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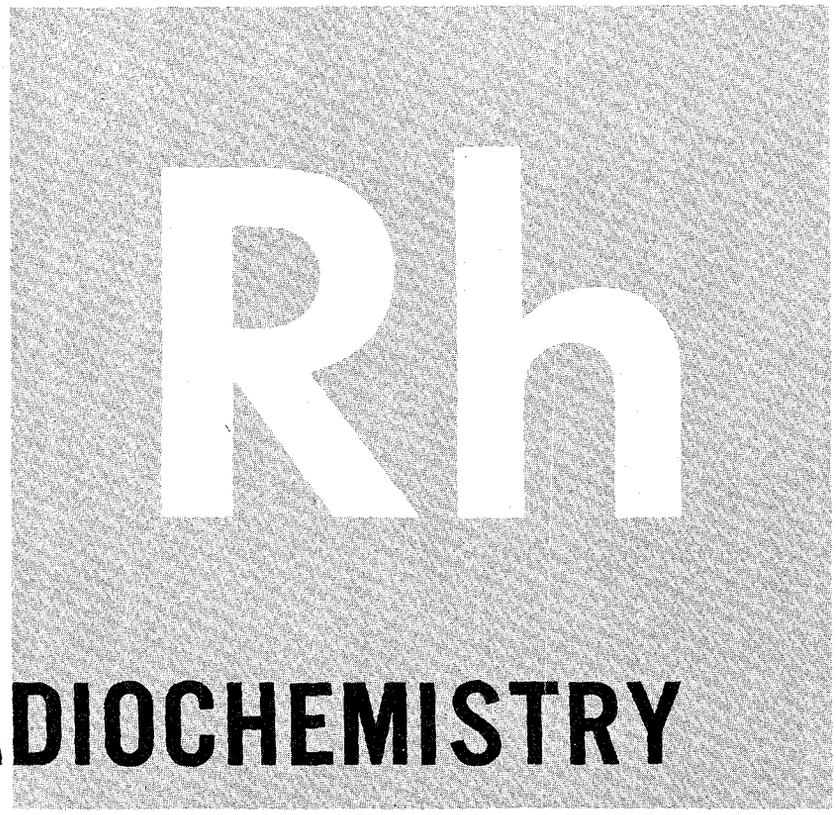

RADIOCHEMISTRY OF RHODIUM

Rev. 1965

NUCLEAR SCIENCE SERIES

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Radiochemistry of Rhodium

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National Academy of Sciences—National Research Council

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FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of radiochemistry and nuclear chemistry. Support for the activities of this and other subcommittees of the Committee on Nuclear Science is provided by a grant from the National Science Foundation.

The Subcommittee has concerned itself with preparation of publications, encouraging and supporting activities in nuclear education, sponsoring symposia on selected current topics in radiochemistry and nuclear chemistry, and investigating special problems as they arise. A series of monographs on the radiochemistry of essentially all the elements and on radiochemical techniques is being published. Initiation and encouragement of publication of articles on nuclear education in various subject areas of chemistry have occurred, and development and imporvement of certain education activities (e.g., laboratory and demonstration experiments with radioactivity) have been encouraged and assisted. Radioactive contamination of reagents and materials has been investigated and specific recommendations made.

This series of monographs has resulted from the need for comprehensive compilations of radiochemical and nuclear chemical information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or with a specialized technique. The U. S. Atomic Energy Commission has sponsored the printing of the series.

Comments and suggestions for further publications and activities of value to persons working with radioactivity are welcomed by the Subcommittee.

N. E. Ballou, Chairman
Subcommittee on Radiochemistry

INTRODUCTION

This monograph on the radiochemistry of rhodium is one in a series covering the radiochemistry of essentially all the elements. It is a revised and expanded version of an earlier monograph. In it are included reviews of nuclear and chemical properties of rhodium, discussions of methods of sample dissolution and of separation reactions, descriptions of counting techniques, and a compilation of radiochemical separation procedures.

As new information accumulates on chemical and nuclear properties of rhodium and on separation and measurement techniques, consideration will be given to further revision of this monograph. Consequently as additional information becomes available in both published and unpublished form, readers are encouraged to bring it to the attention of the author for possible inclusion in future editions of this monograph.

CONTENTS

Radiochemistry of Rhodium

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

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III. ISOTOPES OF RHODIUM

TABLE I

TABLE OF ISOTOPES OF RHODIUM

Nuclide	$T_{1/2}$	Type and Energy (MeV) of Radiation
Rh^{97}	35 m	β^+
Rh^{98}	8.7 m	β^+: 2.5
		γ: 0.65
Rh^{99}	15 d	γ: 0.086 (K/L 5), 0.353
Rh^{99}	4.7 h	E.C. (90%); β^+: 0.74 (10%)
		γ: 0.34 (70%), 0.62 (20%), 0.89, 1.26, 1.41
Rh^{100}	20.8 h	E.C. (95%); β^+ (5%)
		β^+: 2.62 ($^+$45), 2.07 ($^+$39), 1.26 ($^+$13), 0.54 ($^+$3.6), 0.15 ($^+$0.06)
		γ: 0.301, 0.372, 0.442, 0.535, 0.742, 0.823, 1.108, 1.358, 1.557, 1.934, 2.379

III. TABLE (CONTINUED)

Nuclide	$T_{1/2}$	Type and Energy (MeV) of Radiation
Rh^{101}	4.7 d	E.C.
		γ: 0.31
Rh^{101}	5 y	γ: 0.125 ($e_{K/\gamma}$ 0.4), 0.190 ($e_{K/\gamma}$ 0.7)
Rh^{102}	205 d	β^+/β^- 0.84; E.C., β^+~ 7.5%
		β^-: 1.15
		β^+: 1.24 ($^+59$), 0.76 ($^+21$), 0.40 ($^+4$),
		γ: 0.125 ($^+50$), 0.200 ($^+60$), 0.475 ($^+80$),
		0.635 ($^+30$), 0.72 ($^+10$), 0.79 ($^+10$),
		1.08 ($^+60$)
Rh^{102}	1057 d	(Same γ's as above)
*Rh^{103m}	57 m	I.T.
		γ: 0.040 (K/L 0.18, $e_{K/\gamma}$ 40)
Rh^{103}	Stable	(100%)
Rh^{104m}	4,4m	I.T. (99^+%), β^-(~0.1%)
		γ: 0.051 ($e_{K/\gamma}$ 1.9), 0.077 (K/L~0.6)
		(also, Rh^{104} γ's)
Rh^{104}	44 s	β^-: 2.5 (98.5%), 1.9 (1.4%), 0.7 (0.08%)
		γ: 0.556 ($^+100$), 1.24 ($^+5.8$)
Rh^{105m}	45 s	I.T.
		γ: 0.130 (e/γ 3, K/L 1.6) (Also, Rh^{105} γ's)
Rh^{105}	36.5 h	β^-: 0.570 (96%), 0.25 (4%)
		γ: 0.320 (10%, d/γ 0.018), 0.157 (very
		weak)
Rh^{106}	130 m	β^-: 0.7
		γ: 0.220 ($^+18$), 0.435 ($^+43$), 0.515 ($^+100$),
		0.61 ($^+26$), 0.74 ($^+36$), 0.82 ($^+45$),
		0.94, 1.07 ($^+39$), 1.23 ($^+24$), 1.38,

III. TABLE (CONTINUED)

Nuclide	$T_{1/2}$	Type and Energy (MeV) of Radiation
		1.56 ($^{+}$39), 2.26 ($^{+}$1) (Also, Rh^{106} (30 s) γ's)
Rh^{106}	30 s	β^-: 3.53 (68%), 3.1 (11%), 2.44 (12%), 2.0 (3%), others (6%)
		γ: 0.513 (21%, $e_{K/\gamma}$ 0.005), 0.624 (10%), 0.87 (0.3%), 1.045 (1.7%), 1.14 (0.4%), 1.54 (0.2%), 1.76, 2.28, 2.42 (Also, Rh^{106} (130 m) γ's)
Rh^{107}	24 m	β^-: 1.15
		γ: 0.305, 0.385, 0.570, 0.680
Rh^{108}	18 s	β^-: 4.5
Rh^{109}	1 hr	β^-

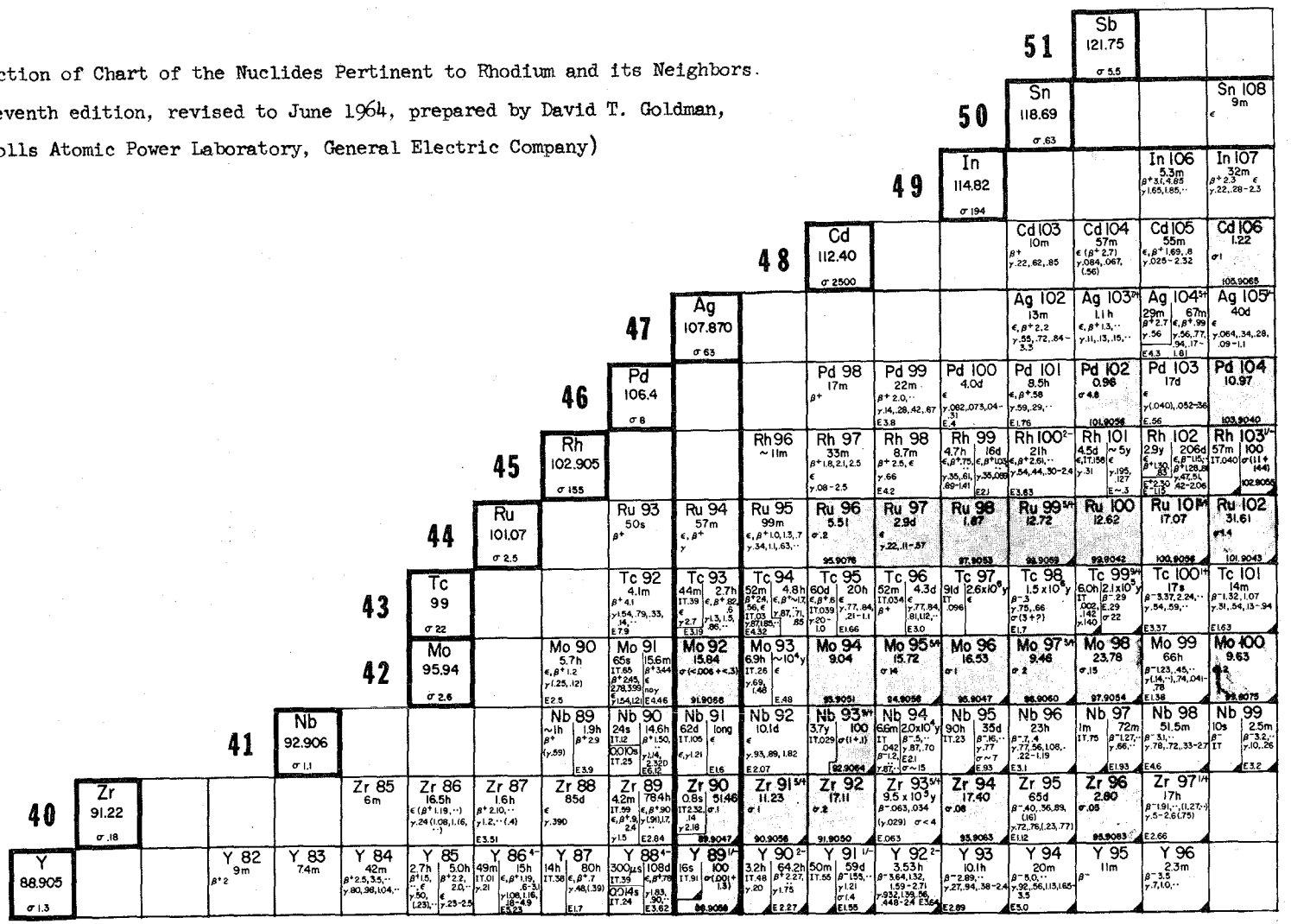
$^{+}$ signified relative intensity

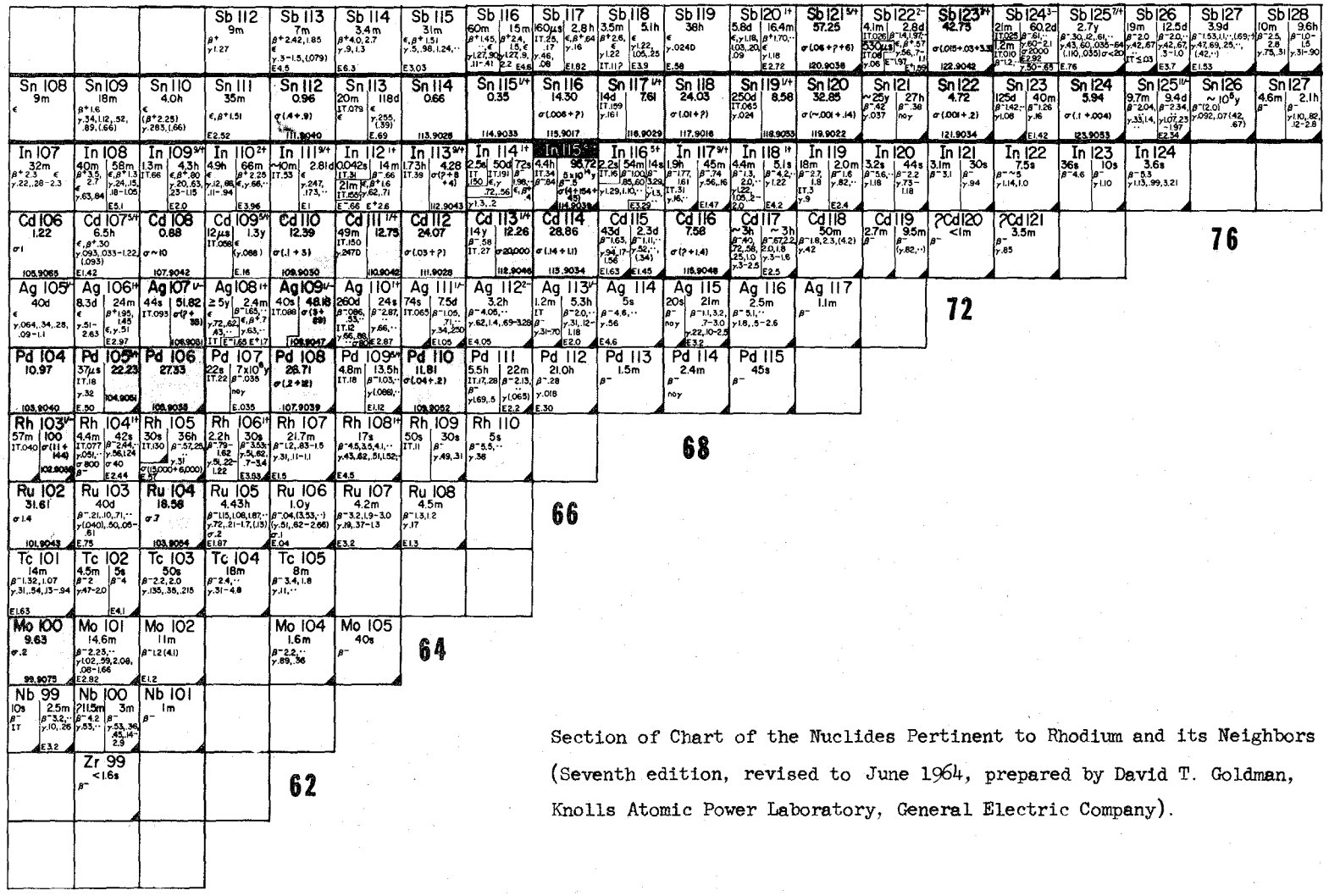
* From Rh^{103} the succeeding isotopes have been identified as fission products.

For a more complete list of the nuclear properties of the rhodium isotopes and references to the original literature, consult: "Table of Isotopes", Strominger, Hollander and Seaborg, Reviews of Modern Physics, 30, 585 (1958).

Section of Chart of the Nuclides Pertinent to Rhodium and its Neighbors.

(Seventh edition, revised to June 1964, prepared by David T. Goldman, Knolls Atomic Power Laboratory, General Electric Company)





Section of Chart of the Nuclides Pertinent to Rhodium and its Neighbors (Seventh edition, revised to June 1964, prepared by David T. Goldman, Knolls Atomic Power Laboratory, General Electric Company).

IV. REVIEW OF THE CHEMISTRY OF RHODIUM

Rhodium is one of the rarest elements, occurring in only one part in 10^9 in the earth's crust. It has not been studied extensively and the interpretation of many of the published results are questionable due to uncertainties of the complex species involved. In general, rhodium chemistry resembles that of cobalt and, to an even greater extent, that of iridium.

A. Metal. Metallic rhodium is harder, tougher and higher melting than platinum or palladium. It, however, is softer, more ductile and less brittle than metallic iridium. It has a lower specific resistance than these latter two metals and maintains a low and stable contact resistance due to the absence of oxide films on its surface. Metallic rhodium behaves more like platinum than palladium with respect to hydrogen. Compact rhodium absorbs very little H_2, while finely divided rhodium absorbs H_2 readily; consequently, powdered rhodium serves as a very active hydrogenation catalyst. Some of the properties of rhodium metal are listed in Table II.

Compact rhodium is quite resistant to chemical attack by acids, even aqua regia, and is attacked only slowly by boiling sulfuric acid. Alkaline fusion is the usual technique for oxidizing the metal. Potassium acid sulfate or potassium pyrosulfate fusion completely converts rhodium to the water soluble $Rh_2(SO_4)_3$. If the fusion is accomplished with $NaHCO_3$ and KNO_3 or with BaO_2, insoluble oxides are formed. Fused metaphosphoric acid will dissolve rhodium to some extent, while a mixture of O_2 and HCl reacts with the metal above 150°C.

A number of reducing agents such as ammonium formate, $TiCl_3$, Mg, etc., will reduce rhodium(III) to a black finely divided form of rhodium metal. This form is readily soluble in aqua regia or hot, concentrated sulfuric acid. The fused salts listed above also dissolve the powdered metal. Solution may be achieved either in concentrated hydrochloric acid under pressure of oxygen or in the presence of sodium chlorate in a sealed tube at temperatures of 125 - 150°C.

TABLE II
PHYSICAL PROPERTIES OF RHODIUM METAL [1,2]

Atomic Number	45
Atomic Weight	102.91
Density	12.42 g/cm^3
Crystal Structure	Face-centered cubic
Metallic Radius	1.247 Å
Atomic Volume	8.29 ml
Thermal Conductivity	0.210 cal/cm sec degree
Electrical Conductance	0.222 μohms/cm
Melting Point	1966°C
Boiling Point	3727°C
Heat of Fusion	5.2 Kcal/mole
Heat of Vaporization	118.4 Kcal/mole
Ionization Potentials (Kcal/g atom)	277 (1st) 417 (est) (2nd) 716 (est) (3rd)
Thermal Neutron Cross Section	140 barns (Rh^{104} 42 s) 12 barns (Rh^{104m} 4.4 m)

Attack by Cl_2 on a wet bed of NaCl yields soluble $RhCl_3$ (or Na_3RhCl_6).

Direct union of rhodium with sulfur yields Rh_2S_5, Rh_2S_3, Rh_3S_4 and Rh_9S_8, but no evidence has been reported for the formation of RhS or RhS_2. At 500 - 600°C fluorine attacks metallic rhodium to form RhF_3 as well as some RhF_4 and RhF_5. At red heat, rhodium slowly oxidizes to Rh_2O_3 in and to $RhCl_3$ in streams of the gases.

B. Oxides. In oxygen, rhodium volatilizes as the dioxide at 800 - 1500°C but decomposes back to the elemental

state above 1100°C in an oxygen deficient atmosphere. Neither Rh_2O nor RhO have been definitely shown to exist. The hydrous oxide formed by the precipitation of Rh^{3+}_{aq} with NaOH is lemon yellow, water insoluble, and acid soluble. Its stoichiometric formula is $Rh_2O_3 \cdot 5H_2O$. Upon heating, the water is lost to form the yellow Rh_2O_3 which is water and acid insoluble. Unpublished work by one of the authors (J.C.A.) using X-ray diffraction has shown that the black amorphous $Rh(OH)_3$ described in Sidgewick's book is actually metallic rhodium.

C. Oxidation States. Rhodium differs from the other Group VIII elements in the unusual stability of the oxidation number III relative to all others. Osmium and ruthenium, in particular, are characterized by a multiplicity of oxidation states. For iridium, which rhodium most closely resembles, the trivalent is the most important state; but compounds of iridium 0, I, II, IV, V and VI are known and those of Ir(IV) have some importance. While cobalt(II) is the characteristic species in many ionic tetrahedral and octahedral complexes, in covalent complexes cobalt is usually in the trivalent state. This is in agreement with the fact that rhodium compounds in general exhibit a high degree of covalency and have a strong preference for the oxidation number III.

Very little is reported concerning the oxidation potentials for rhodium. Latimer [3] has published some estimated values which are summarized in this oxidation potential diagram in acid solution:

$$Rh^0 \xrightarrow{-0.6v} Rh^{+1} \xrightarrow{-0.6v} Rh^{+2} \xrightarrow{-1.2v} Rh^{3+} \xrightarrow{-1.4v} Rh^{2+} \xrightarrow{-1.46v} RhO_4^{-2}$$

$$Rh^0 \xrightarrow{-0.8v} Rh^{3+}$$

Rhodium(0). Several carbonyls have been reported such as $[Rh(CO)_4]_n$, $[Rh(CO)_3]_n$ and $[Rh_4(CO)_{11}]_n$. The first seems to be a yellow dimer, $[Rh_2(CO)_8]$, which decomposes at 76°C.

Rhodium(I). Examples reported are $[Rh(CO)_2Cl]_2$, $[Rh(CNR)_4]X$ $C_8H_8RhCl(AsPh_3)$ and $RhClCO(PEt_3)_2$, where R = p-tolyl, p-chlorophenyl; X = Cl^-, ClO_4^-; $AsPh_3$ = arsines; PEt_3 = phosphines.

Rhodium(II). Although RhO, RhS and $RhCl_2$ have all been reported, there exists doubt about the validity of these reports and it is possible that no simple compounds of this oxidation state exist at all. Some ammines and arsines have also been reported, as well as $[Rhpy_6]X_2$ where

py = pyridine

X - halide.

Several complexes supposedly of rhodium(II) have been shown by nuclear magnetic resonance studies to be rhodium(I).

Rhodium(III). This oxidation state is discussed separately in the following section.

D. Rhodium(III), the most common oxidation state. This is by far the most common and best studied oxidation state. In common with the other platinum group elements, rhodium(III) rarely forms simple compounds but rather shows a strong tendency to form polynuclear complexes. As a result, apparently simple compounds such as $Rh(OH)_3$ and $RhCl_3$ exist in several forms. For example, if $RhCl_3$ is made from rhodium metal heated in a stream of chlorine,

it is insoluble in water and acids; if it is made from the hydrous oxide, $R_2O_3 \cdot 5H_2O$ by the action of hydrochloric acid, it is very soluble. The soluble form can be converted to the insoluble form by high temperatures. If alkali is added slowly to $RhCl_3$ in solution, yellow crystals, having the composition $Rh(OH)_3 \cdot H_2O$ and readily soluble, form. $Rh_2(SO_4)_3$ also exists in two forms--a yellow one and a red one.

M. Lederer and coworkers have made the most detailed study of the problem of the species actually present in some inorganic systems. [4-7] Commercial $RhCl_3$ dissolved in 6N hydrochloric acid reached equilibrium in two days at room temperature as shown by the absorption spectrum. On elution with 6N HCl through Dowex-2 anion-exchange resin, 70% of the rhodium passed through the column rapidly as a red band which was found to have an absorption spectrum in good agreement with that reported by Jorgensen [8] for the hexachlororhodate(III) ion, $RhCl_6^{3-}$. The remainder was in a form which was strongly adsorbed as a red-brown band on the Dowex-2 column.

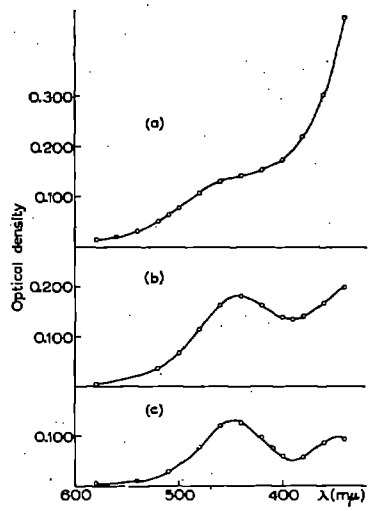


Fig. 1. Absorption spectra of eluate when a solution of rhodium hydroxide in 6 *N* HCl on a Dowex-2 column is eluted with just over 1 column volume of 6 *N* HCl. (a) Aged 1/4 h at room temperature. No adsorption on a Dowex-2 column. (b) Aged 2 days at room temperature. Weak red band ($RhCl_6^{-3}$) and strong tan band ($Rh(H_2O)Cl_5^{-2}$) on a Dowex-2 column. (c) Heated 1 h at 100°. Strong red band ($RhCl_6^{-3}$) and weak tan band ($Rh(H_2O)Cl_5^{-2}$) on a Dowex-2 column. (Ref. 6)

A solution of $RhCl_3$ or $Rh(OH)_3$ in 6N HCl on refluxing at 110°C reached equilibrium in an hour. By a combination of elution from Dowex-2 and absorption spectrometry, evidence was obtained for a series of successive reactions as follows:

$$Rh(OH)_3 + 6N\ HCl \rightarrow \text{cationic and neutral complexes} \rightarrow [Rh(H_2O)_2Cl_4]^{-1} \rightarrow [Rh(H_2O)Cl_5]^{-2} \rightarrow [RhCl_6]^{-3}.$$

At equilibrium, the rhodium is about 95% in the $RhCl_6^{-3}$ form. It was suggested that refluxing in 6N HCl followed by passage through a Dowex-2 column would separate Rh from Co, Cu and Ru. The small amount of rhodium (presumably as polynuclear complexes) which adsorbs strongly on the anion resin would reduce the attractiveness of this technique. Refluxing of ammonium hexachlororhodate in 6N HCl yielded mostly $RhCl_6^{-3}$ but, also, appreciable amounts of another species, which the authors suggest is probably $Rh(NH_3)Cl_5^{-2}$.

In 0.5N HCl rhodium chloride was found to be a mixture of up to six complexes with a slowly-attained equilibrium. The ratio of the complexes depends on the mode of formation and the age of the solution.

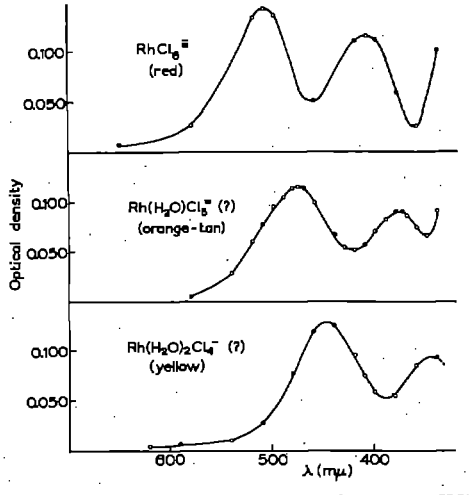
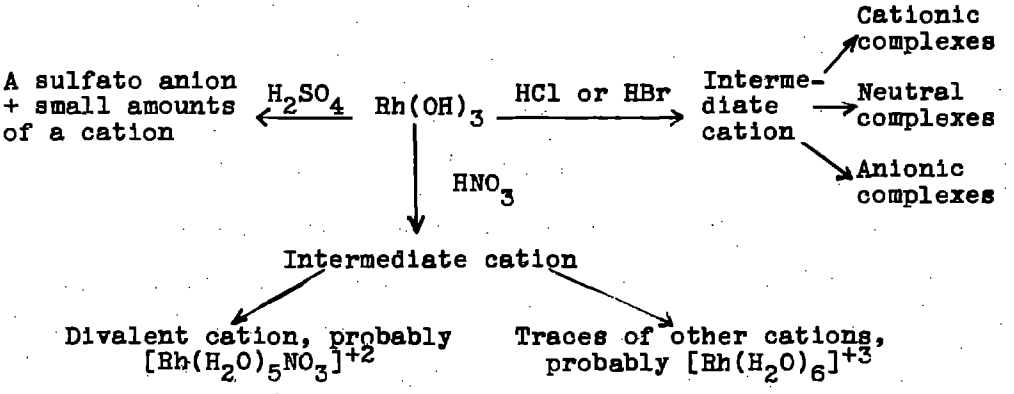


Fig. 2. Absorption spectra of Rh(III) complexes in 6 *N* HCl. (Ref. 6)

Similar results were found for HBr, HNO_3 and H_2SO_4 solutions. An unstable intermediate cation was found to form in all but sulfuric acid. This, as well as the fact that of this group only sulfuric acid can dissolve rhodium metal, reflects the stronger complexing power of sulfate with Rh(III). The observations of Lederer may be summarized thusly:



The yellow rhodium sulfate mentioned previously was shown to have the $[Rh(H_2O)_6]^{+3}$ cation present. The red form is a mixture, one species being the anionic trisulfato complex, $[Rh(SO_4)_3]^{-3}$.

It was shown also that the removal of the coordinated chloro groups from the rhodium-chloro salts is not complete in one precipitation as the hydroxide. To completely remove the coordinated chloro groups from "Rhodium hydroxide" at least six repeated precipitations and dissolutions in $HClO_4$ were required. The final product showed a single band when submitted to paper electrophoresis.

This study by Lederer's group has been complemented by Wolsey, Reynolds and Kleinberg [9] who used Dowex-50 cation exchange resin to separate the species present in the rhodium(III)-chloride system. The complex species were

adsorbed on the resin bed from the chloride solution; they were eluted from the column by means of perchloric acid solutions of Th(IV). The rhodium complexes eluted in separate distinct bands which were analyzed for rhodium and free hydrogen ion. This allowed calculation of the charge on the complex species per rhodium(III) atom. The species were also studied for their absorption bands and molar absorptivity. The authors further were able to calculate the successive formation constants from the equation

$$k_n = \frac{(RhCl_n^{3-n})}{(RhCl_{n-1}^{3-1-n})(Cl^-)}.$$

The results of this investigation are listed in Table III. The two maxima in the absorption spectra for all species is in accord with Jorgensen's predictions that these complexes should exhibit transitions to two singlet and two triplet levels. The absorption maxima of the chloro complexes show a shift to longer wave lengths with increasing number of chloride ligands. The agreement with the spectroscopic measurements of Lederer and coworkers is good for the cationic species. However, the spectra assigned to $RhCl_4^-$ and $RhCl_5^{2-}$ are not in accord with those which Kristjanson and Lederer assigned to these species. Rather, the spectra of these complexes reported by Kristjanson and Lederer resemble roughly the spectra assigned by Wolsey et al. to $RhCl_2^+$ and $RhCl_3$. Otherwise, this work and the studies of Lederer's group are in substantial agreement.

This multiplicity of species is not restricted to the inorganic complexes of rhodium. When pure rhodium(III) hydroxide is heated with oxalic acid, $RhOx_3^{-3}$ is formed to a great extent. [10] The reaction does not go to completion

TABLE III

Species	Max (mμ)	Molar Absorptivity (E)	Formation Constants at 120°C. (k_n)
$Rh(H_2O)_6^{3+}$	311 396	67.4 62.0	
$RhCl^{+2}$	335 426	50.0 50.4	$>10^3$
$RhCl_2^{+1}$	349 450	49.5 64.9	$>10^3$
$RhCl_3$ (cis)	376 474	93.5 68.3	10^3 (cis + trans)
$RhCl_3$ (trans)	370 471	71.6 77.1	
$RhCl_4^{-1}$	385 488	54.1 72.0	250 ± 120
$RhCl_5^{-2}$	402 507	73.4 72.8	25 ± 8
$RhCl_6^{-3}$	411 518	93.8 111.5	0.56 ± 0.18

as other aquo-coordinated oxalato complexes of rhodium are formed in small quantities. In order to obtain complete conversion of rhodium(III) into potassium trisoxalatorhodate(III), the chloride must be refluxed with four to five times its weight of potassium oxalate for at least six hours.

E. Physical Properties of Rhodium(III) Compounds. Reliable data is rather scarce for rhodium(III) compounds. A summary of some data on solubility, melting point, etc., is listed in Table IV.

F. Complexes of Rhodium(III). A relatively large number of rhodium(III) complexes are known. Even the simple salts readily form autocomplexes. In the great majority of

TABLE IV

PHYSICAL PROPERTIES OF Rh(III) COMPOUNDS

Compound	Mol Wt	Color and Crystalline Form	Density	M.P.	B.P.	Solubility
RhF_3	159.91	red, rhomb.	5.38	----	>600 (subl)	Insoluble in H_2O, HCl, HNO_3, H_2SO_4, NaOH
$RhCl_3$	209.28	br. red powd., deliq.	----	450-500(d)	800 (subl)	Insoluble in H_2O, acids, alkalies
$RhCl_3 \cdot xH_2O$	----	dk. red	----	d	----	Soluble in H_2O, HCl, alcohol
RhI_3	590.04	----	----	----	----	Insoluble in H_2O, acids, alkalies
$Rh(NO_3)_3$	288.93	br.-yellow	----	d	----	Soluble in H_2O, insoluble in alcohol

$Rh(NO_3)_3 \cdot 2H_2O$	324.97	red, deliq.	----	----	----	Soluble in H_2O, insoluble in alcohol
Rh_2O_3	253.82	gray, crys. or amor.	----	1100-1150(d)	----	Insoluble in H_2O, acids, alkalies
$Rh_2O_3 \cdot 5H_2O$	343.90	yellow	----	d	----	Soluble in hot H_2O, acids
RhO_2	134.91	brown	----	----	----	Insoluble in H_2O, acids, alkalies
$RhO_2 \cdot xH_2O$	----	olive-green	----	d	----	Soluble in HCl
$Rh_2(SO_4)_3 \cdot 12H_2O$	710.21	yellow	----	----	----	Soluble in H_2O, insoluble in alcohol
Rh_2S_3	302.02	black	----	d	----	Insoluble in H_2O, acids
$Rh_2(SO_3)_3 \cdot 6H_2O$	544.11	yellow	----	d	----	Soluble in H_2O, insoluble in alcohol

cases, rhodium(III) complexes exhibit a coordination number of 6 and an octahedral structure. The bonding is of the inner orbital d^2sp^3 type. The chemistry of Rh(III) complexes in general is rather similar to that of Co(III) complexes and Ir(III) complexes. Due to the lanthanide contraction, the radii of the 4d metal ions are more similar to those of the 5d elements than those of the 3d elements. The 4d and 5d electrons in the second and third transition series are less tightly held to the metal atom than are the 3d electrons in the first transition series. As a consequence, molecular orbital formation occurs more readily. In addition, in a ligand field the crystal field stabilization energy (10Dq) between the split d orbitals is large with the result that charge-transfer states have lower energies than crystal field states. A further problem is that it is not possible to treat spin-orbit coupling as a minor perturbation in the 4d and 5d elements. All this increases the difficulty of interpretation of data on such complexes as those of Rh(III).

One direct consequence of the increased level splitting in 4d elements is a far greater tendency to form low spin (smallest number of unpaired electrons) complexes. In Rh(III) this results in the $t_{2g}^6\ e_g^0$ configuration since the t_{2g} orbitals are lower in energy. Experimental confirmation of this is found in the fact that Rh(III) complexes are diamagnetic.

Jorgensen [11] has studied the absorption spectra of a number of Rh(III) complexes. Again, he assigns the low spin t_{2g}^6 configuration as the ground state. This is designated as $^1A_{1g}$. The singlet excited states are $^1T_{1g}$ and $^1T_{2g}$ belonging to the configuration $(t_{2g}^5)(e_g)$. Some of Jorgensen's results are tabulated in Table V.

TABLE V

SPECTRAL TRANSITIONS IN Rh(III) COMPLEXES

Complex	Transition		
$[RhCl_6]^{3-}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	19,300	$D_q = 2160\ cm^{-1}$
	$^1A_{1g} \rightarrow {}^1T_{2g}$	24,300	
	$^1A_{1g} \rightarrow {}^3T_{1g}$	14,700	Spin forbidden band
$[RhBr_6]^{3-}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	17,900	
$[Rh(C_2O_4)_3]^{3-}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	25,100	
	$^1A_{1g} \rightarrow {}^1T_{2g}$	30,000	
	$^1A_{1g} \rightarrow {}^3T_{1g}$	19,200	Spin forbidden band
$[Rh(H_2O)_6]^{3+}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	26,000	$D_q = 2770\ cm^{-1}$
$[Rh(NH_3)_6]^{3+}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	32,700	
	$^1A_{1g} \rightarrow {}^1T_{2g}$	39,100	
$[Rh(en)_3]^{3+}$	$^1A_{1g} \rightarrow {}^1T_{1g}$	33,400	

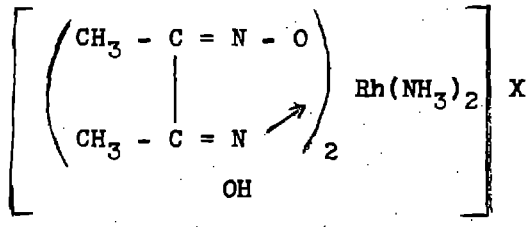
The covalent nature of the Rh(III) complexes is reflected in their relatively inert kinetic behavior. The multiplicity of species isolated by Lederer reflects the slowness of the rate of exchange. In general, Rh(III) complexes aquate at a rate intermediate between those of Co(III) and Ir(III). In contrast to Co(III) and Ir(III), however, the monochloropentaaquorhodium(III) aquates faster than the monobromo analogue. Basolo and Pearson [12] list the rather scanty data on exchange rates in their text. In

general, the cationic and neutral species are more kinetically inert than the anionic complexes. The greater lability of the anionic species has been attributed to a more rapid unimolecular dissociation step. Presumably, the cationic and neutral complexes can react only by undergoing a slow bimolecular substitution.

$[Rh(CN)_6]^{-3}$ is a particularly stable species, being unaffected by prolonged boiling in concentrated sulfuric acid. Four types of halide complexes are known: M_3RhX_6, M_2RhX_5, M_4RhX_7 and $M_3Rh_2X_9$ where M is usually a large cation such as a protonated organic base and X is chloride or bromide. Two anionic complexes, $[RhX_6]^{-3}$ and $[Rh(H_2O)X_5]^{-2}$, where $X = Cl^-$, Br^-, SCN^-, are important in rhodium solution chemistry. It is noteworthy that Co(III) does not form the analogues of these anions. $[Rh(SCN)_6]^{-3}$ is quite stable and as $H_3[Rh(SCN)_6]$ can be extracted with amyl alcohol. The insoluble alkali and alkaline earth salts with the $[Rh(NO_2)_6]^{3-}$ are important in several separation schemes.

Usually it is possible to prepare with a particular ligand a multiplicity of rhodium complexes up to the saturation of the coordination number of six. When one of the oxalato complexes, cis-$K_3[Rh(C_2O_4)_2Cl_2]$, is subjected to prolonged boiling or evaporated to dryness, the trans isomer is formed. However, there is no rapid racemization even at 100°C, so the stability of rhodium complexes is again demonstrated. The malonato complexes show the same stability in solutions as the oxalato complexes. The complexes with ammonia ranging from the hexamine, $[Rh(NH_3)_6]X_3$, to the monamine, $M_2[Rh(NH_3)X_5]$, and pyridine have been studied, and the latter complexes provide the basis for an important extraction separation. With dimethylglyoxime (DMG) rhodium

forms a dichelate complex with the two remaining coordination sites occupied by NH_3 or Cl^-.



This complex is more stable than the corresponding one for cobalt but less so than the one for palladium. As a consequence, it is possible to precipitate palladium with DMG in hydrochloric acid solution while rhodium remains in solution.

Jorgensen [8] has reported on the hydrolysis of rhodium(III). In titrating $Rh(OH)_3$ with $HClO_4$, it was observed that flocculation disappeared about pH 5 but turbidity persisted until pH 3.8. Therefore, Rh(III) would seem to behave to hydrolysis somewhat like the trivalent lanthanides and Cr(III). $[Rh(NH_3)_5(H_2O)]^{+3}$ has a reported value for the pKa of 5.9 at 25°C which is comparable to the analogous cobalt and chromium cations. [12]

It should be kept in mind in working with rhodium complexes that these compounds frequently have more than one formula unit in their molecular structure. A good example of this is the red compound corresponding to the simple formula $K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$. Nuclear magnetic resonance data have provided the basis for assigning to this compound the formula $K_6[Rh(C_2O_4)_3][Rh(C_2O_4)_2(HC_2O_4)(OH)] \cdot 8H_2O$.

V. SEPARATION OF CHEMISTRY

A. Precipitation. Beamish [13] reports that analytical methods for the determination of rhodium are few in number and no gravimetric reagent is specific for a practi-

cal separation. However, since the radiochemical procedures which follow are based in a large part on the standard analytical separation scheme, it is well to describe that standard method.

Osmium is removed first by distillation of OsO_4 from nitric acid solution. RuO_4 distillation from dilute sulfuric acid containing bromate removes ruthenium. Palladium, rhodium, iridium and platinum are precipitated as the hydrous oxides again in the presence of bromate. Hydrolytic precipitation of rhodium is complete at a pH of 6 leaving platinum in the supernatant solution. This precipitation must be repeated if the rhodium is to be quite free of platinum. The oxides are then dissolved in HCl and palladium precipitated with dimethylglyoxime. Rhodium is separated from iridium by reduction to the metal with $TiCl_3$ in hot sulfuric acid. Again, this precipitation may be repeated to eliminate all the iridium. The rhodium metal is dissolved in hot concentrated sulfuric acid and precipitated with H_2S. This is ignited in air, then in hydrogen and, finally, weighed as metallic rhodium.

A colorimetric method using $SnCl_2$ and HCl has been reported by several groups. [14] Both the $SnCl_2$ method and one using 2-mercaptobenzoxazole have been developed for the determination of rhodium in the 25-200 microgram range. [15] Ayres and Young have also reported a colorimetric procedure which is frequently used. [16] A more recent publication describes a colorimetric reagent, 2 ethylaminoethanethiol hydrochloride, which has the advantage of aqueous solubility, for trace amounts of rhodium. [17]

Beamish [18] has recently reviewed the recovery of

rhodium and other platinum group metals from ores and concentrates by wet assay.

Rh, Ir, Pt, Ru and Pd can be isolated from such base metals as gold, copper, zinc, etc., by first converting the former to soluble stable nitrite complexes followed by precipitation of the base metals as hydrous oxides. The nitrite complexes of the platinum group metals are changed to the chloro form and precipitated by ammonium chloride. [19] Rh, Ir and Pd can be separated from Pt by controlled hydrolysis of the chloro complexes in the presence of bromate. [20] Another technique [21] reports a method of separating Rh, Ir and Pd from Pt by oxidation of the metals to their higher valence states and precipitation of Rh, Ir and Pd by hydrolysis of the solution to pH 6-8 with sodium acid carbonate.

Lloyd and Morris [22] have described a procedure for the separation of milligram amounts of iridium and rhodium from each other using calomel and hypophosphorus acid. The final rhodium sample contained only 0.006 mg of iridium when the initial sample contained 30 mg each of rhodium and iridium. It would seem that this method could be adapted profitably to radiochemical separation.

Rhodium as well as iridium and platinum can be quantitatively separated from palladium with dimethylglyoxime [23] or with β-nitroso-α-naphthol. [24] Rhodium can be separated from lead, nickel and zinc with thiobarbituric acid. [25] Similarly, it has been shown that iridium and rhodium can be quantitatively precipitated by thiourea. [26] Incomplete separations of rhodium from iridium have been achieved by selective extraction from fused sodium bisulfate, [27] fusion in lead, [28] and reduction of chloride complexes.

[29] A quantitative separation of rhodium from iridium can be achieved [30] by the reduction of Rh(III) to rhodium metal as described in the standard method described earlier. A number of authors have described other methods of separating rhodium from iridium, most of which involve reduction of Rh(III) to rhodium metal. [31-35]

A method for the determination of rhodium in uranium-rhodium alloys employs absorption spectrometry using $SnCl_2$ reagent. [36] It is recommended that the absorption be measured at 520 mμ rather than at 475 mμ which corresponds to the maximum of the absorption curve. This avoids interference by U(VI) which absorbs strongly at 475 mμ but not at all at 520 mμ.

B. Electrodeposition. MacNevin and Tuthill [37] have reported the selective deposition of rhodium on a platinum cathode by electrolysis of a solution for 1-1/2 hours at a voltage which was decreased steadily from -0.25v to -0.40v. Addition of 3.5M ammonium chloride to the solution produced quantitative separation from iridium in the deposited rhodium. Electrodeposition of rhodium has been studied by Bubernak [38] and reviewed by Fisher and Leonhard. [39]

C. Distillation. Parker and Grunditz [40] have described a separation of Rh^{103} from a ruthenium target. The target was placed on a tungsten filament and heated for one minute. Approximately 20% of the rhodium was collected on a Zapon film.

D. Solvent Extraction. In addition to the standard precipitation techniques, the radiochemist is interested whenever possible in using solvent extraction and/or ion

exchange for separations. Again here, the data on rhodium is best described as fragmentary. Morrison and Freiser [41] present what data there is on solvent extraction as described in the rest of this section.

With the halides, no data exist for fluorides or chlorides. $RhBr_3$ does not extract into isopropyl ether from 3M HBr. With methyl isopropyl ketone, RhI_3 is partially extracted from iodide solution containing 5% HCl. Both rhodium and ruthenium extract quite well in the presence of lead, although their extraction is slight otherwise. The extraction of Rh, Ru, Pd and Te(IV) is less than 5% from 1M nitric acid by dibutylphosphoric acid. Two useful extraction systems do exist with pyridine and with thenoyltrifluoroacetone (TTA), and both of these are described in the separation schemes which follow. Wish and Foti [42] have developed a solvent extraction separation scheme for Ag, Cd and Rh using triisooctylamine.

It has been shown that citrate complex of rhodium can be extracted as a substituted ammonium salt. [43]

E. Ion Exchange. Trivalent rhodium may be absorbed on Dowex-50 cation exchange resin from weak acid solution and subsequently eluted with moderate or strong concentrations of hydrochloric acid. No appreciable absorption was observed on Dowex-50 resin in 0.1 to 12N HCl. [44] This has been confirmed by Nelson, Murase and Kraus, [45] who report that the distribution coefficient is less than unity between 0.2 and 9M HCl. The study by Wolsey et al. of the species in chloride solutions has been discussed earlier.

Berman and McBryde [46] have studied the separation of rhodium from Pt, Pd, Ru and Ir using IRA-400 anion exchange

resin. Rh(III) had a lower K_D (resin distribution coefficient) than any of the other ions in hydrochloric acid and thus could be eluted first. The separations studied were:

a) Rh-Pd: Loaded column in 2M HCl; Rh eluted with 2M HCl, then the Pd with 12M HCl.

b) Rh-Pt: Same procedures as above.

c) Rh-Pd-Pt: Loaded column in 2M HCl; Rh eluted with 2M HCl, Pd with 9M HCl and Pt with 2.4M $HClO_4$.

d) Rh-Ir-Pd: As above in (a); Rh and Ir(III) eluted together in the 2M HCl.

They suggest that Ru(IV), which also has a high K_D, can be used for the separation of Ru from Rh. Ce(IV) would be used to insure formation of Ru(IV) and the rhodium would again be eluted with 2M HCl. However, under these conditions it was not possible to remove the rhodium quantitatively from the resin bed. Cluett et al. [47] had noted earlier that it was more difficult to remove rhodium from anion resin after adsorption from a fresh solution of chlororhodate than from an old one. As a result, it is necessary to use Ir(IV) (which has a very high K_D) in the separation of Rh and Ir with hydrochloric acid eluant. This behavior of fresh vs. old solutions as well as the non-quantitative removal of Rh(III) is explained by the results of Lederer described previously.

Kraus and Nelson [48] also reported low adsorption on Dowex-1 of Rh(III) at all HCl concentrations. Rh(IV) showed strong adsorption in the same system and they reported that it was difficult to remove these complexes by HCl solutions. Shimojiwa [44] observed slight adsorption of Rh(III) on Dowex-1 for solutions between 3 and 12N HCl but significant adsorp-

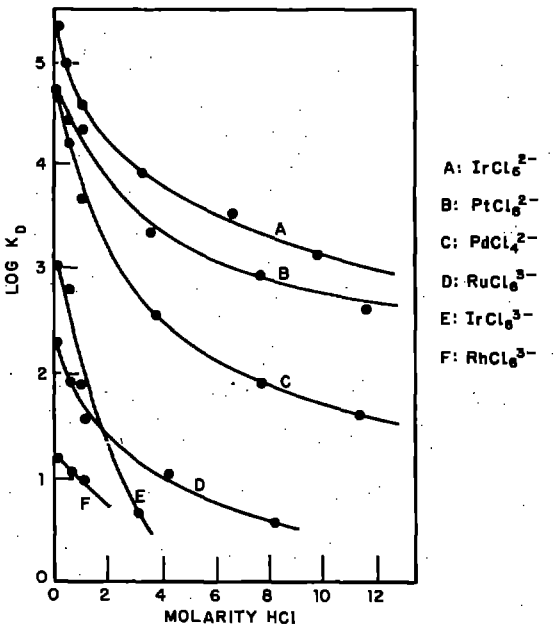


Fig. 3. Distribution Coefficients with Dowex-1 (Ref. 46)

tion at concentrations below 3N. He found that the best way to recover the strongly adsorbed rhodium from the resin was to keep it boiling in 6N HCl for many hours. This presumably allows conversion of the adsorbed polymeric species into the $RhCl_6^{-3}$ form which has a very small distribution coefficient. Other ion exchange techniques involving rhodium separations are reviewed in the book by Samuelson [49]. A recent article by Evans, Bloomquist and Hughes describes the analysis of Rh(III) in Pu-U alloys using separation with Dowex-1 column elution and spectrophotometry [50] (see Procedure 13).

F. Paper and Electro Chromatography. Kember and Wells [51] and Lederer [52] have reported techniques for separation of rhodium by paper chromatography (see Modification II, Procedure 15). Several procedures for chromatographic separation of the platinum group elements, including rhodium, by use of cellulose columns have been described

[53-56]. Two groups have discussed electrochromatographic separations [57,58].

G. Dissolution Techniques. The difficulties of dissolving metallic rhodium have been discussed in an earlier section. It is obvious from that discussion that dissolution of rhodium foils following irradiation is quite difficult. Smith [59] attempted to dissolve a foil after an alpha particle bombardment (to produce Ag^{106}) with KNO_3-KOH and also Na_2O_2 with no success, probably due to the surface formation of insoluble oxides. However, he found that approximately 10% of the Ag^{106} was extracted by the Na_2O_2 melt. It would seem that the sulfate fusions are necessary for successful quantitative dissolution of rhodium foils, whereas aqua regia suffices for the finely divided metal. A private communication to one of the authors [60] outlines a method of dissolving up to two grams of 3 mil rhodium foil. The foil is cut into small pieces and mixed with equal portions of granular bismuth and powdered charcoal in a porcelain crucible. The crucible is then heated with a gas oxygen torch until the bismuth becomes molten. After cooling, the melt is dissolved in concentrated nitric acid. One fusion will dissolve 80 to 90% of the foil. The fusion can be repeated to put the remainder in solution. A satisfactory procedure for dissolution of metal targets is described in Procedure 20.

VI. BIOLOGICAL ASPECTS OF RHODIUM

The biological hazards and the environmental behavior of ruthenium and rhodium are discussed by Auerbach and Olson [61]. These authors pay particular attention to the contamination of our environment due to fission product fallout.

VII. ACTIVATION ANALYSIS

Two groups have used Rh^{104} in neutron activation analysis. The photopeak at 550 kev for Rh^{104} (42 sec. half-life) was measured by Meinke and Steele in a non-destructive method following a 42 sec. irradiation at a thermal flux of 10^{12} n/cm^2/sec. [62]. As little as 0.1 microgram of rhodium was measurable in the absence of interfering materials (Table 6). Miller [63] used Rh^{104m} (4.4 min) and scintil-

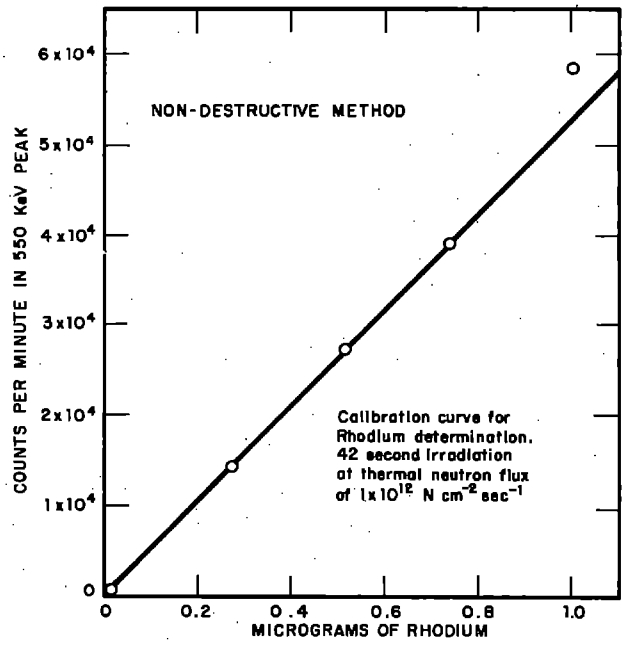


Fig. 4. Curve for non-destructive testing for rhodium, 42 second irradiation at a flux of 10^{12} n/cm^2/sec. (62)

lation spectrometry following a one-minute irradiation at a similar flux. The procedure for activation analysis of rhodium using Rh^{104m} in a destructive method is described in Procedure 1.

VIII. COUNTING TECHNIQUES

Little in the way of unusual methods is reported.

The reader is referred to the monograph by G. D. O'Kelley [65] for a discussion of the normal techniques in Geiger, proportional and scintillation counting. Roos has reported a K

Table 6

Results of Activation Analysis [62]

Matrix	Irradiation Time	Chemical Separation	Micrograms Rh	
			Added	Found
H_2O-HCl	42 s	None	0.01	0.011
H_2O-HCl	42 s	None	0.10	0.095
H_2O-HCl	42 s	None	0.25	0.24
H_2O-HCl	42 s	None	0.50	0.50
H_2O-HCl	42 s	None	0.75	0.74
SiO_2-Al_2O_3	42 s	None	0.50	0.53
SiO_2-Al_2O_3	42 s	None	0.75	0.77
SiO_2-Al_2O_3	42 s	None	1.00	1.02
H_2O-HCl	5 m	Pyridine Extraction	0.10	0.09
H_2O-HCl	5 m	Pyridine Extraction	0.50	0.48
H_2O-HCl	5 m	Pyridine Extraction	1.00	1.01
SiO_2-Al_2O_3	5 m	Pyridine Extraction	1.00	1.04

Day, Fox and Hyder have described [64] an activation technique using the formation of Rh^{103m} after scattering of neutrons above 100 kev energy. This provides a measure of relative fast neutron fluxes. The 57.4 min. Rh^{103m} was measured by scintillation counting. Since the energy dependence of the inelastic scattering cross section of Rh^{103} is similar to that of the fission cross section for U^{238}, the results have direct relevance to reactor calculations.

fluorescent yield of 0.786 ± 0.015 for rhodium [66]. Table 1 is a summary of pertinent data of the isotopes of rhodium which are of importance in choice of a counting system and in quantitative evaluation of the counting data. Figures 5 and 6 are gamma ray spectra reported by Heath [67] for the Ru^{106}-Rh^{106} system. Figures 7 and 8 are similar spectra of Rh^{104m} reported by Miller [63].

IX. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES

Before proceeding to the collection of 20 procedures included here, it must be emphasized that these procedures have not been evaluated by the authors in the laboratory. Procedure 15 has been used with satisfaction following proton bombardment of ruthenium. Of the fission product separations, Procedure 2 by Croall and Glendenin would seem to be very satisfactory. These authors and Chenley, Osmond and Perry (Procedure 3) have evaluated the older methods, and their comments are summarized below.

Chenley, Osmond and Perry: Neither precipitation of $K_3Rh(NO_2)_6$ nor extraction of rhodium by pyridine was sufficient to give radiochemically pure rhodium. In the precipitation of $K_3Rh(NO_2)_5$ it was found necessary to add Te and Sb (to remove Sb^{127}) hold back carriers. They added Ag, Mo, Pd, Te and Sb in addition to rhodium carrier. When Sb and Te are added, the decontamination factor for $K_3Rh(NO_2)_6$ precipitation was higher than for the pyridine extraction method. The latter also suffered from having somewhat lower yields and being lengthy. The lower yields may be due to the difficulty of obtaining complete precipitation of Rh_2S_3 from the pyridine complex.

These workers investigated the possibility of using

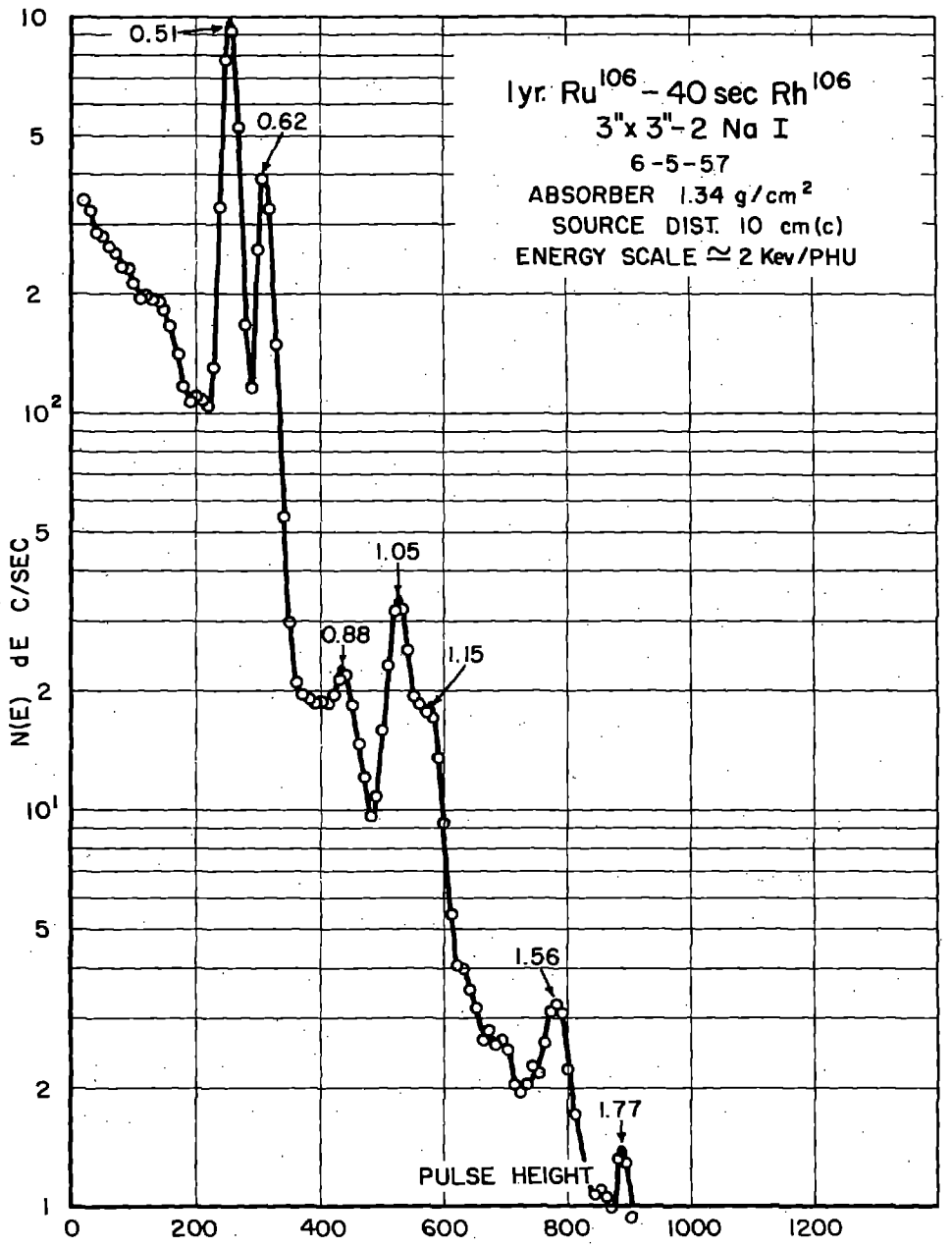


Fig. 5. Gamma-Ray Pulse Height Spectrum of Ru^{106} - Rh^{106}

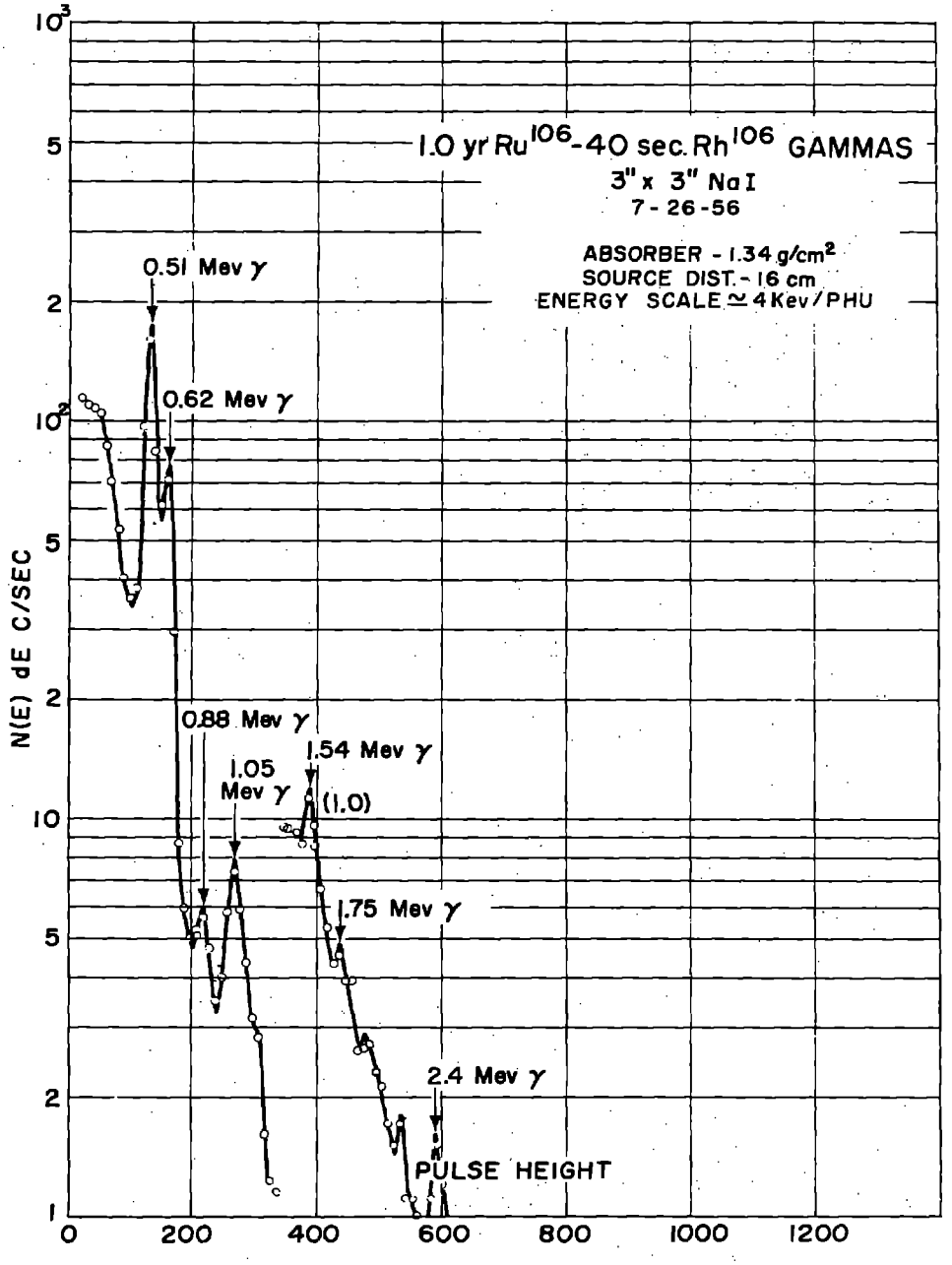


Fig. 6. Gamma-Ray Pulse Height Spectrum of Ru^{106} - Rh^{106}

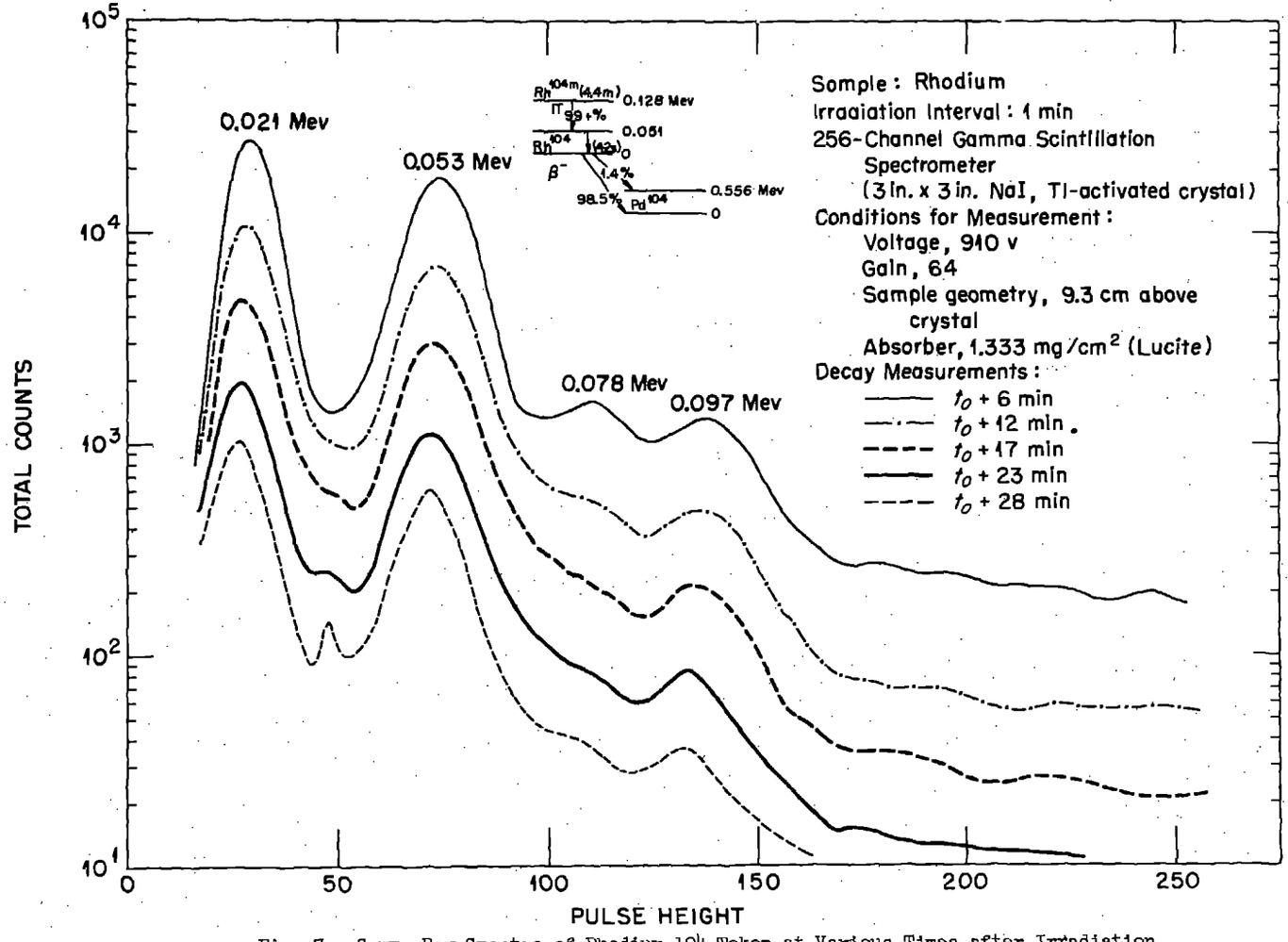


Fig. 7. Gamma-Ray Spectra of Rhodium-104 Taken at Various Times after Irradiation

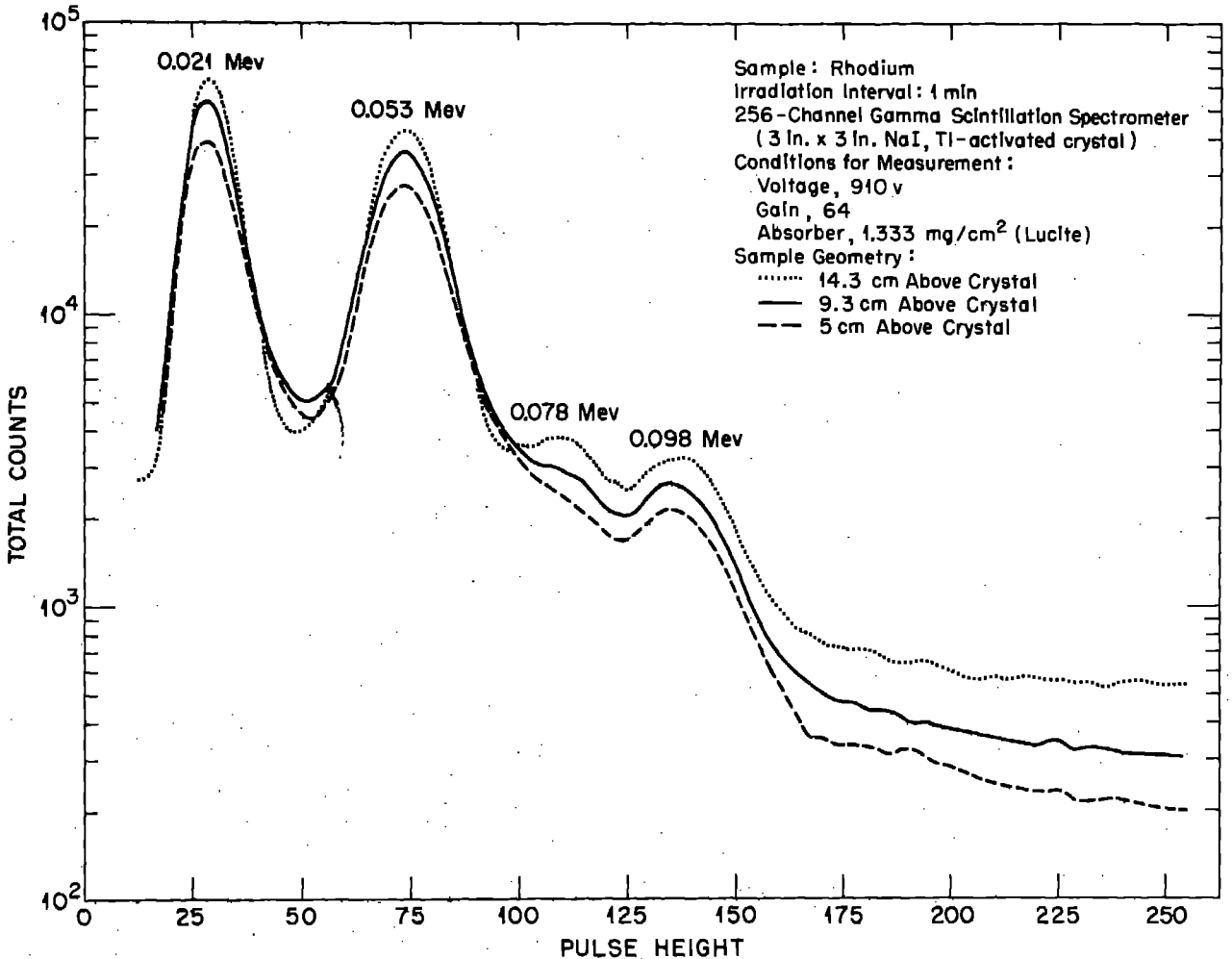


Fig. 8. Gamma-Ray Spectra of Rhodium-104m Taken at Various Times after Irradiation

the very stable complex formed with 2-mercaptobenzoxazole, but its stability is such that it is very difficult to destroy the complex by acid treatment.

The procedure by Croall and Glendenin (Procedure 2) is designed to provide decontamination factors of 10^6 from Zr, Cs, Te and Sb and also to remove Ru within 2-3 minutes to reduce background due to Rh^{105} and Rh^{107}. The Seiler method of $K_3(NO_2)_6$ precipitation gave a decontamination factor of only 5×10^3 from Te. With the pyridine method, it was found necessary to use at least four extractions to obtain the 10^5 decontamination factor and, again, the procedure was found to be lengthy and of low yield. Anion exchange resin column separations using the $RhCl_6^{3-}$ anion gave low yields of rhodium. This is attributed to hydrolysis in dilute acid and is in agreement with the observations mentioned in Section IV on fresh chlororhodinate solutions and anion exchange resins.

Ballou (see the reference for Procedure 7) discussed the problem of Te contamination, but it must be emphasized that this is an earlier reference.

Two English reports may be of some interest in relation to fallout studies. In one report [68] Ru^{106}-Rh^{106} is measured in samples of sea silts and shore sands by simple drying, grinding to a size to pass through a B.S. 60 sieve and counting with a 100 channel pulse height analyzer using a 3 x 3 in NaI(Tl) crystal. The second publication [69] describes a method for the determination of microgram quantities of Rh per liter of sea water. Although this is not a radiochemical separation, it could serve as the first part of a procedure since the recovery from the sea water is 90% for 0.1 to 5.0 micrograms per liter.

A. Activation Analysis.

Procedure 1

Element Separated: Rhodium

Target Material: Synthetic Rock Samples[a]

Type of Bombardment: Neutrons in pneumatic tube 5 min at 1 Megawatt

Procedure by: E. Steele[b]

Time for Separation: 7 minutes

Equipment Required: Spectrophotometer and gamma spectrometer

Yield: 95-100%

Degree of Purification: Sufficient for gamma-spectroscopy (auth.)

Advantage: Rapid separation and chemical yield determination

Procedure:

(1) Irradiate sample for 5 minutes at 1 Megawatt.

(2) Two minutes before end of irradiation, heat 5g of Na_2O_2 to melting in a nickel crucible. Add the sample (caution) and fuse for 1 minute.

(3) Cool the crucible by cautiously dipping it in cold H_2O.

(4) Dissolve melt with 20 ml concentrated HCl (caution!) and add: (a) 5 ml $RhCl_3$ solution (1 mg/ml in 1N HCl); (b) 1 ml 10% tartaric acid; (c) 8 ml pyridine.

(5) Mix well and transfer to separatory funnel by filtering off the silica. Wash precipate with 5 ml 6N HCl and collect this filtrate in the same separatory funnel.

(6) Add 15 ml 12N NaOH to separatory funnel and separate pyridine (upper) layer for analysis in multichannel pulse height analyzer.

(7) Determine chemical yield by measuring the absorbance at 420 mμ of the Rh-pyridine complex.

Notes:

(a) Silica, alumina and $RhCl_3$.

(b) A combination of previously reported methods.

B. Fission Product Separation.

Procedure 2

Target Material: Pu-239 and U-233

Type of Bombardments: Thermal neutrons

Procedure by: Croall and Glendenin, A.E.R.E., Harwell, to be published.

Yield: 55-60%

Separation Time: 2 hours

Decontamination: At least 10^6 from Zr, Cs, Te, and Sb. Also, Ru was removed within 2-3 minutes of the end of the irradiation.

Procedure:

(1) Add the irradiated solution to 3 ml of 70% perchloric acid containing 10 mg Rhodium, 5 mg of Ruthenium and 1 mg of Zr as carriers. Fume off ruthenium tetroxide, cool, add a further 5 mg of Ru and repeat the fuming, finally reducing the volume to 1 ml.

(2) Dilute to 10 ml, add 3 ml of 6M sodium acetate solution (buffer) and 2 ml of 60% sodium nitrate solution. Heat to form the rhodonitrite complex, then add 12 M NaOH until a pH of 9 is reached. At this stage plutonium (or uranium) and zirconium are precipitated.
Centrifuge off this precipitate and scavenge the supernatant solution twice with 1 mg quantities of iron.

(3) Acidify the supernatant from (2) (HNO_3), add 1 ml of 60% KNO_2 solution and centrifuge off the potassium rhodonitrite precipitate. Wash twice with 10 ml of water.

(4) Dissolve the rhodonitrite precipitate by heating with 1 ml of conc. HCl. Dilute to 10 ml, add 3 ml of 6M sodium acetate, and 2 ml of 60% $NaNO_2$ solution, heat. Add 12M NaOH until the pH is 7 to 8. Add 3 drops of saturated sodium carbonate solution and scavenge twice with 1 mg quantities of iron.

(5) Repeat step (3).

(6) Dissolve the rhodonitrite in 1 ml of aqua regia, boiling until no more oxides of nitrogen are evolved. (If necessary add more conc. HCl.) Make up to 2 ml volume with 6M HCl, dilute to 10 ml and add 2 ml of a saturated aqueous solu-

tion of thioacetamide, warm gently for two minutes to allow the rhodium complex to form.

(7) Add 1 mg Te carrier, pass in a little H_2S and centrifuge off the tellurium sulphide. Scavenge twice with 1 mg amounts of antimony. (See Note 1)

(8) Transfer the supernatant from (7) to an Erlemeyer flask containing 5 ml of conc. HCl, boil vigorously almost to dryness, add 1 ml conc. HNO_3 and 3 ml of conc. HCl and again boil down to near dryness.

(9) Dilute to 10 ml, buffer and carry out basic iron scavenges as in step (4).

(10) Repeat step (3).

(11) Dissolve the rhodonitrite in 1 ml conc. HCl, heat. Dilute to 10 ml, buffer with 3 ml 6M sodium acetate, add 10 ml of 60% KNO_2, centrifuge off the potassium rhodonitrite, wash twice with water.

(12) Repeat step (11), mounting the rhodonitrite precipitate on a tared filter paper, wash with water, alcohol and ether, dry at 110° for 10 min and weigh to determine chemical yield.

Notes:

(1) Excessive heating of the thioacetamide solution should be avoided if loss of rhodium is not to occur. Antimony sulphide is precipated simply by the sulphide produced by the hydrolysis of thioacetamide, but to ensure complete precipitation of tellurium it is necessary to pass in hydrogen sulphide gas.

Procedure 3

Target Material: 3 mg samples of uranium

Type of Bombardment: Neutron fission

Procedure by: Chenley, Osmond, and Perry, A.E.R.E. C/R 1870 (1956).

Yield: 45%

Decontamination: Half-life and absorption curves gave no indication of the presence of contamination.

Procedure:

(1) Place the sample (1) in a 4 cm platinum dish. Add 2 ml of following carrier solutions Ag, Pd, Rh, Mo, in this order. Heat on a boiling water bath until dry (2).

(2) Add 1 ml 16M HNO_3, 1 ml 9M $HClO_4$, 1 ml 20M HF. Place 6" away from a 250 watt. infra-red lamp and evaporate slowly until $HClO_4$ fumes appear (2). Cool and add 1 mg Ru carrier. Again place 6" away from I.R. lamp and fume until only a few drops remain. Add 5 drops 9M $HClO_4$ and evaporate slowly until just moist.

(3) Extract the residue in the dish four times with 1 ml 6M NH_4OH, breaking up any lumps, and transfer both the solution and the insoluble to a 10 ml centrifuge tube. Centrifuge and remove the alkaline supernatant to another 10 ml tube. Wash the insoluble three times with 1 ml 6M NH_4OH containing 1 drop saturated NH_4NO_3 solution. Add the washings to the supernatant and reserve for Ag, Pd, Mo separation. Transfer the insoluble to the platinum dish using a little water and heat on a water bath until dry (3).

(4) Dissolve the insoluble in 0.5 ml 6M HNO_3 and transfer to a 10 ml centrifuge tube. Rinse the dish with a few drops of 16M HNO_3 and add to the solution, which should have a final volume of about 1 ml and be approximately 6M in HNO_3 (4).

(5) Make just acid by (a) adding 6M NaOH to the hot solution until a permanent precipitate is just produced and then (b) adding 6M HCl until the precipitate is just dissolved. Add an equal volume of 60% KNO_2 and heat on a water bath for 10 minutes. Cool, centrifuge and discard the supernatant.

(6) Dissolve the precipitate in the minimum amount of aqua regia (approximately 1 ml), heating on

a water bath. Cool, centrifuge (5) and add 6M NaOH until a precipitate just forms.

(7) Add 1 drop 6M HCl to redissolve the precipitate.

(8) Add 1 ml Sb carrier and stir (6). Adjust the acidity as before and repeat the KNO_2 precipitation. Dissolve the precipitate in aqua regia (5) add 1 ml Ab carrier and repeat the KNO_2 precipitation. Wash the precipitate twice with 0.5 ml 2M HCl. Dissolve the precipitate in aqua regia, reduce the acidity, add 1 ml tellurium carrier with stirring, adjust the acidity and repeat the KNO_2 precipitation as before. Wash the precipitate with 0.5 ml 2M HCl twice. Dissolve the precipitate in aqua regia.

(9) Transfer the solution to a silica crucible and evaporate slowly to dryness under an I.R. lamp. (2). Dissolve the residue in 0.5 ml water and remove weighed aliquots for chemical yield and counting.

Notes:

(1) The samples examined contained 0.3 mg uranium.

(2) The residue should on no account be baked.

(3) This is to remove excess ammonia.

(4) Complete solution should be achieved.

(5) Small amounts of insoluble matter should be rejected.

(6) It may be necessary to add a further drop of 6M HCl to maintain a clear solution.

Procedure 4

Target Material: Uranium (1 gm)

Type of Bombardment: 388 MeV alphas

Procedure by: Wolfe, AECD-2738

Yield: 10%

Separation Time: 1.5 days when separated with Pt and Ir.

Decontamination: 10^4 from fission products, (none from Ir)

Procedure:

(1) Cut out 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 determinations of Ba, Ru, and Rh.

(4) To the 20% aliquot add HNO_3, 5 mg Ru carrier and 5 mg I^- and IO_3^-. Boil the solution to expel Os and I. (CAUTION: OsO_4 very poisonous.)

(5) Place the solution in a special all-glass distilling flask like that used for the osmium distillation. Add 0.5 gm $NaBiO_3$, 1 ml conc. H_3PO_4, and 10 ml 70% $HClO_4$. Boil in an air stream without bumping and distill over RuO_4 into 12 ml 6 N NaOH in an ice bath. Distill until 1-2 ml of $HClO_4$ have distilled (2-3 min after fuming begins.)

(6) The residue from this Ru distillation is fumed strongly with the $HClO_4$.

(7) Cool the solution, dilute to 4 N and add 20 ml pyridine.

(8) Boil the solution for five minutes, place in a separatory funnel, and add 19 N NaOH to separate the free-base pyridine layer (the high conc of NaOH is merely to keep the volume low.)

(9) Wash the dark blue pyridine layer three times with equal volumes of dilute HCl, separating the layers each time with 6 N NaOH.

(10) Add a few drops of 6 N NaOH to the pyridine layer and evaporate the pyridine off.

(11) Pass H_2S into the boiling alkaline solution for several minutes, while the solution is acidified dropwise with HCl. Sulfides of Rh and Ir ppt.

Procedure 4 (Cont'd)

(12) Dissolve the ppt in a little aqua regia. Add 5 mg of Au, Pt, and Pd carriers.

(13) Make solution 4 N in HCl and extract twice with equal volumes of butyl acetate to decontaminate from Hg and Au.

(14) Dilute the solution to about 0.5 N in H^+, add 5 ml dimethylglyoxime solution (1% in alcohol) and filter off the Pd ppt.

(15) Fume the remaining solution with H_2SO_4, dilute, neutralize to the brom cresol purple end point, and add BrO_3^- to ppt the hydrated oxides of Rh and Ir, leaving Pt in solution.

(16) Dissolve the oxides in conc HCl and dilute to known volume.

(17) An aliquot of proper size to give about 5000 c/m is withdrawn and a known amount of Rh carrier is added to it.

(18) Fume with H_2SO_4, dilute twenty to one, boil and ppt Rh metal by adding $TiCl_3$ dropwise until a very slight excess is present.

(19) Plate this Rh metal and count.

Remarks:

In uranium bombardments the activity in step 16 is due almost entirely to Rh, the activity of Ir being about 10^{-3} that of Rh--even though no separation has been made from Ir. In some other bombarding arrangement where the activities of Ir and Rh are more closely equal, Ir could be separated from the Rh by a procedure similar to the last part of Procedure 9.

Rh, Ir, and Pt should be separated from one bombardment leaving Cs, Ru, and Pd for a second bombardment unless several people are cooperating on the procedure.

Procedure 5

Target Material: Uranium and thorium

Type of Bombardment: Neutron, alpha and proton

Procedure by: Stevenson, Nervik and Borg, U.C.R.L. 4377

Yield: 70%

Separation Time: 5 hours for 4 samples

Decontamination: 10^{13} atoms of Rh^{105} isolated from a one-day-old mixture containing 10^{15} fissions showed no detectable foreign radioactivity when decay was followed through three half lives.

Procedure:

(1) Add about 20 mg Rh carrier to an aliquot of the active solution in HCl and dilute to about 1M in H^+. Add one drop 1% aerosol (a surface active agent).

(2) At room temperature or slightly above, add 2-3 mg Pd^{++} and precipitate PdI_2 with a slight excess of 1M KI solution. Digest five minutes at room temperature, centrifuge and discard precipitate. Do not heat, repeat scavenge by addition of several drops of Pd^{++} carrier.

(3) Place 1-2 gm KI crystals in a 125-ml Erlenmeyer flask and add 2-3 drops Te carrier. Pour the supernatant from step 2 into the Erlenmeyer, add an equal volume of conc. HCl and boil gently on a hot plate for at least twenty minutes, adding 6M HCl from time to time to maintain volume. Solution must be boiling to ensure reasonable yields. Add one drop aerosol after boiling.

(4) Transfer to 40-ml centrifuge cone, centrifuge and reject supernatant. Wash the precipitate twice with 3-6 M HCl or until the wash is clear and colorless, digesting each wash briefly in a hot water bath.

(5) Slurry the precipitate into a 125-ml Erlenmeyer with water, add 3-4 ml conc. $HClO_4$ and heat cautiously to fuming. If too much heat is applied, some Rh sticks to the flask and is lost. As the I^- is oxidized and removed, some slight foaming may occur. After all the I_2 is driven off, the $HClO_4$ should be driven off cautiously with a microburner until the volume is 1-2 ml. (It may help to add water after first fumes appear and fume again.)

(6) After evaporation to a small volume of $HClO_4$, cool and add 40-50 ml of water and enough Dowex-50 resin (H^+ form) to fill about 8 cm of a 6-mm-diameter column. Warm gently until the yellow Rh color disappears from the solution (five to ten minutes). The resin should be coarse (50-100 mesh, coarse fraction) and free of Cl^-, added as a water slurry.

(7) While the solution and resin are being equilibrated, place about a 1-cm length of the same type resin in a gravity-flow column 6 mm in diameter, and wash with water. When the Rh is adsorbed, decant the liquid and transfer the resin to the top of this column with 10 ml of water. Wash the column with 10 ml of 0.5 M HCl. Elute the Rh with hot 3M HCl (5-15 ml usually required). Catch the eluate in a 125-ml Erlenmeyer flask.

(8) Add five to six drops 1% aerosol to eluate to reduce foaming, then Mg turnings to reduce the Rh to metal. Boil to complete reduction, dissolve excess Mg by addition of conc. HCl and coagulate the metal. Wash metal twice with hot 3M HCl, three times with acetone, and dry at 100°C. Weigh as Rh metal.

Procedure 6

Target Material: Uranium and Thorium

Type of Bombardment: Neutron, alpha and proton

Procedure by: Bonner and Iddings, UCRL-4377

Yield: 80%

Separation Time: 5 hours for one sample (not including electrolysis)

Decontamination: A sample containing less than 20 c/m was obtained from a mixture of fission products from 10^{15} fissions three months old.

Procedure:

(1) To the solution in ~25 ml of 6M HCl, add 20 mg Rh and 10 mg Te carriers.

(2) Boil solution for ~10 minutes (see Note 1).

(3) Cool, add solution to a 60 ml, cylindrical, open-top, separatory funnel containing 25 ml of methyl

isobutyl ketone, and stir vigorously for two minutes.

(4) Draw off aqueous layer into a second separatory funnel containing 25 ml of methyl isobutyl ketone. Stir for two minutes (see Note 2).

(5) Draw off aqueous phase into a 125-ml Erlenmeyer flask containing 2 g of NaI. Discard organic phase. Add 2 mg Te carrier.

(6) Boil for at least 20 minutes (see Note 3). Add more 6M HCl if volume becomes too small.

(7) Transfer to a 40-ml glass centrifuge cone. Centrifuge. Discard supernatant.

(8) Wash with two 20-ml portions of 6M HCl, heating on hot water bath for a short time.

(9) Add ~1/2 mg Te carrier, dissolve RhI_3 by adding 1 ml conc. HNO_3 and 2 ml conc. $HClO_4$ and fuming.

(10) Cool, add 1-2 ml conc. HCl (see Note 4), and take to fumes of $HClO_4$ again.

(11) Cool, add 1 ml conc. HNO_3, fume to ~1/2 ml volume (see Note 4).

(12) Dilute to 2 ml, add 10 M NaOH dropwise until a permanent precipitate just begins to form. Add one drop of conc. $HClO_4$ to redissolve precipitate. Add 10 ml of 0.5 M TTA in acetone and then 1-2 ml of 1 M HAc-1 M NaAc burrer solution. Check pH to be sure it is ~5. Add acetone if solution is not already as one phase.

(13) Heat in boiling water bath until all acetone is driven off (~20 minutes). (The solution will separate into two phases, and the aqueous phase should be colorless.)

(14) Transfer to a 60-ml cylindrical separatory funnel with 30 ml benzene, stir and draw off aqueous layer.

(15) Wash benzene layer with ~15 ml portions of the following for two minutes each, discarding the aqueous layers:
   a. 6 M HCl.
   b. Two portions of 1 M NaOH. (This removes "free" TTA from benzene but leaves Rh-TTA complex.)
   c. Two portions of 8 M HNO_3.
   d. Two portions of 6 M HCl; 2 M HF.
   e. Two portions of 6 M HCl.

(16) Drain benzene layer into a 125 ml erlenmeyer flask and evaporate to dryness. Add 3 ml conc.

Procedure 6 (Cont'd)

H_2SO_4, 2 ml conc. HNO_3, and 1 ml conc. $HClO_4$. Heat to fumes of SO_3 to decompose all organic matter.

(17) Cool, dilute and transfer to an electrolysis cell with a platinum-plate cathode. (Cell and plate must be cleaned very carefully.) Electrolyze overnight at 100 milliamps.

(18) Weigh as Rh metal and count on beta counter.

Notes:

(1) Boiling reduces the Te(VI) to Te(IV) and ensures complete exchange between the Te carrier and the tracer.

(2) This extraction is designed to remove most of the Te activity which tends to be the principal contaminant in most Rh procedures. If desired, the double extraction can be replaced by a triple precipitation of TeI_4 from dilute HI + H_2SO_3.

(3) If the solution is not actually boiled extensively, the RhI_3 remains partially in colloidal form.

(4) The treatment with HCl is to destroy iodate formed in the HNO_3- $HClO_4$ fuming. The HNO_3 treatment destroys any Rh chloride complexes formed.

Procedure 7

Target Material: Uranium

Type of Bombardment: Neutrons

Procedure by: N. Ballou, Paper 263, Radiochemical Studies, Book 3, National Nuclear Energy Series, McGraw Hill, (1951).

Yield: 50-70%

Separation Time: 1-1.5 hrs.

Decontamination: 5×10^3

Procedure:

(1) a. Uranyl Nitrate Solutions. To 5 ml or less of 40 per cent uranyl nitrate add 30 mg of Rh(III) carrier, 5 ml of H_2O, 8 ml of conc. HCl, 10 mg of Te(IV) carrier, and 8 ml of pyridine. Boil gently for 1 min (see Note 1). Add 7 to 9 g of Na_2CO_3 carefully in several portions (see Note 2), stir, and centrifuge. Transfer the liquid

phases to a separatory funnel and separate the pyridine (upper) layer.

b. Heavy-metal Ion Solutions. To a 5-ml sample add 30 mg of Rh(III) carrier, 5 ml of H_2O, 4 ml of conc. HCl, 1 ml of 10 per cent tartaric acid, $H_2C_4H_4O_6$ (see Note 3), 10 mg of Te(IV) carrier, and 8 ml of pyridine. Boil gently for 1 min (see Note 1). Add 15 ml of 12 M NaOH carefully, stir, transfer to a separatory funnel, and separate the pyridine (upper) layer.

(2) Add 5 ml of H_2O, 6 ml of conc. HCl, and 10 mg of Te(IV) carrier to the pyridine layer, and shake. Add 10 ml of 12 M NaOH, shake, and separate the pyridine layer.

(3) Add 5 ml of H_2O to the pyridine layer, shake, add 10 ml of 12 M NaOH, shake, and separate the pyridine layer.

(4) Transfer the pyridine layer to a 50-ml centrifuge tube, add 2 drops of 6 M NaOH, and evaporate to about 0.5 ml. Add 10 ml of H_2O, heat to boiling, and pass in H_2S for 3 min (see Note 4). Add 1 ml of 6 M HCl, heat to boiling (see Note 5), and centrifuge. If all the rhodium has not been precipitated, as shown by the color in the centrifugate, add 1.5 ml of 6 M NaOH to the solution, heat to boiling, pass in H_2S for 1 min, add 2 ml of 6 M HCl, heat to boiling, and centrifuge.

(5) Dissolve the Rh_2S_3 by heating with 1 ml of conc. HNO_3 and 2 ml of conc. HCl. Centrifuge, and wash the precipitate of sulfur by heating with 0.5 ml of conc. HNO_3 and 1 ml of conc. HCl. Add the washings to the rhodium solution.

(6) Add 3 ml of 70 per cent $HClO_4$ and 5 mg of ruthenium carrier to the rhodium solution, stir, and fume for 1 min after the disappearance of the ruthenium color. Cool.

(7) Add 2 ml of 70 per cent $HClO_4$, 5 mg of ruthenium carrier, and 5 drops of 0.035 M HIO_3. Stir, add 10 mg of I^- carrier (see Note 6), and stir. Fume the solution for 1 min after the disappearance of the iodine color, and cool.

(8) Wash the solution into an Erlenmeyer flask with 20 to 30 ml of H_2O. Add two or three 0.1-g portions of magnesium, with several minutes of heating and stirring between each addition (see Note 7). If the reaction becomes too slow at any time, 1 ml of 6 M HCl may be added. After the reduction of the rhodium, excess magnesium is destroyed by the addition of 5 ml of conc. HCl.

(9) Prepare a filter-paper disk by washing in a Hirsch funnel with 5 ml of H_2O and three 5-ml portions of 95 per cent ethanol, dry in an oven at 110°C for 10 min, allow to cool in a desiccator, and weigh.

(10) Filter the metallic rhodium through the weighed filterpaper disk, wash, dry, and weigh as outlined in step 9. Mount on a standard card, and count.

Notes:

(1) Boiling serves to bring about the rapid and complete conversion of all the rhodium to the very stable pyridine complex, thereby effecting a complete exchange between the carrier and the activity.

(2) The use of Na_2CO_3 serves the dual purpose of keeping the larger part of the uranium in solution and of separating the pyridine layer.

(3) Tartaric acid is added to prevent the formation of a large hydroxide precipitate.

(4) Rhodium sulfide is precipitated to free the rhodium from the pyridine. If the rhodium is in the pyridine complex when the final metal reduction is made, an incomplete precipitation of the rhodium metal occurs and the precipitate contains organic impurities that make the determination of the chemical yield incorrect. Because of the danger of explosion it is also desirable to be rid of the pyridine before doing the fuming with the perchloric acid.

(5) The precipitation of Rh_2S_3 from the pyridine complex is not complete within a moderate length of time from either acid or alkaline solution. But if H_2S is passed into the alkaline solution for a short time and if the solution is then made acid and heated, all the rhodium is usually precipitated. If it is not precipitated, a repitition of the process does precipitate it all.

(6) Excess I^- carrier is added to reduce any IO_3^- or BrO_3^- formed in the $HClO_4$ fuming so that the halogens can be expelled by the subsequent fuming.

(7) The reduction by magnesium gives a rhodium precipitate of quite reproducible weight; this weight is slightly greater than the weight of the rhodium metal obtained by hydrogen reduction.

Procedure 8

Target Material: Fall-out fission products

Type of Bombardment: Separation of Rh^{103m} from Ru^{103}

Procedure by: Kimura, Ikeda, and Yoshihara, Bull. Chem. Soc. Japan, 29, 395 (1956).

Separation Time: 2-3 hours

Decontamination: Some Ru^{103} is seen in the final sample.

Procedure:

(1) Dissolve the Ru salt from a RuO_4 distillation in a small amount of HCl and repeat the process of evaporating the Ru sample to dryness and subsequent dissolution in HCl several times.

(2) Adjust acidity to 0.2N HCl and the volume to 10 ml. Prepare a column of Dowex-50 (50-100 mesh) 1 cm I.D. and 6 cm in length and put the solution through this resin bed. After washing the bed with a small quantity of 0.2N HCl, the Rh is eluted with 2N HCl at an elution rate of 1 ml per minute.

(3) The effluent is collected, dried and counted.

Procedure 9

Target Material: 7 weeks old mixture of fission products

Procedure by: N.A. Bonner, Lawrence Radiation Laboratory, U. of California, Livermore (1958).

Yield: 70%

Separation Time: 5 hours (excluding the electrodeposition)

Procedure:

(1) Add the active solution in 6M HCl to 20 mg of Rh carrier, ~2 mg of Te carrier, and 20 mg of Tl carrier in a 125 ml Erlenmeyer flask. Add ~8 ml of conc. $HClO_4$ and 1 ml conc. HNO_3. Evaporate to fumes of $HClO_4$. Fume vigorously until volume of $HClO_4$ is about 4 ml (see Note 1). Cool and add 2 drops each of conc. HCl and conc. HNO_3.

(2) Transfer to a 40 ml centrifuge tube with water and dilute to 20 ml. Add 5 drops of 57% HI (contain-

ing no H_3PO_2) and 2 ml of 6% H_2SO_3 solution. Stir vigorously. Centrifuge off TlI, pour supernatant into a 125 ml Erlenmeyer flask. Wash TlI with ~5 ml of 2 M HCl containing a few drops of HI and 1/2 ml of 6% H_2SO_3. Combine wash with the original supernatant.

(3) To solution in flask, add 10 ml of conc. HCl, 2 ml of 57% HI and boil vigorously for at least 20 min. Add 6 M HCl if necessary to keep volume between 15 and 30 ml. Transfer to 40 ml cent. cone; centrifuge. Wash RhI_3 ppt. with 10-15 ml of 6 M HCl.

(4) To RhI_3, add 3 ml conc. HCl + 1 ml 30% H_2O_2. Mix thoroughly. Warm slightly. After solution has become clear (but very dark), boil to about 1 ml volume. Dilute to 20 ml with H_2O. (If a ppt. of RhI_3 remains, centrifuge it off and dissolve it in HNO_2 + $HClO_4$. Evap. to ~1/2 ml and combine with supernatant). Add 5 ml of saturated $NaNO_2$ (~9 M). After most of the bubbling has stopped, heat on hot water bath for at least 10 min. The solution should be colorless. Add 1 mg of Fe^{+++} carrier, stir vigorously, heat on water bath ~1 min. Centrifuge. Pour supernatant into a clean 40 ml cone and discard ppt of $Fe(OH)_3$.

(5) Add 1 mg of La carrier + a few drops of phenolphthalein and stir. Add 1 M NaOH dropwise until solution turns pink (1 or 2 drops is usually enough). Stir and heat on water bath about 1 min. Centrifuge. Pour supernatant into a clean centrifuge cone and discard $La(OH)_3$ ppt.

(6) Add to the supernatant 2 drops of 6 M HCl, 2 ml of saturated KNO_3 (~3 M), stir vigorously, heat in water bath for at least 2 min., cool to room temperature, and centrifuge. Wash white ppt of $K_3Rh(NO_2)_6$ with 15 ml of 0.1 M HCl (see Note 2).

(7) Dissolve the ppt by adding 3 ml of 6 M HCl and boiling. Evaporate just to dryness. If the solution is not deep ruby red and clear before dryness is approached, take nearly to dryness, add more 6 M HCl and carefully evaporate again to dryness (see Notes 3 and 4).

(8) Dissolve the residue in 5 ml of 0.1 M HCl and transfer to a Dowex-1 anion column. (Cl - form, water washed, 50-100 mesh, x-8 in a column 6 mm in dia. and 5-6 cm long). Rinse contents of tube onto column with another few ml of 0.1 M HCl. Put small glass wool pad on top of ion bed when the solution has all gone through. Wash column with 15 ml of 0.1 M HCl. Discard washes.

Procedure 9 (Cont'd)

(9) Elute Rh from the column with 20 ml of conc. HCl. Collect eluate in a 125 ml Erlenmeyer flask. Add 1 mg of Te carrier and boil for 10 min. If volume gets too small, add 6 M HCl.

(10) Cool to room temp. Add 5 ml of 55% HI and immediately transfer solution to a 60 ml open-top separatory funnel containing 30 ml of hexone. Use 6 M HCl for transfer. Aqueous volume should be 20-30 ml. Stir vigorously for 2 min., allow to settle for a short time after phases have separated. Be extremely careful to prevent any of the organic phase from going with the aqueous phase when it is removed. This step removes the last traces of Te and Ag fission product activities.

(11) Withdraw aqueous phase into a 125 ml Erlenmeyer flask and boil vigorously for at least 20 min to precipitate RhI_3. Add 6 M HCl if necessary to keep volume between 15 and 30 ml. Centrifuge, wash once with 15 ml of 6 M HCl (see Note 5).

(12) Dissolve ppt in 3 ml of conc. H_2SO_4 by heating to fumes of SO_3 until I_2 vapor is no longer visible. Cool to room temp., add 3 ml H_2O and 1 ml of conc. HCl. Boil for brief time, then add 1 ml each of conc. HNO_3 and conc. $HClO_4$. Continue heating until all $HClO_4$ has evaporated and SO_3 fumes are coming off strongly.

(13) Cool to room temp., dilute with 5 ml of water. Transfer to plating cell with water. Plate onto tared Pt plate for at least 8 hours at 100 ma. Rinse, dry and weigh. Mount on flat Al counting plate with no covering on the sample. Count on beta counter.

Notes:

(1) Steps 1-3 correspond more or less to the initial separations procedures ordinarily used. If initial separations are not carried out separately, add 10 ml of conc. HCl to the solution in the flask after the $HClO_4$ fuming in step 1. Boil and evaporate to 10 ml volume, then proceed with step 2. The boiling with HCl will put Te in a form that will be carried on TlI.

(2) Do not allow the $K_3Rh(NO_2)_6$ to stand in the 0.1 M HCl wash solution any longer than necessary. Do not heat the solution. The salt dissolves slowly in 0.1 M HCl.

(3) If more than one sample is being worked up, it saves time to put the ones which have not yet been evaporated on the hot bath while the first samples are being evaporated.

(4) From the time the rhodium chloride is dissolved in 0.1 M HCl (step 8) until it has been eluted from the column (step 9) the procedure should be carried on without stopping. Any appreciable delays will cause loss of Rh.

(5) If large amounts of iridium radioactivity were thought to be present in the original solution, omit step No. 12 and proceed as follows: Dissolve the RhI_3 in 1 ml conc. HNO_3 and 2 ml of conc. $HClO_4$. Heat to strong fumes of $HClO_4$. Cool, add 1 ml conc. HBr and 1 ml conc. HCl. Heat just to fumes of $HClO_4$. Cool, add 1 ml conc. HNO_3 and heat to strong fumes of $HClO_4$. Continue heating until the solution is clear and the volume is 1 ml. Cool, add 5 ml of 6 M $HClO_4$. Transfer the 6-8 M $HClO_4$ solution to a Dowex 50 (100-200 mesh) cation exchange column (6 mm i.d. and 7 cm in length) which has been pre-oxidized with 8 M HNO_3 and washed with 6 M $HClO_4$. Wash the Rh through the resin column with two or three 5 ml portions of 6 M $HClO_4$ into a 125 ml Erlenmeyer flask. (Ir^{+4} adheres to the resin). Add 2 ml of conc. HNO_3 and 3 ml of conc. H_2SO_4 to the Rh solution in the flask. Heat until all $HClO_4$ has evaporated and SO_3 fumes are coming off strongly. Continue to step No. 13 which is a separation from Ir also.

Procedure 10

Target Material: 8 week old fission product mixture

Procedure by: W. H. Hutchin, Lawrence Radiation Laboratory, U. of California, Livermore (1957).

Yield: 60%

Decontamination: No detectable contamination in a sample of 7 c.p.m. (flow proportional counter, 30% geometry). Separated from 10^{15} fissions.

Procedure:

(1) To a solution of the activity add ~4 ml $HClO_4$, 2 mg Te^{+4}, 2 mg La, ~10 mg Zr, 20 mg Rh, ~10 mg Tl and 5 mg Ru carrier. Take to fumes of $HClO_4$ and fume strongly for 20 or 30 seconds (Note 1).

(2) Cool, dilute to ~25 ml with H_2O and add 3 drops H_3PO_4. Stir, centrifuge and discard precipitate.

(3) To the supernatant add ~2 ml 6% H_2SO_3 and 3 or 4 drops 55% HI. Stir and centrifuge, discarding precipitate. Pour supernatant into a 125 ml Erlenmeyer. Add 5 mg Ru.

(4) To the supernatant add 20 ml conc. HCl, ~5 ml 55% HI, 1 mg Te^{+4}. Boil for 20 minutes. Add 6 M HCl if volume gets too small. Transfer to a 40 ml cone with 6 M HCl. Centrifuge and discard supernatant. Wash ppt once with 6 M HCl.

(5) Add 2 mg Te^{+4}, 1 ml conc. H_2SO_4, 1 ml HNO_3, and ~0.5 ml conc. $HClO_4$. Take to fumes of SO_3. Cool to room temperature. Dilute to 15 ml volume with 6 M HCl. Stir and add ~1.5 ml H_3PO_2. Bring to a boil for 10 or 15 seconds to coagulate Te metal. Filter through a 9 cm No. 42 filter paper and wash filter with 6 M HCl. Catch filtrate in a 125 ml Erlenmeyer. Add ~5 ml H_2O_2 (30%) and warm slightly. If reaction gets too violent quency with 6 M HCl (see Note 2). After reaction subsides, boil for at least 5 minutes to destroy H_2O_2.

(6) Repeat step 4 (use 10 ml conc. HCl instead of 20 ml) and step 5 twice.

(7) After cooling solution from step 5, transfer to a 40 ml cone. Make basic with 6 M NaOH. Add 3 ml of a saturated solution of Na_2S and heat in a hot bath for ~15 minutes. Centrifuge and discard supernatant. Wash once with H_2O. Dissolve in 3 ml conc. H_2SO_4, 1 ml conc. HNO_3 and 0.5 ml conc. $HClO_4$. Take to fumes of SO_3. Dilute with H_2O and electroplate overnight at 80 milliamps (see Note 3).

Notes:

(1) The separation from Ir is at least a factor of 10^3. However, if large amounts of Ir activity are thought to be present and added separation may be accomplished as follows: (Rh - Ir separation by G. M. Iddings). After fuming the activities in $HClO_4$, pass the solution through a Dowex 50 x 12 (100-200 mesh) column that has been washed with 8 M HNO_3 and then 6 M $HClO_4$. Column dimensions are ~5 mm I.D. by ~10 cm long. Ir will remain on resin.

(2) The reaction between H_3PO_2 and H_2O_2 will not get too violent and have to be quenched if, while warming, the flask is removed from the heat as soon as bubbles start to form. At this point the reaction will increase on its own and reach a point where it is self-sustaining for a few minutes. After this one can proceed without danger of boiling over.

(3) Electroplating cells and electrodes must be clean and free from all organics (including soap) or else a good plate will not be obtained.

Procedure 11

Target Material: Fission Product (day old mixture).

Procedure by: J. C. Armstrong, Jr., Lawrence Radiation Laboratory, U. of California, Livermore (1959).

Yield: 50%

Separation Time: About 8 hours for 4 samples

Decontamination: Final sample contained 5×10^{8} atoms of Te-132 in 10^{13} atoms of Rh-105. This was the only detectable impurity.

Procedure:

(1) a) In a 125 Erlenmeyer flask, add to the active solution Rh carrier, 2 mg Te hold back, 2mg Ru holdback, 3 ml conc. H_2SO_4, 1 ml conc. $HClO_4$, take to SO_3 fumes gently.

b) While fuming add 2-3 drops H_3PO_2, continue fuming for 30 min. (see Note No. 1).

(2) a) Cool, dilute to ~20 ml, add 5 ml $NaBrO_3$, boil for 10 min.

b) Add 10 ml conc. HCl, continue boiling 10 min.

(3) a) Ice cool, add mg Pd holdback, 4 drops 4% KI, digest in ice bath 5 min., centrifuge, filter supernatant into 125 ml Erlenmeyer flask.

(4) a) Add ~5 ml 5 M NaI, 2 ml H_2SO_3, boil to coagulate RhI_3 ppt, transfer to 40 ml cone, centrifuge.

b) Wash ppt with 1.5 M H_2SO_4.

(5) a) Add to ppt, 2 ml conc. H_2SO_4, 2 mg Te holdback and fume carefully to about 1 ml or less volume.

b) Ice cool, add 5 ml conc. HCl carefully, pass thru Dowex A-1 column preconditioned with conc. HCl. Rh is in eluate.

c) Wash column with ~2 ml conc. HCl.

(6) a) Add 2 mg Te holdback, make basic with NaOH, add 3-4 ml saturated Na_2S solution, digest Rh_2S_3 ppt, in hot bath. Do not wash.

(7) Repeat step 5.

(8) a) Dilute eluate to ~30 ml with water, ice cool, add 5 ml $CrCl_2$, digest cold 10 min.

b) Add 5 ml $CrCl_2$, repeat digestion.

Procedure 11 (Cont'd)

c) Bubble in O_2 for 1 min. centrifuge,

d) Wash Rh° twice with 1M HCl, once with acetone. Dry 10 min. at 110°C. Weigh as Rh°.

Alternate Rhodium metal precipitation

(8) a) Dilute eluate to ~20 ml with water, add 2 ml of a saturated hydroxylamine hydrochloride solution, digest hot for 15 min.

b) Make basic with NaOH, digest hot until reaction ceases.

c) Wash Rh° twice with 1M HCl, once with acetone, dry 10 min at 110°C. Weigh as Rh°. See Note 3.

NOTES:

(1) H_3PO_2 must be added carefully to avoid sputtering out of the flask. If solution is fumed too vigorously at this point, the red rhodium sulfate precipitates. If this forms, centrifuge ppt, and dissolve in a small volume of boiling 6M NaOH, and return to original solution. Continue fuming.

(2) Steps 1 and 2 are done to insure Rh exchange.

(3) This Rh metal precipitation is easier and more complete than the $CrCl_2$ precipitation and also easier to handle.

Procedure 12

Target Material: Fission Products

Procedure by: J. S. Gilmore, LA-1721 (TID-4500, 13th Ed).

Yield: 60%

Separation Time: Six samples can be analyzed per day

Procedure:

(1) To a 125-ml Erlemeyer flask add 3 ml of standard Rh carrier and an aliquot of the sample.

(2) Add 3 ml of conc. H_2SO_4, 2 ml of conc. $HClO_4$, 1 ml conc. HNO_3 and heat until SO_3 fumes appear.[4] Cool, add 2 ml of conc. $HClO_4$, and evaporate to a volume of 1 ml.

(3) Add 3 ml of 6M HCl, 1 ml each of Mo and Co carriers, 1 to 2 g of solid KI and boil for 20 min. adding 6M HCl as needed to keep the volume of solution

approximately constant. Transfer to a 40-ml centrifuge tube, centrifuge, and discard the supernatant. Wash the RhI_3 precipitate with 20 ml of warm 6M HCl and discard the supernatant.

(4) To the precipitate add 3 ml of 3M KCN and heat until solution occurs. Add 1 ml of Te(IV) carrier, 2 ml of 6M HCl, and heat to boiling. While heating, add 5M $NaNO_2$ dropwise until I_2 fumes are no longer visible.

(5) Dilute to 20 ml with H_2O, add 3 drops of Fe carrier, and then conc. NH_4OH until a precipitate just forms. Centrifuge, transfer the supernatant to a clean 40-ml centrifuge tube, and discard the precipitate.

(6) Add 2 ml of conc. NH_4OH, 1 ml of Ba carrier, 3 ml of 0.5M Na_2CO_3 and warm on a steam bath for 5 min. Add 3 drops of Fe carrier, stir, and centrifuge. Transfer the supernatant to a clean centrifuge tube, and discard the precipitate.

(7) Add conc. HCl dropwise until the evolution of CO_2 ceases. Add 1 ml of 6M HCl, 1 ml each of Te(IV)[2] and Sb(III) carriers, and saturate with H_2S. Centrifuge, transfer the supernatant to a clean centrifuge tube, and discard the precipitate.

(8) Boil the solution for about 30 sec to remove H_2S. Add 7 ml of conc. HCl, 2 ml of $Cu(NO_3)_2$ solution, and cool in an ice bath. (The Rh is precipitated, presumably as $Cu_3[Rh(CN)_6]_2$.) Centrifuge and discard the supernatant.

(9) Dissolve the precipitate in 2 ml of conc. NH_4OH and dilute to 10 ml with H_2O. Transfer to the Dowex 50 cation exchange column and allow the solution to pass through under gravity, catching the eluate in a 125-ml Erlenmeyer flask. $[Cu(NH_3)_4]^{+}$ is removed on the column, the $[Rh(CN)_6]^{-3}$ passing through.

(10) Evaporate the solution nearly to dryness, add 3 ml of conc. H_2SO_4, and concentrate to a volume of 1 ml to destroy Rh-cyanide complex.

(11) Repeat Steps 3 through 9, but collect the column eluate in a 40 ml centrifuge tube.

(12) Repeat Steps 6 through 10.

(13) Add 2 ml of conc. $HClO_4$, 1 ml of conc. HNO_3, and heat until SO_3 fumes are evolved. Transfer to the plating cell with 20 ml of H_2O. Electroplate at room temperature and 0.1 amp for 16 hr on a weighed Pt cathode disk. Wash the cathode with H_2O and then with 95% ethanol. Dry in an oven at 110° for 15 min. Cool, weigh, mount, and β-count.

NOTE:

(1) The components of the plating cell must be extremely clean in order to obtain a smooth, adherent cathode deposit.

Procedure 13

Target Material: Air Filter Samples

Procedure by: Anahid Thomasian, A.F. Cambridge Research Laboratories.

Purpose: To separate Rh^{102} in thin samples over a small area for X-ray counting with thin crystals.

Procedure:

(1) Mixing Between Active Sample and Carrier

a. To the active solution add 2 ml $Rh(NO_3)_3 \cdot 2H_2O$ carrier (1.5-2.0 mg Rh/ml), 2 ml Tl_2O_3 (2.5 mg Tl/ml) and 4 drops $TeCl_4$ (10 mg Te/ml).

b. Evaporate gently until the volume is about 2 to 3 ml. Add 10 ml aqua regia and boil to dissolve any insoluble oxides which may be present in the sample.

(2) Conversion to Chloride Salts

a. Evaporate to incipient dryness. (Do not bake)

b. Add 10 ml concentrated HCl, wash sides of beaker thoroughly with 6M HCl and evaporate again to incipient dryness.

c. Repeat 2-b twice to insure complete expulsion of oxides of nitrogen. (See note 1).

(3) Thallium and Tellurium Scavenge

a. To the chloride salts add 2 ml concentrated HCl and heat slightly to dissolve. (See note 2).

b. Add 10 ml H_2O and transfer to a 40 ml centrifuge tube, using H_2O. Total volume should be about 20 ml.

c. To the solution add 2 ml 6% H_2SO_3 and stir. Add approximately 1 ml of 57% HI (Phosphorous free) and stir again. Centrifuge the iodides of tellurium and thallium.

d. Decant supernatant into a 125 ml Erlenmeyer flask. Wash the precipitate with 5 ml of a solution containing 5 ml H_2O, 1 ml concentrated HCl, 0.5 ml 6% H_2SO_3 and a few drops of HI. Centrifuge. Discard precipitate. Add wash to main supernatant.

(4) Precipitation of Rhodium as RhI_3

a. To the combined supernatant and wash, add 10 ml concentrated HCl and 2 ml phosphorous free HI.

b. Boil at least 20 minutes. Keep the volume between 15-20 ml by the addition of 6 M HCl.

c. Allow to stand a few minutes. Transfer to a 40 ml centrifuge tube using 6 M HCl to aid in the transfer. Centrifuge 5 to 10 minutes.

d. Discard supernatant.

e. Wash the RhI_3 precipitate with 10-15 ml 6 M HCl. Centrifuge. Discard wash.

(5) Conversion of Rhodium to the Soluble $NaNO_2$ complex

a. To the RhI_3 precipitate add 2 ml concentrated HCl and 5-10 drops 30% H_2O_2. Heat gently until solution is effected, adding more H_2O_2 if necessary.

b. Boil the solution to a volume of 1 ml. Cool and dilute to 15 ml with H_2O.

c. Cautiously add about 3 ml of a saturated solution of $NaNO_2$, with stirring. After the initial effervescence has subsided, place in a hot H_2O bath for 10 minutes with occasional stirring.

(6) Iron Scavenge

a. Add 1 or 2 drops of $FeCl_3 \cdot 6H_2O$ (5 mg Fe^{+++}/ml), stir, digest for 1 minute in a hot H_2O bath and centrifuge. Transfer supernatant to a 40 ml centrifuge tube. Discard precipitate.

(7) Lanthanum Scavenge

a. To the supernatant add 2 drops of $La(NO_3)_3 \cdot 6H_2O$ (10 mg La/ml) and 1 or 2 drops of phenolphthalein. Stir and add dropwise 1M NaOH until the solution is just alkaline. (See note 3).

b. Digest for 1 minute in a hot H_2O bath. Centrifuge. Transfer supernatant to a 40 ml centri-

fuge tube. Discard precipitate.

(8) Precipitation of $K_2Rh(NO_2)_6$

a. Acidify the supernatant by the addition of 1 drop 3M HCl. Add 2 ml of a saturated solution of KNO_3. Stir vigorously until precipitation occurs.

b. Digest in a hot water bath for at least 15 minutes (see Note 4).

c. Cool to room temperature by immersing sample in cold water bath. Centrifuge. Discard supernatant.

(9) Purification by Ion-Exchange

a. Dissolve the precipitate with 2 or 3 ml 6M HCl and gentle heating. Evaporate to dryness.

b. Cool and dissolve salts with about 3 ml 0.1M HCl.

c. Pass solution through a column of water washed Dowex 1-X 10 resin, Cl^- form, 200-400 mesh. The resin bed should be about 3.3 cm long and 0.4 cm wide.

d. Wash column with 1 or 2 ml 0.1M HCl. Discard washings.

e. Elute rhodium with 15 ml concentrated HCl, collecting the eluate in a clean 125 ml Ehrlenmeyer flask (see Note 5).

(10) Removal of Traces of Silver and Tellurium

a. Add 2 drops of $TeCl_4$ (10 mg. Te/ml) to the eluate and boil until the volume is about 10 ml.

b. Wash sides of flask with 2 or 3 ml H_2O and allow to cool.

c. Add 2 ml 57% HI (phosphorous free) (see Note 6) to the flask and transfer contents to a 125 ml separatory funnel which contains 15 ml of 4-methyl-2pentanone (hexone) previously equilibrated with about 1 ml 57% HI and 5 ml 6M HCl. Wash flask out with a few ml 6M HCl and transfer to the funnel. (The ratio of acid to hexone volumes should be about 1-1).

d. Using a stirring rod, stir vigorously for about two minutes. Allow mixture to stand 10 minutes.

e. Carefully draw off the acid layer into a clean 125 ml Ehrlenmeyer flask.

(11) Precipitation of Rhodium as RhI_3

a. Bring sample to a boil over a hot plate, initially swirling the flask by hand in order to prevent bumping by traces of hexone which may have dissolved in the acid layer. Allow to boil for 15 to 20 minutes to precipitate RhI_3, maintaining the volume at about 10 ml by the addition of 6M HCl.

b. Cool somewhat and transfer to a 40 ml centrifuge tube using 6M HCl to aid in the transfer.

c. Centrifuge for about 10 minutes. Discard supernatant. Wash the precipitate with 10 ml 6M HCl and centrifuge. Discard wash.

(12) Destruction of Iodide-Conversion to Sulfate

a. Transfer the RhI_3 back into the flask in which the precipitation was made, using water. Add 1 ml conc. H_2SO_4 and boil until the fumes of iodine have been expelled.

b. Allow the flask to cool. Wash sides of flask with a few ml water. Add 1 ml conc. HCl and boil until the red color of $RhCl_3$ becomes apparent.

c. Add 1 ml conc. HNO_3, 1 ml conc. $HClO_4$ and boil to the evolution of SO_3 fumes.

d. Allow flask to cool. Transfer the solution of $Rh_2(SO_4)_3$ to a 40 ml centrifuge tube (see Note 7). Wash flask by the dropwise addition of water two or three times. Add each washing to the centrifuge tube.

e. Boil until fumes of SO_3 begin to evolve.

f. Cool. Wash sides of tube with 10-15 drops of H_2O and repeat e.

(13) Determination of Rhodium by Electrodeposition

a. Cool centrifuge tube. Add 5 or 6 drops of water to the H_2SO_4 acid solution and cool again.

b. Transfer solution to the electroplating cell whose volume is approximately 3 ml. Using a medicine dropper wash tube out with water twice, transferring the wash each time to the cell until the volume reaches about 7/8 of the cell capacity.

c. Electroplate the rhodium on to a previously tared platinum disc (3/8 inch in diameter,

Procedure 13 (Cont'd)

1 mil in thickness) for approximately 16 hr. 75 milliamps.

d. Remove the platinum disc. Rinse several times with water and finally with 95% ethyl alcohol.

e. Dry at 110°C. for 15 minutes. Cool in a dessicator and weigh to constant weight as elementary rhodium.

NOTES:

(1) The expulsion of HNO_3 and other oxides of nitrogen is important since they will oxidize the HI which will be subsequently used to precipitate rhodium as RhI_3.

(2) Some heating may be required here also to aid in solution of the salts. If silica is present, centrifuge and discard the latter.

(3) Usually 2 to 3 drops of NaOH is sufficient.

(4) With 3-4 mg quantities of rhodium, the average digestion period has been about 30 minutes. If a larger amount of rhodium is used, the digestion period may be decreased to 5 or 10 minutes.

(5) With larger amounts of rhodium carrier it may be necessary to use 5-10 ml more conc. HCl to elute the rhodium.

(6) For larger amounts of rhodium carrier increase the volume of HI to about 5 ml and the volumes of hexone and acid to about 30 ml each.

(7) This transfer is useful because of the small volume of final rhodium solution, whereby the surface area to be washed is decreased by using a centrifuge tube rather than a flask.

Procedure 14

Target Material: Pu-U Fissium Alloys

Procedure by: Evans, Bloomquist and Hughes, Anal. Chem., 34, 1692 (1962)

Procedure:

(1) Transfer a 0.5-gram sample (or less) of the alloy as turnings to a quartz tube, 12 mm. in outside diameter by 8 mm. in inside diameter and approximately 15 inches in length, which has been sealed and carefully annealed at one end. Slowly add, in small increments, 5 ml of 12M hydrochloric acid. After the evolution of gases has ceased, add 2 drops of 72% perchloric acid. (The volume of liquid should never be greater than one half of the volume of the tube). Seal off the tube at a length of approximately 10 to 12 inches using a gas-oxygen torch and anneal-seal in a gas flame. Place the tube in a steel shell which has been previously hydrostatically tested and x-rayed, and add 40 grams of solid carbon dioxide. Immediately screw on the cap and test for leakage by immersing the shell under water. Place the shell in a muffle furnace maintained at approximately 300° ± 10° C. for 4 hours. (This furnace is specially equipped with temperature control safety devices to obviate electrical failures or human errors).

(2) Remove the shell from the furnace, cool to room temperature, and remove the tube. Inspect for complete dissolution, cool the tube in solid carbon dioxide and open. Transfer the contents to a 50-ml volumetric flask and make the final solution 8M in hydrochloric acid.

(3) Select from the stock solution an aliquot that contains 50 to 150 µg. of rhodium, and transfer it to a 40-ml borosilicate glass graduated centrifuge tube. Adjust the volume to 5 ml and make the final solution 8M in hydrochloric acid. Add 0.5 ml of concentrated nitric acid and heat the solution on a sand bath until gas evolution occurs.

(4) Discontinue heating the sample and permit it to stand for about 2 1/2 hours before transferring to the resin column, prepared as previously described. When the level of the sample solution nears the top of the resin bed, use three 5-ml portions of the eluting solution to wash out the sample containers, and add to the column when the level of the preceding portion of eluant nears the top of the resin bed.

(5) Pass the solutions through the column, with the aid of gentle suction, into a 50-ml volumetric flask, at a drop rate of 35 ± 5 drops per minute. Do not allow the columns to reach dryness. Continue

washing the column with 8M hydrochloric acid until a total volume of 45 to 50 ml has been collected in the flask.

(6) Elute the plutonium from the column with 0.30M hydrochloric acid and transfer to waste. Transfer eluate along with the 8M hydrochloric acid washings to a 150-ml beaker. Slowly add 2 ml of concentrated sulfuric acid, cover the beaker with a Speedyvap cover, and evaporate to fumes.

(7) Add 500 µl. of perchloric acid slowly to the hot sulfuric acid and continue fuming for 1 to 2 minutes. Cool, and rinse the cover with a minimum of water and the sides of the beaker with 8M hydrochloric acid. Again heat to copious fumes of sulfuric acid for 10 minutes, add 2 drops of perchloric acid, and continue fuming for 10 minutes. Cool, repeat the rinsing operation with water and 8M hydrochloric acid, and continue fuming until an estimated volume of 0.5 ml of sulfuric acid remains. Do not allow the acid to fume to dryness and, if necessary, add 0.5 ml of sulfuric acid between the second and the third fuming steps. (The fuming operation will eliminate organic matter, ruthenium, and nitrate ions, which would interfere during the color-development stage).

(8) Development of Rhodium (III) Chloro Complex. To the sulfate solution of rhodium in the beaker, add 10 ml of 2M hydrochloric acid, cover with a watch glass, and heat to boiling. Add 5 ml of 1M tin(II) chloride in 2.5M hydrochloric acid and continue heating at incipient boiling for 2 minutes. (The solution will develop a pink tinge during this period). Transfer the sample to a steam bath, and digest for 1 hour. Allow to cool for 5 minutes. Add another 5 ml of 1M tin(II) chloride solution, and transfer to a 50-ml volumetric flask, using 2M hydrochloric acid as the wash and for dilution to volume. Allow the solution to stand for 30 minutes before measuring the absorbance at 470 mµ.

NOTES:

The method described here consists essentially of three steps: sample preparation, ion exchange separation and spectrophotometric determination. It is readily adapted to routine procedure and is elementary and less time-consuming than the cation application (A) as it requires only one fuming instead of three, control of the acid in the feed is not so critical, prior removal of uranium is not necessary, and separation from plutonium is efficient.

(A) Kartunen, J.O. and Evans, H.B., Anal. Chem., 32, 917 (1960).

C. Spallation Product Separation

Procedure 15

Target Material: Ruthenium

Type of Bombardment: Protons

Procedure by: Gile, Garrison and Hamilton, J. Chem. Phys., 19, 1428 (1951).

Yield: 80-90%

Separation Time: 7-8 hours

Decontamination: 10^3

Procedure:

(1) Fuse the ruthenium powder with 10 gms Na_2O_2 in a nickel crucible at 300°C for 30 minutes.[2] Any Te produced is lost in this step.

(2) Dissolve the fused mass in aqua regia with heating and centrifuge the insoluble material out.

(3) Make the solution basic with KOH, heat to approximately 100°C and pass Cl_2 gas through the solution to volatilize RuO_4.[2] Collect the distillate in 6M NaOH.

(4) After all the Ru has been distilled out as evidenced by the color of the distillate fractions, centrifuge the residual solution. The $Ni(OH)_2$ precipitate carries about 95% of the rhodium.[2]

(5) Wash the precipitate with water and dissolve in a minimum volume of dilute HNO_3. Add 5 mg Fe(III) and precipitate $Fe(OH)_3$ by addition of NH_4OH. The rhodium carries quantitatively on the precipitate while the nickel remains in solution as $Ni(NH_3)_6^{++}$.

(6) Reprecipitate the $Fe(OH)_3$ twice to remove all the nickel. Then dissolve the final precipitate in 6N HCl and extract the iron with ethyl ether.

(7) Evaporate the aqueous phase containing HCl and the rhodium to dryness on 50 mg NaCl and dissolve this quantitatively in 5 ml of distilled water.

I. Modification by Ellis and Choppin, Unpublished data.

(A) In step 5, Rh may not coprecipitate with $Fe(OH)_3$. Saturation of the solution with Cl_2 before precipitation with NH_4OH ensures coprecipitation of the Rh.

(B) The Fe(III) is more rapidly and more completely removed in step 6 by passing the 6N HCl solution through a small bed of Dowex-1 anion resin. The Fe(III) will adsorb much more strongly than the Rh which elutes rapidly.

II. Modification by M. Lederer, Anal. Chim. Acta, 8, 134 (1953).

Some brown residue in Rh due to unextracted Fe(III) is always found after step 6. This may be removed with paper chromatography as follows:

(A) The mixed $Fe(OH)_3$ and $Rh(OH)_3$ precipitate is dissolved in a few drops of HCl and placed on a band of Whatman No. 1 filter paper. This is developed with a mixture of 20 ml butanol and 10 ml concentrated HCl. Fe travels with the liquid front while Rh remains in the R_f 0.1 region. Cut out the radioactive band and extract the Rh repeated with small quantities of 2N HCl, then evaporate to dryness. The dry sample has approximately the same residue as the 2N HCl used for extraction.

Procedure 16

Target Material: Silver

Type of Bombardment: Gammas to produce (γ,α)

Procedure by: de Laboulaye and Beydon, Compt. rend., 239, 411 (1954).

Procedure:

(1) Dissolve the silver target in HNO_3.

(2) Add 10 mg Fe(III) as $Fe(NO_3)_3$ with NH_4OH. Rh coprecipitates, Ag remains in solution.

(3) Dissolve the precipitate in HNO_3 and repeat the precipitation three times.

(4) Dry the hydroxide, cursh it to a fine powder and mount this powder for counting.

Procedure 17

Target Material: Silver (20 gms)

Type of Bombardment: Protons-450 Mev.

Procedure by : L. Marquez, Phys. Rev. 95, 67 (1954)

Procedure:

(1) Dissolve the target in HNO_3 and add 2 mg each of Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, and Cd as carriers.

(2) After long boiling, dilute the solution with H_2O, precipitate the Ag with HCl and filter.

(3) Precipitate the Pd with dimethylglyoxime (DMG) by adding 20 ml of 1% alcohol solution of DMG and neutralizing in part the excess of acid. Centrifuge the solution and decant the supernatant liquid.

(4) Evaporate the supernatant to near dryness, then strongly fume with a mixture of $HClO_4$, $NaBiO_3$ and H_3PO_4 to evaporate the Ru.

(5) Purify the Rh by pyridine extraction as described in Procedure 4.

(6) Alternatively,* after step 4, evaporate with H_2SO_4 to fumes of SO_3, add 20 ml of water (cautiously after cooling and precipitate Rh as the metal by addition of $TiCl_3$. Wash the Rh metal with dilute H_2SO_4, then H_2O. Transfer the Rh metal slurry to a zapon backing, and dry under a heat lamp.

* L. Marquez, Phys. Rev. 92, 1511 (1953).

Procedure 18

Target Material: Palladium Foil

Type of Bombardment: Fast Neutrons

Procedure by: Baro, Seelmann-Eggebert and Zabala, Z. Naturforsch, 10a, 80 (1955).

Procedure:

(1) Dissolve the target foil in HNO_3 to which Rh, Ru, and Ag carriers have been added.

(2) Precipitate the AgCl with HCl and filter.

Procedure 18 (Cont'd)

(3) Add $Ca(OH)_2$ until the solution is almost neutral, then with heating, add $Ca(NO_3)_2$ solution to precipitate $Ca_2Rh(NO_3)_6$.

(4) After filtering, dissolve the precipitate in HCl, add more Ru and Pd carrier and reprecipitate the $Ca_2Rh(NO_3)_6$ salt.

(5) Again filter and dissolve the precipitate in HCl, dilute with H_2O and add Ag^+ and precipitate AgCl until activity is no longer carried down in the AgCl precipitate. Filter the solution.

(6) Precipitate Rh as the metal by addition of a solution of $TiCl_3$ to the filtrate.

Procedure 19

Target Material: Palladium or Silver Foil

Type of Bombardment: Deuterons and Fast Neutrons

Procedure by: Baro, Seelman-Eggebert and Zabala, International Conf. on Peaceful Uses of Atomic Energy, 7, 176 (1955).

Yield: 50-60%

Separation Time: Approximately 1 hour

Decontamination: <.05% of original activity of impuritites remaining.

Procedure: (For Pd Foil)

(1) Dissolve target in a small volume of concentrated HNO_3.

(2) Add 20 mg Rh(III), 10 mg Ru (III), 10 mg Ag(I) and precipitate AgCl with KCl and filter.

(3) Partially neutralize the filtrate with NaOH and add KNO_2.

(4) Bring solution to the boiling point to precipitate $K_3Rh(NO_2)_6$, cool and filter.

(5) Dissolve precipitate in HCl, and again add Ru(III) and Pd(II) carriers.

(6) Repeat $K_3Rh(NO_2)_6$ precipitation twice more.

(7) Using Ag(I) carrier and KCl precipitate AgCl until the precipitate no longer carries any activity down with it.

(8) Precipitate Rh as the metal by addition of $TiCl_3$ solution.

Procedure 19 (Cont'd)

(For Ag Foil)

(1) Dissolve silver target in HNO_3 to which 30 mg Rh(III) and 10 mg Pd(II) have been added.

(2) Precipitate Ag with KCl until AgCl precipitate no longer carries down any activity.

(3) Continue from Step 4 above.

Procedure 20

Target Material: Rhodium Foil

Type of Bombardment: Cockcroft-Walton Accelerator

Procedure by: G. M. Iddings, Lawrence Radiation Laboratory, University of California, Livermore (1964)

(1) Weigh the Rh metal foil. Place ∿ ten times the Rh weight of bismuth metal in a No. 0 porcelain crucible. Add the Rh foil and fill the crucible ∿2/3" full with Norit A (decolorizing carbon). Heat the crucible over a Fisher burner a few minutes at full heat. Cool and wash out the carbon.

(2) Dissolve the Rh-Bi alloy in conc. HNO_3 in a beaker. Boil just to near dryness. Add some conc. HCl and boil to low volume to destroy all of the nitrate.

(3) Take an aliquot of this solution such that one has ∿ 20 mg of Rh in it. Make the solution ∿ 6 M in HCl and 1-2 M in HI. (Use the HI without the H_3PO_2 preservative in it). Make the aqueous layer ∿ 20 ml. Put it into a 60 ml cylindrical separatory funnel. Add ∿ 40 ml of hexone and extract the Bi into the organic layer. Discard the organic layer and repeat the hexone extraction twice adding a ml of conc. HI each time. The solution must not be hot or even warm when the HI is added or the RhI_3 starts to ppt. Discard all organic layers. (These contain BiI_3).

(4) Boil the aqueous layer in a 125 ml Erlenmeyer flask for ∿ 20 minutes to ppt. the RhI_3. Centrifuge and wash the ppt. with 6 M HCl.

(5) Dissolve the ppt. in 3 ml of conc. H_2SO_4 by heating to fumes of SO_3. Cool and add ∿ 2 ml of 6 M HCl. Boil to reduce iodates. Add 1 ml each of conc. HNO_3 and conc. $HClO_4$. Heat to SO_3 fume. Cool, dilute the H_2SO_4 with water and electrodeposit the Rh on a Pt plate, using ∿ 40 ma overnight.

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