the compounds is

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by the action of acid on the tetraamine. The simplest diamine,
$[Pd(NH_3)_2Cl_2]$, is, for example, formed by adding hydrochloric
acid to a solution of tetraaminochloride. The chlorine atoms
in the general formula of the diamines can be replaced by various
other radicals both monovalent and divalent. Well known are
bromides, iodides, nitro-compounds, and oxalato-compounds.

The coordinated molecule Am in the complexes of the type
$[(PdAmCl_2)_2]$ is not an amine, but can be a tertiary phosphine
or arsine, or another molecule such as carbon monoxide or even
ethylene (11).

The anionic complexes are all of the type $M_2^I[PdR_4]$, where
R can be CN, CNS, NO_2, Cl, Br, or I.

There exist also many chelate complexes where the palladium
atom may be attached to nitrogen, oxygen, and/or sulfur atoms.
Many of these complexes are used for the separation and/or deter-
mination of palladium. The chelating agents will be mentioned
in the chapter covering the analytical chemistry of palladium.
Only the glyoxime compounds will be described here as an example
of these chelate complexes. The substituted glyoxime complexes
are dichelate, and of the type:
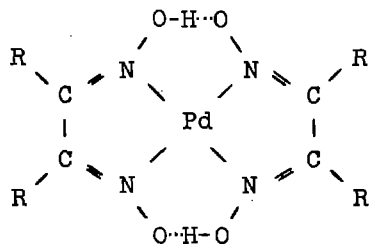
The compounds can be made by the action of the glyoxime on
palladium dichloride in hydrochloric acid solution. Examples
of these glyoxime compounds, which are very slightly soluble in
water, are the complexes of dimethylglyoxime, benzoyl-methyl-
glyoxime, and α-furildioxime.

Complexes of tetravalent palladium are only confined to a few complex sulfides, halides, and amines. The most important are the complex halides of the type $M_2^I[Pd(Hal)_6]$, where (Hal) represents chlorine or bromine. The potassium chloropalladate, [or potassium hexachloropalladate(IV)], $K_2[PdCl_6]$, can for example be obtained by dissolving palladium dichloride in aqua regia, and precipitating the salt by adding potassium chloride to the solution. (Described earlier in this document.) The complex salt dissolves in dilute hydrochloric acid, and is slightly soluble in water. The solubility product of $K_2[PdCl_6]$ in water at 25° C is found to be 6×10^{-6} (13).

IV. THE ANALYTICAL CHEMISTRY OF PALLADIUM

A. Separation by Precipitation

The concentration of palladium from ores prior to a gravimetric determination, can be carried out by cupellation or fire assay methods (14,15,16,39). The results of the analysis based on these methods are too small, however, owing to losses of palladium during the fire assay (15,16).

Palladium may be concentrated from diluted solutions by coprecipitating with elemental tellurium obtained by reduction of a tellurite with stannous chloride or similar strong reducing agents. Gold, silver, and rhodium accompany palladium. Tellurium can be volatilized from the collected precipitate by ignition. Addition of ammonium iodide accelerates the volatilization (17).

Small amounts of palladium may also be recovered from dilute solutions by precipitating palladium with hydrogen sulfide in the presence of lead (18).

Procedures for the systematic separation and determination of the platinum metals may be found in many textbooks of quanti-

tative inorganic chemistry and in published papers (19-23). Having a solution of only platinum metals, one of the standard methods (23) is to remove osmium and ruthenium by distillation of OsO_4 and RuO_4, followed by precipitating rhodium, palladium, and iridium as hydrated oxides (24), leaving platinum in solution. Palladium is then separated from rhodium and iridium by dissolving the hydrated oxides in hydrochloric acid and precipitating palladium with dimethylglyoxime.

The precipitation of palladium as cyanide or iodide has been recommended as a separation from the other platinum metals, as well as from gold and basic metals, except silver, copper, and lead (19).

Palladium can also be separated as the metal from the other platinum metals by reducing out the metal from a hydrochloric acid solution at $80°$ C by ethylene (7). The reaction is reported to be specific for palladium, but two hours are needed for quantitative precipitation.

A literature survey clearly shows that the uppermost used reagent for both separation and determination of palladium is dimethylglyoxime. It was first introduced by Wunder and Thüringer (25), and has together with a few other organic reagents, practically displaced reagents formerly used, such as mercuric cyanide, hydrogen sulfide, and potassium iodide. The dimethylglyoxime complex with palladium is formed in dilute acid solutions, is sparingly soluble in water and dilute hydrochloric or nitric acid, soluble in ammonia, chloroform and benzene, and decomposes in concentrated nitric acid and in aqua regia. For the use of dimethylglyoxime as a reagent for both separation and determination of palladium, see the references (23,26) and the references listed in chapter VII in this monograph.

Many derivatives of glyoxime other than the dimethyl deriva-

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tive have been used as a reagent for the gravimetric determina-
tion of palladium. Holtzer (26) reports that benzoyl-methyl-
glyoxime, as well as dimethylglyoxime (and salicylaldoxime) pre-
cipitates palladium quantitatively from a solution of palladium
dichloride in 2-3 $\underline{M}$ hydrochloric acid. Platinum will not inter-
fere under these conditions. α-furildioxime has also been used
as a precipitant for palladium (27). Other reagents which can
be classified as derivatives of glyoxime are 1,2-cyclohexanedione-
dioxime (28) and 4-methyl-1,2-cyclohexanedionedioxime (29). The
latter reagent is reported to be an excellent reagent for the
gravimetric determination of both palladium and nickel. Nickel
precipitates quantitatively at pH 3, and palladium in the pH
range 0.7 to 5. The reagent is water soluble, and will therefore
form precipitates nearly free from contamination of excess re-
agent. The precipitate filters easily and does not creep. It
seems to have some advantage in preference to dimethylglyoxime
as a precipitant for palladium, but because of its higher equiva-
lent weight, the precipitate is likely to be more bulky than the
precipitate formed by dimethylglyoxime, and thus may involve a
higher degree of coprecipitation.

Other satisfactory reagents used for the precipitation of
palladium are salicylaldoxime (26,30), 1-nitroso-2-naphthol (31,
32), 3-hydroxy-1,3-diphenyltriazine (33), β-hydroxy-naphthaldehyde
(34) and thiourea (35). Fraser et al. (30) have separated 5 mg
quantities of palladium from a concentrated lead solution by a
double precipitation with salicylaldoxime, and Holtzer (26) re-
ports that platinum will not interfere if palladium is precipitated
with the same reagent from 2-3 $\underline{M}$ hydrochloric acid. In addition
to palladium 1-nitroso-2-napthol will precipitate gold and many
other elements from hydrochloric acid solutions, but it will not
precipitate the other platinum metals.

The 3-hydroxy-1,3-diphenyltriazine (33) is not only use-
ful for determination of palladium in the presence of other
members of the platinum group, but it is also a rather specific
reagent when other elements are concerned. Below pH 3 it forms
precipitates only with $Cu(II)$, $Pd(II)$, $Fe(II)$, $Fe(III)$, vanadate,
$V(III)$, $Ti(IV)$, and molybdate. All but those of $Cu(II)$ and
$Pd(II)$ decompose on heating in acidic medium, thus making the
reagent highly selective for $Cu(II)$ and $Pd(II)$. The palladium
complex is granular, not voluminous like the dimethylglyoxime
complex, is more stable toward heat and acid than the same com-
plex, and can be filtered quickly in the hot state. $Au(III)$,
$Ag(I)$ and $Os(IV)$ interfere because they are reduced to the
metallic state by the reagent. The palladium complex is soluble
in a mixture of concentrated sulfur and nitric acid (4:1), and
is also very soluble in benzene and chloroform.

B. Separation by Solvent Extraction

Morrison and Freiser (36-38) have reviewed the applications
of ion association and chelate complex systems to the determina-
tion of most of the elements. Attention should also be given to
the article of McBryde (39), a review of the different methods
which can be used for the separation of gold and the six platinum
metals, and to an article which discusses solvent extraction in
radiochemical separations (40).

The following methods for separating palladium by solvent
extraction have not been reported to have been used in any radio-
chemical separation procedure, except for the extraction of palla-
dium by dimethylglyoxime into chloroform (108, 115). Therefore,
when certain elements in a specific extraction method are re-
ported not to interfere, it means that the elements do not in-
terfere in measurements which are based on principles not in-
volving the detection of radioactive disintegrations. Attention

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should also be paid to the fact that many of the procedures are
only developed for specific purposes which involve separation of
palladium from a restricted number of elements. Even if non-
radiochemical separation methods are concerned, many of the
methods therefore need a more intensive investigation before they
can be used in the general case. This is even more true if palla-
dium is going to be separated radiochemically, because radio-
active contaminants can interfere seriously even if they are
only extracted in extremely small quantities. This review is
therefore mainly meant to be used as a basis for developing
radiochemical separation procedures for palladium.

C. Ion Association Systems

Duke and Stawpert (41) have reported that palladium can be
separated from niobium and zirconium by extraction of the iodide
complex, PdI_4^{2-}, into isobutyl methyl ketone. The aqueous
solution was 20% v/v with respect to sulfuric acid, and con-
tained 4 moles of potassium iodide for every mole of palladium.
The system was not studied exhaustively with regard to inter-
ferences, but they found that chloride ions allowed a partial
extraction of both niobium and zirconium. They also found that
palladium sulfate was extracted 80% into isobutyl methyl ketone
in the presence of only 20% v/v of sulfuric acid. West and
Carlton (42) found that Pd, Bi, Hg, Fe, Pb, Cu, Cd, Rh, Au, and
Ru were extracted at least partially as iodides into several
organic solvents, including methyl isobutyl ketone. The metals
were extracted from solutions of their iodides in the presence
of potassium iodide and hydrochloric acid. McBryde (39) has
found that palladium can be separated from platinum and rhodium
by extracting palladium from a hydroiodic acid solution into
isobutyl methyl ketone, but doubts whether the separation possesses
the practical advantages found in other methods.

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Palladium can be completely extracted into methyl iso-propyl-
ketone from acidic aqueous solutions containing thio-cyanate ions
(43). Fe, Cu, Zn, Hg and Au are also extracted. The thiocyanate
complex of palladium is also reported to be extracted with butyl
or iso-amylalcohol (43). The system needs further investigation
as far as interferences from other elements are concerned.

Between pH 6.3 and 10.3, West et al. (44) were able to ex-
tract copper by a solution of 5% capric acid in ethyl acetate.
Mn, Fe, Ni, Co, Ru and Pd are also extracted to a more or less
extent. The system needs more investigation with regard to ex-
traction of palladium.

The technique of liquid-liquid extraction with high-molecular
weight amines has also been used for extraction of palladium.
Ziegler has extracted the palladium complex formed when a solution
of palladium nitrate is treated with sodium thiosulfate, into
methylene chloride by tributylammoniumacetate. The only elements
interfering are Ag, Pb, V and U (45). Ziegler (46) has also ex-
tracted the citrate and tartrate complexes of palladium into
methylene chloride by tri-n-butylammoniumcitrate and tri-n-butyl-
ammoniumtartrate respectively, using an excess of tri-n-butyl-
amines. Elements which are extracted to a more or less extent
are V, U, Fe, Bi, Au, Rh, Zr and Ce.

D. Chelate Complex Systems

Palladium forms a chelate complex with dimethylglyoxime
which can be extracted into chloroform. Young (47) separated
palladium from platinum, gold and silver by extracting palladium-
dimethyl-glyoximate out of a solution approximately 1 $\underline{M}$ in H$_2$SO$_4$.
Small quantities of nitric acid and hydrochloric acid prevented
gold and platinum from interfering. Fraser et al. (30) report
that palladium was completely extracted with chloroform from
dilute nitric acid after the palladium had been complexed with

dimethylglyoxime. Palladium was separated from Pb, Pt, Ni, Cu and Fe, the latter element causing the only interference. With the use of EDTA (disodium salt of ethylene diaminetetraacetic acid), the interference from iron was prevented.

Glyoxime compounds other than the dimethylglyoxime have also been used for separating palladium. Menis and Rains (48) report that palladium can be separated from gold and the other platinum metals by extracting the palladium-alpha-furildioximate from a solution of hydrochloric acid (0.1-1.4 N HCl) into chloroform. Cyanide ions prevent the formation of the alpha-furildioxime complex.

Sodium diethyldithiocarbamate has proved an effective extraction reagent for almost two dozen metals (36). The selectivity of the reagent can be improved by using sodium ethylenediaminetetraacetate (EDTA) as a masking agent, and by a proper adjustment of the pH. Bode (49) has found that palladium can be extracted as the diethyldithiocarbamate complex from a solution which contains EDTA. At pH 11.0, Cu, Ag, Hg, Bi, Tl(III), Au, Os and Pt are also extracted to a more or less degree. Palladium has also been extracted as the same complex from strong hydrochloric acid solutions into chloroform (50). This latter system needs more investigation when interferences from other elements are concerned.

Cheng (51) has separated palladium from a number of elements by using 2-nitroso-1-naphthol. The palladium complex is formed at a pH 1.5 - 3.5 and after adding EDTA as a masking agent, the solution is made basic with ammonium hydroxide and the palladium naphthalate is extracted into toluene. When measuring spectrophotometrically, Fe, Cu, Ni, Co, Cr and the Pt metals do not interfere. Ross et al. (52) have also used this reagent for separation and determination of palladium in presence of a large

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amount of uranium, containing ruthenium, rhodium and zirconium. Their procedure was based upon Cheng's method, but to avoid precipitation of uranium as a diuranate prior to the extraction of the palladium naphthalate, the extraction was carried out in a pH range of 1 to 2. The excess reagent was also extracted under these conditions, but it could be scrubbed from the toluene phase with a dilute solution of sodium hydroxide. The amount of palladium was measured spectrophotometrically. No interference of U, Ru, Rh and Zr could be detected by this method.

Dithizone in carbon tetrachloride extracts palladium(II) quantitatively from 1 N (and doubtless stronger) hydrochloric acid solutions. Other metals extracted are gold(III), silver, mercury, and copper. Much chloride, and especially bromide, prevents reaction of silver (53). Young (47) found that in the presence of dimethylglyoxime, hydrochloric acid, and nitric acid, dithizone does not react with silver, gold and platinum(IV).

As pointed out earlier in this document, 3-hydroxy-1,3-diphenyltriazine is a specific reagent for palladium. Of all the complexes which are formed at a pH below 3, only those of copper and palladium are stable against heating in acid solution (33). The fact that the complexes are very soluble in benzene and chloroform may perhaps be used as a method of separation of palladium from many other elements by solvent extraction.

8-mercaptoquinoline (thiooxine) has been used as a reagent for colorimetric determination of palladium (54). The complex is stable in strong acid solution, and can be easily extracted by most organic solvents. Palladium has been determined in the presence of Pt, Os, Ru, Rh, Ir, Cu, Ag, Au, Hg, Fe, Ni, Co, Zn, Cd, Ge, Mn, Tl, As, Sb, Bi, Sn, Se, W, Mo, Pb, U and Y.

Cheng et al. (55) have investigated 1-(2-pyridylazo)-2-naphthol as a possible analytical reagent. It forms complexes

with a number of different elements, including palladium. Almost
all of them are soluble in amyl alcohol. A further study with
the reagent, particularly of the effect of pH upon extraction,
might be quite fruitful.

Palladium also forms a complex with phenylthiourea in dilute
hydrochloric acid which is quantitatively extracted into either
ethyl or amyl acetate. 40% of Pt(IV), 16% of Cu, and under 1% of
Ir(IV), Rh(III), Ru(III), Os(IV), Au(III), Fe(III), Co, Ni, and
Cr(VI) are extracted (56).

Beck (57) has shown that thiosalicylideneethylenediimine
forms chloroform-extractable complexes with a number of elements,
including palladium. Mercury(II) forms the most stable complex
and can displace the other metals. The system needs further
investigation.

8-hydroxyquinoline (8-quinolinol, or oxine) are known to
form chelate complexes with a number of elements, including palla-
dium. Oxine extraction has been studied in detail for almost
twenty metals. The pertinent data is summarized by Morrison and
Freiser (36). No separation methods for palladium, based upon
extraction of the oxine complex have been reported, but from the
data given (36) it seems reasonable to assume that palladium may
be extracted from a dilute hydrochloric acid solution into chloro-
form with little interference from other elements.

Other reagents used for extraction of palladium are mentioned
briefly below. p-nitrosodimethylaniline has been used for
separating palladium from platinum by extraction into purified
chloroform (50). p-nitrosodiphenylamine is able to separate
palladium from Pt, Rh and Ir by extracting the palladium complex
into ethylacetate, ether, or chloroform (58,59). Sa (60) has
extracted palladium with 5-methyl-8-quinolinol into chloroform.
Dutt et al. (61) used diallyldithiocarbamidohydrazine and chloro-

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form, and Kodama (62) coniferin, HClO$_4$, and chloroform. Palladium
has also been separated from Pt, Rh and Ir by using antipyrine,
HCl and KI in the aqueous phase and chloroform as the organic
phase (63). Prior to a colorimetric determination of palladium,
Peshkova et al. (64) extracted the element into benzene by
salicylaldehyde from a weakly acid solution containing a large
excess of hydroxylamine, and also by means of 1,2-naphthaquinone,
a large excess of hydroxylamine, and chloroform. Co, Cu, Ni, Fe,
Pt(IV) and Ir(IV) did not interfere.

Clark (65) reports that dibenzoyldithiol, in strong hydro-
chloric acid, only gives a stable complex with Pd(II) and Se(IV).
The extraction of the palladium complex has not been investigated.
Ziegler et al. (66) have used the reaction between palladium and
isopropenylacetylene as a qualitative test for this element. They
report that the isopropenyl-palladiumacetylid formed, is extract-
able into chloroform, and that the reagent used is fairly specific
for palladium. Other reagents which are more or less specific
for detection of palladium are phenoxthin (phenothioxine), thio-
glycolic acid, and thiomalic acid (67). It is possible that these
reagents may prove to be useful in separation procedures for palla-
dium.

E. Separation by Ion Exchange

Stevenson et al. (68) have separated palladium from Pt, Rh,
and Ir by the use of the cation resin, Dowex-50. The solution
of these metals was taken near dryness repeatedly with a mixture
of nitric acid and perchloric acid until every trace of halide
ions was removed, and the ions were left in a small volume of
fuming perchloric acid. The solution was diluted with water and
was run into the top of the resin. Platinum passed through, but
the others were retained. Palladium was then easily stripped from

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the column with dilute (0.05-0.5 $\underline{M}$) hydrochloric acid, while rhodium and iridium were gradually eluted with 2 $\underline{M}$ and 4-6 $\underline{M}$ hydrochloric acid respectively. Karttunen et al. (69) used the same method, and reported that palladium was quantitatively eluted with 0.3 $\underline{M}$ hydrochloric acid.

The behavior of the platinum metals towards both cation and anion exchange resins has been investigated by MacNevin et al. (70). If the chlorides of platinum, palladium, rhodium, and iridium are treated with ammonia and passed through the cation resin, Amberlite IR-100, all the metals, except palladium will be quantitatively eluted. Palladium can be eluted by 1 N HCl. If a mixture of the complex chlorides of the same four elements are run into the anion resin, Dowex-2, all the elements are ad-sorbed. By eluting with an ammonium hydroxide-ammonium chloride solution, palladium will be eluted first, and will be free from the other three metals.

Berman and McBryde (71) investigated the separation of rhodium, ruthenium, palladium, platinum and iridium by the anion resin, Amberlite IRA-400. A solution of all these elements was evaporated to dryness, the residues were dissolved in water, the solution treated with hydroxylamine to reduce iridium(IV) to the trivalent state, and the solution was fed to the resin. Rh, Ru and Ir were eluted with 2 $\underline{M}$ HCl, and palladium by 9 $\underline{M}$ HCl. Palladium was contaminated with platinum, which was due to bivalent platinum obtained when the solution was treated with hydroxylamine. Palladium free from platinum was obtained by oxidizing the bivalent platinum to the quadrivalent state by nitric acid, evaporating to dryness with hydrochloric acid, dissolving the residue in a few milliliters of 2 $\underline{M}$ hydrochloric acid, feed-ing the solution to the resin, and eluting palladium with 12 $\underline{M}$ hydrochloric acid. The removal of the palladium from the resin

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takes a long time and needs a large amount of eluting solution.
Kraus et al. (72,73) found that the adsorbability of the chloro
complex of palladium, even in concentrated hydrochloric acid,
was still sufficiently large to preclude its easy removal from
a resin of Dowex-1, and they recommend a displacement of the
strongly adsorbed Pd(II) complex by other strongly adsorbed
chlorocomplexes, e.g., those of Zn(II) or Cd(II) in 6 $\underline{M}$ HCl.

A systematic investigation of the behavior of the chloro-
complexes of rhodium, ruthenium, palladium, iridium and platinum
toward the strong anion exchange resin, Permutit ES, in the
hydroxyl chloride and acetate form has been performed by Blasius
et al. (74). Rhodium and ruthenium were precipitated out as
hydroxides on the resin in the hydroxyl form, while palladium
could be eluted by 1 N NaOH, free from platinum and iridium.

Other investigations of the behavior of a number of elements,
including palladium, toward different ion-exchange resins, can
be found in the literature. Kraus et al. (73) give adsorption
data for almost all the elements in the periodic table, using
hydrochloric acid with different molarities and the anion resin,
Dowex-1. Buchanan et al. (75) give elution characteristics of
Pu, Zr, Nb, Mo, Ru, Rh, Pd, Ce, U, Am and Fe in nitric acid
medium, using Dowex-1, Faris (76) gives a review of the behavior
of some 50 elements in a hydrofluoric acid medium, using the anion
resin, Dowex-1, and Hicks et al. (77) have investigated the
qualitative anionic behavior of a number of metals toward the
anion resin, Dowex-2. They fed a mixture of the elements in
12 $\underline{M}$ HCl onto the resin, and then eluted selectively by alter-
ing the species and concentration of the eluent. After having
decreased the molarity of the hydrochloric acid in steps from
12 N to below 0.01 N, and treated the resin with 3 $\underline{M}$ HClO$_4$,
palladium was found to be eluted by 1 $\underline{M}$ NH$_4$OH, together with

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Ag, Sb(III) and Sb(IV).

Attention should also be paid to Kallmann et al. (78) who describe a method which allows the determination of Cu, Al, Fe, Ni, Co, Ce, Ag, Au and Pd by using both cation and anion exchange resins, and to Pshenitsyn et al. (79) who separated the platinum metals, Pt, Pd, Rh and Ir, from the base metals, Cu, Ni, Fe and Pb by using a cation exchange resin. Freshly prepared chlorides of the four platinum metals were not adsorbed on the resin from 0.01-0.1 N hydrochloric acid solutions containing about 1 per cent sodium chloride, while the other metals were retained on the resin. These metals could be eluted by 1 N HCl.

F. Separation by Paper Chromatography

Lederer (80) has separated Ag, Cu, Pd, Pt and Au by using n-butanol saturated with 1 N HCl and upward diffusion. He has also separated carrier-free Pd^{103} from rhodium foils, bombarded with deuterons $[Rh^{103}(d,2n)Pd^{103}]$, by the same technique (81). In an attempt to purify a source of Pd^{103}, containing macro amounts of stable palladium ($\sim$ 2 g), he found, by using the same technique as described above, that the palladium activity was contaminated with tracers of radioactive platinum. He was not able to separate this impurity from the palladium, and concluded that although such separations are quantitative for analytical purposes, the overlapping activities are too large to produce a radiochemically pure source even after repeated chromatography.

A description of the qualitative separation of the platinum elements by paper chromatography is given by Burstall et al. (82). They have investigated several systems containing a different combination of the ions Pt^{4+}, Pd^{2+}, Rh^{3+}, Ir^{4+}, Ir^{3+}, Ru^{4+}, Ru^{3+}, Os^{4+}, and Au^{3+}. More or less good separations were achieved depending on the solvent used, the ions present, and the valency

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state of the metals in solution. By using ethyl methyl ketone
or methyl n-propyl ketone containing 30% (v/v) of concentrated
hydrochloric acid (d = 1.18), and downward diffusion, they
separated Au^{3+}, Pt^{4+}, Pd^{2+}, Rh^{3+} and In^{3+} into four bands, one
of which contained both rhodium and iridium. Rh and Ir could be
separated by oxidizing Ir^{3+} to Ir^{4+} by chlorine water and using
acetone containing 5% (v/v) of concentrated hydrochloric acid
as solvent.

Kember et al. (83) have developed methods for the quantita-
tive separation and determination of Pt, Pd, Rh and Ir on the
microgram scale. They make use of downward diffusion of three
solvents, the choice of which depends on the type of mixture to
be analyzed. By using a solvent mixture of isobutyl methyl ketone
(hexone), pentanol, and concentrated hydrochloric acid, in the
proportion 60:10:30 by volume, palladium could be separated from
rhodium, iridium, platinum, gold, and a number of other base
metals. They found that the metal solution must be treated
with sodium chlorate in order to prevent the palladium band
from being contaminated with divalent platinum. The same authors
also achieved a partial separation of gold, platinum, palladium
and rhodium as their chlorocomplexes, by using sheets of paper
prepared from cotton fabrics which had been treated with 2-amino-
ethyl sulfuric acid. A solution of 2 N hydrochloric acid was
used as developing solvent. They report that the bands were
diffuse and slightly overlapping (84).

Separation of Au, Pt, Pd and Rh have also been carried out
by Shibata (85) by using upward diffusion of different solvent
mixtures. Best separation was obtained by a mixture of ether,
butylalcohol and concentrated hydrochloric acid in the ratios
1:2:1.5. Good separations were also achieved by using a mixture
of ether, amylalcohol and concentrated HCl in the ratios 1:2:1.5,

and a mixture of methylethylketone and concentrated HCl in the ratios 7:3.

G. Separation by Electrodeposition

Little work has been done with this technique. As so far is known, the only paper describing this method is presented by Bubernak (86). He investigated the separation of all the platinum metals, except osmium and ruthenium, by electrodeposition. From a solution of the chlorides of palladium, rhodium and iridium, which was 0.5 $\underline{M}$ in hydrochloric acid, 3.0 $\underline{M}$ in sodium chloride, and which contained 8.0 grams hydrazine dihydrochloride added per 175 ml solution (as an anodic depolarizer), Bubernak was able to separate these three metals. At 60° C palladium was deposited at a cathode potential of +0.050 volts vs. the saturated calomel electrode, and rhodium at -0.250 to -0.275 volts. Iridium was precipitated from the solution as the hydrated dioxide and ignited to metal in an atmosphere of hydrogen. The potential range for the reduction process for platinum overlaps those of the other processes, thereby excluding the possibility for separating platinum from the other metals. This was also true when other supporting electrolytes were tried (sulfate, perchlorate, phosphate, oxalate, and others).

V. DISSOLUTION OF SAMPLES CONTAINING PALLADIUM

A very good review of the different methods of dissolution of inorganic and organic samples is given by Willard et al. (87) and Dunlop (88) respectively. A fairly complete review is also compiled by Calkins (89). For choosing the method that is best adapted to the material to be analyzed, attention should also be given to Hillebrand et al. (90), who give a compilation of the different reagents and fusion methods which can be used to dis-

solve minerals and alloys containing the platinum metals and gold.

Many minerals and alloys containing palladium can be dissolved in either aqua regia, nitric acid, or sulfuric acid. For example, Duke et al. (41) dissolved Pd-Zr alloys in aqua regia, Fraser et al. (30) dissolved lead buttons containing gold, silver, and platinum metals in 1:2 nitric acid, and Young (47) dissolved lead buttons containing the same metals in 1:1 sulfuric acid.

With given mineral acids, aqueous bases, and oxidizing or reducing agents, there is little doubt that most samples can be attacked. Wichers et al. (91) found, for example, that refractory platiniferous material could be brought completely into solution by heating in contact with hydrochloric acid containing a suitable oxidizing agent (Cl_2) in a sealed glass tube at an elevated temperature. But the extent of such attack is often inadequate if a short dissolution time is required.

A much more rapid dissolution of the sample can be achieved by fusion with acidic or alkaline fluxes. Examples of fluxes which dissolve complex silicates and alloys containing palladium or any of the other platinum metals are: sodium peroxide, barium peroxide, sodium hydroxide mixed with 25% sodium peroxide, or sodium hydroxide mixed with 25% sodium nitrate. Sodium peroxide is the most effective flux, and rapid dissolution can be accomplished. Schindewolf et al. (92) have, for example, brought crushed rocks and organic materials into solution using a very rapid fusion (less than 2 min.) in sodium peroxide. Occasionally they found samples which combusted with explosive violence, and adequate safety precautions (such as the use of heavy plastic shielding) must therefore be taken.

The fusion with sodium peroxide is most often carried out in a nickel crucible. Because the reagent is both a strong base and a powerful oxidizing agent, macro amounts of the crucible are

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dissolved. Recently crucibles of metallic zirconium have been
recommended as specially resistant to the action of fused sodium
peroxide (93), and they can be used in cases where the macro
amounts of dissolved nickel will interfere with the subsequent
separations.

For further information about the fusion techniques with
sodium peroxide, see reference (94).

When rapid dissolution procedures are concerned, consider-
able attention should also be paid to the "explosive" method of
attack with sodium peroxide (95). In this method 0.5-1.0 gram
of the granular sample is mixed with 15 gram of sodium peroxide
and 0.7 gram of sugar carbon (prepared by igniting granulated
sugar in a covered porcelain crucible) in a nickel crucible. The
covered crucible is placed in a cold water bath, and the mixture
is ignited by inserting a burning cotton string through a hole
in the cover. After cooling, the solid melt is easily removed
from the crucible by only tapping it sharply against the desk.
Only minor amounts of nickel are reported to be dissolved by this
method. Though this method has many advantages, obviously dis-
advantages are present. For the first, undissolved residues are
often left after the reactions have ceased, and for the second,
the amount of sodium peroxide needed is greater than the amount
needed when the sample is fused with sodium peroxide over open
flame.

Organic materials can be rapidly dissolved by fusion with
sodium peroxide (92). If the reaction is too violent, the
ordinary method of wet ashing, i.e., digestion with H_2SO_4-$HClO_4$-
HNO_3 mixtures while being heated (88) can be tried.

VI. COUNTING TECHNIQUES FOR RADIOACTIVE PALLADIUM ISOTOPES

Table I of this monograph shows some of the nuclear char-
acteristics of each of the known radioactive isotopes of palla-
dium. The radioactive isotopes usually encountered by the radio-
chemist are Pd^{109m}, Pd^{109} and Pd^{103}. Pd^{109m} has a half life of
4.75 min and the radiation emitted is best detected by a scin-
tillation counter. Pd^{109} has a half-life of 13.5 hours, and
decay by both β^- and γ emission, with the γ-ray relatively highly
converted ($e/\gamma > 11$). The radioactivity from Pd^{109} can therefore
be detected by Geiger-Mueller counters, proportional counters,
and scintillation counters. Pd^{103} which has a half-life of 17
days, decays by electron capture and γ emission, and is therefore
counted by using either an x-ray proportional counter or a scin-
tillation counter.

The $Pd^{109m-109}$ gamma spectrum is presented in Fig. 1. The
Pd^{103} gamma spectrum has a weak gamma peak at 40 kev (from 57
min. Rh^{103}) and a Rh-x-ray peak at 20 kev, both peaks super-
imposed on the spectrum of the internal Bremsstrahlung.

It is frequently possible to detect and measure the radio-
activity emitted by a given palladium nuclide in a mixture of
several other radioactive nuclides by means of gamma-ray spec-
trometry. References (96-102) give the information and describe
the techniques needed.

VII. COLLECTED RADIOCHEMICAL PROCEDURES FOR PALLADIUM

All the procedures listed in this chapter, except procedure
18, use dimethylglyoxime as a selective reagent for palladium.
Procedures 1-8 and 10-17 precipitate palladium as a dimethyl-
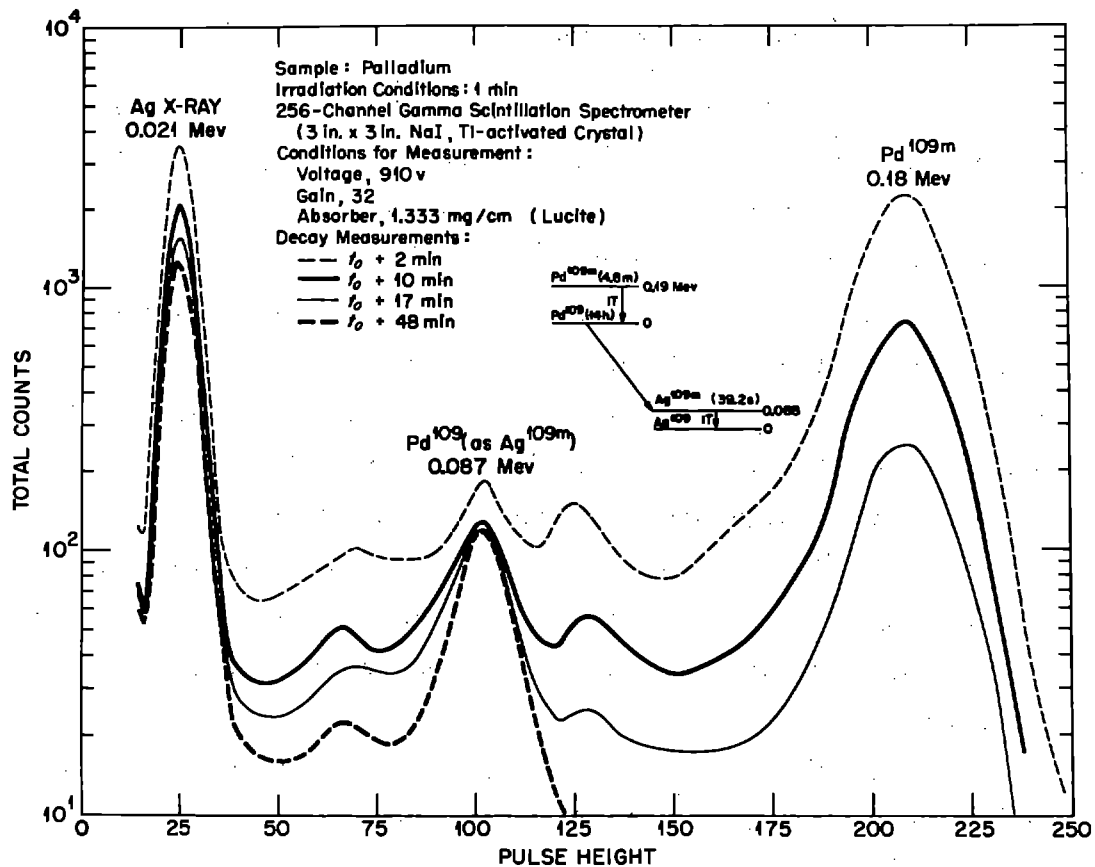glyoximate, while 9 and 17 extracts the complex into chloroform.

Fig. 1—Gamma-ray spectrum of Palladium-109.

The reduction of palladium to the metallic state is used as a separation step in procedures 8, 9 and 16, and in procedures 15 and 16, palladium is precipitated with salicylaldoxime and α-furildioxime respectively. As decontamination steps, the procedures (except 18) use either one or a combination of $Fe(OH)_3$, $La(OH)_3$, $Zr(OH)_4$, AgCl, and AgI scavengings. Procedure 18 is used for a carrier-free separation of the nuclide Pd^{103}, and is based on a coprecipitation on Se metal followed by a distillation of the selenium.

Many of the procedures listed represent a more or less modification of the procedures developed by Seiler (103) and Glendenin (104).

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PROCEDURE 1

This procedure is developed by Seiler (103) for separating palladium activity from the other fission products produced by pile neutron irradiation of uranium (metal and uranyl nitrate).

In a separation of palladium from irradiated uranium metal, very effective decontamination from the other fission products was obtained by this procedure.

1) Add palladium carrier to a uranyl nitrate solution, stir, and make basic with conc. NH_4OH until the heavy precipitate does not redissolve in the HNO_3 present. Then acidify with 6 N CH_3COOH or 6 N HCl. Heat until the precipitate dissolves, add 1 per cent dimethylglyoxime solution in ethanol (3 to 5 ml), heat for a few minutes, and then centrifuge. Wash two or three times with 2 per cent CH_3COOH or HCl.

2) Dissolve in 1 ml of aqua regia and destroy the dimethylglyoxime by boiling for a few minutes. Add 1 ml of conc. HCl, 10 mg of zirconium carrier, and 5 mg of lanthanum carrier. Make distinctly basic with NH_4OH and centrifuge off the $Zr(OH)_4$ and the $La(OH)_3$. Repeat the scavenging with zirconium and lanthanum hydroxides a second time by adding more zirconium and lanthanum carriers to the basic solution.

3) Add 10 mg of silver carrier to the above solution, acidify with HNO_3, boil for a few minutes, and filter off the AgCl.

4) Precipitate the palladium by adding 3 to 5 ml of 1 per cent dimethylglyoxime. Wash.

5) Repeat steps 2 to 4 twice and filter the final palladium dimethylglyoxime onto a weighed filter-paper disc in a Hirsch funnel. Dry with alcohol, heat in an oven for 10 min. at 110° C, and weigh as the dimethylglyoxime.

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Notes: Dimethylglyoxime is highly specific for palladium in acid solution. Selenium is the only fission product that precipitates with palladium. In freshly irradiated uranyl nitrate, short-lived selenium activity is a contaminant. Other contaminants are zirconium and silver, but these are effectively removed by the $La(OH)_3$, $Zr(OH)_4$, and AgCl scavengings.

PROCEDURE 2

This procedure is developed by Glendenin (104) mainly for separating palladium from uranium irradiated by pile neutrons. The procedure is not much different from the procedure developed independently by Seiler (103).

In a separation of palladium from a very active concentrate of plutonium fission products, a decontamination factor of 10^6 was obtained.

1) Add 20 mg of palladium carrier to the uranyl nitrate sample. Make the solution 0.4 $\underline{M}$ in HNO_3 or HCl, add 3 to 5 ml of 1 per cent dimethylglyoxime, and centrifuge. Discard the supernatant solution and wash the palladium precipitate.

2) Dissolve the precipitate in 1 ml of hot conc. HNO_3. Cool, dilute with 10 ml of H_2O, add 5 mg of iron carrier, and make basic with excess NH_4OH. Add 10 mg of silver carrier and just enough I^- carrier to precipitate all the silver (Note 1).

3) Centrifuge, and discard the precipitate. Repeat the precipitation by adding 5 mg more of iron carrier and 10 mg of silver carrier, heating, and centrifuging.

4) Acidify the supernatant solution to 0.4 $\underline{M}$ with HCl and centrifuge off any AgCl precipitate.

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5) Add 3 to 5 ml of 10 per cent dimethylglyoxime to the solution and filter.

6) Wash the palladium precipitate with water and ethanol and dry at 110° C for 10 min. Weigh and mount the final sample.

Note 1: If needed, another purification cycle of Fe(OH)$_3$ and AgI scavengings and dimethylglyoxime precipitation may be carried out, since the fission yield of palladium is low.

Note 2: Selenium, which is reduced to the element under the conditions used, will coprecipitate with palladium dimethylglyoxime. Purification is effected by the Fe(OH)$_3$ and AgI scavengings. The principal contaminants in the final sample are zirconium and silver.

PROCEDURE 3

This procedure which has been used by Goeckermann in bombardment work at the University of California Radiation Laboratory, Berkeley, California, is reproduced from a compilation written by Meinke (105).

Target material: ~1 g Bi metal   Time for sepn: ~ 2 hrs.

Type of bbdt: 388 Mev α particles   Equipment required: centrifuge,
348 Mev protons   tubes, 110° oven
194 Mev deuterons

Yield: ~ 60%

Degree of purification: Decontamination factor >10^4 from fission and spallation products

Advantages: Fair yield of pure Pd

Procedure:

1) To aliquot of HNO_3 soln. of target add 10 mg Pd^{2+}, make up to 20 ml 0.5 N HCl, add 5 ml dimethylglyoxime solution (1% in alcohol). Wash with dilute HCl.

2) Dissolve precipitate in 1 ml conc. HNO_3, dilute with 10 ml H_2O, add 5 mg Fe^{3+} and make basic with NH_3.

3) Add 10 mg Ag to supernatant and enough I^- to precipitate all the Ag. Repeat AgI scavenging.

4) Make supernatant 0.5 N in HCl and centrifuge out any AgCl. Add 5 ml dimethylglyoxime solution. Wash.

5) Repeat purification cycle if needed for higher purity.

6) Filter last Pd-dimethylglyoximate, wash with H_2O and C_2H_5OH, dry 10 min at 110° C. Weigh as Pd-dimethylglyoximate (20.70 mg per 10 mg Pd).

Remarks:

Zr and Ag are the principal contaminants of the dimethyl-glyoxime ppt.

PROCEDURE 4

This procedure, which has been used by Folger and Hicks in bombardment work at the University of California Radiation Laboratory, Berkeley, California, is reproduced from a compilation written by Meinke (105).

Target material: ~ 4 g U metal   Time for sepn: ~ 2 hrs.

Type of bbdt: 388 Mev α particles   Equipment required: centri-

348 Mev protons   fuge, cones, vac. filter

194 Mev deuterons

<u>Yield</u>: ~ 60%

<u>Degree of purification</u>: ~ 10^4 from all fission product activities.

<u>Advantages</u>: Good yield of pure Pd

<u>Procedure</u>:

1) Add 10 mg Pd^{2+} and 10 mg Ni; make 0.4 N in HNO_3 or·HCl, add 3-5 ml dimethylglyoxime solution (1% in alcohol). Wash with dilute HCl or NHO_3 (0.2 N).

2) Dissolve precipitate in 1 ml conc. HNO_3, dilute with 5 ml H_2O, add 2 mg Fe^{3+} and make basic with NH_3. Centrifuge and repeat $Fe(OH)_3$ scavenging.

3) Add 10 mg Ag^+ to supernatant and enough I^- to precipitate all the Ag. Centrifuge and repeat AgI scavenging.

4) Make supernatant 0.4 N in HCl and centrifuge out any AgCl. Add 3-5 dimethylglyoxime solution. Wash.

5) Repeat purification cycle (steps 2,3,4) if needed for higher purity.

6) Filter last Pd-dimethylglyoximate, wash with H_2O and C_2H_5OH, dry 10 min at 110° C. Weigh as Pd-dimethylglyoximate (20.70 mg per 10 mg Pd).

<u>Remarks</u>:

Pd-dimethylglyoximate is quite bulky and may not centrifuge. In such a case, filter with suction. The ppt. may be dissolved by adding conc. HNO_3 and catching the solution which runs through the filter.

PROCEDURE 5

This procedure, which has been used by Lindner in bombardment work at the University of California Radiation Laboratory, Berkeley, California, is reporduced from a compilation written by Meinke (105).

Target material: ~ 0.5 g Sb metal   Time for sepn: ~ 1 hr.

Type of bbdt: 388 Mev α particles   Equipment required: Lusteroid
            194 Mev deuterons   tubes, centrifuge, cones

Yield: >50%

Degree of purification: Factor of at least 100

Procedure:

1) To dissolve the Sb metal, add 15 drops of 27 N HF to it in a Lusteroid tube in a hot water bath. Add conc. HNO_3 dropwise until dissolved (~ 10 min). Dilute to ~ 20 ml.

2) To the SbF_4^- solution add 20 mg of Te, Sn, In, Cd, Ag, Pd, Ru, Mo and Y carriers as soluble salts. Add 2 drops conc. HCl. Centrifuge the YF_3 and AgCl ppts.

3) To half of the supn. add 5 ml of 1% dimethylglyoxime in alcohol. Centrifuge.

4) Wash the Pd-"DMG" ppt. with water and dissolve in aqua regia. Evaporate to dryness. Add 10 ml 2 N HCl. Add 1 mg Sb, Sn, In and Cd holdback carriers and 5 ml 1% "DMG" reagent in alcohol.

5) Repeat 4) twice (do three times altogether).

6) Wash the ppt. with water and then alcohol.

7) Plate the Pd-"DMG" ppt.

PROCEDURE 6.

This procedure has been used by Newton (106) and is reproduced from Meinke (105).

Target material: 0.1-1.0 g Th metal   Time for sepn: ~ 1 hr.

Type of bbdt: 37 Mev α particle   Equipment required: standard

Yield: ~ 80%

Degree of purification: 10^6 except from Ag^+

Procedure:

The Th metal is dissolved in conc. HCl plus a few drops 0.2 M solution of $(NH_4)_2SiF_6$ to clear up black residue. The solution is diluted to 2 N in HCl and an aliquot taken.

1) To sample add 20 mg Pd^{2+}. If sample in HCl, must add HNO_3 to oxidize Pd. (See Note).

2) Add 3-5 ml of a solution of 1% dimethylglyoxime in ethanol. Centrifuge the ppt. and wash with water.

3) Dissolve ppt. in 1 ml conc. HNO_3, cool, dilute with 10 ml H_2O, add 5 mg Fe^{3+}, make basic with excess NH_4OH. Add 10 mg Ag^+ and enough I^- to ppt. Ag. Centrifuge and repeat scavenging.

4) Make 0.4 N in HCl and centrifuge out any AgCl. To supernatant add 3-5 ml of the dimethylglyoxime solution. Wash.

5) Repeat purification cycle in steps 3 and 4 for further purity.

6) Wash dimethylglyoxime ppt. with H_2O and EtOH. Dry 10 min. at 110° C. Weigh.

Remarks:

Zr and Ag^+ are principal contaminants. 10 mg Pd = 31.6 mg $PdC_8N_4O_4H_{17}$.

Note:

The Pd is in Th as colloidal metal. It is not oxidized to Pd^{2+} by HCl and does not exchange with carrier.

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PROCEDURE 7

This procedure has been used by Wolfe and is reproduced from Meinke (105).

Target material: Uranium metal

Type of bbdt: 388 Mev α-particles

Yield: ~ 50%

Degree of purification: 10^3 from fission products

Time for sepn: ~ 1 day when separated with Os and Ru

Equipment required: Special distilling flask, centrifuge, sep. funnel, Lusteroid tubes, standard

Procedure:

1) Cut off the central portion of the target and boil with conc. HCl to dissolve it and to expel Ge.

2) Add 5 mg I^- and IO_3^- and boil the solution again to expel iodine.

3) Add 20 mg Os, Ir, Pt and Au carriers plus 20 mg Ba, Ru, Rh and Pd carriers. Withdraw a 20% aliquot for later determinations of Ba, Ru, and Rh.

4) Place the remaining solution in a special all-glass distilling flask having a thistle tube entry and an air entry. Add conc. HNO_3 through the thistle tube, and distill OsO_4 into 6 N NaOH in an ice bath. (Save for Os determination).

5) Place the residue from the Os distillation in a beaker, add 10 ml 70% $HClO_4$ and boil the solution to fume off $HClO_4$ to expel Ru.

6) Dilute the solution, add 5 mg more Ru carrier, and 5 mg more I^- and IO_3^- and repeat the fuming.

7) Add one ml dilute HCl, dilute the solution to 4 N and extract twice with equal volume butyl acetate to decontaminate from Hg and from Au.

8) Dilute the solution to ~ 0.5 N in H^+, add 5 ml dimethyl-

glyoxime solution (1% in alcohol) and filter off the palladium ppt.

9) Dissolve ppt in HNO_3, dilute to 0.5 N in H^+, and reppt. the Pd-DMG.

10) Dissolve ppt. in HNO_3, add 2 mg La^{3+} carrier and ppt the hydroxide by adding NH_4OH. Repeat the $La(OH)_3$ scavenging twice more.

11) Add 10 mg Ag^+ to suspn. and enough Cl^- to ppt all the Ag. Centrifuge and repeat AgCl scavenges twice. Centrifuge off all AgCl.

12) Dilute supn. to known volume, transfer to a plastic lusteroid container (to prevent adsorption of Ag daughter activity on glass walls) and wrap in parafilm to prevent evaporation.

13) Allow the soln. to stand for 12-16 hours until the 3.2 hr Ag^{112} daughter of 21 hour Pd^{112} has grown into equilibrium. Thereafter at intervals of about a day, known aliquots are "milked" of the Ag^{112} daughter by AgCl pptns in order to determine decay of Pd^{112}.

Remarks:

Os, Ru and Pd can be taken from one bombardment leaving Rh, In and Pt for a second bombardment unless several people are cooperating on the procedure.

PROCEDURE 8

This procedure represents a modification by Melnick of the method developed by Glendenin (104). It is in part reproduced from a compilation written by Kleinberg (107).

Pd sep. from: Fission products   Time for sepn: ~ 5 hrs. for

Yield: ~ 75%   duplicate analysis

Degree of purification: Selenium   Equipment required: Centrifuge,

    is the only fission product   tubes, standard

    contaminating the final sample

Procedure:

1) Pipet an aliquot of the sample into a 125 ml Erlenmeyer
flask. Add 2.0 ml of Pd carrier (10 mg Pd/ml as $PdCl_2$ in H_2O)
and make the solution about 0.4 $\underline{M}$ in HCl. Evaporate to dryness
and then dissolve the residue in about 5 ml of conc. HCl. Reduce
Pd to the metallic state with Mg powder and dissolve the excess
Mg in conc. HCl (Note 1). Transfer the contents of the flask to
a 40 ml conical centrifuge tube.

2) Centrifuge the Pd metal and discard the supernate. Wash
the precipitate with about 2 ml of conc. HCl and discard the
washings. Dissolve the Pd in a minimum of aqua regia and make
the resulting solution 0.4 $\underline{M}$ in HCl. Add 5 ml of dimethylgly-
oxime reagent (1% solution in 95% ethanol) and centrifuge, dis-
carding the supernate.

3) Dissolve the precipitate in 1 ml of conc. HNO_3 contain-
ing a few drops of conc. HCl. Dilute the solution with 10 ml of
H_2O, add 1 ml of Ag carrier (10 mg Ag/ml as $AgNO_3$ in H_2O), and
centrifuge. Transfer the supernate to a clean 40 ml centrifuge
tube.

4) Add 1 ml of Fe carrier (10 ml Fe/ml as $FeCl_3 \cdot 6H_2O$ in
very dilute HCl) and make the solution basic with conc. NH_4OH
(Note 2). Centrifuge, transfer the supernate to a clean 40 ml
centrifuge tube, and discard the precipitate.

5) Make the supernate 0.4 $\underline{M}$ in HCl and add 5 ml of dimethyl-

glyoxime reagent. Centrifuge and discard the supernate.

6) Repeat steps 3, 4, and 5 two additional times.

7) Filter the precipitate onto a weighed No. 50 Whatman filter circle, 7/8" diameter, using a ground-off Hirsch funnel and chimney. Wash the precipitate with small portions of H_2O and 95% ethanol. Dry at 110° C for 5 min, cool, weigh and mount (Note 3).

Notes:

1) Conversion of palladium to the metal promotes exchange between the carrier and active species. It also serves as a volume regulating step.

2) In the $Fe(OH)_3$ scavenging steps the precipitation of palladium is prevented by the formation of the $Pd(NH_3)_4^{2+}$ complex ion.

3) Beta counting is begun about 15 hours after completion of the chemistry to permit 3.2 h Ag^{112} to grow into equilibrium with 21 hour Pd^{112}. Absorbers are used in the counting to separate the 13.5 h Pd^{109} and the 21 h Pd^{112} activities. A 54.5 mg/cm^2 Al absorber is first used and permits the counting of both Pd^{109} and Pd^{112} activities. The sample is then counted with a 637 mg/cm^2 Al absorber; the count is that of the Pd^{112} activity decreased by a factor resulting from the thickness of the absorber. (This factor is obtained by bombarding Pu, separating Pd, permitting the latter to decay sufficiently so that the Pd^{109} activity is down to about 1% of the original value, and counting through each of the two absorbers described above. This permits determination of Pd^{112} activity in the combined Pd^{109} and Pd^{112} activities.) Pd^{109} has a 0.95 Mev beta which passes through the light absorber but not the heavy one. The Ag^{112}, which has grown

into equilibrium with Pd^{112}, has a 3.6 Mev beta and a 0.86 Mev gamma; these activities are counted through both absorbers. The light absorber cuts out the 0.2 Mev beta of Pd^{112}.

PROCEDURE 9

This procedure has been developed and used by Alexander, Schindewolf and Coryell (108) for a fast separation of palladium from deuteron induced fission in uranium (15 Mev d). They report that the time required for the chemical separation was three minutes. They give no information about the degree of purification. The activity from the final sample was analyzed by a multichannel gamma spectrometer.

Procedure:

1) The bombarded U foil was dissolved in aqua regia containing ~ 2 mg Pd(II) carrier. After diluting, AgCl was precipitated by the addition of 10 mg Ag carrier.

2) Transfer the supernatant to a separatory funnel and extract Pd into chloroform as the dimethylglyoxime complex using 1 ml 1% dimethylglyoxime in methanol per 20 ml chloroform.

3) Wash the organic phase twice with dilute HNO_3 and back extract into concentrated ammonia.

4) Add Fe(III) carrier and centrifuge. Discard the precipitate.

5) Reduce Pd to the metal state with Zn powder, filter, wash and count.

This procedure has been used by Brown and Goldberg (109) in a pile neutron activation analysis of Pd in iron meteorites. The procedure represents a slight modification of the procedure developed by Seiler (103).

Procedure:

1) Dissolve the sample of irradiated meteorite in hot conc. HCl in a 50 ml centrifuge tube covered with a watch glass. Add 10 mg of Pd^{2+} carrier. Keep tube in ice bath in order to inhibit oxidation of Fe^{2+} (Pd will not precipitate easily in presence of Fe^{3+}).

2) Add ammonium hydroxide until solution is 0.4 M in acid. Add 3 to 5 ml of 1% dimethylglyoxime solution. Allow solution to stand for 40 minutes. Centrifuge.

3) Dissolve precipitate in 1 ml of hot conc. HNO_3. Cool and dilute with 10 ml of water. Add 5 mg of Fe^{3+} carrier. Add excess ammonium hydroxide to precipitate iron (this step removes a number of extraneous activities). Add 10 mg of Ag^+ carrier and enough iodide to precipitate all silver. (This step removes any silver activity present).

4) Centrifuge and discard the precipitate.

5) Repeat steps 3) and 4).

6) Adjust acidity to 0.4 M. Centrifuge solution to remove any AgCl precipitate formed.

7) Add 3 to 5 ml of 1% dimethylglyoxime solution and allow solution to stand 40 minutes. Filter.

8) Wash the precipitate with hot, then cold, water and ethyl alcohol. Determine the weight of the sample after heating at 110° C for 10 minutes. The sample is now ready to count. The sample is now ready to count.

PROCEDURE 11

This procedure was used by Parker et al. (110) for separating Pd from the fission product sulfide concentrates available at Oak Ridge National Laboratory, Oak Ridge, Tennessee, as a product of the large scale separation of Tc^{99}. The sulfide concentrates were obtained as follows.

From a solution of high activity uranium (2-3 N in HCl), having a two year cooling period, the sulfides were precipitated after Pt was added as a carrier. Palladium and technetium were carried well on the platinum sulfide, together with some ruthenium, zirconium and niobium. Technetium was distilled with sulfuric acid from the dissolved sulfides, followed by a distillation of the ruthenium with permanganate in sulfuric acid. After a second distillation of ruthenium with carrier, the solution was treated with an excess of ammonium hydroxide and filtered. The ammonia was boiled off, aqua regia was added to decompose NH_4^+ salts, and excess HNO_3 was evaporated. Acidity was adjusted to 3 N in HCl, and the sulfides were precipitated.

Procedure:

1) Dissolve sulfides in NH_4OH and H_2O_2. Boil off NH_3. Dissolve in 0.3 N HCl. Precipitate Pd with dimethylglyoxime in ethyl alcohol. Filter.

2) Dissolve residue in aqua regia. Boil off HNO_3. Take up in 0.3 N HCl and repeat dimethylglyoxime cycle until filtrate is inactive.

3) To residue add Mo, Ru, Re (for Tc), Ag, Cd, As, Sb, Sn, I and Fe as carriers. Make alkaline with excess NH_4OH and centrifuge. Discard precipitate.

4) Centrifugate contains $Pd(NH_3)_4^{2+}$. Boil off NH_3. Take up in 0.3 N HCl. Add excess dimethylglyoxime. Filter.

5) Dissolve in aqua regia and filter.

6) Boil off HNO_3. Take up in 0.3 N HCl. Repeat dimethyl-glyoxime precipitation. Dissolve in aqua regia. Boil off HNO_3. Take up in 0.3 N HCl. Electro-deposit aliquot for counting and weighing.

PROCEDURE 12

This procedure has been developed and used by Zvyagintsev and Kulak (111) in a pile neutron activation analysis of Pd in silver samples.

Procedure:

1) 1.5 gm of silver in the form of thin shavings is dissolved after irradiation by heating in HNO_3 (1:3).

2) After the dissolution, solutions of the salts of Au, Pt, Pd, In and Cu are added as carriers in the following quantities. Au - 20 mg, Pt - 20 mg, Pd - 15 mg, Ir - 20 mg, Cu - 20 mg.

3) The solution, with a precipitate of AgCl formed on heating, is treated with aqua regia, and evaporated to dryness. The residue is dissolved in hot water, and filtered off from the precipitate of AgCl.

4) 5 mg Ag is added to the solution, AgCl is precipitated and filtered off.

5) Evaporate the solution to dryness twice with conc. HCl, and dissolve in hot water. Gold and copper are precipitated by treatment with nitrite. The precipitate is separated from the solution by centrifugation and used for Au and Cu determinations.

6) To the nitrite solution add 10 mg Cu and 5 mg Au, and precipitate Cu and Au again. Filter.

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7) From the nitrite solution, precipitate palladium by dimethylglyoxime. Centrifuge.

8) Dissolve the precipitate in aqua regia, and add 3 mg each of salts of Pt and Ir. From the hydrochloric acid solution, precipitate Pd as dimethylglyoxime.

9) Repeat step 8) once more.

10) The precipitate is filtered off on ash-free filter paper and washed with water and dried. Activity is measured.

11) The precipitate with the filter is placed into a weighed muffle, and is calcinated together in a current of hydrogen and cooled in a current of carbon dioxide. The yield of the carrier is determined.

PROCEDURE 13

This procedure has been developed and used by Zvygintsev and Kulak (111) in a pile neutron activation analysis of Pd in cathode nickel.

Procedure:

1) 1.5 gm of nickel in the form of shavings is dissolved in dilute nitric acid. Add carrier of Au, Pt, Pd, Ir and Cu as indicated in step 2) of the preceding procedure. Evaporate the solution to dryness. Treat with aqua regia. Evaporate twice from conc. HCl.

2) From the hydrochloric acid solution, Au, Pt, Pd, Ir and Cu are precipitated, upon heating by hydrogen sulfide. Filter off the sulfide precipitates.

3) Wash the precipitate and dissolve in aqua regia.

Evaporate twice from conc. HCl and dissolve residue in aqua regia.

4) Proceed with steps 5) to 11) in the preceding procedure.

PROCEDURE 14

This procedure has been used by Vincent and Smales (112) in a pile neutron activation analysis of Pd in igneous rocks. The procedure represents a modification of the procedure used by Goldberg and Brown (109).

Procedure:

1) 100-200 mg of very finely ground rock powder is weighed into polyethylene tubing and sealed. Irradiate for about twelve hours. Mix the irradiated rock powder with about 0.5 gm sodium peroxide in a silicon crucible and heat at 480-500° C in a muffle for ten minutes [T. A. Rafter, Analyst 75, 484 (1950)].

2) Transfer the cooled sintered cake to a small beaker, moisten with water, and add 10 mg Pd foil and 30 mg Au foil. Add aqua regia to the crucible and loosen any adhering material by scraping 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 carriers. Repeat the acid digestion in the crucible and transfer the contents to the beaker, finally rinsing in with a little water. The solution should be quite clear, except for a few flecks of silica. Evaporate the contents of the covered beaker to dryness on the hot plate, cool, add fresh aqua regia, and repeat the evaporation. Take up the residue in 1 ml

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HCl and 20 ml water and transfer to a centrifuge tube.

3) Centrifuge off the silica and transfer the supernatant liquid to a fresh tube. Wash the silica twice with hot, dilute HCl, adding the washings to the main solution. Reject the silica to active waste.

4) To the main solution add 1 ml each of hold-back carrier solutions of $NaNO_3$, KCl, $CuCl_2$ (10 mg each cation), and 1 ml of a composite hold-back carrier for Co, Zn, and Mn (5 mg each element as nitrate), followed by sufficient Mg powder to precipitate the Pd and Au metals and leave a slight excess. Warm the tube to expel hydrogen, cool, and centrifuge. Decant the supernatant liquid to active waste, and wash the precipitated metals twice with hot water. From this stage onwards, activity is reduced to tracer levels.

5) Dissolve the precipitated metals in a few drops of aqua regia and evaporate nearly to dryness. Dissolve the residue by warming with 15 ml of 10% HCl, and transfer the solution to a separating funnel. Extract with 30 ml of ethyl acetate, allow the layers to separate, and run the lower aqueous layer, containing the Pd, into a centrifuge tube.

6) Add hold-back carriers for Na, K, Cu, Co, Zn, and Mn to the slightly acid aqueous solution, heat nearly to boiling, and precipitate the Pd by the addition of 5 ml of a 1% solution of dimethylglyoxime in methanol. Allow to stand for a few minutes, centrifuge and wash the precipitate twice with water.

7) Warm the Pd-glyoximate with ∼ 2 ml of aqua regia, finally boiling to dissolve the precipitate and destroy organic matter. Cool, add 5 ml of water, followed by 1 ml $FeCl_3$ solution (10 mg Fe), 1 ml $MnCl_2$ solution (5 mg Mn), and 2 ml bromine

water. Warm, add excess ammonia, boil and filter through a fast paper into a fresh centrifuge tube. Wash the precipitate two or three times with water.

8) Make the filtrate just acid with HCl, add hold-back carriers, heat nearly to boiling, and reprecipitate the Pd with dimethylglyoxime. Wash the precipitate twice, redissolve in aqua regia, add 5 ml water and 1 ml $FeCl_3$ solution, and repeat the ferric hydroxide scavenge.

9) To the ammonical filtrate add 1 ml $AgNO_3$ solution (10 mg Ag) followed by 1 ml (slight excess) KI solution. Boil to coagulate the silver iodide, and filter into a fresh tube.

10) Make the filtrate just acid with HCl, add hold-back carriers and 5 ml dimethylglyoxime solution. Warm to precipitate the Pd-dimethylglyoximate.

11) Centrifuge, wash twice with water, dissolve in aqua regia, reprecipitate palladium glyoximate in the presence of hold-back carriers. Repeat the solution and reprecipitation once more.

12) Finally, wash twice with water and once with 50% alcohol. Slurry and transfer the precipitate with a pipette to a weighed aluminum counting tray. Dry under an infra-red lamp and weigh to establish the chemical yield. ($\sim$ 50-60%).

PROCEDURE 15

This method has been used by Dzantiev et al. (113) for separating radioactive palladium produced by a (n,α) reaction on cadmium, and for a subsequent separation of the isomers Pd^{111m} and Pd^{111}.

The separation of palladium is performed by a simple precipitation of palladium salicylaldoximate, followed by an extraction of the organic complex into benzene. The chemical separation of the isomers Pd^{111m} and Pd^{111} is based on the Szilard-Chalmers effect. In an isomeric transition which has been completely or partly converted, the atoms in the ground state are multiply ionized, that is, they change their valance and consequently their chemical properties and can under certain conditions be separated from the atoms of the parent isomer by ordinary chemical methods. In the present method the isomer in the higher excited state enters an organic compound (salicylaldoxime) which is soluble in an organic solvent (benzene) and practically insoluble in water. The inorganic ions of the daughter isomer leave the organic molecules after the isomeric transition, and are simply washed out with water and precipitated by dimethylglyoxime in the presence of a Pd carrier.

Procedure:

1) Irradiate 400 g of cadmium nitrate for 4 hours in a 14 Mev neutron beam of $\sim 10^7$ n cm^{-2} sec^{-1}.

2) Dissolve the salt in water, add 100 mg Pd carriers and precipitate out palladium salicylaldoxime.

3) Pour off the solution above the precipitate, and wash the precipitate several times with a 1% solution of HNO_3 until the wash water shows no trace of unbound salicylaldoxime.

4) Dissolve the washed precipitate in 200 ml of hot benzene, and dilute the solution with 2 liters of cold benzene.

5) Transfer the solution to a separatory funnel and wash the organic phase a few times with water and a few times with an acid aqueous solution of $Pd(NO_3)_2$ (pH $\sim$ 1).

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6) Ten hours after the end of the irradiation, the benzene solution is rigorously shaken with 150 ml of an acid aqueous solution of $Pd(NO_3)_2$ [pH ~ 1, 50 mg $Pd(NO_3)_2$].

7) Transfer the water phase to a beaker and precipitate the palladium in it by adding dimethylglyoxime. Wash the precipitate, dry it, and count its radioactivity by a Geiger counter.

Remarks:

In developing a method for separating palladium isomers, several organic reagents which form water insoluble compounds with palladium were tested. These reagents include dimethylglyoxime, acetoxime, salicylaldoxime, and α-nitroso-β-naphthol. The most suitable was salicylaldoxime, which selectively precipitates palladium from strongly acid aqueous solutions in the form $Pd(C_7H_6O_2N)_2$. The precipitate after drying at 110° C is of constant composition: 28.17% Pd. 70 mg Pd-salicylaldoximate is soluble in 100 ml benzene. The distribution coefficient for Pd-salicylaldoximate between water and benzene was found to be equal to 1.5 x 10^{-4} by using Pd^{109} tracer.

PROCEDURE 16

This procedure was developed during a survey of the fission yield of the longer-lived activity produced in the thermal neutron bombardment of U^{233} and U^{235} (114).

U metal and U^{233} as the black oxide were irradiated in a reactor for 57 days and allowed to cool for several weeks before chemical investigation was started. The procedure described gave samples of satisfactory radiochemical purity from fission

product solutions containing 10^4-10^6 times the activity of the
separated product. The chemical yield was better than 90%.

Procedure:

1) Dissolve the irradiated sample in fuming nitric acid,
dilute with water, and add palladium and carriers for other
sulfide group elements, Sr, Ba, Ce, Cs, etc.

2) Reduce the palladium to metal by boiling in 1 N HCl
solution with N_2H_4-HCl.

3) Dissolve the metal in strong nitric acid, add hold-back
carriers for the other sulfide group elements and the rare earths,
and adjust the solution to about 2 N in HNO_3.

4) Precipitate palladium by adding a slight excess of di-
methylglyoxime or α-furildioxime. Wash the precipitate.

5) Dissolve the precipitate in aqua regia, add holdback
carriers and reprecipitate Pd as the oxime. Wash.

6) Repeat step 5).

7) Dissolve the precipitate in aqua regia, evaporate nearly
to dryness, take up the residue in diluted hydrochloric acid and
reduce the palladium to the metallic state by heating the solution
with formic acid. Filter, wash, dry, weigh and count.

PROCEDURE 17

This procedure has been used by Killick and Morris (115)
in their determinations of palladium in samples of platinum by
neutron-activation analysis.

The samples for analysis were in the form of metal sponge
and were ground to small fragments. Suitable quantities (~ 0.1

g) were weighed and sealed in silica ampoules made from silica tubing of internal diameter 4 mm. Standards were prepared by adding weighed portions (~ 0.05 g) of a standard solution of palladium (27.6 mg of Pd/liter) to 0.1 g samples of the platinum in silica ampoules. The liquid in the tubes was allowed to soak into the metal powder and then was carefully evaporated to dryness, after which the ampoules were sealed.

Standards containing the added palladium and samples to which no palladium had been added were packed together with silica wool in standard aluminum cans, 3 in. x 1 in., for irradiation in a reactor. Irradiation was for periods of up to 3 days in a thermal neutron flux of 10^{12} n cm^{-2} sec^{-1}. After irradiation, the samples and standards were analyzed radiochemically for Pd^{109} (13.5 h).

Procedure:

Carriers were employed in the isolation of the radio-palladium. An initial separation was achieved by precipitation of palladium dimethylglyoxime from dilute acid solution and additional purification was attained by precipitation of hydrous palladium dioxide. Further reduction in the contamination of the palladium was attained by precipitation and solvent extraction of the dimethylglyoxime derivative. Although gold is reported not to be precipitated by dimethylglyoxime under the conditions employed in the procedure[*], it was necessary to remove the final traces of the element by extraction with ethyl acetate. By this stage Pd^{111} had completely decayed away and any residual silver activity was removed by a silver chloride scavenge. The purified palladium

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[*]R. R. Barfoot and F. E. Beamish, Analyt. Chim. Acta 9, 49 (1953).

was finally precipitated and counted as the dimethylglyoxime derivative. Experimental details are as follows:

1) Transfer the irradiated samples and standards to 250 ml beakers. Wash out the irradiation ampoules with warm 6 $\underline{M}$ HCl and add the washings to the beakers. To each sample add 1 ml of Pd carrier (7 mg of Pd/ml as $PdCl_2$ in dil. HCl, standardized gravimetrically as palladium dimethylglyoximate). Add 5 ml of aqua regia and slowly dissolve the platinum. Dilute to 200 ml with cold water.

2) Add 2 ml of a 1% solution of dimethylglyoxime in 95% ethanol and stir vigorously until the precipitated palladium complex has been coagulated. Collect the precipitate by filtration on a No. 41 Whatman paper and wash it with small portions of cold 2 $\underline{M}$ HCl and cold water.

3) Transfer the precipitate to a 250 ml beaker, and evaporate with two 3 ml portions of 16 $\underline{M}$ HNO_3. Dilute to 100 ml with water, add 5 ml of 5% $Hg(NO_3)_2$ solution and boil. Add 5 ml of 10% $NaBrO_3$ solution and digest on a hot plate until the blackish brown precipitate of hydrous PdO_2 has settled. Collect the precipitate on a No. 41 Whatman paper and wash it with hot water.

4) Transfer the precipitate to a 250 ml beaker, add 3 ml of 12 $\underline{M}$ HCl, and dilute with exactly 100 ml of cold water. Add 2 ml of 1% dimethylglyoxime reagent and stir for 2 min. Add 30 ml of 12 $\underline{M}$ HCl, stir, and transfer the suspension to a 250 ml separating funnel. Extract the palladium complex into a 50 ml and two 10 ml portions of $CHCl_3$.

5) Combine the organic extracts and evaporate to dryness. Dissolve the precipitate in 1 ml of 16 $\underline{M}$ HNO_3 containing a few drops of 12 $\underline{M}$ HCl. Add 2 mg of Au carrier (as $AuCl_3$ in 1 $\underline{M}$ HCl)

and 5 ml of 12 $\underline{M}$ HCl, and boil for 5 min. Dilute the solution to 100 ml with water and extract the gold with three 10 ml portions of ethyl acetate. Retain the aqueous phase in two clean 50 ml centrifuge tubes.

6) To each portion of the aqueous solution add 2 mg of Ag carrier (as $AgNO_3$ in water) and centrifuge. Transfer the supernates to two clean 50 ml centrifuge tubes. To each add 2 ml of dimethylglyoxime reagent. Centrifuge and discard the supernates. Combine together the two precipitates of palladium dimethylglyoximate and wash with small portions of water and 95% ethanol. Slurry the precipitate with 95% ethanol onto a weighed aluminum counting tray by using a transfer pipette. Make sure that the distribution of the precipitate on the tray is uniform. Dry at 110° C for 15 min., cool, and weigh to establish the chemical yield.

Final precipitates of the palladium dimethylglyoximate complex, $Pd(C_4H_7N_2O_2)_2$, prepared by the above procedure from analysis samples and standards were counted under identical conditions with a thin end-window Geiger-Müller counter. All observed counting rates were corrected for coincidence, background and chemical yield. No correction for self-absorption of β-radiation in the precipitates was necessary as they were all kept nearly the same in weight. Decay characteristics of all the precipitates were measured to ensure that the activities were due to Pd^{109}.

Gile et al. (116) have produced Pd^{103} by a (d,2n) reaction
on rhodium, followed by a carrier-free separation of the same
nuclide. The procedure used for the isolation is not available
in the literature in a detailed form. A summary of the proce-
dure is given by Garrison and Hamilton (117) and is reproduced
below.

Procedure:

The Rh is fused with $KHSO_4$ and the fused mass is dissolved
in water. HCl is added together with mg amounts of H_2SeO_4 and
the solution is saturated with SO_2. The Pd^{103} is carried quan-
titatively on the Se metal. Se is removed by distillation with
$HClO_4$-HBr.

REFERENCES

1. D. Strominger, J. M. Hollander, G. T. Seaborg. Rev. Mod. Phys. 30, No. 2, Part II, pp. 679-81 (1958).

2. "Nuclear Data Sheets". National Academy of Sciences - National Research Council, 2101 Constitution Avenue, Washington 25, D. C.

3. C. O. Fairchild, W. H. Hoover, M. F. Peters. Journ. Research Bur. Stands. 2, 931 (1929).

4. H. St. C. Deville, H. Debray. Ann. Chim. Phys. 56 (3), 385 (1859).

5. J. Violle. Compt. Rend. 87, 981 (1878); 89, 702 (1879).

6. M. A. Whiteley (editor). "Thorpe's Dictionary of Applied Chemistry", Vol. IX, p. 209, Longmans, Green and Co., New York, 1949.

7. S. C. Ogburn, W. C. Brastow. J. Am. Chem. Soc. 55, 1307 (1933).

8. D. H. Templeton, G. W. Watt, C. S. Garner. J. Am. Chem. Soc. 65, 1608 (1943).

9. I. K. Taimni, G. B. S. Salaria. Anal. Chim. Acta 11, 329 (1954).

10. J. R. Partington. "A Textbook of Inorganic Chemistry", p. 957, MacMillan and Co. Ltd., London, 1950.

11. N. V. Sidgwick. "The Chemical Elements and Their Compounds", Vol. II, pp. 1553-77, Oxford Press, London, 1950.

12. H. D. K. Drew, F. W. Pinkard, G. H. Preston, W. Wardlaw. Journ. of the Chem. Soc., London, 1932, 1895.

13. H. B. Wellmann. Journ. of Am. Chem. Soc. 52, 985 (1930).

14. J. Seath, F. E. Beamish. Ind. Eng. Chem. Anal. Ed. 12, 169 (1940).

15. J. G. Fraser, F. E. Beamish. Anal. Chem. 26, 1474 (1954).

16. J. C. Hagen. Thesis, Massachusetts Institute of Technology, June 1954, unpublished.

17. E. B. Sandell. "Colorimetric Determination of Traces of Metals", 3rd ed., p. 719, Interscience Publishers Inc., New York, 1959.

18. G. Lunde. Mikrochemie 5, 119 (1927).

19. W. R. Schoeller, A. R. Powell. "Analysis of Minerals and Ores of the Rarer Elements", pp. 205-11, Charles Griffin and Co., London, 1919.

20. J. W. Mellor, H. V. Thompson. "A Treatise on Quantitative Inorganic Analysis", 2nd ed., pp. 459-480, Charles Griffin and Co., London, 1938.

21. W. W. Scott. "Standard Methods of Chemical Analysis", N. H. Furman, editor, Vol. I, 5th ed., pp. 710-72, D. van Nostrand Co. Inc., New York, 1939.

22. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. I. Hoffman. "Applied Inorganic Analysis", 2nd ed., pp. 271-83, John Wiley and Sons Inc., New York, 1953.

23. R. Gilchrist. Journ. Research Bur. Stands. 12, 291 (1934).

24. R. Gilchrist, E. Wichers. J. Am. Chem. Soc. 57, 2565 (1935).

25. M. Wunder, V. Thüringer. Z. Anal. Chem. 52, 101, 660, 740 (1913).

26. H. Holzer. Z. Anal. Chem. 95, 392 (1933).

27. S. A. Reed, C. V. Banks. Proc. Iowa Acad. Sci. 55, 267 (1948).

28. R. C. Voter, C. V. Banks, H. Diehl. Anal. Chem. 20, 652 (1948).

29. C. V. Banks, D. T. Hooker. Anal. Chem. 28, 79 (1956).

30. J. G. Fraser, F. E. Beamish, W. A. E. McBryde. Anal. Chem. 26, 495 (1954).

31. K. Tanii, H. Hoshimiya, M. Ikeda. Nippon Kagaku Zasshi 61, 269 (1940); U. S. Atomic Energy Commission AEC-tr-3441.

32. W. B. Pollard. Analyst 67, 184 (1942).

33. N. C. Sogani, S. C. Bhattacharyya. Anal. Chem. 28, 81 (1956).

34. A. S. Pesis. Zhur. Anal. Khim. 16, 253 (1961); Nucl. Sci. Abstr. 15, 19350 (1961).

35. N. K. Pshenitsyn, I. V. Prokof'eva. Zhur. Neorg. Khim. 3, 996 (1958); Nucl. Sci. Abstr. 12, 15344 (1958).

36. G. H. Morrison, H. Freiser. "Solvent Extraction in Analytical Chemistry", John Wiley and Sons Inc., New York, 1957.

37. G. H. Morrison, H. Freiser. Anal. Chem. 30, 632 (1958); Anal. Chem. 32, 37R (April 1960).

38. G. H. Morrison, H. Freiser. "Comprehensive Analytical Chemistry", Vol. 1A, pp. 147-209, C. L. Wilson and D. W. Wilson, eds., Elsevier Publishing Co., Amsterdam-New York, 1959.

39. W. A. E. McBryde. Analyst 80, 503 (1955).

40. H. Freiser, G. H. Morrison. "Solvent Extraction in Radio-chemical Separations", Ann. Review of Nucl. Science, Vol. 9, pp. 221-44. E. Segre, ed., Annual Reviews Inc., Palo Alto, 1959.

41. J. F. Duke, W. Stawpert. Analyst 85, 671 (1960).

42. P. W. West, J. K. Carlton. Anal. Chim. Acta 6, 406 (1952).

43. E. S. Przheval'skii, V. I. Shlenskaya, L. F. Maternykh. Vestnik Moskov Univ. 9, No. 6, Ser. Fiz.-Mat-i Estestven Nauk. No. 4, 71 (1954); Chem. Abstr. 47, 4789 (1953); Chem. Abstr. 49, 96 (1955).

44. P. W. West, T. G. Lyons, J. K. Carlton. Anal. Chim. Acta 6, 400 (1952).

45. M. Ziegler. Naturwissenschaften 46, 353 (1959).

46. M. Ziegler. Naturwissenschaften 46, 492 (1959).

47. R. S. Young. Analyst 76, 49 (1951).

48. O. Menis, T. C. Rains. Anal. Chem. 27, 1932 (1955).

49. H. Bode. Z. Anal. Chem. 144, 165 (1955).

50. J. H. Yoe, J. J. Kirkland. Anal. Chem. 26, 1335 (1954).

51. K. L. Cheng. Anal. Chem. 26, 1894 (1954).

52. L. E. Ross, G. Kesser, E. T. Kucera. Anal. Chem. 32, 1367 (1960).

53. E. B. Sandell. "Colorimetric Determination of Traces of Metals", 3rd ed., p. 713, Interscience Publishers Inc., New York, 1959.

54. Yu. A. Bankovskii, A. F. Ievinsh. Zhur. Anal. Khim. 13, 507 (1958); Nucl. Sci. Abstr. 13, 1176 (1959).

55. K. L. Cheng, R. H. Bray. Anal. Chem. 27, 782 (1955).

56. G. H. Ayres, B. L. Tuffly. Anal. Chem. 24, 949 (1952).

57. G. Beck. Mikrochemie ver. Mikrochim. Acta 33, 188 (1947).

58. D. E. Ryan. Analyst 76, 167, 310 (1951).

59. J. H. Yoe, L. G. Overholser. J. Am. Chem. Soc. 61, 2058 (1939); J. Am. Chem. Soc. 63, 3224 (1941).

60. A. Sa. Rev. asoc. bioquim. Argentina 16, 7 (1949).

61. N. K. Dutt, K. P. Sen Sarma. Science and Culture (India) 23 (5), 249 (1957).

62. K. Kodama. Nagoya-shi Kogyo Kenkyujo Kenkyu Hokoku 19, 1 (1958).

63. E. Sudo. Sci. Repts. Research Insts. Tohoku Univ. Ser. A 8, 367 (1956).

64. V. M. Peshkova, V. I. Shlenskaya, A. I. Rashevskaya. Izvest. Sektora Platiny i Drug. Blagorod. Met. Inst. Obshchei i Neorg. Khim., Akad. Nauk SSSR 32, 61 (1955); Anal. Abstr. 4, 2623 (1957).

65. R. E. D. Clark. Analyst 82, 182 (1957).

66. M. Ziegler, O. Glemser. Z. Anal. Chem. 153, 246 (1956).

67. O. König, W. R. Crowell. Microchem. ver. Mikrochim. Acta 33, 300 (1948).

68. P. C. Stevenson, A. A. Franke, R. Borg, W. Nervik. J. Am. Chem. Soc. 75, 4876 (1953); U. S. Atomic Energy Commission UCRL-2329 (1953).

69. J. O. Karttunen, H. B. Evans. Anal. Chem. 32, 917 (1960).

70. W. M. MacNevin, W. B. Crummett. Anal. Chem. 25, 1628 (1953); Anal. Chim. Acta 10, 323 (1954).

71. S. S. Berman, W. A. E. McBryde. Can. J. Chem. 36, 835 (1958).

72. K. A. Kraus, F. Nelson, G. W. Smith. J. Phys. Chem. 58, 11 (1954).

73. K. A. Kraus, F. Nelson. Intern. Conf. on the Peaceful Uses of Atomic Energy, Geneva, Vol. 7, 113 (1955) (P/837).

74. E. Blasius, U. Wachtel. Angew. Chem. 66, 305 (1954); Z. anal. Chem. 142, 341 (1954).

75. R. F. Buchanan, J. P. Faris, K. A. Orlandini, J. P. Hughes. U. S. Atomic Energy Commission TID-7560 (1958).

76. J. P. Faris. Anal. Chem. 32, 520 (1960).

77. H. G. Hicks, R. S. Gilbert, P. C. Stevenson, W. H. Hutchin. U. S. Atomic Energy Commission Rept. LRL-65 (1953).

78. S. Kallmann, R. Liu, H. Oberthin. Nucl. Sci. Abstr. 14, 15602 (1960). (WADC-TR-59-325). Available from OTS under PB-161295.

79. N. K. Pshenitsyn, K. A. Gladyshevskaya, L. M. Ryakhova. Zhur. Neorg. Khim. 2 (5), 1057 (1957); Eng. transl. 2 (5), 115 (1957).

80. M. Lederer. Nature 162, 776 (1948); 163, 598 (1949).

81. M. Lederer. Anal. Chim. Acta <u>8</u>, 134 (1953).

82. F. H. Burstall, G. R. Davies, R. P. Linstead, R. A. Wells. J. Chem. Soc., London <u>1950</u>, 516; Nature <u>163</u>, 64 (1949).

83. N. F. Kember, R. A. Wells. Analyst <u>80</u>, 735 (1955).

84. N. F. Kember, R. A. Wells. Nature <u>175</u>, 512 (1955).

85. M. Shibata, T. Uemera. J. Chem. Soc. Japan <u>72</u>, 757 (1951).

86. J. Bubernak. Univ. Microfilms (Ann Arbor, Mich.), Publ. No. 12010. Dissertation Abstr. <u>15</u>, 955 (1955).

87. H. H. Willard, C. L. Rulfs. "Treatise on Analytical Chemistry", Part I, Vol. 2, Chap. 24, pp. 1027-50. I. M. Kolthoff, P. J. Elving, eds., Interscience Publishers, New York-London, 1961).

88. E. C. Dunlop. "Treatise on Analytical Chemistry", Part I, Vol. 2, Chap. 25, pp. 1051-1093, I. M. Kolthoff, P. J. Elving, eds., Interscience Publishers, New York-London, 1961.

89. V. P. Calkins. U. S. Atomic Energy Commission Rept. AECD-4175.

90. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, J. F. Hoffman. "Applied Inorganic Analysis", 2nd ed., pp. 343-51, John Wiley and Sons Inc., New York, 1953.

91. E. Wichers, W. G. Schlecht, C. L. Gordon. J. Research Nat. Bur. Stands. <u>33</u>, 363, 451, 457 (1944).

92. U. Schindewolf, M. Wahlgren. Geochim. et Cosmochim. Acta <u>18</u>, 36 (1960).

93. Oregon Metallurgical Corp., P. O. Box 484, Albany, Oregon, U.S.A.

94. T. A. Rafter. Analyst <u>75</u>, 484 (1950).

95. W. F. Muehlberg. Ind. Eng. Chem. <u>17</u>, 690 (1925).

96. C. E. Crouthamel. "Applied Gamma-Ray Spectrometry", Pergamon Press, New York, 1960.

97. R. L. Heath. U. S. Atomic Energy Commission IDO-16408 (1957).

98. L. Salmon. U. Kingdom Atomic Energy Authority, AERE-C/M-206 (1954).

99. C. E. Miller. U. S. Atomic Energy Commission, ORNL-2715 (1959).

100. R. E. Connally, M. B. Leboeuf. Anal. Chem. <u>25</u>, 1095 (1953).

101. W. Lee. Anal. Chem. <u>31</u>, 800 (1959).

102. D. G. Olson. U. S. Atomic Energy Commission IDO-14495 (1959).

103. J. A. Seiler. "Radiochemical Studies: The Fission Products", National Nuclear Energy Series, Div. IV, Vol. 9, p. 1573, Paper 264. C. D. Coryell, N. Sugarman, eds., McGraw-Hill Book Co., Inc., New York, 1951.

104. L. E. Glendenin. "Radiochemical Studies: The Fission Products", National Nuclear Energy Series, Div. IV, Vol. 9, p. 1575, Paper 265. C. D. Coryell, N. Sugarman, eds., McGraw-Hill Book Co., Inc., New York, 1951.

105. W. W. Meinke. U. S. Atomic Energy Commission, AECD-2738 (1949).

106. A. S. Newton. Phys. Rev. 75, 17 (1949).

107. J. Kleinberg. U. S. Atomic Energy Commission, LA-1721, 2nd ed. (1958).

108. J. M. Alexander, U. Schindewolf, C. D. Coryell. Phys. Rev. 111, 228 (1958).

109. H. Brown, E. Goldberg. U. S. Atomic Energy Commission, AECD-2296 (1948); Science 109, 347 (1949).

110. G. W. Parker, G. E. Creek, G. M. Hebert, P. M. Lantz. U. S. Atomic Energy Commission, ORNL-336 (1949).

111. D. E. Zvygintsev, A. I. Kulak. Zhur. Neorg. Khim. 2 (7), 1687 (1957); Engl. Transl. 2 (7), 376 (1957).

112. E. A. Vincent, A. A. Smales. Geochim. et Cosmochim. Acta 9, 154 (1956).

113. B. G. Dzantiev, V. N. Levkovskii, A. D. Malievskii. Doklady Akad. Nauk SSSR 113, 773 (1957); Transl. Soviet Phys. Doklady 2, 154 (1957).

114. G. Wilkinson, W. E. Crummitt. Nucleonics 9 (3), 52 (1951); Nature 158, 163 (1946); 161, 520 (1948).

115. R. A. Killick, D. F. C. Morris. Talanta 8, 601 (1961).

116. J. D. Gile, H. R. Haymond, W. M. Garrison, J. G. Hamilton. Unpublished.

117. W. M. Garrison, J. G. Hamilton. U. S. Atomic Energy Commission, UCRL-1067 (1950).