

1946

The chelate compounds of plutonium

Frederick John Wolter
Iowa State College

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Physical Chemistry Commons](#)

Recommended Citation

Wolter, Frederick John, "The chelate compounds of plutonium " (1946). *Retrospective Theses and Dissertations*. 14179.
<https://lib.dr.iastate.edu/rtd/14179>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

NOTE TO USERS

This reproduction is the best copy available.

UMI[®]

130

THE CHELATE COMPOUNDS OF PLUTONIUM

by

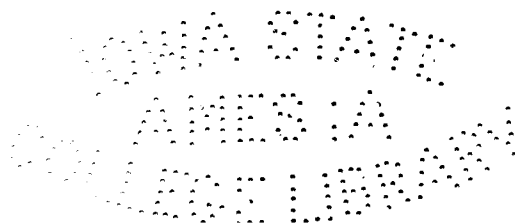
Frederick John Wolter

**A Thesis Submitted to the Graduate Faculty
for the Degree of**

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:



Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1948

UMI Number: DP13061

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI[®]

UMI Microform DP13061

Copyright 2005 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

CONFIDENTIAL
WASDC
c.1

1128-129

TABLE OF CONTENTS

| | Page |
|--|------|
| I INTRODUCTION | 1 |
| 1.1 History of the Plutonium Problem | 1 |
| 1.2 The Chemical Properties of Plutonium | 3 |
| 1.2.1 Oxidation states | 4 |
| 1.2.2 Oxidation and reduction of plutonium | 6 |
| 1.2.3 Ionic species and complex formation | 10 |
| 1.2.4 The position of plutonium in the periodic table | 12 |
| 1.3 Statement of the Problem | 15 |
| II THE NATURE OF CHELATE COMPOUNDS | 16 |
| 2.1 Nomenclature | 16 |
| 2.2 Properties of Chelate Compounds | 17 |
| 2.3 Factors Involved in the Formation of Chelate Compounds | 19 |
| 2.3.1 General conditions for complex formation | 19 |
| 2.3.2 The chemical bonds formed in complex compounds | 20 |
| 2.3.3 Functional groups in chelating reagents | 21 |
| 2.3.4 The nature of the donor atom | 22 |
| 2.3.5 The nature of the acceptor atom | 24 |
| 2.3.6 Ring formation | 26 |
| 2.3.7 The possible complexing properties of plutonium | 28 |

T12204

| | Page |
|---|-----------|
| III EXPERIMENTAL METHODS AND TECHNIQUES | 29 |
| 3.1 Extractions on the Tracer Scale | 29 |
| 3.2 Extractions on the Micro Scale | 30 |
| 3.3 Radioactive Assays | 32 |
| 3.3.1 Plutonium assays | 32 |
| 3.3.2 Other radioactive assays | 34 |
| IV MATERIALS USED | 36 |
| 4.1 Plutonium | 36 |
| 4.2 Other Radioactive Isotopes | 36 |
| 4.3 Solvents | 36 |
| 4.4 Organic Reagents | 37 |
| V THE CHELATE COMPOUNDS OF PLUTONIUM(IV). | 40 |
| 5.1 Exploratory Experiments on the Tracer Scale | 40 |
| 5.1.1 Introduction | 40 |
| 5.1.2 Experiments with bidentate reagents | 40 |
| 5.1.3 Experiments with quadridentate reagents | 45 |
| 5.1.4 Discussion | 51 |
| 5.2 Extended Studies with Disal | 55 |
| 5.2.1 Conditions for preparing the Pu(IV)-disal complex on the micro scale | 55 |
| 5.2.2 The composition of the Pu(IV)-disal complex | 57 |
| 5.2.3 The use of various solvents for disal extractions | 59 |

| | Page |
|---|-----------|
| 5.2.4 Behavior of the Pu(IV)-disal complex toward dilute acids | 60 |
| 5.2.5 Interfering substances | 62 |
| 5.2.6 Discussion | 64 |
| 5.3 The Plutonium(IV)-Ferron Complex | 67 |
| 5.3.1 Introduction | 67 |
| 5.3.2 Experimental | 69 |
| 5.3.3 Discussion | 76 |
| VI THE CHELATE COMPOUNDS OF PLUTONIUM(III). | 78 |
| 6.1 Introduction | 78 |
| 6.2 Experimental | 78 |
| 6.2.1 General procedure | 78 |
| 6.2.2 The behavior of plutonium(III) with hydroxamic acids | 80 |
| 6.2.3 The behavior of plutonium(III) with amide oximes | 85 |
| 6.2.4 The behavior of plutonium(III) with miscellaneous bidentate reagents | 87 |
| 6.3 Discussion | 89 |
| VII THE USE OF ORGANIC REAGENTS FOR THE DECONTAMINATION AND PURIFICATION OF PLUTONIUM | 93 |
| 7.1 Introduction | 93 |
| 7.2 Experimental | 94 |
| 7.2.1 The behavior of various cations with disal | 94 |
| 7.2.2 Attempts to adapt disal extractions to the separation of plutonium from zirconium and thorium | 98 |

| | Page |
|--|------|
| 7.2.3 The behavior of various cations with hydroxamic acids | 100 |
| 7.2.4 The behavior of various cations with amide oximes | 103 |
| 7.3 Discussion | 105 |
| VIII SUMMARY | 109 |
| IX LITERATURE CITED | 113 |
| X ACKNOWLEDGEMENTS | 119 |

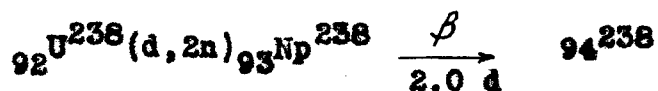
I INTRODUCTION

1.1 History of the Plutonium Problem

The first transuranium element was discovered in May, 1940 by McMillan and Abelson (1), who found a radioactivity with a 2.3 day half-life formed by irradiation of uranium with neutrons, and emitting negative β -rays. After showing that it differed from uranium and the fission products they identified this activity as the daughter of 23 minute β -active U^{239} which is formed by the radiative capture of neutrons by U^{238} . The new element therefore has an atomic number one greater than that of uranium and is element 93.

Their work on the tracer scale showed that element 93 has at least two oxidation states, and that oxidation to the higher state requires more vigorous conditions than the corresponding oxidation of uranium. The new element was given the name neptunium.

The next transuranium element discovered was element 94. Late in 1940, Seaborg, McMillan, Wahl, and Kennedy (2) identified as element 94 the α -active element formed by the decay of the intermediate neptunium produced by a d, 2n reaction on U^{238} .



Element 94 was named plutonium. The isotope ${}_{94}\text{Pu}^{238}$ is an α -emitter with a half-life of about 115 years. Early experiments with tracer amounts of Pu^{238} showed that the element had at least two oxidation states, and that for producing the higher oxidation state even more vigorous oxidizing agents were required than for the corresponding operation with neptunium.

The isotope of plutonium which is of greatest importance is the long-lived α -emitter Pu^{239} , the daughter of 2.3 day Np^{239} . Consideration of the Bohr-Wheeler theory of fission (3) and of certain empirical relations among heavy nuclei by L. A. Turner (4) and others had suggested that Pu^{239} would be a long-lived α -emitter and that it might be fissionable by slow neutrons.

It had been found by the middle of 1940 that neutrons were emitted in the process of fission of uranium (5). Thus at that time many of the prerequisites for a serious study of the production of atomic energy were at hand.

The dramatic history of the development of the atomic bomb has been described in the now-famous Smyth report (6).

The Metallurgical Project had as its object a method for obtaining large quantities of pure Pu^{239} . The first aspect of the problem was the development of a controllable

chain reacting structure which would produce Pu²³⁹ in a matrix of uranium. The second part of the problem was to learn enough of the chemistry of plutonium to devise an efficient method of separating the Pu²³⁹ from uranium and highly radioactive fission products and of producing Pu²³⁹ in a state of purity useful for military purposes.

These goals were achieved by a research program in which many of the chemical studies were done with microscopic and submicroscopic quantities of material. In fact it was not until August of 1942 (7) that the first pure compound of plutonium free from carrier material and other foreign matter was prepared. Milligram quantities did not become available until much later. Since early 1944 investigations have been continued with increasingly larger amounts of plutonium, until plutonium has been brought from the realm of little-known elements to a position where its chemical and physical properties are as well or better understood than those of many other elements.

1.2 The Chemical Properties of Plutonium

Any reasonably complete discussion of the chemical properties of plutonium would require volumes. The purpose of this brief discussion is to summarize a few of the more important properties of plutonium as they apply to a study of the chelate compounds of plutonium. No attempt will be made to make specific references to the original

project reports in which the work was described, as this has been done in the report of Thomas and Warner (8) and will be covered completely in the forthcoming volumes of the Plutonium Project Record (9).

1.2.1 Oxidation states.

The dipositive state. Of the compounds of Pu(II), PuO is the best known. It is readily soluble in dilute HCl with the liberation of hydrogen, so apparently Pu(II) is not stable in acid solution. The dipositive state is produced by metallic reduction of solid compounds of higher oxidation states.

The tripositive state. Plutonium(III) in aqueous solution has a blue to violet color. The absorption spectrum of Pu(III) solutions has several absorption bands, some of which are narrow. They are useful in identifying the oxidation state of plutonium in solution. The narrow bands are similar to those found for elements containing more than one 4f electron. The narrow absorption bands of the rare earths, for example, are due to electrons rearranging themselves in deep-lying subshells (4f). These transitions are thus protected from the ions' environment.

The general aqueous solution chemistry of Pu(III) is quite similar to that of the rare earth ions. In some compounds, Pu(III) has an ionic radius about like that of Pr(III).

The tetrapositive state. The color of aqueous solu-

tions of Pu(IV) varies from green to brown, depending on the anions present. The explanation of this in terms of complex ion formation will be discussed later. The absorption peaks of Pu(IV) are sharp and narrow, and serve as a means of identifying Pu(IV) in aqueous solution.

The chemistry of Pu(IV) is very similar to that of U(IV), Ce(IV) and Th(IV), except in its oxidation-reduction properties. It is much more stable than U(IV), and its ionic radius is slightly less than that of Ce(IV). The hydroxide of Pu(IV) is amorphous and extremely insoluble. It shows no amphoteric properties. This hydroxide has a tendency to form a green solution containing various sized aggregates, some of which have been found to be of colloidal dimensions. The hydroxides of Th(IV), U(IV) and Ce(IV) also exhibit this same phenomenon of dispersion into colloidal particles. The polymeric form of the hydroxide of Pu(IV) requires heating in concentrated acid for solution, and in dilute acids the transformation from colloidal to ionic form is often very slow.

In certain media Pu(IV) is the easiest of the various oxidation states to maintain.

The pentapositive state. Only one compound of Pu(V), believed to be potassium plutonite, has been described, although there is some evidence of PuF₅ compound. Pu(V) has been detected spectrophotometrically as an intermediate state in the reduction of Pu(VI) with hydroxylammonium ion, SO₂,

and H_2 . Apparently Pu(V) is unstable with respect to Pu(III), Pu(IV) and Pu(VI).

The hexapositive state. The compounds of Pu(VI) and their aqueous solutions exhibit colors from pink through orange to brown, and the aqueous solutions have the characteristic sharp absorption bands in their spectra.

The aqueous chemistry of Pu(VI) is very similar to that of U(VI), and the plutonyl and plutonate salts resemble very closely the corresponding uranyl and uranate compounds. The ionic radius of Pu(VI) is only slightly smaller than that of U(VI), and Pu(VI) exists as PuO_2^{++} ion in the absence of complexing anions.

There is no fluorescence corresponding to that exhibited by the UO_2^{++} ion.

Higher oxidation states. There have been various attempts to prepare plutonium of oxidation number greater than six, but they have been unsuccessful.

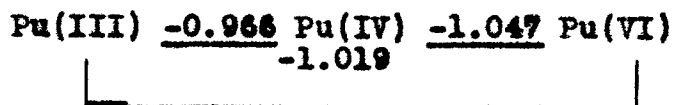
1.2.2 Oxidation and reduction of plutonium

Formal potentials between Pu(III), Pu(IV) and Pu(VI).

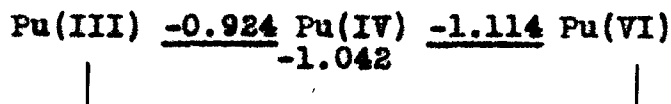
The determination of the potentials between various oxidation states of plutonium was one of the important objectives in the research program on the chemistry of plutonium.

The various potentials listed below are the best values obtained from direct cell measurements, polarographic determinations, and spectrophotometric measurements of disproportionation equilibria. All values are in 1 M acid at 25°C.

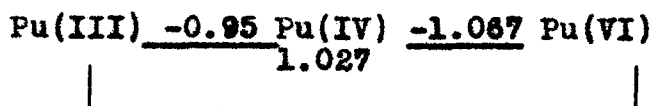
HCl



HNO₃



HClO₄



H₂SO₄



The Pu(IV)-Pu(VI) couple in 1 M H₂SO₄ is estimated from measurements of irreversible cells (10). There have been no direct measurements in neutral and alkaline solutions, in which the relationships are much more complicated.

Formal potentials of the Pu(III)-Pu(IV) couple. The potentials of the Pu(III)-Pu(IV) couple have been measured under many conditions which are of general interest in the chemistry of plutonium. Reference to Table 1 will show the evidence of complexing of Pu(IV) by various anions (10, 11).

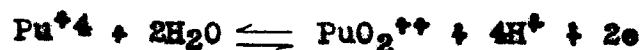
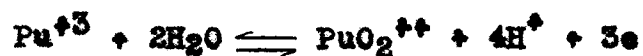
Table 1

Formal Potentials of the Pu(III)-Pu(IV)
Couple in Various Media at 25°C

| Solution | E.M.F. |
|---|--------|
| 1 M HAc, 1 M NaAc | -0.398 |
| 0.3 M HAc, 0.1 M NaAc, 0.05 M Na ₂ SO ₄ | -0.281 |
| 1 M HCl, 1 M HF | -0.50 |
| 1 M HCl, 0.1 M H ₃ PO ₄ | -0.80 |
| 1 M HCl, 0.6 M H ₃ PO ₄ | -0.59 |
| 0.5 M H ₂ SO ₄ , 0.6 M H ₃ PO ₄ | -0.60 |
| 0.05 M H ₂ SO ₄ , 9 M NH ₄ F | L-0.87 |
| 0.02 M H ₂ SO ₄ , 0.18 M H ₂ C ₂ O ₄ , 0.18 M K ₂ SO ₄ | -0.234 |
| 0.05 M H ₂ C ₂ O ₄ , 0.75 M K ₂ C ₂ O ₄ , 0.05 M K ₂ SO ₄ | -0.082 |

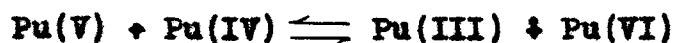
Disproportionation equilibria. In solutions in which there are no anions which will stabilize one oxidation state of plutonium through complex formation, disproportionation among the various oxidation states occurs, as a consequence of the fact that the potentials of the Pu(III)-Pu(IV)-Pu(VI) couples are so nearly equal in value. The existence of these equilibria greatly complicates the aqueous solution chemistry of plutonium.

The Pu(IV) ion is relatively unstable. In dilute solutions of HCl, HNO₃ or HClO₄ it undergoes partial disproportionation into Pu(III) and Pu(VI). In 0.5 M HCl, the value of the equilibrium constant (in molar concentrations) is 0.052 at room temperature for the reaction



In H_2SO_4 solutions and in other media in which Pu(IV) is stabilized by complex formation the equilibrium constant for the disproportionation reaction becomes very small.

The equilibria in the reaction



have not been studied so thoroughly, and values of the equilibrium constant range from 5.4 to 8.8.

Oxidation-reduction reactions. Reference to the formal potentials of couples of the various oxidation states of plutonium will suggest what media might be necessary for various oxidation reduction reactions.

For the oxidation of Pu(III) to Pu(IV), oxygen in the presence of H_2SO_4 is effective, as are concentrated HNO_3 , Cl_2 , and $\text{Cr}_2\text{O}_7^{--}$ with HNO_3 . For the oxidation to Pu(VI), sodium bismuthate, BrO_3^- , $\text{Cr}_2\text{O}_7^{--}$, Ag^{++} and $\text{S}_2\text{O}_8^{--}$, KMnO_4 , Ce^{++++} , and electrolytic oxidation have been used.

For the reduction of Pu(VI) to Pu(IV), fuming with H_2SO_4 is particularly effective. For the reduction of Pu(IV) to Pu(III) NH_3OH^+ , H_2 , and SO_2 have been used most extensively. Other reductants which have had wide application in various operations are Fe^{++} , NH_3NH_2^+ , I^- , H_2O_2 , formic acid, and formaldehyde.

Stabilization in any particular oxidation state is often determined by the presence of complexing anions.

The kinetics of oxidation-reduction reactions have been studied only rather superficially.

1.2.3 Ionic species and complex formation

Various methods, such as E. M. F. determinations, solubility measurements, absorption spectra, and electrical transference experiments, have been used to determine the nature of the ions of plutonium which exist in aqueous solution.

Ionic species and complexes of Pu(III). The absorption spectra of Pu(III) in 1 M solutions of HCl, HNO₃, H₂SO₄ and HClO₄ are closely similar, suggesting that the same ionic species, probably hydrated Pu⁺⁺⁺, is present. However, there is some evidence from chemical studies and electrical migration data for possible complexing of Pu(III) by H₂SO₄. E. M. F. measurements on the Pu(III)-Pu(IV) couple in H₂SO₄ do not shed any light on this, because of the very strong complexing of Pu(IV) by sulfate ion.

Evidence of complexing by oxalate ion is observed in the solution of the insoluble Pu(III) oxalate in saturated K₂C₂O₄ solution.

Ionic species and complexes of Pu(IV). Absorption spectra and E. M. F. data have revealed no evidence of complexing of Pu(IV) by HCl and HClO₄.

Nitrate ion complexes Pu(IV) quite strongly. The exist-

tence of $\text{Pu}(\text{NO}_3)^{4+}$ and $\text{Pu}(\text{NO}_3)_2^{2+}$ ions has been shown by absorption spectra measurements, and the complex anion $\text{Pu}(\text{NO}_3)_6^{4-}$, analogous to hexanitratocerate, has been found from electrical migration experiments to exist in 8 to 10 M HNO_3 .

E. M. F. measurements have indicated the complexing action of SO_4^{2-} , and absorption spectra determinations have been interpreted by assuming the existence of complex sulfated cations. In 0.1 to 1.0 M H_2SO_4 solutions, electrical migration data have shown that Pu(IV) exists predominantly as an anion.

The formation of oxalate complexes of Pu(IV) has been shown by solubility studies of the oxalate in various oxalic acid concentrations. Similarly, there is evidence of a citrate complex in the observation that $\text{Pu}(\text{IO}_3)_4$ dissolves in sodium citrate solution.

The acetate complex of Pu(IV) is apparently quite stable, preventing the precipitation of the hydroxide at pH's as high as 5, as compared to precipitations at pH's below 3 in the absence of acetate. In 1 M acetate solutions at pH 3.5, Pu(IV) exists as an anion, and when a Pu(IV) solution is treated with excess sodium acetate, the color changes from green or brown to a purplish orange.

Ionic species and complexes of Pu(VI). There is no spectrophotometric evidence for complex formation by Pu(VI) in either HNO_3 or HClO_4 at 1 M concentrations. However, in

9.4 M HNO_3 some complex ion formation does occur. There is some complex ion formation in 1 M H_2SO_4 and in HCl of concentrations as low as 0.5 M.

By analogy with UO_2^{++} it was proposed that Pu(VI) would probably exist as PuO_2^{++} . The Pu(III)-Pu(VI) and Pu(IV)-Pu(VI) couples have a fourth power hydrogen ion dependence, in accordance with the reactions discussed in the section on disproportionation equilibria (1.2.2).

The existence of PuO_2^{++} is supported by a great mass of chemical and physical evidence showing its similarity to UO_2^{++} .

In contrast to Pu(IV), PuO_2^{++} does not precipitate as the hydroxide when its solutions are made basic. Plutonates or polyplutonate double salts appear when PuO_2^{++} solutions are made basic with NaOH. They precipitate more slowly and are more soluble than the corresponding UO_2^{++} compounds.

The presence of a holding oxidant is usually necessary to maintain plutonium in the hexavalent state.

1.2.4 The position of plutonium in the periodic table

Before the discovery of the transuranium elements there was considerable speculation about the possible electronic configurations of the elements beyond uranium (12). The fact that not a great deal was known about the chemical properties of the elements immediately preceding uranium in the periodic table added to the uncertainty.

After the discovery of the transuranium elements through

element 96, enough chemical information about the heavy elements was accumulated to make possible certain deductions about the atomic structures of the elements in this region of the periodic table.

It had been thought possible that a transition group should appear in the neighborhood of these elements. If a 6d transition group (similar to the 5d group from hafnium to gold and the 4d group from yttrium to silver) were being formed, neptunium would be expected to resemble rhenium, and plutonium might resemble osmium. However, neptunium and plutonium are much more electropositive than rhenium and osmium. There is no evidence for a volatile PuO_4 , in contrast with volatile osmium and ruthenium oxides, and the oxidation state of eight has never been described for plutonium. Thus it seems likely that the transition in the elements from 89 to 96 does not involve the simple filling of 6d orbitals.

There is considerable evidence that in this transition group the 5f shell is being filled, and that the series begins with actinium in the same sense that the rare earth series begins with lanthanum (7). It has been called the "actinide" series, by analogy with the "lanthanide" series for the rare earths.

The valence states of the elements from 89 through 96 can be explained in the same manner as the valence states of the rare earths (13). Thus it would be expected that elements 95 and 96 should exhibit very stable tripositive states,

and that 96 should exist almost exclusively in the tripositive state, because with its seven 5f electrons, its electronic structure should be analogous to that of gadolinium, which has seven 4f electrons. Chemical studies have shown that the tripositive state is characteristic for element 96. On this basis the names proposed for elements 95 and 96 are "americium," Am (by analogy with europium) and "curium," Cm (by analogy with gadolinium) (14).

Other evidence substantiating the hypothesis of an "actinide" series includes measurements of the magnetic susceptibility of uranium and plutonium, the sharpness of the absorption bands in the spectra of aqueous solutions of these ions, and evidence of a coordination number of eight for U(IV) and Pu(IV).

The relationships may not be so sharply defined as in the "lanthanide" series, because the energy difference between the 5f and 6d shells is probably very small, and changes in environment and state of chemical combination might determine the positions of the electrons with respect to the 5f and 6d orbitals.

The emission spectrum of plutonium is too complex to be of any value at present in determining the electronic configuration of plutonium.

1.3 Statement of the Problem

In connection with studies on the general chemistry of plutonium, a program was authorized for a study of the chelate compounds of plutonium extractable into organic solvents. If suitable organic reagents specific for plutonium could be found, they might prove of value for such operations as extraction, decontamination, concentration or purification of plutonium.

Decontamination is the process of elimination of the highly radioactive fission products which are formed along with plutonium in the chain reacting pile. The chemical separation of gram amounts of plutonium from ton amounts of uranium is a complex problem, as the requirements for the decontamination and purification of plutonium from troublesome elements are very rigid.

This thesis contains part of the results of the studies designed to find such organic reagents for plutonium.

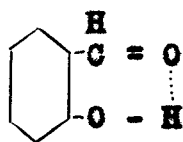
II THE NATURE OF CHELATE COMPOUNDS

2.1 Nomenclature

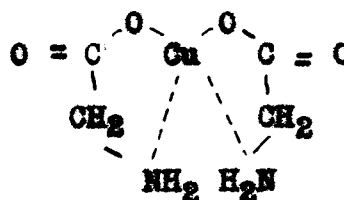
The term "chelate", proposed by Morgan and Drew (15) to designate those cyclic structures formed by the union of metallic atoms with organic and inorganic molecules, is derived from the Greek chela, which refers to the great claw of the lobster. The term is applicable to these ring systems since the associating molecules are characterized by a pincer-like structure.

More generally, chelate rings refer to cyclic structures which arise through intramolecular coordination in systems containing a donor and acceptor center or through intermolecular coordination in systems capable of forming two or more coordinate links.

Examples of intramolecular coordination are salicylaldehyde (I) and copper glycine (II):

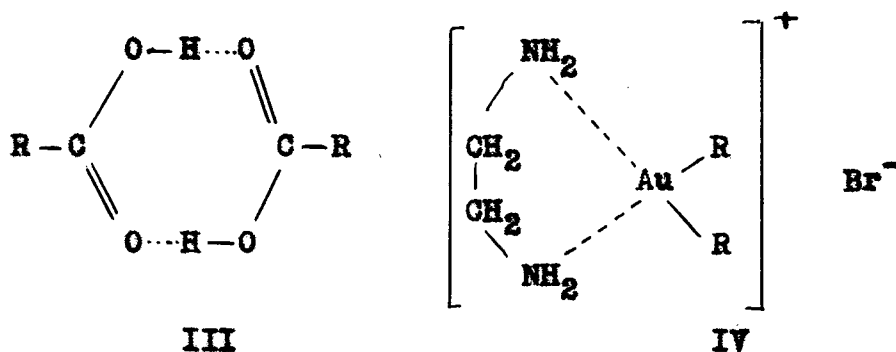


I



II

Examples of the intermolecular type are the dimers of carboxylic acids (III) and the Werner complexes derived from ethylenediamine (IV):



The cyclic structures may be formed by primary valences (those in which hydrogen is replaced by metal), by secondary or coordination valences, or by combinations of the two. Reagents capable of forming cyclic complex structures have been classified as bidentate ("two-toothed"), tridentate, quadridentate, and so on, in which the functional groups may be acidic, coordinating, or both. Diehl (17) has published an excellent survey of chelate rings based on the above system of classification.

2.2 Properties of Chelate Compounds

The non-electrolyte chelate compounds, those in which all of the primary and secondary valences are satisfied to produce a complex with a zero net charge, are of special interest in

analytical chemistry. These are known as inner complexes. Such compounds are usually highly colored, are insoluble in water and other polar solvents, and are quite soluble in non-polar organic solvents. These solubility properties lead to unique uses in analytical chemistry. Thus, if an organic reagent is specific in forming a true inner complex of the element in question, there are several advantages of extraction methods over precipitation procedures. Solvent extraction of inner complexes can effect much greater separation of a major element from minor amounts of impurities than is possible by precipitation methods because two-phase extraction separates elements without the presence of a solid phase capable of adsorbing or occluding undesired ions. These factors make solvent extraction of inner complexes particularly applicable to the separation, without carriers, of minor components from large amounts of other metals not complexed by the chelating reagent.

Actually, the search for a specific reagent is a rather ambitious plan. Although a great deal of work has been done in the preparation of chelate compounds and upon their structure, there apparently is still no method for predicting the specificity of a reagent for a particular metal ion. We may draw upon many generalizations that have accumulated first from the vast amount of classical work on Werner complexes and more recently from developments in studies on the nature

of the chemical bond in complex compounds.

However, the search for more or less specific reagents still must be conducted in the laboratory, using as a guide certain rules based on experimental results obtained in studies on all kinds of complex compounds. One author has been led to state that "in extrapolating past experience---we must be careful not to leave the laboratory long to theorize on what we think should happen with an untried reagent" (18).

2.3 Factors Involved in the Formation of Chelate Compounds

2.3.1 General conditions for complex formation

Complex formation depends on the nature of the acceptor and donor atoms and the types of bonds which may be formed between them. The stereochemical factors are of prime importance, too. The subtle relationships among these factors are too complex to permit predictions of quantitative behavior, so the usual approach is to study the variables separately.

In addition to the structural relationships mentioned above, there are also peculiar effects of hydrogen ion concentration which determine the specificity of reagents for certain cations. For example, diphenylthiocarbazono forms chloroform-soluble complexes with many metals, but by controlling the hydrogen ion concentration of the medium in which complex formation takes place, the specificity of the reagent can

be improved (ref. 19a, p. 91). Cupferron and 8-hydroxyquinoline are also examples of rather rapid complex-forming reagents whose specificity can be improved by proper control of hydrogen ion concentration.

There are several reference books on the use of organic reagents for metallic ions (19) which might serve as source material for a study of the problem of finding new reagents for metallic ions. The work of Sidgwick (20,21) and of Pfeiffer (22,23,24) has opened the way for the systematic search for new organic reagents for metallic ions.

2.3.2 The chemical bonds formed in complex compounds

The binding forces in complex compounds may be due to electrostatic attraction for the surrounding ions or oriented dipoles, or to true covalent binding, or to some combination of these types. Pfeiffer (23) contends that in inner complex compounds the primary and secondary valence bonds differ only in the origin of the binding electron pair.

In $\text{Fe}(\text{H}_2\text{O})_6^{+++}$, $\text{Ni}(\text{H}_2\text{O})_5^{+++}$, $\text{Ni}(\text{NH}_3)_4^{++}$, FeF_6^{---} and many similar complex ions, the bonds between the central atoms and the surrounding molecules result in a large part from ion-dipole attraction. Electrostatic bonds might result from the attraction of an ion for the induced dipole of a polarizable molecule.

Covalent bonds involve the sharing of electron-pairs between two atoms. Such bonds may be formed by each atom fur-

nishing one electron or by both electrons being furnished by one atom (the donor) to fill a vacant orbital of the acceptor atom. In most cases, the bonds are formed by "hybridization," which is a combination of s and p and other orbitals. The application of magnetic measurements to the study of complex compounds is due largely to Pauling (25) and most of the recent literature on the subject is expressed in terms of atomic orbitals and other characteristics of Pauling's nomenclature.

Kimball (26) has summarized the possible bond types for various coordination numbers, giving electronic configurations, geometrical arrangements and relative bond strengths. Further discussion of these factors will be considered in Section 2.3.5.

2.3.3 Functional groups in chelating agents

In the formation of non-electrolyte complexes two kinds of reactive groups are involved, acidic groups and coordinating groups.

Among the various functional groups which may unite with metals by primary valence by replacing hydrogen by metal are the following:

carboxylic acid - COOH

sulfonic acid - SO₃H

enolic or phenolic hydroxyl - C-OH

oxime-nitrone - = NOH

primary amino - -NH₂

secondary amino - = NH

The secondary valence groups, which contain so-called donor atoms with an unshared pair of electrons, form coordinate bonds by the donation of this unshared pair into vacant orbitals of the metal ion to form homopolar bonds. These donor atoms are contained in such groups as the following:

primary amino - -NH_2
secondary amino - =NH
tertiary amino - $\text{-}\overset{\cdot}{\text{N}}$
cyclic tertiary amino - $\overset{\cdot}{\text{N}}$
imino - =N-
oxime - =NOH
alcoholic hydroxyl - OH
carbonyl - C=O
thioether - -S-

These lists could be expanded, but with little point, as most of the known chelate rings involve combinations of the functional groups given above.

Most of the organic reagents known and commonly used are of the bidentate type, containing one acidic and one coordinating (or secondary valence) group.

2.3.4 The nature of the donor atom

In complexes containing the coordinate structure $\text{A} \leftarrow \text{BC}$, in which B is the donor atom, the strength of the coordinate

bond can seldom be determined. As a rule we can discover the affinity of particular donor atoms for particular acceptor atoms only in a qualitative way from a consideration of the number and stability of the complexes formed by the two kinds of atoms.

The nature of a substituent (C) on the donor atom may modify the strength of the $A \leftarrow B$ link. This has been noted in the change of stability in the amines of Cu(II), Co(II) and Ni(II) when the hydrogen of NH_3 is replaced by hydrocarbon radicals (21), and in the base strengths of various amines. In many organic compounds the effect of substituents on the donor atom appears to be due to the polarization from the inductive effect (27) proposed by Ingold to explain the effects of substituents on reactivities of organic compounds. Orleman (28) has used the idea of the inductive effect to explain the coordination effects noted in the extraction of plutonium nitrate from aqueous solutions by various ethers and ketones.

The stability of the $A \leftarrow B$ link in the $A \leftarrow BC$ complex also depends on the nature of the groups attached to A by acidic linkages. Spacu and Voichescu (29), in studying the vapor pressures of NH_3 over amines of various cupric salts, found that the strength of the $Cu \leftarrow NH_3$ bond was inversely proportional to the base strength of the anion of the salt under otherwise comparable conditions. Calvin and Wilson (30)

have reported that in the cupric chelate compounds with substituted salicylaldehydes and β -diketones there is a direct relationship between the stability of the complex and the acid strength of the reagent.

The generalizations observed in the study of non-chelate complex compounds can be used as an approach in the study of chelate compounds, but only to a limited extent. This is true because in the polydentate organic reagents both acidic and coordinating groups must be in the same molecule. For example, the same substituent groups that increase acidity will decrease the donor power of a donor group. In an organic reagent containing both acidic and donor groups the proper balance between these two opposing effects must be attained.

2.3.5 The nature of the acceptor atom

Long before the electronic configurations of the elements had been determined, it had been observed from experimental facts that the transition elements are most easily introduced into complex compounds, even though many other elements also display complex-forming properties.

Sidgwick (20,21) attempted to explain complex formation with the idea of the "effective atomic number" (E. A. N.) of an element, which is the total number of electrons either possessed completely by the atom or shared with other atoms in covalent or coordinate bonds. Sidgwick postulated that the

tendency for complex formation could be explained by assuming that an ion tended to achieve the E. A. N. of the next inert gas by gaining electrons from a donor atom. Thus he explained the formation of $\text{Ni}(\text{CO})_4$ on the basis that ^{28}Ni , with E. A. N. = 28 added 4 pairs of electrons from CO molecules to form $\text{Ni}(\text{CO})_4$ with E. A. N. = 36, the E. A. N. of krypton. While Sidgwick's idea would explain the formation of many complex compounds, it had many shortcomings, especially in that it could not explain the valences of complex ions of the transition metals. In the extremely stable acetylacetonates of Mg, Zn, Al, and Th the E. A. N. is that of an inert gas, but with Ni and Fe the acetylacetonates are stable and seem to exist without respect to the E. A. N.

After more was known about the electronic structure of the elements and after the quantum mechanical approach put the nature of the covalent bond on a somewhat more rigorous basis (25), it was possible to explain differences in the complexing properties of various ions (31,32). The modern explanation for the complex-forming properties of the transition elements is that they have low-lying vacant orbitals which can form homopolar bonds by accepting electron pairs.

The concept of hybrid bonds has been substantiated by magnetic measurements, stereochemical evidence, and chemical properties. Thus in $\text{Zn}(\text{CN})_4$ -- the sp^3 bonds give a tetrahedral configuration, $\text{Ni}(\text{CN})_4$ -- with dsp^2 bonds is square,

and $\text{Pd}(\text{Cl})_6^{--}$ with d^2sp^3 bonds is octahedral.

Selwood (33) has discussed complex compounds quite thoroughly with respect to the use of magnetic measurements in showing what orbitals are involved in the actual structure of complexes.

In complexes in which all of the bonds are not covalent but in which some of the bonds may be partly ionic or electrostatic, it has been found that the coordinating tendency of the metal ions increases with the charge density on the central atom. That is, the bonds are stronger the greater the charge and the less the ionic radius of the central atom.

2.3.6 Ring formation

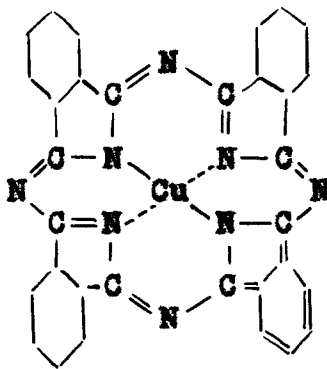
The possibility of closed rings in coordination compounds was first suggested by Tschugaeff in 1907 (34) to explain the behavior of metal compounds with biuret and similar substances. Werner (35) developed the idea immediately afterwards, and since then many generalizations have been used to explain the stability of chelate compounds.

Ring formation generally increases the stability of complexes. For example, ethylenediamine forms more stable complexes than primary amines. Phenol is a weak complexing agent, yet catechol forms complexes with many ions. Oxalate complexes are far more numerous and more stable than complexes with monocarboxylic acids.

If there are no resonance possibilities, the most stable

rings are those of five or six members, as might be expected from strain theory. However, chelate rings with as many as thirteen members have been described (26). Pfeiffer (23) and Sidgwick (20) have classified the most common ring types in chelate compounds in which various combinations of C, N, O and metal atoms are considered.

In structures containing possibilities for resonance, ring stability is greatly increased. Thus chelate rings, formed from β -diketones, β -keto esters and compounds in which the ring includes part of an aromatic structure may be stabilized by resonance. A classic example of stabilization through resonance is copper phthalocyanine, which is so stable that it resists boiling HCl and molten caustic, and can be sublimed unchanged at 580°C at reduced pressure in nitrogen atmosphere (37).



It has been suggested (38) in the case of nickel dimethylglyoxime that the electronic structure of the divalent nickel is an essential factor in establishing the resonance of the whole complex. Similarly, it has been proposed that organic

reagents which are specific for particular ions owe their specificity to the electronic arrangement in the central atom and the participation of the central atom in the resonance of the whole complex.

2.3.7 The possible complexing properties of plutonium

If chemical experience had shown that plutonium resembles osmium and ruthenium (the transition elements in which the 5d and 4d orbitals, respectively, are being filled) we might expect plutonium to be an active complex former. However, it appears quite certain that the transition group of which plutonium is a member is formed by the filling of 5f orbitals.

Therefore, it is not expected that plutonium should be uniquely active in complex formation. The principal approach, then, would be to determine the coordination number of Pu(III) and Pu(IV) by the use of reagents known to complex many elements. Then, knowing the coordination number associated with each valence state, the polydentate reagents tried should be those which could lead to non-electrolyte complexes soluble in nonpolar solvents.

While Pu(VI) might form inner complexes, the necessity of using "holding oxidants" to maintain the hexapositive state makes it impossible to use some organic reagents which are sensitive to oxidation.

III EXPERIMENTAL METHODS AND TECHNIQUES

3.1 Extractions on the Tracer Scale

In all of the exploratory experiments with tracer plutonium, the experimental procedure was essentially the same. The aqueous solution containing tracer was buffered to the desired pH with sodium or ammonium acetate and acetic acid in solutions 0.1 to 1.0 M in total acetate. When only approximate values of pH were desired, indicator paper ("Hydrion" paper, manufactured by Micro Essential Laboratory) was used. For more precise values, glass electrode pH meters (Beckman Model G, Leeds and Northrup Model 7661-A1) were used.

The usual solvent was chloroform, since it has rather exceptional solvent properties for most true inner complexes. In cases in which the organic reagent was relatively soluble in water, the reagent was added to the buffered tracer solution. When the reagent was insoluble in water, it was contained in the chloroform.

In all of the exploratory experiments reported, the volume of the solvent layer was equal to that of the aqueous solution. The volumes were usually from 10 to 15 ml, and the amounts of reagent were from 10 to 20 mg. The extractions were carried out by agitating the two phases vigorously in an ordinary separatory funnel.

After separation of the phases, the aqueous phase was evaporated to a small volume for assay. For analysis of the organic phase, the solvent was evaporated and the organic residue was destroyed with fuming HNO_3 and HClO_4 , and taken up in water for assay.

In some cases, carrier ions, known to react with the chelating reagents under investigation, were added.

3.2 Extractions on the Micro Scale

For operations with amounts of plutonium ranging from 50 μg to 2 or 3 mg, specially designed micro equipment had to be used.

The pipets used were designed by R. R. Baldwin, and a representative type is shown in Figure 1. The actual pipet is of quartz (A) and is sealed into the sheath (B) with deKhotinsky cement (E). To fill the pipet the hole (C) is closed with the finger tip while gentle suction is obtained with a hypodermic syringe attached at (D). The liquid fills the entire pipet. To empty the pipet, pressure is exerted on the hypodermic syringe.

The pipets were calibrated "to contain" by weighing the volume of mercury which they contained. In order to effect complete transfer of solution, two or three washes were necessary. Excellent reproducibility could be obtained with pipets with capacities from 1 to 300 microliters.

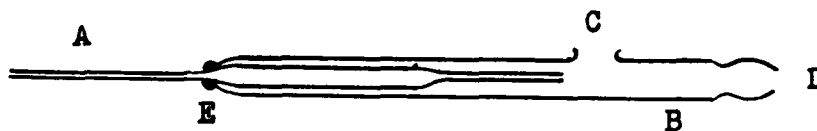


Fig. 1. Cross Section of Micro Pipet

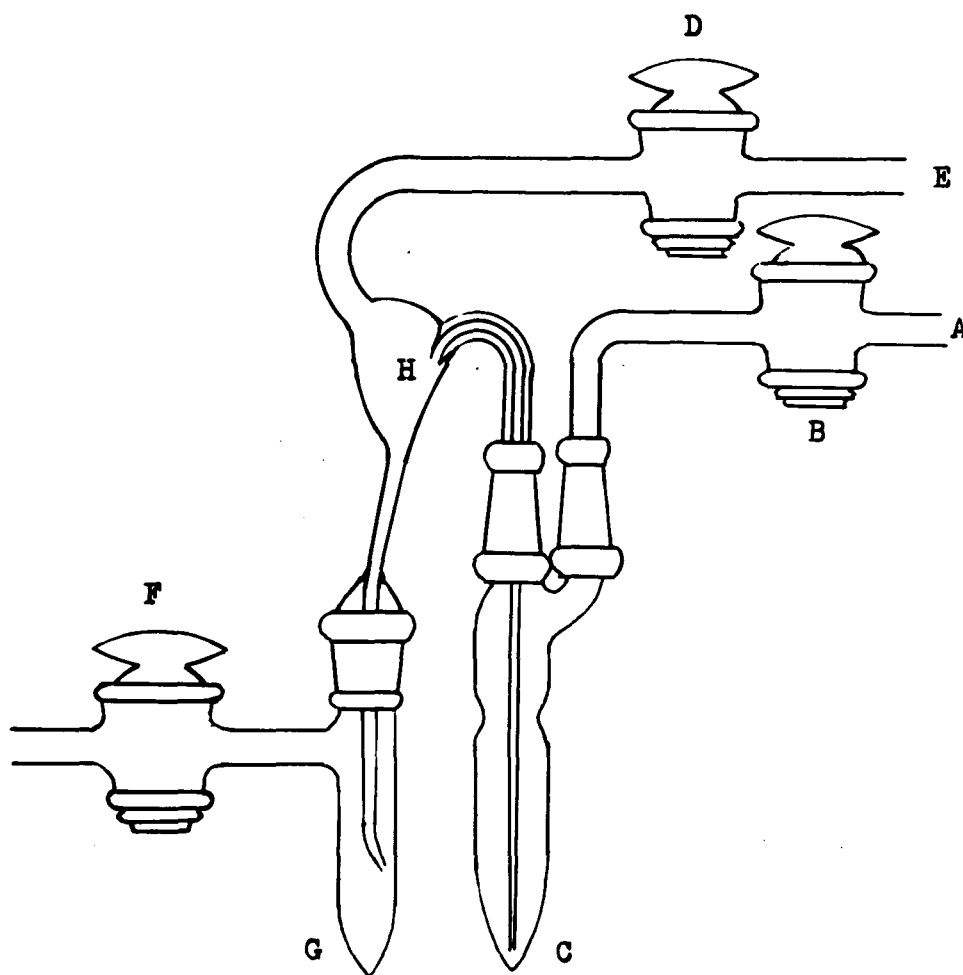


Fig. 2. Micro Extraction Apparatus

With amounts of plutonium exceeding 100 μg , separatory funnels could not be used for two-phase extractions. Therefore, a micro-extraction apparatus, adapted from a design by Langham (39) was used. This apparatus is shown in Figure 2. The extraction thimble (C) contained about 1 ml of the aqueous solution or suspension to be extracted by chloroform. Chloroform (1 ml) was introduced into the sidearm of the thimble. For agitation of the two-phase system stopcocks D and B were opened, stopcock F was closed, and an inert gas (helium or nitrogen) was introduced at E at a rate slow enough to agitate the two phases in the extraction thimble with the desired vigor. When extraction was complete stopcock D was closed and stopcock F was opened. Then the inert gas was introduced very carefully at A. The heavier solvent layer was forced up the tube and drained into the receptacle G. The flow of gas was stopped the instant the chloroform-water interface reached the tip of the tube at H.

The water layer in C and the chloroform layer in G were then analyzed in the usual manner.

3.3 Radioactive Assays

3.3.1 Plutonium assays

The alpha particles from Pu^{238} and Pu^{239} have ranges of about 3.5 to 4 cm of air. This corresponds to a mass range

of about 4.9 mg/cm^2 in air, or of about 10 mg/cm^2 for the carriers usually used. Therefore, to avoid low results due to self-absorption in the sample, very thin samples had to be prepared for alpha counting.

For analyses on the tracer scale, the samples were prepared in the following manner. The aqueous solution was treated with H_2O_2 or SO_2 to produce the fluoride-insoluble Pu(III) or Pu(IV) state, La^{+++} ion was added as carrier and LaF_3 precipitations were made from solutions 1 to 5 M in HF. The fluoride precipitations were done in specially prepared Lusteroid centrifuge tubes with bottoms flattened to form a smooth surface. The suspension was then centrifuged, the supernatant poured off, the precipitate carefully washed with a fine stream of water and centrifuged again. With proper care, a uniformly thin LaF_3 precipitate could be deposited on the bottom of the lusteroid tube. After the second centrifugation, the supernatant was poured off, and the precipitate on the bottom of the tube carefully dried by a gentle stream of air while the tube was gently warmed above a hot plate. After the precipitate had dried, the bottom of the tube was cut off with a razor blade to form a very shallow cup with walls about $1/32$ to $1/16$ of an inch high. This disc with its LaF_3 deposit of less than 1.5 mg/cm^2 was then used as the sample for alpha-counting.

For assays on the micro scale no LaF_3 precipitations were

used. Suitable aliquots of solutions were transferred with micro pipets to platinum foils and carefully evaporated to produce a uniformly thin deposit. The margins of the platinum foil were coated with Zapon lacquer to prevent the solution from creeping over the edges of the foil. Sometimes a drop of ethylene glycol was added to aid in the slow evaporation to a uniformly thin deposit. After the solution was evaporated to dryness, the foil was heated to a dull red heat to get rid of organic matter and volatile salts. This foil, with its extremely thin deposit, was used as the sample for alpha-counting.

The alpha activities, if less than 3000 counts per minute, were measured on a standard alpha counter (40), with a scale of sixty four circuit and mechanical recorder. The geometry of the counter, as determined by R. R. Baldwin, was 51.6%. For activities greater than 3000 counts per minute, and for samples with a high β -activity, a methane chamber proportional counter, with a scale of one hundred twenty eight circuit was used. The geometry of the proportional counter was 50% (41).

3.3.2 Other radioactive assays

In experiments dealing with radioactivities of fission products and consisting of β - and γ -rays, samples for measurement were prepared either by evaporation of aliquots on platinum foils or small watch glasses, or by precipitation with

carriers. Less care had to be taken in the preparation of thin samples than in preparing plutonium samples, because of the greater penetration of the β - and γ -rays.

The radioactivities were measured on an electroscope or a Geiger counter depending on their strength. The electroscope used was of the Lauritsen quartz fiber type with a 2.4 mg/cm² aluminum window. The samples were measured by placing them under the ionization chamber in a holder which kept them in a reproducible position. The Geiger-Muller counter was of the copper wall type with a mica window 5.2 mg/cm² in thickness. A scale of sixty four circuit and mechanical recorder were used.

IV MATERIALS USED

4.1 Plutonium

The supply of Pu²³⁸ was isolated from uranium metal bombarded with deuterons at the Berkeley cyclotron.

Solutions of pure Pu²³⁹, isolated from pile uranium, were obtained from the Clinton Laboratories. Dilute solutions of Pu²³⁹, used in tracer experiments, were obtained by processing slugs of uranium subjected to slow neutron irradiation in the Clinton pile.

4.2 Other Radioactive Isotopes

In some of the studies on the specificity of organic reagents, other radioactive isotopes were used. Solutions of 24 day Th²³⁴ (UX₁) were prepared by the ether extraction of uranyl nitrate. Other radioactivities, including 33 year Cs¹³⁷, 28 day Ce¹⁴¹, 275 day Ce¹⁴⁴, 57 day Y⁹¹, 68 day Zr⁹⁵ and 12.8 day Ba¹⁴⁰, were obtained from supplies of activities which various members of the Ames project had isolated in other studies.

4.3 Solvents

The chloroform and carbon tetrachloride were reagent

grade, obtained from General Chemical Company. All of the other solvents used were obtained from Eastman Kodak Company.

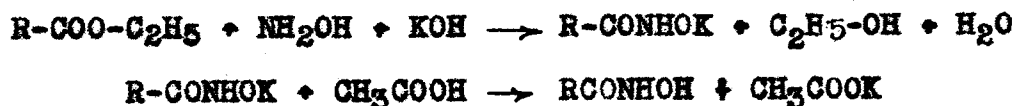
4.4 Organic Reagents

The following compounds, which were used directly in examinations for complex formation, were obtained from Eastman Kodak Company: quinalizarin, benzoin, α -benzoin oxime, acetylacetone, benzoylacetone, dibenzoylmethane, α -nitroso- β -naphthol, β -nitroso- α -naphthol, dimethylglyoxime, isonitrosoacetophenone, isatin, 8-hydroxyquinoline, 7-iodo-8-hydroxyquinoline-5-sulfonic acid, diphenylthiocarbazone, diphenylthiourea, α -picolinic acid (hydrochloride), diphenylcarbazide, o-aminophenol, and anthranilic acid.

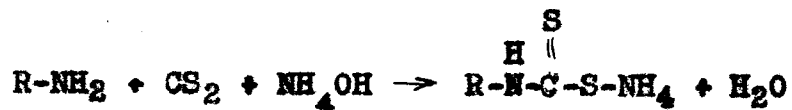
Trifluoroacetylacetone was obtained from M. Calvin, of the University of California at Berkeley.

All oximes were prepared by methods commonly known. The monoimines of o-hydroxyaldehydes were prepared by refluxing equivalents of the aldehyde and amine in ethanol (42).

All of the hydroxamic acids were prepared by general methods adapted from that described in "Organic Syntheses" (44):

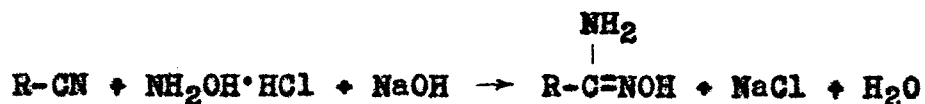


The dithiocarbamates were prepared by the method of Delephine (45) using the general reaction:

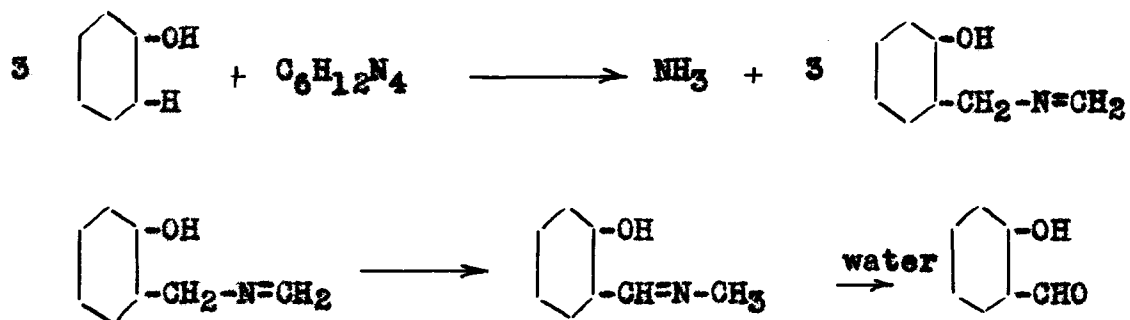


Di-substituted dithiocarbamates were prepared by a similar reaction using a secondary amine as starting material.

All amide oximes were prepared by the same general method, adapted from that of Tiemann and Kruger (46):



For the experiments with the diimines of o-hydroxyaldehydes, many of the diimines were obtained from Dr. Harvey Diehl. In the other cases, the diimines were prepared by refluxing the aldehyde with the appropriate diamine in ethanol, and the Schiff's base crystallized from ethanol (47). For the preparation of the o-hydroxyaldehydes not directly obtainable, the method of Duff (48) was used. The synthesis consists essentially in causing hexamethylenetetramine and a phenol to react in the presence of anhydrous glycerol and glyceroboric acid at a temperature of 150 to 160°C. The o-hydroxyaldehyde in nearly pure form is obtained by steam distillation of the acidified reaction mixture. The mechanism suggested by Duff is



Other miscellaneous compounds were prepared by methods described in the literature, and included acetylacetone monoimide (49), salicylalphenylhydrazone, *o*-hydroxyacetophenone semicarbazone, α -azobenzene- β -ketobutyric acid (50), *N*-methyl salicylamide (51), and *N,N'*-diphenylformazylbenzene (52).

V THE CHELATE COMPOUNDS OF PLUTONIUM(IV)

5.1 Exploratory Experiments on the Tracer Scale

5.1.1 Introduction

Most of the organic reagents commonly used for metal ions are bidentate molecules, in consequence of the fact that the coordination number is generally twice the primary valence. Therefore, the most obvious approach to the problem of finding organic reagents that complex plutonium is to make use of the more active reagents known to complex many ions. From the data obtained in this way it should be possible to determine the coordination number of Pu(IV).

Then, knowing the coordination number of Pu(IV), a more systematic study of group interactions and the effect of chelate ring size could be made to obtain more specifically the requirements of organic reagents which will form chelate compounds with Pu(IV).

5.1.2 Experiments with bidentate reagents

All of the bidentate reagents, containing one donor and one acidic group, which were examined for complexing activity with Pu(IV) tracer were known to form true inner complexes with some other elements. In all of the tracer experiments the procedure was essentially that described in Section 3.1.

Chloroform was used as the solvent in all of the extractions except in the experiments with quinalizarin, in which aniline was used, and in those with trifluoroacetylacetone, in which benzene was the solvent. The results obtained in single extractions with a volume of solvent equal to that of the aqueous phase are summarized in Table 2.

Table 2
 Behavior of Tracer Plutonium(IV)
 with Various Bidentate Organic
 Reagents in Acetate-Buffered Solutions

| Class of Compound | Reagent | pH of Aqueous Solution | Per Cent Pu Ex-tracted |
|--------------------------------|-----------------------------|------------------------|------------------------|
| Hydroxy keto compounds | Quinalizarin (with aniline) | 2.11 | 95.1 |
| | | 3.80 | 70.3 |
| | | 4.65 | 94.8 |
| | | 5.54 | 95.5 |
| | Benzoin | 2 to 8 | 2.2 |
| | 2-Hydroxybenzophenone | 2.6 to 6.3 | 2.6 |
| | | 8.3 | 18.6 |
| 2-Hydroxy-5-methylbenzophenone | 1.5 to 6.2 | 0.3 | |
| | 8.47 | 10.1 | |
| β -Diketones | Benzoylacetone | 3.75 | 3.0 |
| | | 4.69 | 7.0 |
| | | 5.47 | 7.0 |
| | | 8.52 | 25.0 |
| | Dibenzoylmethane | 1.80 | 0.7 |
| | | 4.20 | 1.5 |
| | | 4.80 | 11.0 |
| 5.70 | | 36.0 | |

Table 2 - Continued

| Class of Compound | Reagent | pH of Aqueous Solution | Per Cent Pu Ex-tracted | |
|--|---------------------------------------|---------------------------------|------------------------------|------|
| | Trifluoroacetylacetone (with benzene) | 2.5 3.5 4.5 5.0 5.6 | 20 36 57 86 93 | |
| Oximes and Nitroso Compounds | α -Nitroso- β -naphthol | 2 to 8 | <10.7 | |
| | β -Nitroso- α -naphthol | 2 to 8 | <7.6 | |
| | o -Hydroxyacetophenone Oxime | 2 to 4 6 8 | <0.1 13.0 2.7 | |
| | α -Benzoin Oxime | 2 to 8 | <3.7 | |
| | Isonitrosoacetophenone | 2.6 to 5.8 8.45 | <1.9 44.2 | |
| | Isatin- β -oxime | 1.7 to 6.7 | <2.5 | |
| | Dimethylglyoxime | 2 to 8 | <4.2 | |
| | Acetylacetone dioxime | 1.5 to 8.0 | <1.5 | |
| | Monoimines | Acetylacetone monoimide | 1.8 to 5.3 | <1.0 |
| | | Salicylal methylimine | 4 to 8 | <8.4 |
| Salicylal ethylimine | | 4 to 8 | <6.0 | |
| Salicylal- β -hydroxyethyl- γ -imine | | 4.9 to 6.6 | <1.0 | |
| Salicylal phenylimine | | 2 to 6 | <7.2 | |
| Salicylal- β -hydroxyphenyl- γ -imine | | 5.68 5.94 6.16 6.44 | 42.5 47.3 49.6 49.2 | |

Table 2 - Continued

| Class of Compound | Reagent | pH of Aqueous Solution | Per Cent Pu Ex-tracted |
|------------------------|---|------------------------|------------------------|
| o-Hydroxyazo Compounds | 2-Hydroxy-5-methylazobenzene | 3.3 to 5.8 | <1.0 |
| | 1-Benzeneazo-2-hydroxynaphthalene | 2.95 to 8.70 | <1 |
| | p-Nitrobenzeneazoresorcinol | 2 to 6 8 | <5.4 14.0 |
| Hydroxamic Acids | Benzohydroxamic acid | 1.88 to 5.20 | <21.5 |
| | | 5.69 | 29.4 |
| | | 6.02 | 42.1 |
| | | 6.40 | 41.9 |
| | | 6.72 | 48.7 |
| | | 7.61 | 65.5 |
| | 8.02 | 60.0 | |
| | o-Hydroxobenzohydroxamic acid | 0.98 to 5.97 | <3.6 |
| | o-Furohydroxamic acid | 3.28 to 6.72 7.92 | <5.9 16.0 |
| Dithiocarbamates | Ammonium phenyldithiocarbamate | 3.75 to 8.18 | <1.0 |
| | | | |
| | Ammonium morpholine-dithiocarbamate | 1.55 to 5.45 | <1.1 |
| | | 8.38 | 43.8 |
| | Potassium pentamethylenedithiocarbamate | 4.00 | 7.4 |
| | | 4.95 | 7.1 |
| | | 5.95 | 7.4 |
| | | 7.07 | 14.1 |
| | | 8.95 | 8.8 |
| | | 8.97 | 7.7 |
| | Potassium N,N-diethylthiocarbamate | 4.15 | 0.9 |
| | | 5.05 | 1.8 |
| | | 6.05 | 16.9 |
| 7.07 | | 6.0 | |
| 8.03 | | 2.2 | |
| 9.01 | | 7.2 | |

Table 2 - Continued

| Class of Compound | Reagent | pH of Aqueous Solution | Per Cent Pu Ex-tracted |
|----------------------------------|---|------------------------|------------------------|
| Amide Oximes | Benzamide oxide | 3.00 to 8.08 | <2.5 |
| | Phenylacetamide oxime | 3.12 | 11.5 |
| | | 4.30 | 6.8 |
| | | 5.00 | 8.3 |
| | | 6.10 | 21.6 |
| | | 7.00 | 8.9 |
| | 7.95 | 11.6 | |
| Miscellaneous Bidentate Reagents | Diphenylthiocarbazone | 4 to 10 | <1.0 |
| | <u>sym.</u> -Diphenylthiourea | 2 to 8 | <4.5 |
| | α -Picolinic acid | 2 to 8 | <1.0 |
| | Diphenylcarbazide | 4.55 to 6.94 | <6.7 |
| | Salicylalphenylhydrazone | 3.04 to 7.06 | <1 |
| | <u>o</u> -Hydroxyacetophenone Semicarbazide | 2 | 2.1 |
| | | 4 | 5.5 |
| | | 6 | 14.1 |
| | | 8 | 15.9 |
| | <u>8</u> -Hydroxyquinoline | 3.00 | 2.3 |
| | | 4.04 | 2.3 |
| | | 5.00 | 5.8 |
| | | 5.90 | 19.7 |
| 6.86 | | 38.9 | |
| 8.10 | | 51.3 | |
| <u>o</u> -Aminophenol | 1 | 2.6 | |
| | 6 | 4.3 | |
| | 9 | 14.3 | |
| Anthranilic acid | 3.9 to 6.1 | <2.3 | |
| N-Methylsalicylamide | 1.84 to 8.42 | <8.8 | |

Table 2 - continued

| Class of Compound | Reagent | pH of Aqueous Solution | Per Cent Pu Ex-tracted |
|-------------------|--|------------------------|------------------------|
| | α -Azobenzene- β -keto butyric acid | 3.20 to 5.55 | < 1.0 |
| | N,N'-Diphenylform-azylbenzene | 1.82 to 5.92 | < 1.2 |

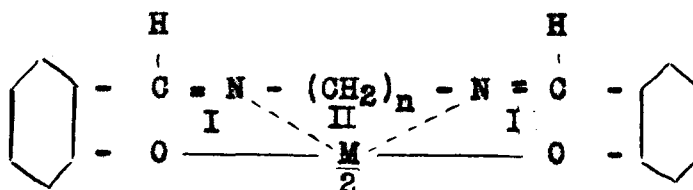
From the results listed in Table 2 there appears to be definite evidence of complexing of Pu(IV) by quinalizarin, the β -diketones, benzohydroxamic acid, 8-hydroxyquinoline, and salicylal- β -hydroxyphenyl-imine.

5.1.3 Experiments with quadridentate reagents

It was evident from the results of the experiments with bidentate reagents that the coordination number of Pu(IV) is eight. Therefore, it appeared worthwhile to investigate the properties of quadridentate reagents containing two acidic groups and two coordinating groups per molecule. If proper reactivity and spatial relationships could be found, quadridentate might be more likely to complex Pu(IV) than bidentate reagents.

Negative results were obtained with the ethylenediimines of o-hydroxyacetophenone and acetylacetone at pH's from 2 to 8. Exploratory experiments with disalicylaethylenediimine, how-

ever, gave promising results. The generalized structure for such compounds would be represented in the figure below, where M represents a quadrivalent metal.



The results of a series of experiments designed to determine the effect of changing the size of ring II are given below.

Table 3

Behavior of Tracer Plutonium(IV) with Derivatives of Salicylaldehyde in Acetate-Buffered Solutions

| Addendum | pH of Aqueous Solution | Per Cent Pu Extracted |
|----------------------------|------------------------|-----------------------|
| Hydrazine | 2 to 8 | < 9.4 |
| Methylenediimine | 2 to 8 | < 3.1 |
| Ethylenediimine | 4.59 | 20.5 |
| | 5.00 | 76.6 |
| | 5.52 | 93.0 |
| | 6.01 | 98.6 |
| Trimethylenediimine | 4.38 | 25.0 |
| | 4.90 | 12.5 |
| | 5.40 | 1.3 |
| <u>o</u> -Phenylenediimine | 4 | 22.5 |
| | 6 | 14.0 |
| | 8 | 3.5 |

The results shown in Table 3 indicate that chelation is accomplished most easily with the ethylenediimine, so the next efforts were directed toward finding derivatives of disalicyl-alethylenediimine which complex Pu(IV) at pH's below that at which the hydroxide precipitates. The results of several such experiments are summarized in Table 4.

Table 4

Extraction of Plutonium(IV) Tracer by Chloroform
and Schiff's Bases of Ethylenediamine

| Parent Aldehyde | pH of Aqueous Solution | Per Cent Pu Ex-tracted |
|------------------------------------|------------------------|------------------------|
| 2-Hydroxy-3-methoxybenzaldehyde | 2 | 0.3 |
| | 4 | 54.4 |
| | 6 | 14.0 |
| | 8 | 1.5 |
| 2-Hydroxy-5-methylbenzaldehyde | 3.20 | 11.8 |
| | 4.25 | 22.8 |
| | 4.82 | 31.3 |
| | 5.38 | 57.0 |
| | 5.68 | 87.0 |
| | 6.09 | 97.4 |
| 2,3-Dihydroxy-6-phenylbenzaldehyde | 1.12 | 0 |
| | 2.85 | 43.8 |
| | 4.00 | 56.8 |
| | 5.12 | 59.1 |
| | 5.55 | 67.2 |
| | 5.98 | 86.0 |

Table 4 - Continued

| Parent Aldehyde | pH of Aqueous Solution | Per Cent Pu Extracted |
|--|------------------------|-----------------------|
| 2-Hydroxy-3-nitrobenzaldehyde | 3.35 | 4.1 |
| | 3.98 | 5.2 |
| | 4.50 | 1.7 |
| | 4.92 | 2.8 |
| | 5.39 | 2.0 |
| | 5.95 | 11.8 |
| 2-Hydroxy-3-bromobenzaldehyde | 2.61 | 28.8 |
| | 3.20 | 49.5 |
| | 3.48 | 47.2 |
| | 3.88 | 26.0 |
| | 5.05 | 20.2 |
| | 5.30 | 34.2 |
| | 5.80 | 39.7 |
| 6.30 | 75.5 | |
| 2-Hydroxy-3-bromo-5- <u>tert.</u> -butylbenzaldehyde | 1.98 | 0.8 |
| | 3.12 | 36.0 |
| | 3.22 | 40.4 |
| | 3.59 | 71.0 |
| | 3.95 | 39.5 |
| | 4.53 | 43.0 |
| | 5.09 | 49.0 |
| | 5.19 | 54.0 |
| | 5.50 | 65.0 |
| | 5.90 | 86.0 |
| 5.98 | 92.0 | |
| 2-Hydroxy-5-chlorobenzaldehyde | 2.33 | 26.2 |
| | 3.30 | 85.5 |
| | 3.69 | 65.5 |
| | 4.20 | 50.8 |
| | 4.55 | 42.8 |
| | 5.02 | 47.0 |
| | 5.31 | 58.0 |
| | 6.15 | 82.0 |

Table 4 - Continued

| Parent Aldehyde | pH of Aqueous Solution | Per Cent Pu Ex-tracted |
|---|------------------------|------------------------|
| 2-Hydroxy-3-chlorobenzaldehyde | 2.29 | 25.4 |
| | 2.88 | 82.0 |
| | 3.36 | 69.5 |
| | 4.42 | 57.2 |
| | 5.45 | 75.6 |
| | 6.00 | 71.4 |
| 2-Hydroxy-3,5-dichlorobenzaldehyde | 2.48 | 54.4 |
| | 3.28 | 83.9 |
| | 3.92 | 60.0 |
| | 4.55 | 53.8 |
| | 5.00 | 63.0 |
| | 5.85 | 71.0 |
| 2-Hydroxy-3-chloro-5- <u>tert.</u> -butylbenzaldehyde | 2.08 | 59.0 |
| | 2.75 | 97.1 |
| | 3.62 | 99.5 |
| | 4.12 | 99.4 |
| | 4.61 | 97.1 |
| | 5.66 | 94.0 |
| 2-Hydroxy-3-isopropyl-5-chloro-6-methylbenzaldehyde | 3.61 | 46.0 |
| | 4.70 | 81.0 |
| | 5.23 | 89.0 |
| | 5.82 | 89.0 |
| 2-Hydroxy-3,5-dimethylbenzaldehyde | 2.72 | 50.7 |
| | 3.90 | 61.8 |
| | 4.38 | 45.5 |
| | 5.00 | 61.7 |
| | 5.48 | 71.4 |
| | 5.98 | 85.6 |
| 2-Hydroxy-3-chloro-4- <u>tert.</u> -butylbenzaldehyde | 2.23 | 58.2 |
| | 2.91 | 83.3 |
| | 3.85 | 71.8 |
| | 4.59 | 52.4 |
| | 5.16 | 75.6 |
| | 5.75 | 92.6 |

Table 4 - Continued

| Parent Aldehyde | pH of Aqueous Solution | Per Cent Pu Ex-tracted |
|---|------------------------|------------------------|
| 2-Hydroxy-5- <u>tert.</u> -butylbenzaldehyde | 2.89 | 41.0 |
| | 4.52 | 89.0 |
| | 5.16 | 91.4 |
| | 5.45 | 91.0 |
| | 6.08 | 84.7 |
| | 6.98 | 21.0 |
| 2-Hydroxy-5-chloro-6-methylbenzaldehyde | 2.75 | 9 |
| | 4.30 | 17 |
| | 4.91 | 37 |
| | 5.92 | 58 |
| 2-Hydroxy-5- <u>tert.</u> -amylbenzaldehyde | 2.20 | 1.3 |
| | 2.62 | 6.9 |
| | 3.52 | 54.2 |
| | 4.62 | 69.3 |
| | 5.28 | 80.0 |
| | 6.14 | 77.7 |
| 2-Hydroxy-4,6-dimethylbenzaldehyde | 4.08 | 4.5 |
| | 4.91 | 31.4 |
| | 5.47 | 85.7 |
| | 6.22 | 84.7 |
| 2-Hydroxy-3-methyl-5- <u>tert.</u> -butylbenzaldehyde | 2.55 | 0.8 |
| | 3.10 | 2.4 |
| | 3.76 | 2.2 |
| | 4.54 | 1.5 |
| | 5.37 | 2.1 |
| | 5.92 | 12.4 |

Table 4 - Continued

| Parent Aldehyde | pH of Aqueous Solution | Per Cent Pu Ex-tracted |
|---|------------------------|------------------------|
| 2,3-Dihydroxy-5 or 6- <u>tert.</u> -butyl-benzaldehyde* | 1.55 | 3 |
| | 1.98 | 83.5 |
| | 2.28 | 86.9 |
| | 2.75 | 97.2 |
| | 2.90 | 88.5 |
| | 2.95 | 99.9 |
| | 3.55 | 98.6 |
| | 3.98 | 99.6 |
| | 4.42 | 99.7 |
| | 4.64 | 99.4 |
| | 4.92 | 98.0 |
| | 5.02 | 99.1 |
| | 5.30 | 98.8 |
| | 5.60 | 99.2 |
| 5.98 | 97.4 | |
| 6.40 | 91.0 | |

5.1.4 Discussion

There are several factors to be considered in tracer studies on inner complexes of plutonium. The stability of many organic complexes is quite critically dependent on the pH of the medium in which the complexes are formed. There-

*The position of the tert.-butyl group is not definitely known. The aldehyde was prepared by the Duff reaction from 2-hydroxy-4-tert.-butylphenol, and the tert.-butyl group in the aldehyde might be in either the 5- or 6- position. Positive proof of structure depended on the oxidation of the tert.-butyl radical to a carboxyl group, and tertiary alkyl radicals are particularly resistant to oxidation. However, the more likely structure might be the 5-substituted compound, as judged from the reactivity of other 5-substituted compounds with Pu(IV).

fore, in order that no reagent be overlooked in its possibility of complexing plutonium, a rather wide pH range was investigated. The buffer systems were limited to acetates, because the anions present in other buffer systems (citrate, tartrate, etc.) form very strong complex ions with Pu(IV), and might lead to erroneous conclusions about the behavior of Pu(IV) with some organic reagents.

Tracer scale extractions can lead to results which are of great value, even though some of the data may not be conclusive on a quantitative basis. If there is high extractability into a solvent which will not extract plutonium in the absence of the organic reagent, the results can be taken as presumptive proof of inner complex formation. If the extractability is low (less than 2 per cent) it is not likely that complex formation takes place. Low but still measurable extractabilities (less than 5 or 10%) are almost ambiguous in their meanings.

Many of the compounds which gave promising results on the tracer scale were later studied more thoroughly on the micro scale using visible amounts of plutonium.

The high extractions obtained with quinalizarin and aniline are difficult to interpret, because aniline alone effected about 85 per cent extraction of tracer Pu(IV). This may be due to selective wetting of the hydroxide which might be precipitated at the pH produced by the solubility of ani-

line in water. Quinalizarin with ether, tert.-amyl alcohol, and nitromethane effected no extraction of Pu(IV) tracer. The extraction of tracer Pu(IV) by tannic acid and aniline (53) has been reported, but there has been no elucidation of the chemistry involved. Later, in connection with experiments designed for other purposes, it was found that micro amounts of Pu(IV) formed a reddish-purple complex at pH = 5 with quinalizarin, and that the compound was soluble in and extractable from water by cyclohexanone.

The β -diketones had obvious possibilities as chelating compounds, since acetylacetone long has been known to complex many metals, including Th(IV) (54), Zr(IV) (55), U(IV) (55) and Ce(IV) (56). Considerable work has been done by other laboratories on Pu(IV)-acetylacetonate (57). In our work we did not stress the study of β -diketones because as a rule their complexing activity is quite general for many elements. However, it was found later by Calvin and co-workers, that certain trifluoromethyl β -diketones exhibit some specificity for forming stable Pu(IV) complexes (58, 59, 60, 61, 62).

None of the nitroso compounds or oximes possess complexing activity for Pu(IV). Cowan and Goldsmith (63) also observed negative results with α -nitroso- β -naphthol, dimethylglyoxime, and salicylaldoxime on the tracer scale. The only nitroso compound whose complexing activity with Pu(IV) is important is cupferron (64).

Of all of the other miscellaneous bidentate reagents listed in Table 2, only benzohydroxamic acid and 8-hydroxyquinoline showed appreciable complexing activity with Pu(IV). Early experiments (65, 66) had indicated that the 8-hydroxyquinolates of UO_2^{++} , Ce(III) and Ce(IV) when precipitated at a pH of 4 carried plutonium. Considerably later, Patton's analysis of Pu(IV)-8-hydroxyquinolate on the micro scale gave conclusive proof that the coordination number of Pu(IV) is eight (67).

Many of the bidentate reagents listed in Table 2 are remarkably active in forming inner complexes with many metals, especially those in the so-called transition groups. That so few of them react with Pu(IV) may constitute evidence that plutonium does not resemble the transition elements in which d orbitals are being filled.

The results obtained with quadridentate reagents are interesting in that they show the structural relationships necessary for the formation of complexes with Pu(IV).

Tracer scale experiments with di-acetylacetonone ethylenediimine gave negative results, and attempts by others (68) to prepare the U(IV) and Pu(IV) complexes, by the method used by Combes (69) for the preparation of the Cu(II) complex, were unsuccessful.

The results summarized in Table 3 show quite well the effect of chelate ring size on the stability of the Pu(IV)

complexes with disalicylal diimines. Copper and nickel derivatives of this type have been studied quite extensively by Pfeiffer (70), and he has described complexes in which there are as many as ten methylene groups between the two imino nitrogen atoms. Pfeiffer (71) prepared UO_2^{++} complexes of disalicylal diimines, and the U(IV) complex of disalicylaethylenediimine is stable with a melting point above $300^{\circ}C$ (72).

Actually for compounds of this type, little quantitative work has been done on the correlation of structure with stability of complexes with disalicylal diimines. The recent studies of Duffield and Calvin (73) on the exchange reactions of copper chelated compounds mark a step in the right direction.

The ethylenediimines exhibited the greatest tendency for complex formation, and the nineteen compounds listed in Table 4 were studied to determine the effect of various substituent groups. The peculiar effect of the tert.-butyl group in the 5-position is evident, as is the effect of a chloro or phenolic group in the 3-position. There appears to be no obvious electronic explanation for the effects of these groups in enhancing the complexing activity of the reagent.

5.2 Extended Studies with Disal*

5.2.1 Conditions for preparing the Pu(IV) complex on the micro scale

In experiments on the tracer scale, disal proved to be the most promising of the reagents examined for complexing activity with Pu(IV) in the pH range 2 to 6.4. Because tracer scale experiments can sometimes lead to questionable results it was necessary to check the validity of the results with microgram and milligram amounts of plutonium.

Several experiments were performed to determine the optimum conditions for preparing the complex with micro amounts of Pu(IV). In all of the experiments, the Pu(IV) was in 1 ml of acetate-buffered solution at pH 4. The solid reagent was added (usually twice the theoretical amount needed) and the slurry agitated while complex formation took place. During the course of the reaction, the solid phase (the suspended organic reagent) changed from the yellow color of the reagent to the purple black color of the Pu(IV) complex.

Chloroform extractions, with 1- to 2-ml portions of solvent, were done in the micro extraction apparatus described in Section 3.2.

The results of several experiments are summarized in Table 5.

*The word "disal" will be used in the rest of this thesis as an abbreviated notation for di-(2,3-dihydroxy-5 or 6-tert.-butylbenzal)-ethylenedimine.

Table 5

The Extraction of Plutonium(IV)
on the Micro Scale by Chloroform
and Disal from Acetate
Solutions at pH 4

| Amount of Pu(IV) | Reaction Conditions | | Per Cent Pu Extracted into Chloroform |
|---------------------|---------------------|------------|---|
| | Temp. °C | Time, Hrs. | |
| 0.950 mg | 25 - 30 | 36 | 88.4 |
| 1.019 | 25 - 30 | 48 | 98.1 |
| 0.356 | 65 - 70 | 2.5 | 88.6 |
| 0.356 | 95 | 2.5 | 97.5 |
| 0.356 | 95 | 1.0 | 96.5 |

The relative slowness of the reaction is doubtless due to the fact that the reaction takes place in a two-phase system. The reagent is quite insoluble in water.

5.2.2 The composition of the Pu(IV)-disal complex

Disal is a quadridentate reagent with two acidic and two coordinating groups, and it was assumed from the results of tracer experiments that two molecules of reagent were involved in complexing one atom of Pu(IV). To establish this with certainty, the weight percentage of plutonium in the disal complex was determined.

To an acetate-buffered solution containing 2.79 mg of Pu(IV) at pH 4 was added an amount of disal less than that required for reacting with all of the Pu(IV) present. The suspension was agitated for 12 hours at 80 to 90°C for com-

pletion of the reaction. The organic complex was extracted with chloroform and the organic layer washed with water.

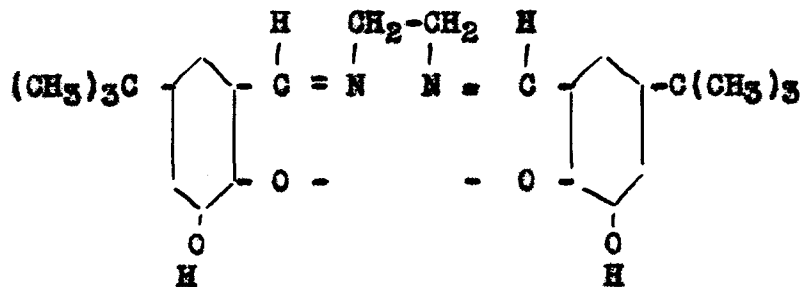
The chloroform solution of the complex was evaporated and the residue dried to constant weight at 100°C. The complex, almost black in color, was weighed, destroyed by digestion with HNO₃, and the resulting solution assayed for plutonium.

The data are summarized in Table 6. The formula PuR_{1.98} (where R = disal radical) is close enough to PuR₂ to indicate that two molecules are involved with one atom of Pu(IV). No molecular weight determinations were attempted.

Table 6
Composition of the Plutonium(IV)-
Disal Complex

| | |
|---|---------------------|
| Weight of plutonium taken | 2.790 mg |
| Weight of dried complex | 11.302 mg |
| Weight of plutonium in complex, by radioactive assay | 2.569 mg |
| Formula of complex, calculated from the above data | PuR _{1.98} |

where R* is



*Assuming the tert.-butyl group to be in the 5-position.

5.2.3 The use of various solvents for disal extractions

In most of the tracer scale extractions chloroform was used as the solvent. If there should ever be a need for a solvent more adaptable than chloroform for continuous counter current extractions, the behavior of various solvents toward the Pu(IV)-disal complex would have to be known.

The data summarized in Table 7 were obtained by using the usual tracer extraction techniques, using 20 ml of aqueous solution at pH 5.6 and 20 ml of solvent in separatory funnels.

Table 7

Extraction of Tracer Plutonium(IV)
by Disal and Various Solvents
from Acetate Solutions at pH 5.6

| Class of Compound | Solvent | Per Cent Pu Extracted | Remarks |
|--------------------------|-------------------------|-----------------------|-------------------------------|
| Hydrocarbons | Pet. Ether (35-55°C) | 95.0 | Preferential wetting of disal |
| | Benzene | 98.9 | |
| | Toluene | 98.0 | |
| | p-Xylene | 99.4 | |
| Chlorinated Hydrocarbons | Chloroform | 99.5 | |
| | Carbon tetrachloride | 50.6 | |
| | Trichlorethylene | 86.9 | |
| Alcohols | Benzyl alcohol | 98.4 | |
| | Cyclohexanol | 98.1 | Considerable Intersolubility. |

Table 7 - Continued

| Class of Compound | Solvent | Per Cent Pu Extracted | Remarks |
|-------------------|------------------------|-----------------------|---------|
| Ethers | Di-isopropyl ether | 99.1 | |
| | Diethyl ether | 98.9 | |
| Esters | n-Butyl acetate | 99.7 | |
| Ketones | Methyl isobutyl ketone | 99.0 | |
| | Cyclohexanone | 99.3 | |

The results indicate that several solvents are effective for disal extractions of plutonium.

5.2.4 Behavior of the Pu(IV)-disal complex toward dilute acids

Several experiments were conducted to determine the nitric acid concentration necessary to extract tracer Pu(IV) from chloroform and methyl isobutyl ketone solutions of the disal complex. The results of these experiments are summarized in Table 8. In all cases, the disal extractions were done under pH conditions which lead to virtually complete extraction of Pu(IV). Copper(II) carrier was used to obtain a qualitative idea of the relative stabilities of the Cu(II)- and Pu(IV)-disal complexes toward nitric acid.

Table 8

Stability of Tracer Plutonium(IV)-Disal
Toward Dilute Nitric Acid

| Solvent | Carrier | pH | Per Cent Pu Ex- tracted | Molar- ity of HNO ₃ | Per Cent Pu Ext'd. by HNO ₃ | Total Per Cent Yield | Remarks |
|------------------------------|------------------|------|-------------------------------|--------------------------------------|--|----------------------------|---|
| Chloro- form | Cu ⁺⁺ | 3.91 | 99.7 | 0.05 | 83.7 | 82.6 | Cu ⁺⁺ complex stable |
| | | 3.92 | 99.0 | 0.2 | 99.2 | 97.9 | " " " |
| | | 3.98 | 98.7 | 0.4 | 99.6 | 98.6 | Cu ⁺⁺ complex de- stroyed |
| | | 3.93 | 98.7 | 1.0 | 99.5 | 99.2 | Reagent attacked |
| Methyl isobutyl ketone | None | 5.6 | 99.6 | 0.1 | 94.8 | 94.4 | The reagent was par- tially attacked by all of these concen- trations of acid. The solubility of HNO ₃ in the ketone is consi- derable |
| | | 5.6 | 99.8 | 0.2 | 95.2 | 95.0 | |
| | | 5.6 | 99.5 | 0.4 | 97.8 | 97.4 | |
| | | 5.6 | 99.4 | 0.6 | 96.6 | 96.0 | |
| | | 5.6 | 99.4 | 0.8 | 96.6 | 96.9 | |
| | | 5.6 | 99.4 | 1.0 | 98.6 | 98.1 | |

In order to determine the effectiveness of oxalic acid in extracting Pu(IV) from the chloroform solution of the disal complex, tracer Pu(IV) was extracted with disal and chloroform from acetate-buffered solutions at pH 4.6. Then the chloroform solution of the complex was agitated with an equal volume of dilute oxalic acid solution and the two final fractions were then analyzed for plutonium. With 0.04 M oxalic acid, 53.5 to 58.6 per cent of the plutonium was extracted from the chloroform solution, and with 0.10 M oxalic acid the extractions ranged from 58.2 to 71.4 per cent.

5.2.5 Interfering substances

Sulfate, oxalate, and ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) were found to prevent complexing of Pu(IV) by disal.

The results of several tracer scale extractions with equal volumes of organic and aqueous phases are summarized in Table 9.

Table 9
Interferences in the Extraction
of Plutonium(IV) by Disal
and Chloroform

| Substances Added | pH of Aqueous Solution | Per Cent Pu Extracted by Chloroform |
|--|--|-------------------------------------|
| None | 5.2 | 99.0 |
| 0.1 M Na ₂ SO ₄ | 5.2 | 91.6 |
| 0.2 M Na ₂ SO ₄ | 5.2 | 81.2 |
| 0.3 M Na ₂ SO ₄ | 5.2 | 74.5 |
| 0.4 M Na ₂ SO ₄ | 5.2 | 70.1 |
| 0.6 M Na ₂ SO ₄ | 5.2 | 68.1 |
| 0.8 M Na ₂ SO ₄ | 5.2 | 70.9 |
| 1.0 M Na ₂ SO ₄ | 5.2 | 70.4 |
| 0.63 M Na ₂ SO ₄ | 1.90 | 4.9 |
| | 2.58 | 4.8 |
| | 3.17 | 23.2 |
| | 3.81 | 61.0 |
| | 5.22 | 67.8 |
| | 0.4 M C ₂ O ₄ ⁼ | 2.68 to 5.00 |
| Ferron (0.5 mg/ml) | 2.02 | 17.8 |
| | 2.51 | 53.6 |
| | 3.01 | 49.0 |
| | 3.52 | 51.9 |
| | 4.00 | 62.5 |
| | 4.51 | 53.6 |
| | 5.00 | 42.9 |

The data indicate that at pH's at which disal extractions are complete from acetate solutions, the Pu(IV) complexes with SO₄⁼, C₂O₄⁼ and ferron are strong enough to limit the complexing of Pu(IV) by disal.

5.2.6 Discussion

Composition of the Pu(IV)-disal complex. The chemical evidence obtained by analysis of the Pu(IV)-disal complex indicates with considerable certainty that the coordination number of Pu(IV) is eight. In this respect the behavior of Pu(IV) is analogous to that of U(IV), which forms complexes with disal (72). Th(IV) and Ce(IV) also form chelate compounds compatible with a coordination number of eight for the metal (54, 56, 74, 75).

Very little is known about the stereochemistry of compounds of elements with a coordination number of eight, even though many such compounds are known. The isomer tables of Marchi, Fernelius and McReynolds for coordination number eight (76) indicate that complete configurational studies of coordination number eight by chemical methods would be a formidable task. Hoard and Nordsieck (77) have shown by x-ray studies that the molybdooctacyanide ion is dodecahedral, and recently Marchi and McReynolds (78) have resolved potassium tetra-oxalato-uranium-(IV) into optical isomers, and postulate that the oxalato-uranium ion is either antiprismatic or dodecahedral.

The studies of chelate compounds of Pu(IV) were designed to concentrate on chemical properties, so there were no attempts to study stereochemical configurations. However, it

might be interesting to speculate briefly about the stereochemical properties of Pu(IV) complexes with relation to the position of plutonium in the periodic table.

Present opinion tends toward the view that plutonium is a member of an "actinide" series in which the 5f subshell is being filled. On the basis of this view, the configuration of Pu(IV) might be $5f^4$, with the 6d, 7s, and 7p orbitals vacant. Thus, to form a complex compound with coordination number eight, Pu(IV) must accept eight pairs of electrons. These are available in two disal radicals. There are no known cases in which f orbitals are involved in bond formation (26), so it is not likely that any of the electrons donated by the reagent would be accommodated in the 5f orbitals. However, the 6d, 7s, and 7p orbitals are available, and might receive the electrons to form stable bonds. According to Kimball (26), in his analysis of coordination number eight, d^5p^3 bonds could be formed to give the antiprismatic configuration, but d^4sp^3 bonds would be much more stable. These would lead to antiprismatic or dodecahedral configurations. These predictions were substantiated by chemical studies on tetraoxalato-uranium-(IV) (78). In order to obtain cubic structures, d^3fsp^3 or d^3f^4s bonds would be necessary (26).

Magnetic measurements would be of great value in determining whether 5f orbitals are involved in the formation of Pu(IV) complexes. Chemical studies designed to determine the configuration of complexes might be quite difficult.

Chemical properties of the Pu(IV)-disal complex.

The reason for the slow reaction of micro amounts of Pu(IV) to form the disal complex is probably that the reaction medium is heterogeneous, due to the low solubility of the reagent in water. The reaction rate could undoubtedly be increased by the use of mixed solvents, such as dioxane-water mixtures, but this would lead to decreased efficiency in the extraction by chloroform.

The data summarized in Table 7 show that several solvents are available for disal extractions if solvents with particular physical properties should be needed.

From the behavior of Pu(IV) and Cu(II) disal complexes with dilute nitric acid, one might surmise that even though several elements were complexed by disal a fractionation still might be possible by judicious choice of the acid concentration used to destroy the complex. In fact there are considerable differences in the stabilities of metal complexes of compounds of this type. Pfeiffer and co-workers (79) have studied the stability of complexes of disalicylaethylenediimine with various

elements by means of displacement reactions and have found the relative strengths of complexes to be in the order $\text{Cu} > \text{Ni} > \text{V}$, $\text{Fe} > \text{Zn}$, $\text{H} > \text{Mg}$. Thus, it is possible that the specificity of disal for plutonium might be increased by proper use of an acid re-extraction cycle.

The low re-extractions of Pu(IV) by oxalic acid were surprising in view of the fact that oxalate interferes so strongly in the complexing of Pu(IV) by disal. See Table 9. It is interesting to note that oxalic acid in concentrations as low as 0.05 M will remove Pu(IV) from the cupferron complex (80).

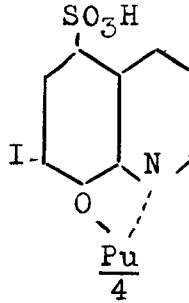
The interferences of sulfate, oxalate and ferron with disal extractions are ascribed to the fact that these substances form very strong water-soluble complexes with Pu(IV). The Pu(IV)-ferron complex is so stable that ferron prevents the adsorption of Pu(IV) on Amberlite IR-1 resin (81). Attempts to destroy the Pu(IV)-ferron compound by addition of Fe^{+++} ion to form the more stable Fe(III)-ferron did not lead to any success in improving the yields in disal extractions from solutions containing ferron.

5.3 The Pu(IV)-Ferron Complex

5.3.1 Introduction

Ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid)

forms an extremely stable complex with Pu(IV) in the pH range 4 to 8. The formula of the complex is probably



When ferron is present in a solution of Pu(IV) at the proper pH, complex formation prevents adsorption of Pu(IV) by Amberlite IR-1 resin. This makes possible the separation, in the adsorption process, of plutonium from elements not complexed by ferron (81).

The work described in this section was designed to learn some of the chemistry of the Pu(IV)-ferron complex, especially that of analytical importance.

In 1932, Yoe (82) reported a method for the colorimetric determination of ferric iron with ferron. Very few cations (only copper, cobalt, nickel, chromium and aluminum) were reported to interfere. Later, Yoe and Hall (83) and Swank and Mellon (84) published additional data on the ferron method for iron. They stated that very few ions other than Fe(III) form colored complexes with ferron. Therefore when Ayres (81) found that Pu(IV) formed

a stable complex with ferron, it was of interest to determine whether the complex was colored, and whether it might have any peculiar properties which might be of use, in the analytical chemistry of plutonium.

In the experimental work described below all of the spectrophotometric measurements were made with the Beckman Model DU Spectrophotometer.

5.3.2 Experimental

The absorption curves for ferron. In most spectrophotometric work the optical behavior of the solution studied is compared with that of a "blank" solution. In studies with ferron, for example, the sample would contain ferron, a buffer, and the cation under consideration, while the "blank" would contain only ferron and buffer. The color characteristics of ferron itself change with pH, so spectrophotometric curves for the reagent are necessary to determine how much care must be exercised in preparing the "blank solutions".

The absorption curves for ferron are shown in Figure 3. All of the measurements were made with 1 cm cells filled with a buffered solution 0.000228 M in ferron against a blank containing the buffer. It is obvious that in the region below 500 m μ care must be exercised in preparation of the blank solution.

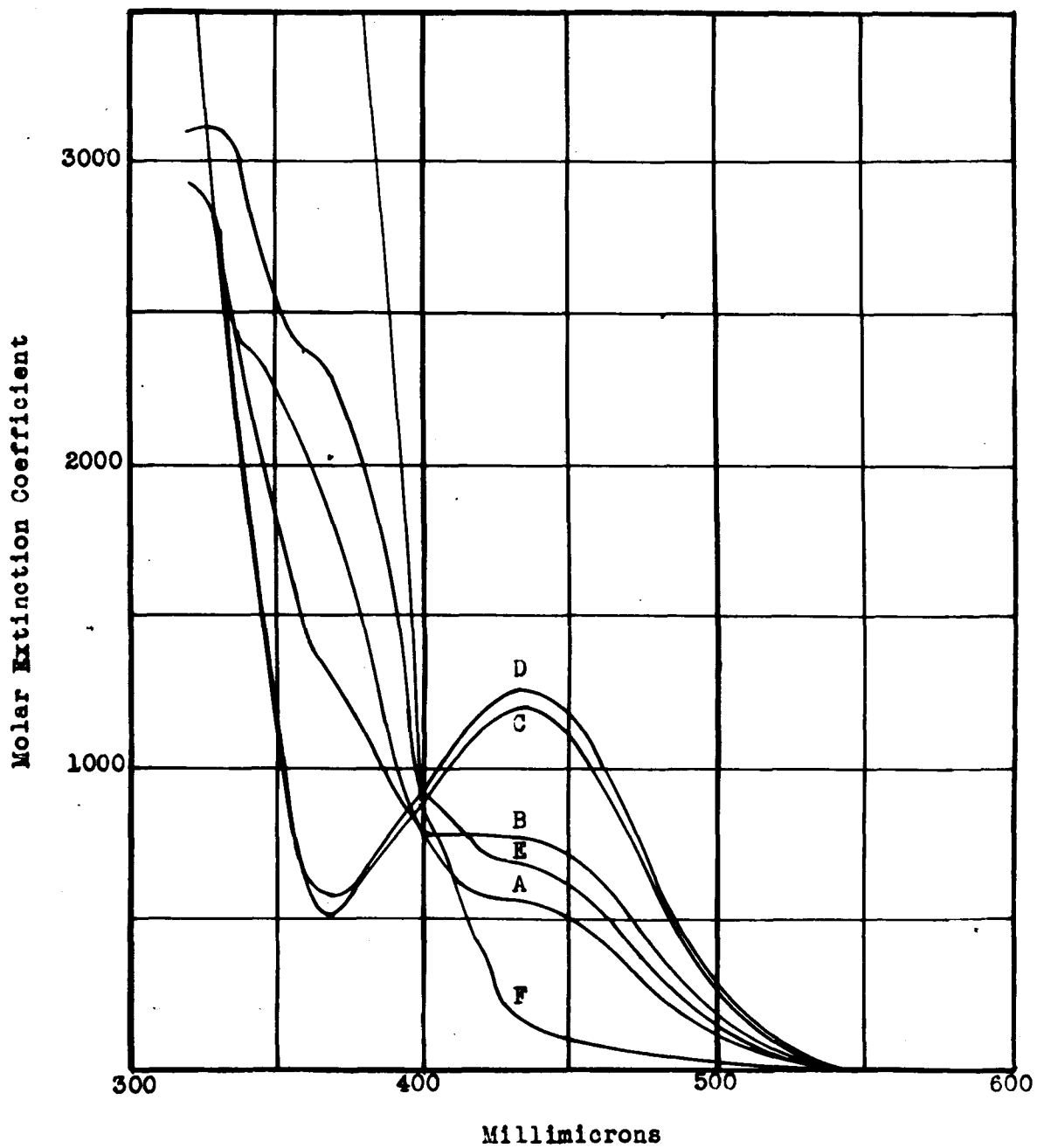


Fig. 3. Absorption Curves for Ferron at Different pH's
A: pH 2.31; B: pH 3.06; C: pH 3.36
D: pH 5.49; E: pH 7.10; F: pH 7.98

Absorption curves for the Pu(IV)-ferron complex.

In Figure 4 are shown absorption curves for the Pu(IV)-ferron complex at pH's 3.61 to 4.88. In all cases, ferron was added in excess of that required to complex the Pu(IV), and the blank contained the same buffer and an amount of ferron equal to the excess used in the preparation of the complex.

Two of the curves were obtained from solutions of plutonium purified by peroxide precipitations. The curve at pH 3.61 was obtained from a solution containing 20.3 μg Pu(IV)/ml. The solution had a very slight green color. At pH 4.68, the ferron solution containing 4.63 μg Pu(IV)/ml had a faint greenish-yellow color.

The third curve, for a solution of Pu(IV)-ferron at pH 4.88 containing 17.0 μg Pu(IV)/ml, was prepared from plutonium by fluoride precipitation.

The absorption curves for the Fe(III)-ferron complex.

In Figure 5 are shown the absorption curves for the Fe(III)-ferron complex, as calculated from the data of Mellon and Swank (84). They measured transmittancies against a blank containing only the buffer and no ferron. Therefore, the curves below 500 $m\mu$ are not particularly useful, because ferron itself has marked absorption peaks in the region 430 to 440 $m\mu$. However, the peaks in the region 600 to 620 $m\mu$ are certainly due only to the Fe(III)-ferron complex.

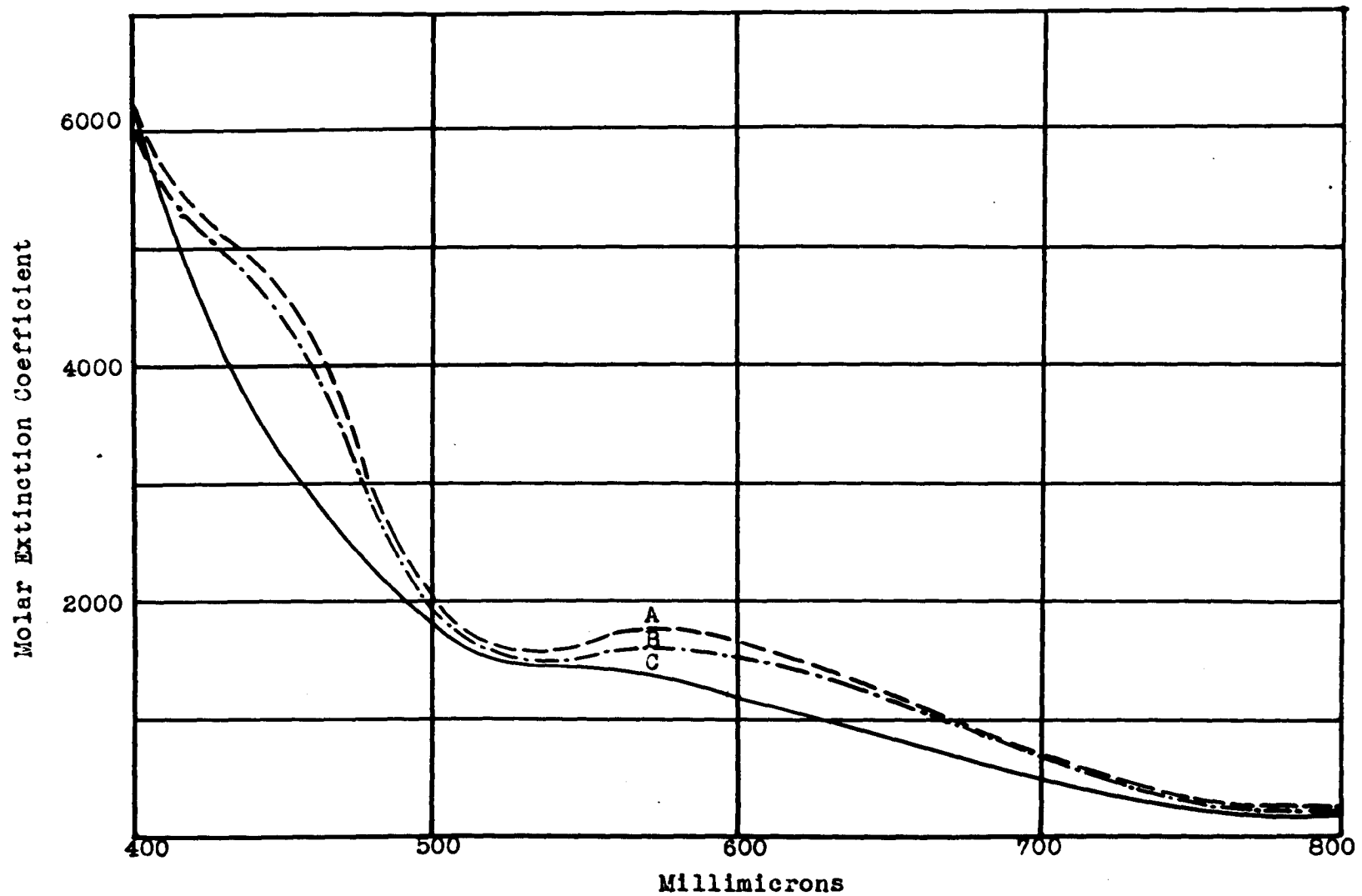


Fig. 4. Absorption Curves of the Pu(IV)-ferron Complex at Different pH's
 A: pH 4.68 B: pH 3.61 C: pH 4.88

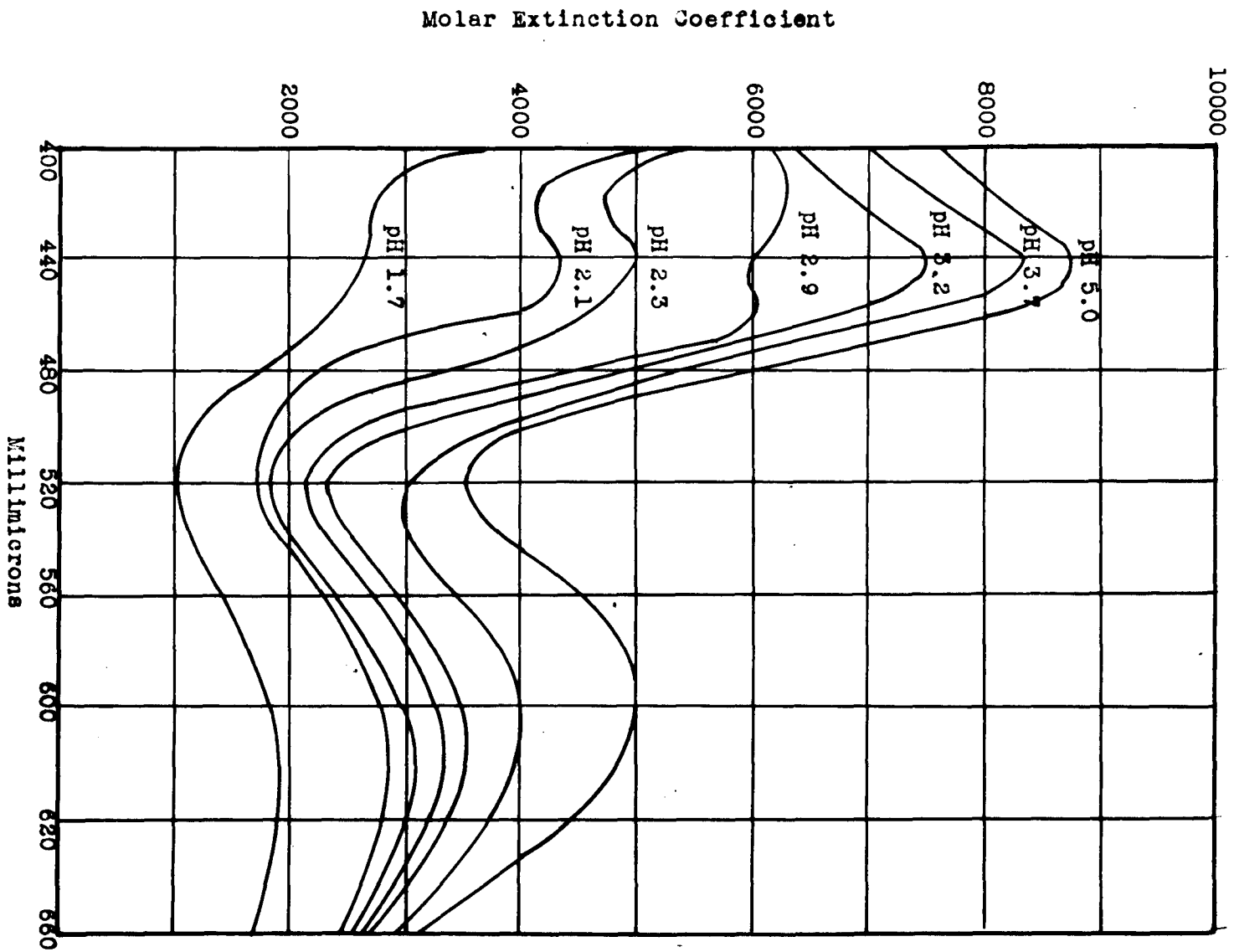


FIG. 5. Absorption Curves of Fe(III)-Ferron Complex

Spectrophotometric estimation of iron in plutonium using ferron as reagent. Yoe and Hall (83) report that Beer's law holds in the ferron determination of iron if the ratio of ferron to iron is kept constant. Of course, this constancy is not a condition commonly realized in analytical practice.

Some solutions, with an unknown iron content, containing 8.113 μg Pu(IV)/ml and more than four-fold excess of ferron, were prepared. The pH range was 1.02 to 2.77. The Pu(IV)-ferron complex is relatively unstable at pH's below 2.5, so in these experiments most of the ferron was used by the iron. The solutions were placed in 1 cm absorption cells, and the absorption curves obtained are plotted in Figure 6.

The data of Swank and Mellon (84) can be used to estimate the iron content in these solutions of plutonium. Beer's law was assumed to hold, since the ferron/iron ratio was constant, and the linear relationship of absorption (at 600 to 620 $m\mu$) with pH was used.

The results of the experiments are shown in Table 10.

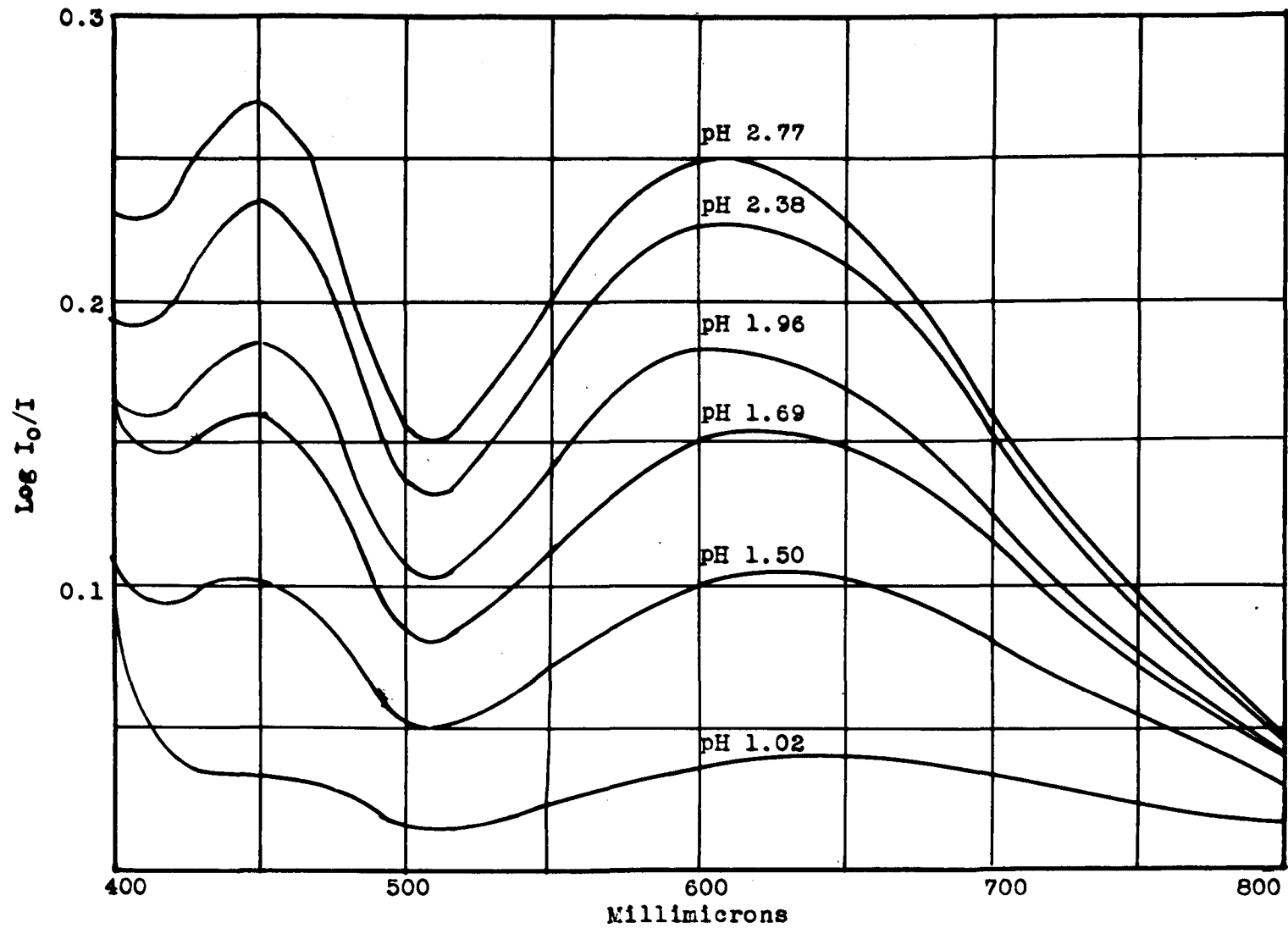


Figure 6. Absorption Curves of Pu(IV)-Fe(III) Solutions Containing Ferron

Table 10

Spectrophotometric Estimation of Iron in Plutonium
with Ferron as Reagent, Using
the 600-620 m μ Band

| pH of Solution | ϵ_m of Fe(III)-ferron | Log I_0/I from Fig. 6 | g Fe/ml |
|----------------|--------------------------------|-------------------------|---------|
| 1.02 | * | 0.038 | |
| 1.50 | * | 0.106 | |
| 1.69 | 1900 | 0.154 | 4.5 |
| 1.96 | 2550 | 0.183 | 4.0 |
| 2.38 | 3000 | 0.225 | 4.2 |
| 2.77 | 3300 | 0.250 | 4.2 |

*Linearity between ϵ_m and pH no longer holds.

5.3.3 Discussion

There are indications that the ferron method can be adapted for the estimation of iron in plutonium, because Pu(IV)-ferron has no marked absorption in the 600 to 620 m μ region of the characteristic peak for Fe(III)-ferron.

The absorption curves for Pu(IV)-ferron in Figure 4 indicate that some iron might be present in the peroxide-purified plutonium, because of the slight inflections around 590 m μ . The corresponding inflection in the curve obtained from fluoride-purified plutonium is not so marked, indicating less possibility of iron contamination. The inflections at about 450 m μ are not so

significant, because ferron itself has an adsorption peak in this spectral region, and the inflections could have been due to slight errors in blank corrections.

VI THE CHELATE COMPOUNDS OF PLUTONIUM(III)

6.1 Introduction

Exploratory attempts to produce tracer Pu(III) did not prove particularly successful, especially at pH's high enough for the formation of stable organic complexes. The anions present in the common buffer systems complex Pu(IV) quite strongly, and consequently shift the potential of the Pu(III)-Pu(IV) couple. Therefore, on the tracer scale, even though proper reducing conditions have been used for production of Pu(III), there is always uncertainty about the identity of the oxidation state of plutonium in the buffer system.

For these reasons, it was necessary to conduct all of the exploratory experiments with micro amounts of Pu(III), so that oxidation states could be identified with more certainty by spectrophotometric methods.

6.2 Experimental

6.2.1 General procedure

In the exploratory experiments, the amounts of plutonium used varied from 106 to 500 μ g. In the volumes of solutions

used, these quantities of plutonium usually were sufficient to make possible the identification of the oxidation state by spectrophotometric analysis (85). For identification of Pu(III) in solution, the absorption bands at 560 and 600 $m\mu$ were used. When reductions were complete, the characteristic 480 $m\mu$ band of Pu(IV) was absent. All spectrophotometric measurements were made with the Beckman Model DU spectrophotometer. After spectrophotometric measurements had shown that the reduction procedure was effective it was assumed in most of the succeeding experiments that Pu(III) was the oxidation state present in solution. Later, however, in the determination of the composition of Pu(IV)- α -naphthohydroxamate, it was found that in acetate solutions, oxidation to Pu(IV) may take place to a certain extent.

The usual reduction procedure was to remove most of the nitrate present in the aliquot of stock solution by several evaporations with HCl. The plutonium solution then was made 1.0 to 1.5 M in hydroxylammonium ion and 1.0 to 1.5 M in HCl. The time for reduction was always at least an hour. In general, the volume of solution was kept below 1.5 ml. In the more concentrated solutions, the color change from brownish green to blue was evident as reduction to Pu(III) occurred.

The organic reagent, either as the solid or in ethanol solution, and in five to ten-fold excess, was added to the Pu(III) solution. The theoretical amounts of reagent were

based on the assumption that the coordination number of Pu(III) is six. After addition of the reagent, the pH of the solution or suspension was raised gradually by addition of NH_4OH and ammonium acetate until the acetate concentration was about 1 M. At least two hours were allowed for reaction to take place.

Chloroform extractions were made in the micro-extraction apparatus with the volume of solvent equal to that of the aqueous phase. The fractions were analyzed for plutonium by evaporating aliquots on platinum foils and checking their alpha activities.

6.2.2 The behavior of plutonium(III) with hydroxamic acids

It is generally assumed that the tautomers (I and II) of the monohydroxamic acids are capable of existence, but that the oxime structure (II) is necessary for chelate ring formation (86).



The hydroxamic acids are quite active in forming chelate compounds, and therefore it seemed worthwhile to examine their activity with Pu(III).

The results of several exploratory experiments are sum-

marized in Table 11. In all cases, the experimental procedure used was that described in the preceding section.

Table 11
The Behavior of Micro Amounts of
Plutonium(III) with Various Hydroxamic Acids

| Reagent | pH of Solution | Per Cent Pu Extracted by Chloroform |
|---------------------------------------|----------------|-------------------------------------|
| Benzohydroxamic Acid | 5 | 43.3 |
| | 6 | 92.5 |
| <u>m</u> -Nitrobenzohydroxamic Acid | 6 | 74.8 |
| <u>o</u> -Hydroxybenzohydroxamic Acid | 6 | 33.0 |
| α -Naphthohydroxamic Acid | 2 | 2.2 |
| | 4 | 94.3 |
| | 6 | 97.4 |
| α -Furohydroxamic Acid | 6 | 1.2 |
| Phenylacetohydroxamic Acid | 5 | 47.2 |
| | 7 | 79.5 |
| Acetohydroxamic Acid | 5 | 1.2 |
| <u>n</u> -Propanohydroxamic Acid | 6 | 5.0 |
| <u>n</u> -Valerohydroxamic Acid | 4 | 96.4 |
| | 6 | 98.6 |

The data in Table 11 show definite evidence of complex formation by Pu(III) with several of the hydroxamic acids. In all cases in which there was extraction of plutonium by chloroform, the color of the Pu(III) complex was reddish-orange. The corresponding hydroxamates of Fe(III) have a more nearly purple color.

In tracer scale extraction experiments with Pu(IV) (see

Table 2), benzohydroxamic acid showed definite evidence of complexing Pu(IV). However, it was possible that some of the Pu(IV) might have been reduced to Pu(III) by the hydroxamic acid, which is really an acyl derivative of hydroxylamine.

It was found with milligram amounts of plutonium in the tetrapositive state that α -naphthohydroxamic acid and chloroform effected 39.0 per cent extraction of Pu(IV) from a solution of pH 6. Similar experiments with Pu(III) showed that naphthohydroxamic acid and chloroform effected 97.4 per cent extraction from a solution at the same pH. Therefore it was of interest to determine the oxidation state of the plutonium in the hydroxamates listed in Table 11.

The composition of the α -naphthohydroxamate was determined in a way similar to that used for determining the composition of the Pu(IV)-disal complex (Section 5.2.2). The α -naphthohydroxamate was chosen for the gravimetric analytical work because of the relatively high molecular weight of the parent acid. Two determinations of the composition were made.

In the first experiment, Pu(III) was prepared by reduction in hydroxylammonium chloride and the identity of the oxidation state checked spectrophotometrically. This solution containing 2.972 mg of Pu(III) was buffered in ammonium acetate to pH 4, and as the pH was raised the color of the solution changed from blue to pink. To the

3 ml of solution were added 5.433 mg of α -naphthohydroxamic acid. A brown color developed almost immediately, and the suspension was agitated with helium for 7 hours for completion of the reaction. Extraction was made with 3 ml of chloroform. The complex dissolved readily in the chloroform to form an orange solution, leaving the aqueous layer colorless. The chloroform solution of the complex was carefully evaporated in a weighed micro platinum dish and dried to constant weight. The plutonium content was determined by destroying the organic matter with nitric acid and assaying the solution for plutonium by alpha counting.

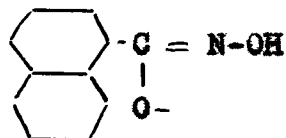
In the second experiment, no acetate buffer was used. The solution, containing 2.535 mg of Pu(III), was prepared by reduction in hydroxylammonium chloride. To 1 ml of this solution were added 3.648 mg of α -naphthohydroxamic acid. As the pH was raised to 6 by the addition of NH₄OH the suspension acquired almost immediately the characteristic brown color of the hydroxamate. The suspension was agitated with a helium stream for 7 hours for completion of the reaction. Extraction was made with 2 ml of chloroform. The chloroform solution of the complex was evaporated and analyzed in the same way as that described in the preceding paragraph.

The results of the two determinations are shown in Table 12.

Table 12
Composition of Plutonium(III)- α -Naphthohydroxamate

| | Conditions for the Preparation of the Complex | |
|--------------------------------|---|----------------------|
| | 1 M Acetate Solution, pH 4 | No Acetate, pH 6 |
| Weight of Plutonium Used | 2.972 mg | 2.535 mg |
| Weight of Organic Reagent | 5.433 mg | 3.648 mg |
| Weight of Complex Formed | 8.250 mg | 4.928 mg |
| Weight of Plutonium in Complex | 2.199 mg | 1.432 mg |
| Composition of Complex* | PuR ₃ .53 | PuR ₃ .14 |

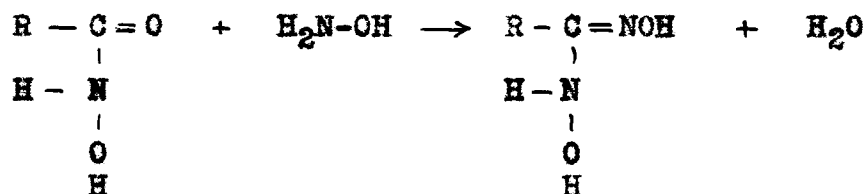
*Where R = α -naphthohydroxamate radical



The data indicate that Pu(III) is not very stable in acetate solutions. Even though in the first experiment all of the plutonium was originally in the tripositive state, addition of acetate ion may have caused some oxidation of Pu(III) to Pu(IV) because of the stabilization of Pu(IV) by formation of the complex acetate ion. The change of Pu(III) to Pu(IV) in acetate solutions probably becomes more appreciable with longer time for reaction. In the first experiment summarized in Table 12, 7 hours were allowed for reaction, and in the exploratory experiments summarized in Table 11 the reaction period was from 2 to 4 hours. Thus, even though it is possible that some oxidation to Pu(IV)

may have occurred, it still appears that the positive results summarized in Table II indicate complexing of Pu(III) by certain hydroxamic acids.

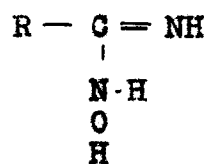
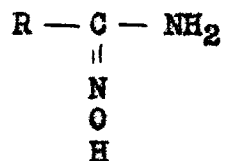
Another factor had to be considered in the reactions of hydroxamic acids. In all of the experiments with Pu(III) and hydroxamic acids, hydroxylammonium chloride was used as the reductant. There was the possibility that at the relatively high pH's used for preparing the complexes, some free hydroxylamine might have reacted with one of the tautomers of the hydroxamic acid to form the corresponding N,N'-dihydroxyamidine according to the following reaction



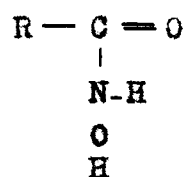
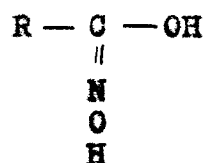
Experiments with benzohydroxamic acid and hydroxylammonium chloride with conditions identical with those used for Pu(III)-complex formation showed that the hydroxamic acid was unchanged. After 2 hours in the reaction medium, the melting point of the benzohydroxamic acid was unchanged (129°C). N,N'-Dihydroxybenzamidine melts at 115°C. (H. Ley, Ber., 31, 2127 (1898)).

6.2.3 The behavior of plutonium(III) with amide oximes

The amide oximes constitute an interesting group of compounds which apparently exist in two tautomeric forms



in which they resemble the hydroxamic acids:



It was thought that the amide oximes might also resemble the hydroxamic acids in their reactions with Pu(III).

The experimental procedure for examining the activity of amide oximes was the same as that described above for the hydroxamic acids. The results of several exploratory experiments are summarized in Table 13.

Table 13

The Behavior of Micro Amounts
of Plutonium(III) with Various
Amide Oximes

| Reagent | pH of Solution | Per Cent Pu Ex-tracted by Chloroform |
|----------------------------|----------------|--------------------------------------|
| Benzamide Oxime | 6 | 0.3 |
| p-Toluamide Oxime | 4.1 | 0.9 |
| | 5.8 | 13.8 |
| α-Naphthamide Oxime | 5 | 1.6 |
| | 6 | 10.9 |
| Phenylacetamide Oxime | 3.0 | 1.8 |
| | 4.1 | 0.2 |
| | 5.0 | 98.5 |
| | 6.0 | 77.9 |
| <u>n</u> -Valeramide Oxime | 4 | 3.2 |
| | 5 | 46.5 |
| | 6 | 92.0 |

Both phenylacetamide oxime and n-valeramide oxime complex Pu(III) quite completely to form compounds deep purple in color. In connection with some other studies it was found that phenyl-acetamide oxime also reacted with Pu(IV). When 826 μg of peroxide-reduced Pu(IV) (with no Pu(III) or Pu(VI) present, as shown by spectrophotometric analysis) were allowed to react with phenylacetamide oxime at pH 5 to 6, one chloroform extraction removed 89.2 per cent of the plutonium. The Pu(IV)-phenylacetamide oxime is brownish-orange in color.

6.2.4 The behavior of plutonium(III) with miscellaneous bidentate reagents

The analysis of Pu(III)- α -naphthohydroxamate gave definite evidence that the coordination number of Pu(III) is six. Therefore, the type of reagent most likely to form chelate compounds of Pu(III) is the bidentate reagent containing one acidic and one coordinating group.

The results obtained in cursory experiments with Pu(III) and several miscellaneous bidentate reagents are summarized in Table 14. The usual experimental procedure was used. Most of the reagents examined exhibit rather general complexing action with many metals.

Table 14

The Behavior of Micro Amounts of
Plutonium(III) with Various
Miscellaneous Bidentate Reagents

| Reagent | pH of Solution | Per Cent Pu Extracted by Chloroform |
|--|----------------|-------------------------------------|
| Salicylaldoxime | 4 | 0.67 |
| | 6 | 0.35 |
| α -Nitroso- β -naphthol | 5 | 9.8 |
| Dimethylglyoxime | 6 | 1.2 |
| Diphenylthiocarbazone | 6 | 3.2 |
| Isatin- β -oxime | 6 | 5.5 |
| α -Benzoin Oxime | 6 | 3.3 |
| Phenylglyoxaldioxime | 6 | 1.4 |
| Diphenylthiocarbazide | 5 | 6.6 |
| s-Diphenylthiourea | 6 | 6.3 |
| β -Hydroxyquinoline | 5 | 10.6 |
| | 6 | 51.6 |
| Ammonium Morpholine- dithiocarbamate | 6 | 0.3 |
| Potassium Pentamethylene- dithiocarbamate | 7 | 1.8 |
| Potassium N,N-diethyldithio- carbamate | 6 | 0.1 |

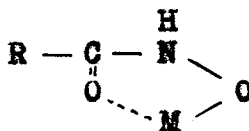
It can be seen that 8-hydroxyquinoline is the only reagent listed in Table 14 showing evidence of complexing Pu(III).

6.3 Discussion

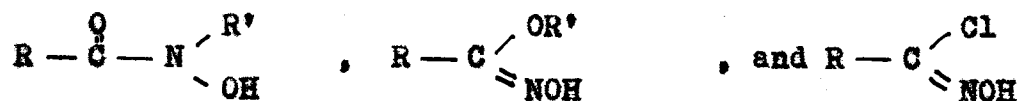
The analysis of Pu(III)- α -naphthohydroxamate constitutes good evidence that the coordination number of Pu(III) is six. If the electronic configuration of Pu(III) is $5f^5-6s^26p^6$, the 6d, 7s, and 7p orbitals are available for receiving electron pairs to form covalent bonds. According to Kimball (26) d^2sp^3 (common in Co, Pd, and Pt complex ions), d^4sp , d^5p , and d^3p^3 configurations are possible for covalent bonds for coordination number six. It is possible, of course, that the bonds in Pu(III) complexes may be partly ionic in character.

Of the reagents examined for complexing activity with Pu(III), only the hydroxamic acids and amide oximes shown any particular reactivity.

The hydroxamic acids are quite active chelating agents, forming complexes with Fe^{+++} , Ni^{++} , Co^{++} , Cu^{++} , UO_2^{++} , Y^{+++} , ZrO^{++} , Th^{++++} , and Ce^{+++} (27). Werner (27) postulated that the structure of the complexes of hydroxamic acids is



However, it has been found that derivatives of the general formulas $RCONHOR'$ or $RC(OH) = NOR'$ do not give color reactions with ferric chloride, while compounds of the structures



do, so it is believed that the $=NOH$ grouping is necessary for the formation of chelate compounds (86). If this be true, the hydroxamic acids and amide oximes are the only compounds with $=NOH$ groupings which show chelating activity with plutonium.

Phenylaceto- and n-valerohydroxamic acids are quite soluble in water, as are the phenylacet- and n-valeramide oximes. These solubility properties make these compounds much more useful as reagents for plutonium.

Salicylaldoxime was of some interest. In early work on the tracer scale (88), when Co^{++} carrier was used with salicylaldoxime and chloroform extractions of Pu(IV) tracer, partitions as high as 80 per cent were obtained. The experimental results were erratic, however, and were difficult to duplicate. Even the carrier seemed to have some effect. However, if true inner complex formation occurs, and if all of the inner complex dissolves in the organic solvent, as is the case with copper and cobalt salicylaldoximes, the erratic results cannot be explained by the carrying properties of the precipitates.

Table 15

Extraction of Plutonium Tracer
with Salicylaldoxime and Chloroform
from Acetate-buffered Solutions

| pH | Carrier in 20 ml Solution | Amount of Reagent | Per Cent Pu Extracted | Conditions |
|------------------------------|---------------------------------|-------------------------|-----------------------------|---|
| 3.12 to 6.66 | None | 15 mg | 14.1 | No NH_3OHCl present |
| 3.04 to 6.58 | 1 mg Cu^{++} | 15 mg | 10.0 | No NH_3OHCl present |
| 3.08 to 5.52 6.11 6.58 | 2 mg Co^{++} | 15 mg | 0.7 33.5 11.3 | No NH_3OHCl present |
| 5.54 5.65 5.73 | 5 mg Co^{++} | 40 mg | 64.6 52.5 60.7 | No NH_3OHCl present |
| 6.07 | 2 mg Co^{++} | 20 mg | 63.3 | Solution 0.1 M in NH_3OHCl |

From the results of the tracer experiments, some factors indicated that the salicylaldoxime might have complexed Pu(III) instead of Pu(IV). The greatest extractions were obtained when hydroxylamine was present, or when a fairly large amount of cobalt was used as carrier. Hydroxylamine is known to produce Pu(III) and certain cobaltous complexes are known to be among the most powerful reducing agents known (89). However, with Pu(III) on the micro scale (See Table 14) there was no evidence for complex formation with salicylaldoxime. So far, no explanation for these discrepancies has been evolved.

VII THE USE OF ORGANIC REAGENTS
FOR THE DECONTAMINATION AND
PURIFICATION OF PLUTONIUM

7.1 Introduction

After several reagents had been found to form chelate compounds with Pu(III) and Pu(IV) efforts were directed toward the determination of the specificity or selectivity of the reagents. Some of the elements whose behaviors were studied were those considered in the purification of plutonium; others were the fission products which had to be removed sometime during the processing of plutonium from the uranyl nitrate dissolver solution to the final form in which plutonium was desired. During the course of the investigations, emphasis on various aspects of the decontamination and purification problems was changed. Therefore, some of the specificity experiments described below are rather limited in their scope.

Extended studies were conducted only with the reagents which exhibited considerable complexing activity with plutonium. For Pu(IV), the best reagents studied in the Amex laboratories were dialicylaethylenediimine and disal (di-2,3-dihydroxy-5 or 6-tert.-butylbenzal-ethylenediimine). The best reagents for Pu(III) were benzohydroxamic acid,

α -naphthohydroxamic acid, and phenylacetamide oxime.

Although none of the reagents discussed in this section has been tested directly with dissolver solutions some have been tested with a number of cations, individually and collectively. Many of the ions tested are found in various process solutions, and others are frequently encountered in laboratory recoveries of plutonium.

7.2 Experimental

7.2.1 The behavior of various cations with disal

This reagent effects greater than 95 per cent complexing of Pu(IV) and the pH range 2.75 to 5.98. The behavior of this reagent with various cations was examined by extractions of tracer amounts and of milligram amounts of ions from acetate-buffered solutions (0.1 to 1.0 M in total acetate) by disal and chloroform. Extractions were made either in separatory funnels or in an extraction apparatus (somewhat larger than that shown in Figure 2) in which agitation of phases was produced by a gas stream. In all cases the volume of chloroform was equal to that of the aqueous phase.

Radioactive 33 year Cs¹³⁷ was used to determine the distribution of cesium in disal extractions. Activities were measured by checking the radioactivity of CsClO₄ precipitates from the aqueous and organic fractions with the Geiger-Müller counter.

The behavior of barium was determined over a wide pH range with 12.8 day Ba^{140} . The tracer was recovered from the fractions as $BaCO_3$ and the activity determined with the electroscope.

A solution of UX_1 activity (24 day Th^{234}) was prepared by ether extraction of uranyl nitrate. The buffered solution was extracted with disal and chloroform, and the tracer recovered by $La(OH)_3$ precipitations.

For extractions of zirconium, a sample of carrier-free zirconium tracer was obtained from Clinton pile material. Absorption measurements showed that the activity was at least 90 per cent pure 68 day Zr^{95} . The tracer was recovered by $Fe(OH)_3$ precipitations and the activities determined with the electroscope.

The behavior of disal with tracer amounts of various cations is summarized in Table 16.

Table 16

The Extraction of Various Radioactive Elements by Disal and Chloroform from Acetate Solutions

| Ion | pH of Aqueous Solutions | Per Cent Activity Extracted by Chloroform |
|--------------------------------------|-------------------------|---|
| Cs ⁺ | 3.88 | 0.02 |
| | 4.28 | 0.02 |
| Ba ⁺⁺ | 1.93 | 0.24 |
| | 3.35 | 12.5 |
| | 4.02 | 13.5 |
| | 4.80 | 17.9 |
| | 5.12 | 22.6 |
| | 5.80 | 21.5 |
| Ce ⁺⁺⁺ , Y ⁺⁺⁺ | 3.28 | 0.09 |
| | 3.85 | 0.37 |
| Th ⁺⁺⁺⁺ | 2.50 | 12.6 |
| | 3.08 | 14.7 |
| | 3.82 | 25.0 |
| | 4.53 | 21.4 |
| | 5.40 | 51.2 |
| | 6.20 | 61.0 |
| ZrO ⁺⁺ | 1.20 | 12.2 |
| | 2.00 | 60.3 |
| | 2.90 | 63.3 |
| | 3.96 | 61.2 |
| | 4.70 | 82.6 |
| | 5.25 | 85.4 |

The data indicate that good separations of Pu(IV) from alkali metals and rare earths are possible, but that direct separations of Pu(IV) from barium, thorium and zirconium are much less effective.

The behavior of iron with disal was studied using milligram amounts of iron. The Fe^{+++} solution was prepared from 99.8 per cent pure iron wire. Extractions were made from 20 ml of aqueous solution, 1 M in acetate, containing 2.50 mg of Fe^{+++} . In each extraction 40 mg of disal was used with 20 ml of chloroform. Iron in the fractions was determined spectrophotometrically as the ferrous orthophenanthroline complex ion. The results of several experiments are listed in Table 17.

Table 17

The Extraction of Iron
by Disal and Chloroform
from Acetate Solutions

| pH of Aqueous Solution | Per Cent Iron Extracted by Chloroform |
|------------------------|---------------------------------------|
| 2.62 | 7.2 |
| 3.13 | 2.8 |
| 4.02 | 23.0 |
| 4.78 | 46.4 |
| 5.34 | 53.8 |
| 6.08 | 41.0 |

Cursory experiments showed that the iron in the disal complex was in the ferrous state. In these experiments the chloroform solutions were shaken with 1.5 M HCl to destroy the complex. The ferrous iron in the HCl solution was de-

terminated spectrophotometrically as the orthophenanthroline complex ion. From 72.8 to 88.0 per cent of the iron in the HCl solution was present in the ferrous state.

Very stable emulsions were formed in disal-chloroform extractions of 5 to 10 mg quantities of UO_2^{++} , U^{+4} , Th^{+4} and ZrO^{++} ions, making impossible accurate estimates of distribution of such quantities of material.

7.2.2 Attempts to adapt disal extractions to the separation of plutonium from zirconium and thorium

Both zirconium and thorium are quite effectively complexed by disal in the pH range in which Pu(IV) is complexed. The following experiments were designed to determine whether there are any conditions with which practical fractionations can be obtained.

Zirconium. The stability of the Zr(IV)-disal complex toward dilute HNO_3 was compared with that of the Pu(IV)-disal complex in the following experiment. Disal extractions were performed from acetate-buffered solutions (pH 4.3 to 4.6) of zirconium tracer in the usual way, the chloroform solutions from these extractions were shaken with equal volumes of dilute HNO_3 and the chloroform and HNO_3 phases were analyzed for zirconium activity.

Table 18
 Stability of Disal Complexes
 Toward Dilute Nitric Acid

| Normality of Nitric Acid | Per Cent Activity Removed from Chloroform by One Acid Wash | |
|--------------------------|--|------|
| | Zr | Pu |
| 0.05 | 62.0 | 83.7 |
| 0.10 | 63.8 | ---- |
| 0.20 | 51.6 | 99.2 |
| 0.40 | 52.2 | 99.6 |
| 0.60 | 63.7 | ---- |
| 0.80 | 93.5 | 99.5 |

When chloroform solutions of the Zr(IV)-disal complex were agitated with equal volumes of 1.0 M aqueous KF solution, 75.5 to 80.6 per cent of the zirconium activity was transferred from the chloroform to the aqueous phase.

The stability of the Zr(IV)-disal complex toward oxalic acid was determined by agitating chloroform solutions of Zr(IV)-disal complex with equal volumes of 0.04 M oxalic acid. From 73.4 to 87.0 per cent of the zirconium activity was transferred from the chloroform solution into the oxalic acid.

Zirconium and thorium. Because disal is a quadridentate reagent, it would not be expected to complex Pu(III). Therefore, there was a possibility that plutonium could be separated from Zr(IV) and Th(IV) by treating a chloroform solution of

the disal complexes with a reducing solution. Used in such experiments were hydroxylammonium and hydrazinium chloride and solutions of sodium bisulfite. In all experiments the disal reagent was attacked by the reducing solutions, and no fractionations were obtained.

7.2.3 The behavior of various cations with hydroxamic acids

Benzohydroxamic acid. Benzohydroxamic acid has been found to effect some complexing of Pu(IV) tracer (See Table 2), but the complexing of Pu(III) is more nearly complete (See Table 11). It was of interest to determine the behavior of certain other elements with benzohydroxamic acid in the pH range in which greater than 90 per cent complexing of Pu(III) takes place.

In qualitative tests of the behavior of various cations with benzohydroxamic acid, 3 to 5 mg of the cation were added to 3 ml of 1.0 M sodium acetate solution. The organic reagent was added to this solution and the pH adjusted by addition of acetic acid or ammonium hydroxide. Precipitation and extraction behavior with chloroform were observed as summarized in Table 19.

Table 19

Qualitative Behavior of Various Cations with
Benzohydroxamic Acid and Chloroform (Acetate Buffer)

| Cation | pH | Precipitate in H ₂ O | Solubility in CHCl ₃ | Remarks |
|-------------------------------|-----|------------------------------------|------------------------------------|---------------------------------------|
| Cr ⁺⁺⁺ | 6 | None | - | Slight turbidity in H ₂ O. |
| Ni ⁺⁺ | 6 | None | - | No visible change. |
| Co ⁺⁺ | 6 | None | - | Brown water soluble color at pH=8. |
| Mn ⁺⁺ | 7 | Brown | Sl. sol. | Emulsion formed. |
| Cd ⁺⁺ | 6-8 | None | - | No visible change. |
| Al ⁺⁺⁺ | 3 | White | - | Turbid emulsion formed. |
| Mg ⁺⁺ | 5 | Faint | Insol. | |
| Cu ⁺⁺ | 5-6 | Green | Sl. sol. | CHCl ₃ layer turbid. |
| Hg ⁺⁺ | 3-6 | Pale Yellow | Sl. sol. | Extraction better at higher pH. |
| Ag ⁺ | 5-6 | Purplish-Black | Sol. | |
| Fe ⁺⁺⁺ | 4-5 | Red | Sol. | |
| UO ₂ ⁺⁺ | 3-4 | None | - | Water-soluble brick-red color. |
| Bi ⁺⁺⁺ | 5-6 | None | - | |
| Y ⁺⁺⁺ | 6 | None | - | |
| Ce ⁺⁺⁺ | 5 | Brown | Sol. | |
| Th ⁺⁺⁺⁺ | 3 | White | Insol. | |
| ZrO ⁺⁺ | 5-6 | White | Insol. | |
| Ca ⁺⁺ | 5 | None | - | Slight turbidity in H ₂ O. |
| Mg ⁺⁺ | 6 | None | - | |
| La ⁺⁺⁺ | 5 | None | - | |
| U ⁺⁺⁺⁺ | 5 | Orange | Sol. | |

The results indicate that benzohydroxamic acid forms chelate compounds with so many cations that it cannot be regarded as a selective reagent.

α -Naphthohydroxamic acid. It was important that the behavior of this reagent with zirconium and thorium (UX₁) be investigated. The tracer scale extractions were done in the usual way, using 68 day Zr⁹⁵ and 24 day Th²³⁴ (UX₁) activities. Under the same conditions under which Pu(III) extractions are nearly complete, Er(IV) and Th(IV) extractions are appreciable. Table 20 contains the results of two such experiments.

Table 20

Extraction of Tracer Zirconium
and Thorium by α -Naphthohydroxamic
Acid and Chloroform from
Acetate Solutions

| Element | pH of Aqueous Solution | Per Cent Activity Extracted by Chloroform |
|-----------|------------------------|---|
| Thorium | 3.72 | 0.85 |
| | 4.39 | 58.2 |
| | 4.90 | 62.5 |
| | 5.40 | 71.9 |
| Zirconium | 4.04 | 94.5 |
| | 4.50 | 92.5 |
| | 4.96 | 86.0 |
| | 5.40 | 86.6 |

The data show the similarity of Th(IV) and Zr(IV) to

Pu(III) in their activity toward chelating reagents!

7.2.4 The behavior of various cations with amide oximes

To obtain a qualitative idea of the specificity or selectivity of phenylacetamide oxime, a series of experiments was performed in which 3 to 5 mg of cation were allowed to react with phenylacetamide oxime in 3 ml of acetate-buffered solution at pH 5 to 6. Precipitation and solubility properties are compiled in Table 21.

Table 21

Qualitative Behavior of Milligram Amounts of Various Cations with Phenylacetamide Oxime in Acetate Solutions at pH 5 to 6

| Cation | Precipitate | Solubility of Precipitate in Chloroform |
|-------------------------------|----------------|---|
| UO ₂ ⁺⁺ | Yellow-orange | Soluble |
| Cu ⁺⁺ | Olive green | Soluble |
| Ni ⁺⁺ | None | ----- |
| Fe ⁺⁺⁺ | Red | Soluble |
| Bi ⁺⁺⁺ | White | Insoluble (Hydroxide) |
| La ⁺⁺⁺ | None | ----- |
| Ce ⁺⁺⁺ | White | Insoluble (Hydroxide) |
| Th ⁺⁺⁺⁺ | White | Insoluble (Hydroxide) |
| U ⁺⁺⁺⁺ | Greenish-brown | Soluble |

It can be seen that phenylacetamide oxime is very similar to benzohydroxamic acid in its reactions with various cations.

For the experiments designed to study the possible separation of Pu(III) from Zr(IV) a solution containing both activities was obtained from J. A. Ayres. Each experiment (Table 22) involved the use of about 43 μ g of plutonium and about 160,000 counts per minute of zirconium activity in 2 ml of acetate-buffered solution. In all of the experiments, phenylacetamide oxime, which is fairly soluble in water, was added to the buffered solution and allowed to react for 2 hours before extraction with chloroform. The extraction step was preceded by a reduction step. Three different reducing agents were studied to compare the effect of different media on phenylacetamide oxime.

Table 22

The Extraction of Plutonium(III) and Zirconium(IV) by Phenylacetamide Oxime and Chloroform from Acetate Solutions at pH 5 to 6

| Conditions for Reducing Plutonium | Per Cent Activity Extracted by Chloroform | |
|---|---|--------|
| | Pu(III) | Zr(IV) |
| Saturated SO ₂ solution, 4 hrs. | 0.1 | 0 |
| 2 M NH ₂ OH·HCl, HCl, 4 hrs. | 91.9 | 37.0 |
| 2 M N ₂ H ₄ ·HCl, HCl, 4 hrs. | 64.2 | 59.2 |

Again, Zr(IV) shows the same persistent similarity to Pu(III) in its reactivity with organic reagents.

7.3 Discussion

None of the reagents discussed above is applicable to the direct extraction of plutonium from dissolver solutions of uranyl nitrate. Disal, α -naphthohydroxamic acid, and phenylacetamide oxime form chelate compounds with UO_2^{++} and U^{+4} ions, as well as with many other ions. However, some of the reagents find practical use in many laboratory operations with plutonium.

Disal effects very good separations of plutonium from the rare earths. This reagent will remove tracer amounts of Pu(IV) from solutions containing large amounts of lanthanum. Since LaF_3 is a very common carrier for tracer amounts of Pu(III) or Pu(IV), disal extractions make available a versatile method of recovering plutonium from miscellaneous solutions. In a typical recovery procedure, LaF_3 precipitations are made from solutions to concentrate the plutonium. The fluoride is converted to the sulfate by fuming to dryness with H_2SO_4 , the sulfate taken into solution and buffered to pH 3 to 4 for disal extractions. In this way, plutonium is separated from rare earths and lanthanum without the oxidation-reduction procedures used earlier in project history. Disal extractions have been used repeatedly in this labora-

tory for recovery purposes and have been found to give consistently good results.

It can be seen from the data in Table 17 that disal extractions are not applicable to the separation of plutonium from iron. However, by preceding disal extractions with the fluoride precipitation step described above, very good separations from iron are obtained.

The behavior of Th(IV) and Zr(IV) with organic reagents for plutonium was of especial interest. The solution chemistry of these two elements is quite similar in many respects to that of plutonium. This is especially true in the adsorption process for extraction and decontamination of plutonium (81). The principal contaminants in the product solution from this process are Zr(IV), one of the fission products, and Th(IV) as UX₁, the daughter of U²³⁸ by α -emission.

The behavior of Th(IV) and Zr(IV) with disal is remarkably like that of Pu(IV). In extractions with disal and chloroform, Zr(IV) is extracted almost as completely as Pu(IV) in comparable pH ranges, and the stability of the Zr(IV)-disal complex toward dilute HNO₃ is too similar to that of the Pu(IV)-disal complex to make possible practical separations of Zr(IV) from Pu(IV) by appropriate acid re-extraction cycles. The same phenomena are true for oxalic acid re-extractions. The relative efficiency of disal extractions of Th(IV) is

somewhat less than that for Pu(IV) at different pH's, but the differences are not great enough to be of use in separating Pu(IV) from Th(IV).

The similarity of Th(IV) and Zr(IV) to Pu(IV) in reactions with chelating reagents has been noticed by others, and some investigators have used Th(IV) as a "stand-in" substitute for Pu(IV) in exploratory studies with organic reagents (91).

A possibility for separating Zr(IV) and Th(IV) from plutonium arises from the fact that the chelating properties of Pu(III) differ from those of Pu(IV). Some of the β -diketonates, for example, complex Pu(IV) and Zr(IV), but not Pu(III) (92). Thus, a benzene solution of the Pu(IV) and Zr(IV) chelates is treated with a reducing solution, such as hydroxylammonium chloride, hydrosulfite or stannous solution, so that the Pu(III) formed is transferred to the aqueous layer, leaving the Zr(IV) chelate in the benzene.

Similar reduction procedures are not effective with disal complexes. The disal complexes are less stable toward acids than are the diketonates, and will not withstand the acid concentrations necessary for the reduction of Pu(IV) to Pu(III). At pH's high enough for stable disal complexes, hydroxylammonium chloride converts the Schiff's base to the corresponding oxime of the aldehyde, and SO₂ reduces the diimine to a diamine which has no complexing properties.

The hydroxamic acids are quite reactive in forming che-

late compounds with many cations (87, 93), so their applicability to the decontamination and purification of plutonium is rather limited. The behavior of Zr(IV) and Th(IV) with α -naphthohydroxamic acid (See Table 20) is so similar to that of Pu(III) that separations of the three elements cannot be achieved in a single operation. Oxidation-reduction cycles, in combination with extraction operations, are of no value, either, because α -naphthohydroxamic acid also complexes Pu(IV).

The amide oximes are quite similar to hydroxamic acids in their reactions with many cations (93), and their applicability to general problems of decontamination and purification of plutonium is limited. Like α -naphthohydroxamic acid, phenylacetamide oxime does not effectively separate Pu(III) from Zr(IV). With hydroxylammonium chloride as reductant, however, phenylacetamide oxime extractions removed 37 per cent of Zr(IV) compared with 86 per cent extraction of Zr(IV) by α -naphthohydroxamic acid under similar conditions. Phenylacetamide oxime in the presence of SO₂ was inactive toward both Pu(III) and Zr(IV), probably because of reduction of the oxime to an amine. Phenylacetamide oxime has some activity for Pu(IV), as well as for Pu(III) so oxidation-reduction cycles would be of no value in plutonium-zirconium separations.

VIII SUMMARY

1. A brief discussion of the chemical properties of plutonium has been presented, with emphasis on the solution chemistry of plutonium. The general chemical properties of plutonium and other transuranium elements, along with the absorption spectra of their aqueous solutions, indicate that they may be members of a transition group in which the 5f subshell is being filled.

2. The various factors involved in the formation of chelate compounds have been reviewed.

3. Exploratory experiments with organic reagents and tracer plutonium have been shown to be satisfactory for qualitative tests for chelating activity of organic reagents for plutonium. In most of the tracer scale experiments, the concentrations of plutonium were of the order 10^{-10} to 10^{-8} M. Except in the case of salicylaldehyde, positive results obtained from exploratory tracer scale experiments were verified in experiments in which amounts of plutonium from 100 μ g to 3 mg were used.

4. In exploratory experiments with Pu(IV) tracer, 45 different bidentate reagents were examined for chelating activity. All of the reagents examined were known to form chelate compounds with certain metal ions. Chloroform was used as the solvent in most of the experiments, and, using

a volume of chloroform equal to that of the buffered aqueous solution, extractabilities greater than 10 per cent were taken as evidence of complex formation. Bidentate reagents which formed inner complexes with Pu(IV) include quinalizarin, o-hydroxybenzophenone, benzoylacetone, dibenzoylmethane, trifluoroacetylacetone, benzohydroxamic acid, phenylacetamide oxime, isonitrosoacetophenone, salicylal- $\sqrt{2}$ -hydroxyphenyl $\sqrt{7}$ -imine, o-hydroxyacetophenone semicarbazide, and 8-hydroxyquinoline.

5. Systematic studies of the behavior of 26 quadridentate reagents with Pu(IV) tracer were made. The most active quadridentate chelating reagents are the Schiff's bases prepared from ethylenediamine and various derivatives of salicylaldehyde. Nineteen different derivatives of disalicylaldehyde ethylenediimine were compared in their chelating activity with Pu(IV) tracer. The Schiff's base which effected most complete chelating activity with Pu(IV) over the greatest range of hydrogen ion concentration was di- $\sqrt{2}$,3-dihydroxy-5 or 6-tert.-butyl-benzal $\sqrt{7}$ -ethylenediimine, referred to in this thesis as "disal".

6. Exhaustive attempts to prove the position of the tert.-butyl radical in disal were unsuccessful. Positive proof of structure depended on the oxidation of the tert.-butyl radical to a carboxyl group, and tertiary alkyl radicals are peculiarly resistant to oxidation.

7. Fourteen different solvents, including hydrocarbons,

chlorinated hydrocarbons, alcohols, ethers, esters, and ketones were found to be satisfactory for extractions of the Pu(IV)-disal complex.

8. The determination of the composition of the Pu(IV)-disal complex gave definite evidence that the coordination number of Pu(IV) is eight. Orbitals which might be involved in 8-coordinate complexes were discussed.

9. The spectrophotometric behavior of the Pu(IV)-ferron complex was studied, and it was suggested that a method for the spectrophotometric estimation of iron in plutonium, with ferron as reagent, is possible.

10. Twenty-seven different bidentate reagents were examined for their chelating activity with Pu(III). Reagents which form chelate compounds with Pu(III) include 8-hydroxyquinoline, benzohydroxamic acid, m-nitrobenzohydroxamic acid, o-hydroxybenzohydroxamic acid, α -naphthohydroxamic acid, phenylacetohydroxamic acid, n-valerohydroxamic acid, phenylacetamide oxime and n-valeramide oxime.

11. The composition of Pu(III)- α -naphthohydroxamate was determined, and it was shown that the coordination number of Pu(III) is six. Orbitals which might be involved in 6-coordinate complexes were discussed.

12. All of the organic reagents found to form chelate compounds with Pu(III) and Pu(IV) also exhibit rather general complexing activity with many other cations. These

factors limit the use of organic reagents for the decontamination and purification of plutonium.

13. Disal extractions were found to be effective for separating plutonium from alkali metals and rare earths. Partial separations of plutonium from barium can be achieved, but no method could be devised for adapting disal extractions to the separation of plutonium from zirconium and thorium. The use of oxidation-reduction cycles for separating plutonium from zirconium and thorium was found ineffective because the media necessary to reduce Pu(IV) to Pu(III) destroy the organic reagent.

14. Phenylacetamide oxime and α -naphthohydroxamic acid were found to complex Pu(III) quite completely and Pu(IV) to a lesser degree. The reactivities of both of these reagents with thorium and zirconium are too similar to their reactivities with plutonium to make possible the separation of plutonium from zirconium and thorium.

IX LITERATURE CITED

1. McMillan, E. M., and P. H. Abelson, Phys. Rev., 57, 1185 (1940).
2. Seaborg, G. T., E. M. McMillan, A. G. Wahl, and J. W. Kennedy, Phys. Rev., 69, 366, 367 (1946),
3. Bohr, N., and J. A. Wheeler, Phys. Rev., 55, 420 (1939).
4. Turner, L. A., Phys. Rev., 57, 950 (1940).
5. Anderson, H. L., E. Fermi, and H. B. Hanstein, Phys. Rev., 55, 797 (1939).
6. Smyth, H. D., "Atomic Energy for Military Purposes", Princeton University Press, Princeton, 1945.
7. Seaborg, G. T., Chem. Eng. News, 23, 2190 (1945).
8. Thomas, G. A., and J. C. Warner, "The Chemistry, Purification and Metallurgy of Plutonium", Manhattan District, 1945.
9. "Plutonium Project Record", Division IV of the Manhattan Project Technical Series, 1946, Volumes XIVA and XIVB.
10. Hindman, J. C., Metallurgical Project Report CN-1587, p. 2, May 1, 1944.
11. Waters, J. I., Metallurgical Project Report CK-1371, p. 10, March 1, 1944.
12. Quill, L. L., Chem. Rev., 23, 98 (1938).
13. Yost, D. M., H. Russell and C. S. Garner, "Advanced Inorganic Chemistry", privately printed in the U. S. A., 1944, Ch. 13.
14. Seaborg, G. T., Chem. Eng. News, 24, 899 (1946).
15. Morgan, G. T., and H. D. K. Drew, J. Chem. Soc., 117, 1456 (1920).
16. Johnson, J. R., in "Organic Chemistry", edited by Henry Gilman, John Wiley and Sons, New York, 1943, p. 1868.

17. Diehl, H., Chem. Rev., 21, 39 (1937).
18. Mellon, M. G., "Colorimetry for Chemists", G. F. Smith Chemical Co., Columbus, Ohio, 1945, p. 11.
19. (a) Mellan, I., "Organic Reagents in Inorganic Analysis", Blakiston Company, Philadelphia, 1941.
(b) Yoe, J. H., and L. A. Sarver, "Organic Analytical Reagents", John Wiley and Sons, New York, 1941.
(c) Feigl, F., "Specific and Special Reactions for Use in Quantitative Analysis", (translated by R. E. Oesper), Elsevier Publishing Company, New York, 1940.
(d) Prodinger, W., "Organic Reagents Used in Quantitative Inorganic Analysis", (translated by S. Holmes), Elsevier Publishing Company, New York, 1940.
(e) Hopkins and Williams, "Organic Reagents for Metals", Hopkins and Williams, Ltd., London, 1944.
20. Sidgwick, N. V., "Electronic Theory of Valency", Oxford University Press, Oxford, 1929.
21. Sidgwick, N. V., J. Chem. Soc., 1941, 433.
22. Pfeiffer, P., in K. Freudenberg's "Stereochemie", Franz Deuticke, Leipzig, 1933, pp. 1200-1377.
23. Pfeiffer, P., Angew. Chem., 53, 93 (1940).
24. Pfeiffer, P., J. prakt. Chem., 162, 279 (1943).
25. Pauling, L., "The Nature of the Chemical Bond", 2nd ed., Cornell University Press, Ithaca, N. Y., 1942, pp. 92-123.
26. Kimball, G. E., J. Chem. Phys., 8, 188 (1940).
27. Ingold, C. K., Chem. Rev., 15, 225 (1934).
28. Orlemann, E. F., Metallurgical Project Memorandum, MUC-GTS-888, July 17, 1944, p. 8.
29. Spacc, G., and P. Voichescu, Z. anorg. allgem. Chem., 226, 273 (1936).

30. Calvin, M., and K. W. Wilson, J. Am. Chem. Soc., 67, 2003 (1945).
31. Bailar, J. C., Chem. Rev., 23, 65 (1938).
32. Copley, M. J., L. S. Foster, and J. C. Bailar, Chem. Rev., 30, 227 (1942).
33. Selwood, P. W., "Magnetochemistry", Interscience Publishers, New York, 1943, Ch. 6.
34. Tschugaeff, L., J. prakt. Chem., 75, 153 (1907).
35. Werner, A., Ber., 41, 1062 (1908).
36. Pfeiffer, P., E. Breith, E. Lübke, and T. Tsumaki, Ann., 503, 84 (1933).
37. Dent, C. E., and R. P. Linstead, J. Chem. Soc., 1934, 1027.
38. Blanchard, A. A., J. Chem. Education, 20, 459 (1943).
39. Langham, W. H., Metallurgical Project Report CK-2254, no date, p. 9.
40. Metallurgical Project Handbook CL-697, 2nd ed., 1945, Ch. VII.
41. Simpson, J. A., Metallurgical Project Report CP-1817, May 8, 1945.
42. Dennstedt, M., and J. Zimmermann, Ber., 21, 1553 (1888).
43. Elkins, M., and L. Hunter, J. Chem. Soc., 1935, 1598.
44. Blatt, A. H., "Organic Syntheses", Collective Volume II, John Wiley and Sons, New York, 1943, p. 67.
45. Delephine, M., Bull. soc. chim., /4/, 3, 641 (1908).
46. Tiemann, F., and P. Krüger, Ber., 17, 1685 (1884).
47. Liggett, L. M., "The Synthesis of o-Hydroxyaldehydes", Ph. D. Thesis, Iowa State College, Ames, 1943.
48. Duff, J. C., J. Chem. Soc., 1941, 547.
49. Combes, A., and C. Combes, Bull. soc. chim., /3/, 7, 779 (1892).
50. Meyer, V., Ber., 10, 2075 (1877).

51. McConnan, J., and M. E. Marples, J. Chem. Soc., 91, 194 (1907).
52. Bamberger, E., and W. Pemsel, Ber., 36, 62 (1903).
53. Rollefson, G. K., and H. W. Dodgen, Metallurgical Project Report CK-1148, December 13, 1943.
54. Urbain, M. C., Bull. soc. chim., /3/ 15, 347 (1896).
55. Biltz, W., and J. A. Clinch, Z. anorg. Chem., 40, 218 (1904).
56. Job, A., and P. Goissedet, Compt. rend., 157, 50 (1913).
57. Dixon, J. S., Metallurgical Project Report CK-2089, September 1, 1944, p. 16.
58. Calvin, M., Metallurgical Project Report CN-2486, December 1, 1944.
59. Blaedel, W. J., A. J. Margolis, and J. Seidlet, Metallurgical Project Report CN-2496, January 1, 1945, p. 33.
60. Crandall, H. W., J. R. Thomas, and J. C. Reid, Metallurgical Project Report CN-2657, January 15, 1945.
61. Winner, B. M., Metallurgical Project Report CN-2887, April 28, 1945, p. 7.
62. Crandall, H. W., and J. R. Thomas, Metallurgical Project Report CN-2999, May 9, 1945.
63. Cowan, G. A., and M. Goldsmith, Metallurgical Project Report CK-1552, April 1, 1944, p. 5.
64. Langham, W. H., G. A. Cowan, S. Wexler, H. S. Dunham, and H. A. Potratz, Metallurgical Project Report CK-2254, no date, p. 9.
65. Thompson, S. G., Metallurgical Project Report CN-328, October 31, 1942, p. 10.
66. Willard, J. E., and E. E. Turk, Metallurgical Project Report CN-282, September 30, 1942, p. 7.
67. Patton, R. L., Metallurgical Project Report CK-1587, April 1, 1944, p. 15.
68. Dixon, J. S., Metallurgical Project Report CK-1763, July 1, 1944, p. 4.

69. Combes, A., and C. Combes, Compt. rend., 108, 1252 (1889).
70. Pfeiffer, P., and H. Pfitzner, J. prakt. Chem., 145, 243 (1936).
71. Pfeiffer, P., T. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, J. prakt. Chem., 149, 217 (1937).
72. Dixon, J. S., Metallurgical Project Report CK-1763, July 1, 1944, p. 4.
73. Duffield, R. B., and M. Calvin, J. Am. Chem. Soc., 68, 557 (1946).
74. Hecht, F., and W. Reich-Rohrwig, Monatsh., 53-54, 596 (1929).
75. Frere, F. J., J. Am. Chem. Soc., 55, 4362 (1933).
76. Marchi, L. E., W. C. Fernelius, and J. P. McReynolds, ibid., 65, 329 (1943).
77. Hoard, J. L., and H. H. Nordsieck, ibid., 61, 2853 (1939).
78. Marchi, L. E., and J. P. McReynolds, ibid., 65, 333 (1943).
79. Pfeiffer, P., H. Thielert, and H. Glaser, J. prakt. Chem., 152, 145 (1939).
80. Clark, R. E., Metallurgical Project Report CN-2519, August 1, 1944, p. 54.
81. Ayres, J. A., Metallurgical Project Report CN-2718, May 11, 1945.
82. Yoe, J., J. Am. Chem. Soc., 54, 4139 (1932).
83. Yoe, J., and R. T. Hall, ibid., 59, 872 (1937).
84. Swank, H. W., and M. G. Mellon, Ind. Eng. Chem., Anal. Ed., 9, 406 (1937).
85. Hindman, J. C., and D. Ames, Metallurgical Project Report CN-2289, November 1, 1944.
86. Yale, H. L., Chem. Rev., 33, 209 (1943).
87. Werner, A., Ber., 41, 1062 (1908).

88. Wolter, F. J., and H. D. Brown, Metallurgical Project Report CN-1495, April 10, 1945, p. 17.
89. Latimer, W. M., "Oxidation Potentials", Prentice-Hall, Inc., New York, 1938, p. 201.
90. Wolter, F. J., H. D. Brown, J. M. Wright and R. R. Raeuchle, Metallurgical Project Report CN-1783, August 10, 1944, pp. 13-19.
91. Cowan, G. A., R. E. Fryxell, and H. A. Potratz, Metallurgical Project Report OK-993, October 9, 1943.
92. Crandall, H. W., and J. R. Thomas, Metallurgical Project Report CN-2999, May 9, 1945.
93. Lossen, W., Ann., 161, 347 (1872).

X ACKNOWLEDGMENTS

The writer expresses his indebtedness to those who have helped make these studies possible.

Dr. F. H. Spedding, as Project Director, suggested the problem, and has given overall supervision and encouragement during the development of the problem.

Dr. A. F. Voigt was in immediate charge of the writer's research, and his suggestions and constant cooperation are deeply appreciated.

Dr. Harvey Diehl, as consultant for the Project, gave many worthwhile suggestions, and furnished many of the organic compounds used in the work.

H. D. Brown assisted in much of the work with tracer and micro amounts of plutonium, and J. M. Wright did many of the exploratory tracer scale experiments. R. F. Rauehle assisted in the preparation of several of the organic reagents examined.

Other members of the Project have also given their complete cooperation, without which many of the studies would have been much more difficult.

Sincere appreciation goes to Dr. I. B. Johns, who directed the writer's graduate studies before they were interrupted by the war.

The research described in this thesis was sponsored

by the Corps. of Engineers, Manhattan District, United States Army, and the funds for its support came from Contract W-7405-eng-82 between the Manhattan District and Iowa State College.