ON THORIUM OXINATES

AND

THEIR ANALYTICAL PROPERTIES

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By

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SCOPE AND CONTENTS:

    2-Methyloxine is shown to be superior to oxine as a reagent for
the determination of thorium. The conditions under which thorium is
precipitated quantitatively and solely as 1:4 thorium 2-methyloxinate
have been carefully investigated, and the results shown to lead to
precise, accurate, and sensitive gravimetric, bromometric, and polaro-
graphic methods for the determination of thorium. The polarography of
2-methyloxine in alkaline solution has been studied, and an attempt to
elucidate the reduction process has been made.

    In contrast to 2-methyloxine, and in contrast to what has been
believed, oxine precipitates thorium only as a compound of 1:5 stoichio-
metry. An accounting for this difference is made in terms of steric
considerations. The structural nature of 1:5 thorium oxinate is con-
sidered, this being based on studies involving radioactive oxine and
the stoichiometry of the heretofore unprepared thorium 3- and 4-methyl-
oxinates.

ACKNOWLEDGEMENTS

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GENERAL INTRODUCTION

Oxine (8-hydroxyquinoline, 8-quinolinol) reacts with metal ions to form chelate compounds, having five-membered rings, which are of considerable analytical importance. Indeed, for purposes of inorganic analytical chemistry, no organic reagent has been more extensively investigated than oxine. The literature pertaining to analytical applications of this reagent is profuse: books have been devoted to it (1), and studies of the usefulness of oxine in quantitative determinations, qualitative detections, or in separations of metal ions continue to appear every month in the literature.

Much of the attention that oxine has claimed from analytical chemists stems from the very unusual versatility of this compound. Gravimetric, absorptiometric, fluorimetric, polarographic, and nitrometric methods have all been developed for the determination of one metal ion or another. A variety of titrimetric methods have also been developed: these include bromometric, photometric, potentiometric, coulometric, and amperometric titrations.

Oxine is non-selective in its reaction with metal ions. This catholicity in reactivity, which in instances limits the usefulness of the reagent, is a characteristic which, among organic reagents, is not peculiar to oxine, although it can be a more serious limitation with this reagent than with others.

Certain measures, however, can be taken to increase the selectivity of oxine for the purpose at hand. For example, by appropriate

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control of pH, or by "masking" interfering ions by appropriate com-
plexing agents, or by both, the requisite selectivity may be achieved.
Judicious control of pH and of the use of complexing agents have been
exploited in both precipitations for gravimetric purposes and in solvent
extractions for absorptiometric determinations. The increased knowledge
in recent years about the nature and stability of complexes has some-
what reduced the importance that has been accorded organic reagents that
are inherently more selective in their reactivity than oxine.

An interesting derivative of oxine, 2-methyloxine (2-methyl-8-
hydroxyquinoline, 8-hydroxyquinaldine), attracted attention when it was
discovered (2) that, unlike oxine, it does not precipitate aluminium.
The failure of 2-methyloxine to precipitate aluminium has been attri-
buted (3,4,5,6,7) to a steric effect, imposed by the methyl group, which
prevents the grouping of the three organic ligands about the small
aluminium ion (the smallest of all the metal ions precipitated by oxine).
Although the methyl group in the 2-position, close to the chelating
nitrogen atom, decreases the stability of the metal chelates of 2-methyl-
oxine (at least in aqueous dioxane solutions (8,9)), the compound is not,
nevertheless, much more selective than oxine. It forms precipitates
with the same metal ions, with the exception of aluminium, that oxine
does. Even so, 2-methyloxine has achieved some significance as an
analytical reagent: a reasonable number of methods (e.g., 2,10,11,12,13)
which make use of 2-methyloxine have been proposed.

At the time the present work was begun, there existed some evi-
dence - although not well established evidence - that oxine and 2-methyl-
oxine react differently with thorium. Oxine gives with thorium a com-

pound of 1:5 stoichiometry, whereas there was an indication that 2-methyloxine reacts with thorium to give a compound of 1:4 stoichiometry. Although several aspects of the chemistry of oxine and thorium are unclear, the 1:5 thorium oxinate has long been known and analytical use has been made of it. Thorium 2-methyloxinate, essentially unknown, had acquired no analytical significance in determinations of thorium.

Thorium has been one of the so-called less common elements, the analytical chemistry of which has been less well developed than that of the traditional elements. The discovery of fission and subsequent developments in the nuclear field have made thorium an important element and, as a consequence, its analytical chemistry has received greatly increased study in recent years.

Included in this study have been investigations of a massive number of organic reagents as means of determining thorium. Many, in fact most, of these reagents have been only sparingly studied (14). For example, the pH range over which quantitative precipitation may be obtained has often not been defined, and matters such as contamination of the precipitate by the organic reagent, and the effect on the composition of the precipitate of variations in pH and other conditions of precipitation, are frequently given little or no attention. On examination of the voluminous literature, the feeling emerges that more thorough studies of fewer organic precipitants for thorium would have been more desirable.

Almost all of the organic reagents proposed for thorium have proven unsuitable or have serious drawbacks (14). A large number of

these reagents appear to yield precipitates of variable composition (mixtures of basic compounds); other reagents appear to precipitate thorium quantitatively in the form of compounds of fixed stoichiometry, but with thermal characteristics that preclude direct weighing. In such instances the favourable gravimetric factor inherent in the thorium-organic compound is lost.

Oxine is one of the few of the many organic reagents studied that has been proven to react with thorium to give a non-basic, stoichio-metric compound. It was anticipated that 2-methyloxine, a close relative, would also yield with thorium a non-basic, stoichiometric compound, but with possibly improved thermal stability.

This thesis is concerned with thorium oxinates, this expression being here used in a general way to refer to the compounds that deriva-tives of oxine, as well as oxine itself, form with thorium. Study is given to several such oxinates, but particularly to those derived from oxine and 2-methyloxine. In the present work, an investigation is made of some aspects of the chemistry of oxine and thorium about which there is confusion and disagreement, with particular attention being given to the composition of the thorium oxinate precipitated from cold solution, and to the structural nature of the long-known 1:5 thorium oxinate. An investigation is made also of the reaction of 2-methyloxine with thorium, with a view to obtaining quantitative precipitation of thorium as a non-basic, stoichiometric 2-methyloxinate, and to the development of ana-lytical methods for the determination of thorium based on this reagent.

HISTORICAL INTRODUCTION

PART A   Thorium and Oxine

The earliest work with oxine and thorium appears to be that of Hecht and Reich-Rohrwig (15). These workers thought the orange-red precipitate obtained from hot aqueous solution to be a hydrated compound of 1:4 stoichiometry, $Th(C_9H_6ON)_4 \cdot xH_2O$. Frere (16) showed subsequently that the compound was of 1:5 stoichiometry, containing one molecule of oxine in excess of the normal valence requirement of Th(IV). In a later paper, Hecht and Ehrmann (17) substantiated this finding. Since Frere's work, the compound has usually been formulated as $Th(C_9H_6ON)_4 \cdot C_9H_7ON$.

Several workers have shown that thorium can, under appropriate conditions, be quantitatively precipitated by oxine from aqueous solution as $Th(C_9H_6ON)_4 \cdot C_9H_7ON$ (16,17,18). Unfortunately, this compound has poor thermal stability.

The 1:5 stoichiometry of the orange-red compound precipitated from hot solution and the quantitative precipitation of thorium by oxine are the only significant aspects of the chemistry of thorium and oxine about which workers are unanimously agreed. In other aspects, the literature is marked by an impressive amount of confusion and disagreement. For the sake of clarity, these aspects are treated in separate sections below.

(a) Composition of Thorium Oxinate Precipitated from Cold Solution: When thorium is precipitated by oxine from cold aqueous solution (i.e.,

50°C. and lower), the precipitate is yellow and more voluminous than the orange-red precipitate obtained from hot aqueous solution. Hecht and Reich-Rohrwig (15) considered this yellow precipitate to be the normal 1:4 compound, $Th(C_9H_6ON)_4$, without water of crystallization, although they gave no analytical data to support this view. They apparently identified this compound with the yellow substance (believed to be $Th(C_9H_6ON)_4$) that may be obtained by appropriately heating, or extracting with ethanol, the orange-red compound.

The same identification, again without supporting experimental data, was made in a review (19) of the analytical chemistry of thorium. The reviewers state that Frere "pointed out that the yellow material [that Hecht and Reich-Rohrwig (15) obtained by precipitation in the cold] corresponded to $Th(C_9H_6ON)_4$." Frere, in fact, did not point this out; he was not even concerned with the yellow substance obtained by low-temperature precipitation. His interest, rather, was with a yellow material, which he believed to be $Th(C_9H_6ON)_4$, obtained by appropriately heating the orange-red precipitate. The reviewers, if they did not misread Frere's paper, assumed that the yellow substance that Frere prepared thermally was the same chemical entity that can be obtained by precipitation at low temperature.

The belief that a yellow 1:4 compound can be precipitated from aqueous solution at 50°C. and lower temperatures appears again in two papers by Indian workers (20,21). In one of these (20), the authors claim to have precipitated the 1:4 compound, and to have confirmed the formula both by igniting a weighed sample to thorium dioxide and by bromometric titration of the oxine groups, but they give no data to

reinforce this claim. Yet, in their paper, the authors give in detail other experimental data of substantially lesser significance. In the light of this and much evidence (22) indicating that these workers have misread the literature, their claim cannot be taken seriously.

Finally, in a rather recent paper in Chemical Reviews (23), there appears the definite statement: "By precipitation from a cold solution it is possible to obtain directly the normal thorium oxinate, $Th(C_9H_6ON)_4$." This statement was probably made by the reviewers on the basis of uncritical acceptance of the paper by Eswaranarayana and Rao (20), and carelessness in the treatment of the literature.

There is no acceptable experimental data in the literature to establish that thorium can be precipitated by oxine as $Th(C_9H_6ON)_4$. The idea appears to have been propagated through a sequence of mis-readings and misinterpretations. As shall be shown in this thesis, the composition of the yellow thorium oxinate precipitated from cold aqueous solution is not $Th(C_9H_6ON)_4$, in contrast to the several statements in the literature that it is.

(b) Thermal Stability of 1:5 Thorium Oxinate: The thermal stability of the orange-red 1:5 compound has been investigated by several workers, but the extent of their agreement is very modest (Table I).

Despite an earlier claim to the contrary (16), it is now esta-blished that the decomposition of 1:5 thorium oxinate begins below $100^{\circ}C$. (probably at about $80^{\circ}C$.). All the thermogravimetric studies (26,27,28,29) are in agreement on the instability below $100^{\circ}C$. (although there are some major differences in the findings in other respects); so

Table I

THERMAL STABILITY OF 1:5 THORIUM OXINATE

Observations and Claims	Source
1:5 compd. stable to 100-110°C.; begins to lose wt. slowly at 130-140°C.; 1:4 obtained by heating at 160-170°C. for 3 hrs.	Frere (16)
1:5 compd. loses wt. at 100-105°C.	Hecht and Ehrmann (17)
1:5 compd. decomposes to 1:4 by heating at 150-160°C. No time specified.	Berg (24)
1:5 compd. decomposes to 1:4 by heating at 170°C. No time specified.	Ishimaru (25)
Irregular wt. losses throughout range of 20-945°C. No heating rate given.	*Dupuis and Duval (26)
1:5 compd. begins to lose wt. slowly at about 80°C., more rapidly at 130°C.; 1:4 not formed till 275°C. and is stable to 345°C.; ThO$_2$ obtained below 700°C. (heating rate = 3°C./min.).	*Borrel and Pâris (27)
1:5 compd. stable up to 80-85°C.; slow wt. loss thereafter to about 120°C. and then more rapid wt. loss. 1:4 obtained by heating 1:5 at 120-125°C. for 5 hr. and at 135°C. for one hr.	Moeller and Venkataramaniah (18)
1:5 compd. stable to 80°C.; 1:4 obtained at 250°C. and is stable to 310°C.; ThO$_2$ obtained at 600°C. (heating rate = 4.5°C./min.).	*Wendlandt (28)
1:5 compd. stable to about 55-60°C.; 1:4 obtained at about 255°C. but wt. is not constant (heating rate = 3.8°C./min.).	*Van Tassel and Wendlandt (29)

* denotes thermogravimetric studies; heating rates, where reported, are given.

also are the thermal studies of Moeller and Venkataramaniah (18).

The idea that the 1:5 compound can be used for gravimetric pur-
poses after heating it to temperatures above 100°C. has unfortunately
been propagated in some respected books (30,31). This is not to say
that gravimetric determinations of thorium cannot be made using oxine.
Indeed, good determinations can be made (EXPERIMENTAL AND RESULTS,
PART B) if a sufficiently low drying temperature is used over an ex-
tended period of time.

When the 1:5 compound is heated strongly at several hundred
degrees, it decomposes to thorium dioxide. Under milder heating con-
ditions it is possible, according to the claims of most workers
(Table I), to prepare the normal 1:4 compound, but there is much dis-
agreement about the conditions for its formation. Although the claims
for the preparation of the 1:4 compound are many, the evidence in the
literature is actually sparse, consisting of observations made from
thermograms (27,28) and only a single elemental analysis (18). There
appears to be no sound experimental basis for the views expressed in
certain textbooks to the effect that the 1:4 compound can be the basis
of a gravimetric method after the precipitated 1:5 compound has been
heated at 150-160°C. (32,33) or 275-345°C. (34).

In view of the considerable amount of disagreement among
workers and of the lack of sufficient analytical data, it must be
considered that the thermal preparation of the pure 1:4 compound from
the 1:5 has not been established.

That the preparation is possible is demonstrated in this thesis
and use of it made in work concerned with the structural nature of 1:5

thorium oxinate.

(c) Reaction of Oxine with 1:4 Thorium Oxinate: Frere (16)
observed that, when the thermally prepared 1:4 thorium oxinate is
placed in a solution containing oxine, the oxinate reacts with oxine
to give an orange-red substance approaching in composition the
1:5 thorium oxinate.

Close study of Frere's paper reveals several deficiencies.
There is no assurance that the starting material, which Frere assumed
to be pure 1:4 thorium oxinate, was indeed pure. Frere prepared the
1:4 compound from the 1:5 compound using his own thermal conditions.
He gives no analyses to prove that the product obtained from his
heating procedure was the pure 1:4 compound and, in fact, there is
reason to believe that it was not (EXPERIMENTAL AND RESULTS, PART A,
(b)). Next, the conditions under which the experiments were done are
given in only barest outline. The solvent for oxine, the volume of
oxine solution used, and the temperature and time of the addition
reaction are not reported. Lastly, Frere misinterpreted his data when
he calculated that the conversion of the 1:4 to the 1:5 compound is
practically quantitative (about 97 per cent). The conversion, when
calculated correctly from Frere's data is, at best, about 85 per cent.

The deficiencies in Frere's paper do not vitiate his point
that oxine reacts with 1:4 thorium oxinate for, even after consideration
of these, it is obvious that some conversion of the 1:4 to the 1:5
compound occurs. It is equally obvious, however, that a more careful
study of this addition reaction is necessary, particularly in view of
the use to be made of it in this thesis.

(d) Structural Nature of 1:5 Thorium Oxinate: When oxine (HON) reacts with metal ions, it normally gives five-membered ring chelates having the general formula $M(ON)_x$, where M is a metal ion of charge x and ON is the oxine anion.

With thorium (16), scandium (35), uranium(VI) (15), and plutonium(VI) (36), however, oxine yields metal chelates having the general formula $M(ON)_x \cdot HON$, in which there is one molecule of oxine in excess of the valence requirement of the metal ion. The nature of the forces binding the "extra" molecule of oxine have been the subject of a few investigations, some of which (18,20,29) have been concerned with the 1:5 thorium compound, $Th(ON)_4 \cdot HON$.

Two views about the structural nature of 1:5 thorium oxinate have been advanced. In one (18,29), the "extra" molecule of oxine is considered to be a component of the crystal lattice, where it is held by weak lattice forces, the other four oxine ligands being chelated to the central thorium atom. In the other (20), all five oxine groups are thought to be equivalent, each directly associated with the central thorium atom. The evidence leading to these views follows.

Moeller and Venkataramaniah (18) studied the absorption spectra of the 1:4 and 1:5 thorium oxinates in chloroform. They found that the addition of an equivalent quantity of oxine to a chloroform solution of the 1:4 chelate gives an absorption spectrum nearly identical to that of the 1:5 chelate, suggesting strongly to them that upon dissolution of the 1:5 chelate, the "extra" molecule of oxine is lost.

These investigators also determined the values for the interplanar "d" spacings for both the 1:5 and the 1:4 compounds by X-ray

diffraction. From the data they concluded that in the solid state the two compounds are different. A comparison of the "d" values of the 1:5 and 1:4 compounds with those for oxine, and of an equimolar mixture of the 1:4 compound and oxine, indicated further that in the 1:5 compound some form of bonding involving the "extra" molecule of oxine must occur, rather than a simple physical mixing. The investigators concluded that although in the solid state the 1:5 compound is a different species from the 1:4 compound, in solution they become indistinguishable, and that, probably, the "extra" molecule of oxine in the 1:5 compound is only a component of the crystal lattice.

Using a calorimetric method, Van Tassel and Wendlandt (29) determined the heat of interaction for the reaction, represented by the equation below, between the "extra" molecule of oxine and the 1:4 chelate.

$$Th(ON)_4{}_{solid} + HON_{solid} = Th(ON)_4 \cdot HON_{solid}$$
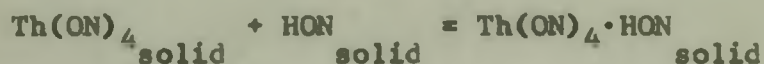
According to the investigators, the low value (-6.5 ± 0.2 Kcal./mole) obtained for the heat of interaction supports the view that the additional molecule of oxine is held in the crystal lattice.

This interpretation of the measured heat of interaction has been criticized (37). It ignores any energy involved in the rearrangement of the normal 1:4 complex on removal of the "extra" molecule.

The validity of claims based on the experimental work by Moeller and Venkataramaniah and by Van Tassel and Wendlandt is open to some question. The 1:4 thorium oxinate used by both pairs of workers was prepared thermally from 1:5 thorium oxinate by a method (18) that is

questionable (EXPERIMENTAL AND RESULTS, PART A, (b)). This casts some
doubt on the purity of the 1:4 compound used in these absorptiometric
(18) and calorimetric (29) investigations.

The structural nature of 1:5 thorium oxinate has also been
studied absorptiometrically by Eswaranarayana and Rao (20). These
workers found that, in dilute hydrochloric acid, the absorption of the
1:5 compound is just that which would be due to five oxine groups,
suggesting dissociation of the compound into its constituent parts. The
absorption of the 1:4 thorium oxinate in dilute hydrochloric acid is
less than that due to four oxine groups, indicating incomplete dissoci-
ation of the 1:4 compound. This implies that the 1:4 compound is more
stable than the 1:5 compound. From this evidence the authors concluded
that, in the 1:5 compound, all five oxine groups are bonded to the thor-
ium atom, and that the compound should be formulated as $Th(ON)_5$.

This formulation is open to more than one criticism. Firstly,
since the ON residues are anions, resulting from the ionization of the
phenolic hydrogen in the oxine molecule, the formulation implies that
thorium exists in an oxidation state +5. Since thorium has not yet
been found to exist in any oxidation state other than +4 (38), more
evidence than that presented by the authors is necessary to establish
a +5 oxidation state for this element. Secondly, since by appropriate
heating of the 1:5 compound oxine is liberated, any formulation of the
1:5 compound must allow for the presence of a proton which, with an ON
residue, can yield oxine when the 1:5 compound is heated. The formu-
lation $Th(ON)_5$ makes no provision for this proton.

These criticisms are of the authors' formulation of 1:5 thorium

oxinate as $Th(ON)_5$, and not of their contention that all five oxine groups are bonded to the thorium atom. Their formulation would better have been made as $H\left[Th(ON)_5\right]$ (DISCUSSION, PART A, (d)), which would meet the two objections raised against the formulation $Th(ON)_5$.

A more serious criticism of this work concerns the source of 1:4 thorium oxinate used in it. The authors claim to have prepared the 1:4 compound by precipitating it from aqueous solution at below $50^{o}C$. As has already been pointed out, there is no experimental evidence to show that 1:4 thorium oxinate can be precipitated from cold solution. In fact, work reported in this thesis (EXPERIMENTAL AND RESULTS, PART A, (a)) proves that 1:5 and not 1:4, thorium oxinate is precipitated from cold solution. This makes it difficult to attribute validity to the work of Eswaranarayana and Rao unless, after precipitation, the 1:5 compound (which they thought to be the 1:4 compound) was converted inadvertently to the 1:4 compound by washing liberally with an organic solvent such as ethanol (17).

Clearly, further studies concerning the structural nature of 1:5 thorium oxinate are desirable. This thesis is concerned in part with these.

PART B   Thorium and 2-Methyloxine

At the time this work was begun, little attention had been given to the reaction between thorium and 2-methyloxine. In fact, the reaction had been reported in only one paper (39), a broad study concerned only in part with thorium and 2-methyloxine. This work, very modest in scope, indicated that thorium is precipitated quantitatively

by 2-methyloxine as a compound of 1:4 stoichiometry, $Th(C_{10}H_8ON)_4$, rather than, as by the parent reagent oxine, a compound of 1:5 stoichiometry.

Repetition of this work showed that the thorium compound precipitated by 2-methyloxine is indeed of 1:4 stoichiometry, but quantitative precipitation of this 1:4 chelate could not be obtained using the sparse directions given (39). Although the precipitate contained all the thorium sought (as shown by ignition to thorium dioxide), it had only 95 per cent, at most, of the thorium as the 1:4 2-methyloxinate. It appeared that a significant amount of the thorium was being precipitated as hydrous thoria or other hydroxo complexes.

In the present work there has been made a careful study of the variables that affect the quantitative precipitation of thorium by 2-methyloxine as the 1:4 chelate. This has led to gravimetric, bromometric, and polarographic methods for the determination of thorium. The gravimetric method takes advantage of the thermal stability of this chelate; the bromometric method takes advantage of the ease with which 2-methyloxine can be quantitatively dibrominated, and the polarographic method takes advantage of the reducibility of 2-methyloxine, a particularly valuable characteristic as thorium cannot be directly determined polarographically (40).

During the course of this study, two papers having to do with thorium and 2-methyloxine appeared. In one of these (41), concerned with a thermogravimetric study of 1:4 thorium 2-methyloxinate, the investigator reported that the chelate possessed thermal stability favourable for analytical purposes. The data given was consistent with that found

in the present study. The other paper (42) is somewhat curious.
Firstly, it in part contradicts the earlier report from the same
laboratory (41) with regard to the thermal stability of the 1:4 thor-
ium 2-methyloxinate. Secondly, it claims a preparation for a compound
of thorium and 2-methyloxine of 1:5 stoichiometry, by precipitation
from aqueous solution.

Close examination of the work concerned with the preparation
of this compound reveals deficiencies in it. The quantity of 2-methyl-
oxine used in the precipitation is about three per cent short of the
theoretical quantity required to give the 1:5 compound. Because of the
extent of hydrolysis of thorium in aqueous solution (even when the
solution is acidic), it is usually necessary, for the preparation of a
pure thorium chelate uncontaminated by basic thorium compounds, to have
present a substantial excess of the chelating agent. Next, the identity
of the 1:5 compound is apparently based on a single precipitation and
single determinations of the thorium and the 2-methyloxine content of
the precipitate. Finally, samples of the supposed 1:5 compound which
were taken for analysis were previously dried at 75°C. for 30 minutes,
but the workers later state that thermogravimetric experiments showed
the "extra" molecule of 2-methyloxine began to sublime at 70°C. In
view of this, it is difficult to see how determination of the thorium
and 2-methyloxine in the compound that these workers obtained yielded
data almost precisely that expected for a 1:5 compound.

When the precipitation described by the investigators was
repeated in the present work, their results were not confirmed.

The polarography of 2-methyloxine had been given some study prior

to the present work. Fernando and Phillips (43) found that 2-methyloxine is reducible at the dropping-mercury electrode throughout the pH range, the form of the polarographic wave varying markedly with changes in pH. In strongly acid solution, the reduction wave was thought likely due to 2-methyl-8-hydroxyquinolinium ion. In weakly acid and weakly alkaline solution, the appearance of the wave is more complicated, and no interpretation of it was attempted. In alkaline solutions of about pH 11 the wave is better defined and the claim was made that the diffusion current is proportional to concentration. At about this pH, the reduction of 2-methyloxine was thought to involve one electron. The relationship in alkaline solution between the half-wave potential $(E_{\frac{1}{2}})$ and pH was given as $-E_{\frac{1}{2}} = 0.59 + 0.084$ pH.

It is difficult to reconcile this relationship with the one-electron process proposed for the reduction. In the polarographic reduction of an organic compound, the electrode reaction is usually of the form:

$$R + aH^+ + ne = RH_a$$
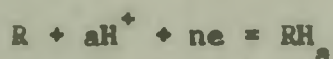
where n represents the number of electrons, e, taking part in the electrode reaction, and RH_a (neglecting the charge) is the reduced form of the organic compound, R. For such a reaction the effect of pH on the half-wave potential is given (44) by:

$$\frac{\Delta E_{\frac{1}{2}}}{\Delta pH} = -0.059 \frac{a}{n}$$

For a one-electron reduction of 2-methyloxine involving one hydrogen ion, $a = n = 1$. Therefore, a plot of $-E_{\frac{1}{2}}$ vs. pH should yield a straight line

with slope 0.059 rather than, as Fernando and Phillips report (43), a slope of 0.084.*

A further and more detailed investigation of the polarographic reduction of 2-methyloxine was thought desirable; this was made, over the pH range 7.6 - 14.2.

Other work with which this thesis is concerned includes an investigation of the stoichiometry of the compounds that thorium forms with 3- and 4-methyloxine and its significance, and bromination studies on several derivatives of oxine. Neither of these topics has been previously investigated. Some investigation of the nature of the brown precipitate (45,46) that can form during the bromometric analysis of oxine and 2-methyloxine and other derivatives of oxine has also been made. This brown compound, at least the one encountered in bromometric titrations of oxine, has been thought (46) to be either a polyiodide of the bromination product 5,7-dibromo-oxine, or an "absorption complex" of iodine and the dibromo compound.

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*The number of hydrogen ions (a) involved in the polarographic reduction of an organic compound is usually equal to the number of electrons (n). Even when this is not so, however, the slope of the straight line should be, for a one-electron reduction, an integral multiple of 0.059 - which 0.084 is not.

EXPERIMENTAL AND RESULTS

Apparatus

Calibrated weights were used throughout this work. Calibrated volumetric ware was used whenever this was appropriate.

Measurements of pH were made with a Beckman Model G pH meter (Beckman Instruments Inc., South Pasadena, U.S.A.) using a #1190-80 glass electrode for pH values below 10 and a #11-505-75 electrode for values above that, each coupled with a saturated calomel reference electrode. The pH meter was standardized each time before use with an appropriate standard buffer solution.

The thermobalance was a Chevenard-type photographically recording instrument (TBP Nr. 27, S.A.D.A.M.E.L., La Chaux de Fonds, Switzerland). The rate of heating was $2.5^{o}C$./min. and the sensitivity was 0.85 mm./mg. Temperature readings were made with a platinum-platinum (90 per cent), rhodium (10 per cent) thermocouple in association with a potentiometer (No. 8662, Leeds and Northrup, Philadelphia, U.S.A.).

All polarographic measurements were made at $25.5^{o}C. \pm 0.1^{o}C.$ using a pen-recording Tinsley polarograph, Type 14/3 (Tinsley Industrial Instruments, Ltd., London, England). The capillary for the dropping mercury electrode was a 6.0-cm. length of marine barometer tubing (S-29417, E. H. Sargent and Co., Chicago, U.S.A.). The capillary characteristics in a 0.10 M potassium chloride solution and on open circuit were: t = 7.67 sec.; m = 0.956 mg./sec. Under experimental conditions t was reduced to 3-4 seconds. Exact values of t, and of m,

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are given later. A conventional H-type polarographic cell was used, electrolytic contact to the saturated calomel reference cell being made through a potassium chloride-agar bridge.

The apparatus for the wet oxidation of compounds containing carbon-14 and the collection of radioactive carbon dioxide from the oxidation has been described (47). The carbon dioxide was collected in a stainless-steel Borkowski ionization chamber (Applied Physics Corporation, Pasadena, U.S.A.). Measurements of carbon-14 radioactivity were made by a "rate-of-drift" method (48), using a vibrating-reed electrometer (Model 30, Applied Physics Corporation) with a head capacity of 13 uuf. A combination of the techniques referred to above for carbon-14 determinations has been reported (49) to yield results with a precision of 0.2 per cent.

The cryoscopic molecular weight determinations were done using the apparatus and method described in Daniels, Mathews, and Williams (50).

Reagents

All common laboratory chemicals were either analyzed grade or of sufficient purity for the purpose they were used, and were obtained from reputable suppliers.

The thorium nitrate (tetrahydrate) was a highly purified product (Code 103, Lindsay Chemical Co., West Chicago, U.S.A.). Stock solutions of thorium, containing 1.3 - 1.4 mg. Th/ml., were kept at a pH of just below 2 with hydrochloric acid. These solutions were standardized by methods that are described later.

The benzene for the molecular weight determinations was a "spectranalyzed" grade (Fisher Scientific Co., Toronto) which was redistilled

(the first 10 per cent of the distillate being discarded) and stored over sodium wire.

The inactive oxine was obtained commercially (Analar, British Drug Houses, Poole, England). The 2-methyloxine was either a commercial product (Aldrich Chemical Co., Milwaukee, U.S.A.) that was further purified by steam distillation and then recrystallization from aqueous ethanol, or was synthesized. All other organic precipitants used in this work were obtained by synthesis, the methods for which are given below.

Solutions of the organic precipitants were made by dissolving an appropriate amount of the organic compound in 6.3 ml. of glacial acetic acid and diluting the solution to 100 ml. with water. The concentrations of these solutions are referred to below in w/v per cent.

Syntheses

$2,4-C^{14}$-oxine: This compound was prepared from $1,3-C^{14}$-glycerol (0.5 mc., Volk Radiochemical Co., Chicago, U.S.A.) and o-aminophenol, by means of the Skraup reaction. The use of $1,3-C^{14}$-glycerol places carbon-14 atoms in positions 2 and 4 of the quinoline ring, although, for the work in this thesis, the particular positions of the carbon-14 atoms are not significant.

The procedure used by Manske, Ledingham and Ashford (51) for the preparation of (inactive) oxine was adopted in the main. Modifications made by these workers in the normal procedure for carrying out the Skraup reaction afford unusually high yields.

The active oxine was prepared as follows. Into a three-necked, 250-ml. flask equipped with a mechanical stirrer, reflux condenser, and

thermometer were put 7.3 g. of o-nitrophenol and 1.0 g. of iron(II) sulphate heptahydrate. The flask was heated to 110°C. (in a liquid paraffin bath) in readiness to receive a "premix" of the other reactants.

The "premix" was prepared in the following manner. To 17.0 ml. of 96 per cent sulphuric acid were added slowly, with stirring, 11.3 g. of freshly recrystallized o-aminophenol, the temperature of the reaction being kept below 80°C. by occasional cooling in a water bath. Next, 0.5 mc. of $1,3$-C^{14}-glycerol (less than 50 mg.) was diluted with 28.7 g. of inactive glycerol and added to the mixture of sulphuric acid and o-aminophenol. The "premix" was then maintained at 60-70°C. to keep it fluid.

The temperature of the mixture of o-nitrophenol and iron(II) sulphate was raised to 135°C., after which the "premix" was added in 6 portions at 10-minute intervals. During the additions, the temperature was kept at 135-145°C. After all of the "premix" had been added, the mixture was refluxed for $4\frac{1}{2}$ hours, during which time the temperature of the reaction decreased to 127-133°C.

The mixture was next transferred to a 500-ml., round-bottomed flask, 50 ml. of water were added, and the mixture was steam-distilled to remove unreacted o-nitrophenol. The mixture was partially neutralized with sodium hydroxide and then fully with sodium carbonate, and the oxine obtained by further steam-distillation.

The product was dried by suction for several hours, allowed to sit overnight, and then dried further for 2 hours at 55-60°C. The weight of crude material was 9.6 g., corresponding to a yield of 64 per cent.

The crude oxine was recrystallized twice from aqueous ethanol. After each recrystallization, the product was nearly snow-white and melted over the same temperature range, 73-74°C. (lit., 72-74°C., 73-74°C., etc., (52)).

The activity of the carbon-14 labelled oxine was determined using the wet oxidation and "rate-of-drift" technique referred to earlier. The data are given in Table II.

Table II

ACTIVITY OF 2,4-C^{14}-OXINE

Sample Wt. (mg.)	Rate of Drift* (mv./sec.)	Activity mv./sec./mg.
2.71	12.0	4.43
3.50	15.4	4.40
4.59	20.1	4.38

* corrected for background

From these data and the head capacitance of the vibrating-reed electrometer, the specific activity of the oxine can be calculated to be 1.59 mc./mole. Although this value of the specific activity is not needed, it is pointed out because it agrees so well with the expected value** of 1.6 mc./mole.

An attempt was made to produce carbon-14 labelled oxine by

**The specific activity of the glycerol is $\dfrac{0.5 \text{ mc. } \times 92 \text{ g./mole}}{29 \text{ g.}}$ = 1.6 mc./mole. Since one mole of glycerol leads to one of oxine, the specific activity of the oxine should be 1.6 mc./mole.

irradiation of inactive oxine (intimately mixed with urea, a good source of nitrogen atoms) in the McMaster nuclear reactor. It was hoped that the desired labelling could be achieved by means of the nuclear reaction $N^{14}(n,p)C^{14}$ followed by subsequent random replacement of carbon-12 atoms in the quinoline ring by carbon-14 atoms. The attempt was unsuccessful.

2-methyloxine: The procedure was that used by Merritt and Walker (2). The yield of crude material was 21 per cent. Four recrystallizations from aqueous ethanol gave white needle-like crystals melting at 71.5 - 72.0°C. (lit., 72°C., (2)).

2-phenyloxine: The general procedure recommended by Phillips, Elbinger and Merritt (53) for the preparation of 2-aryloxines was used. The product was a dark oil (b.p., about 235°C. at a pressure of 20 mm.) which could not be crystallized. Pure 2-phenyloxine is a low-melting solid (59°C., (53)).

The oil was dissolved in hot 3.0 M hydrochloric acid, the solution boiled with decolourizing carbon, and the mixture was filtered. Long, yellow needle-like crystals were obtained on crystallization. The substance was filtered and recrystallized twice from 3.0 M hydrochloric acid and then from a solution consisting of 80 per cent (by volume) methanol and 20 per cent 12 M hydrochloric acid. The crystals were washed with methanol and dried at 110°C. for one hour. The melting range was 190-194°C., a little wider than that (190-191°C.) reported for 2-phenyloxine hydrochloride (54).

Thermogravimetric experiments with the salt yielded a horizontal plateau which corresponded to that expected for anhydrous 2-phenyloxine hydrochloride. Bromometric analyses confirmed this composition.

3-methyloxine: This compound has been previously synthesized, in low yield (4 per cent), by Phillips (55). The synthesis described below provides the compound in much higher yield (31 per cent of crude 3-methyloxine).

To a 500-ml., three-necked flask, fitted with a mechanical stirrer, reflux condenser and dropping funnel, were added 65 g. of o-aminophenol dissolved in 150 ml. of 12 M hydrochloric acid. After the addition of 28 g. of o-nitrophenol, the flask was heated to 100°C. in a liquid-paraffin bath and 77 g. of 2-methylpropenal were slowly added over a period of 45 minutes. The mixture was refluxed for 5 hours at $100-105^{\circ}$C., after which it was steam-distilled to remove volatile impurities. The mixture was carefully neutralized with a solution of sodium hydroxide and the steam distillation continued, this time to remove the 3-methyloxine.

The crude material was recrystallized from aqueous ethanol. White crystals were obtained, melting at $112-113^{\circ}$C. (lit., $112-113^{\circ}$C., (55)).

4-methyloxine: The procedure described by Phillips, Elbinger and Merritt (53) was employed with one modification, this being the use of o-nitrophenol as an oxidizing agent. No oxidant was used in the original procedure. A yield of 26 per cent (crude 4-methyloxine) was obtained by use of the oxidant, representing an absolute increase in yield of only 5 per cent. The crude product was recrystallized from aqueous ethanol, the purified product melting at $141-142^{\circ}$C. (lit., 141°C., (53)).

6-methyloxine: Although several methods have been reported (56,

57,58) for the synthesis of 6-methyloxine, a different approach for this synthesis was taken in this work. This involved a Skraup reaction between glycerol and 2-amino-5-methylphenol. The 2-amino-5-methylphenol was unobtainable commercially and so was synthesized by preparing (59), and reducing (60), 2-nitro-5-methylphenol.

The Skraup synthesis was done using the procedure given (61) for the synthesis of 5-methyloxine, with substitution of 2-amino-5-methylphenol for 2-amino-4-methylphenol. Only 0.50 g. (3.1 per cent yield) of crude 6-methyloxine were obtained. Two recrystallizations from aqueous ethanol gave 0.22 g. of an off-white product melting at 94-95°C. (lit., 95-96°C., (56,57)).

The low yield was probably due to the oxidation of reactants caused by inadequate temperature control.

PART A   Thorium and Oxine

(a) Composition of Thorium Oxinate Precipitated from Cold Solution: The precipitation was done as follows. Into a 150-ml. beaker were pipetted 25.00 ml. of a thorium stock solution (1.34 mg. Th/ml.), that had been standardized bromometrically through 2-methyloxine (EXPERIMENTAL AND RESULTS, PART B, (c)). The solution was diluted to about 50 ml. with water and cooled to 0°C. in a water-ice bath. Then 8.0 ml. of the oxine solution (1.79%), previously cooled to 0°C., were added slowly, followed by 15 ml. of an aqueous solution (also cooled to 0°C.) containing 2.0 g. of ammonium acetate. This solution was added dropwise with efficient stirring. Next, 10-13 ml. of 1.0 M aqueous ammonia were added in the same careful manner. A voluminous yellow precipitate formed, which

gradually settled. The beaker walls were washed down with water, bringing the volume to about 90 ml., and the precipitate was allowed to sit for one hour in the bath. It was then filtered into a fritted-glass crucible (medium porosity) and washed with about 100 ml. of cold water adjusted to pH 8.0 with aqueous ammonia.

After drying for 10 hours at 60°C., the precipitate was cooled in a desiccator and later weighed. It was next dissolved from the crucible (using 50 ml. of warm 4.0 M HCl followed by 50 ml. of water) into an iodine flask and the oxine content in the precipitate determined bromometrically. In some experiments, the precipitate was ignited to thorium dioxide; in these, Selas porcelain filtering crucibles (medium porosity), instead of fritted-glass crucibles, were used.

The results of the analyses are given in Table III.

In another experiment the precipitate, obtained at 0°C., after drying was sealed in a glass tube approximately one foot long. The end of the tube containing the sample was placed in a drying oven while the other end, projecting through a hole in the oven, was placed in a water-ice bath. After the sample had been heated at 165°C. for two hours, the sealed tube was broken. A white solid (m.p. 73-74°C.) was recovered from the cold end, indicating that oxine (m.p. 72-74, 73-74, etc., (52)) had sublimed from the original compound. A similar observation has been reported previously (16) for the orange-red 1:5 thorium oxinate obtained from hot solution.

(b) Thermal Stability of 1:5 Thorium Oxinate: The orange-red 1:5 thorium oxinate used in this work was precipitated exactly as was the yellow 1:5 thorium oxinate discussed in the previous section, except that

Table III

PRECIPITATION OF THORIUM BY OXINE AT $0^{\circ}C$.

pH of precipitation (determined on filtrate at room temp.): 7.0 ± 1.1

Th taken: 33.4 ± 0.1 mg. (equivalent to 38.0 ± 0.1 mg. ThO_2)

For $Th(C_9H_6ON)_4 \cdot C_9H_7ON$: expected wt. of ppte. is 137.3 ± 0.4 mg.
expected wt. of oxine is 104.4 ± 0.3 mg.

For $Th(C_9H_6ON)_4$: expected wt. of ppte. is 116.5 ± 0.3 mg.
expected wt. of oxine is 83.6 ± 0.2 mg.

Wt. of Ppte. (mg.)	Wt. of Oxine (mg.)	Wt. of ThO_2 (mg.)
136.8	104.2	
136.3	104.0	
137.5	104.6	
136.7	103.8	
136.8	103.9	
136.7	103.9	
137.5		38.2
137.0		38.1
136.8		38.1

the temperature of precipitation and digestion was $70^{\circ}C$. rather than $0^{\circ}C$.
After digestion for one hour at $70^{\circ}C$., the orange-red precipitate was
filtered into a fritted-glass crucible (medium porosity) and washed with
100 ml. of hot water adjusted to pH 7.5 ± 0.5 with aqueous ammonia. The
compound was then dried at $60^{\circ}C$. for 10 hours.

The dry compound was finely powdered and samples were then
accurately weighed into crucibles previously brought to constant weight
at $165^{\circ}C$. The samples were heated at $125^{\circ}C$. for 5 hours and then at
$135^{\circ}C$. for one hour, this being the method by which Moeller and
Venkataramaniah (18) claim to have prepared the 1:4 compound from the
1:5. The results are given in Table IV.

Table IV

THERMAL DECOMPOSITION OF 1:5 THORIUM OXINATE
(Method of Moeller and Venkataramaniah (18))

Wt. of 1:5 Compd. Taken (mg.)	Wt. of 1:4 Compd. Expected (mg.)	Wt. of Product Obtained (mg.)
106.4	90.2	98.1
106.0	89.9	97.0
99.5	84.4	93.3

The data of Table IV show that the 1:5 compound has not, by this heat treatment, attained a weight corresponding to the formation of the pure 1:4 compound. Only about 50 per cent conversion has occurred. Even on stronger heating, at 165°C. for 3 hours (Frere's method (16)), the samples decreased in weight by only an additional 3 mg. and were still far from being pure 1:4 thorium oxinate.

After several preliminary experiments, it was found that when samples of 1:5 thorium oxinate were heated at 200°C. for $2\frac{1}{2}$ hours, weights corresponding very closely to those expected for the pure 1:4 compound were obtained (Table V).

That the compound prepared was substantially pure 1:4 thorium oxinate is shown not only by the agreement between the figures in the last two columns of Table V, but also by bromometric determinations of the oxine content of the products. The data for these are given in Table VI.

In each instance, both in the experiments of Table V and Table VI, the weight obtained is very slightly lower (on average, less than 0.4%)

Table V

THERMAL PREPARATION OF 1:4 THORIUM OXINATE

Wt. of 1:5 Compd. Taken (mg.$\pm$0.1 mg.)	Wt. of 1:4 Compd. Expected (mg.$\pm$0.1 mg.)	Wt. of Product Obtained (mg.$\pm$0.1 mg.)
107.1	90.8	90.4
102.3	86.7	86.4
99.7	84.5	84.3
98.4	83.4	83.1
90.1	76.4	76.0
89.5	75.9	75.6

Table VI

OXINE CONTENT OF THERMALLY PREPARED 1:4 THORIUM OXINATE

Wt. of Product Taken (mg.$\pm$0.1 mg.)	Wt. of Oxine Expected (mg.$\pm$0.1 mg.)	Wt. of Oxine Obtained (mg.$\pm$0.1 mg.)
58.5	42.0	41.8
55.6	39.7	39.7
54.3	39.0	38.9
54.0	38.8	38.6
54.0	38.8	38.7
53.3	38.3	38.1

than the weight expected. Slow volatilization or decomposition of the
product probably has occurred. The use of a shorter heating period or
of a somewhat lower temperature would have been desirable.

(c) Reaction of Oxine with 1:4 Thorium Oxinate: The 1:4 thorium
oxinate for these experiments was prepared thermally from the 1:5 compound
as described in the preceding section. Finely powdered samples of the
1:4 compound were weighed accurately into 50-ml. beakers, to which were
then added 10.0 ml. of an ethanolic solution of oxine (2.00 g. of oxine

dissolved in 100 ml. of 95 per cent ethanol). The mixture was allowed

to stand at room temperature (25-27°C.) for 45, 60 or 90 minutes, with

periodic stirring. Then the product was quantitatively transferred

(using 5 ml. of ethanol) to filter paper (Whatman No. 42) previously

wet with ethanol. The beaker and product were then washed with 200 ml.

Table VII

REACTION OF OXINE WITH 1:4 THORIUM OXINATE

1:4 Compd. Taken (moles x 10^5)	Oxine Content of 1:4 Compd. (moles x 10^4)	Oxine Content of Product (moles x 10^4)	Oxine Acquired (moles x 10^5)	Per Cent* Addition	Av.
Reaction Time: 45 minutes					
7.56	3.02	3.50	4.8	63	
7.52	3.01	3.45	4.4	59	62%
7.58	3.03	3.51	4.8	63	
Reaction Time: 60 minutes					
7.58	3.03	3.50	4.7	62	
7.54	3.02	3.49	4.7	62	
7.59	3.04	3.49	4.5	59	
7.58	3.03	3.47	4.4	58	
7.56	3.02	3.51	4.9	65	
7.53	3.01	3.52	5.1	68	62%
7.60	3.04	3.48	4.4	58	
7.48	2.99	3.46	4.7	63	
7.54	3.02	3.48	4.6	61	
7.52	3.01	3.47	4.6	61	
7.49	3.00	3.47	4.7	63	
Reaction Time: 90 minutes					
7.57	3.03	3.49	4.6	61	
7.56	3.02	3.51	4.9	65	63%
7.54	3.02	3.50	4.8	64	

*Per cent addition was obtained by dividing the fourth column by
the first. This assumes that no significant amount of the 1:4 thorium
compound dissolved in the ethanolic solution of oxine. The solubility
appears to be so slight that the assumption is likely valid.

of hot water adjusted to pH 7.5 ± 0.5 with aqueous ammonia. The product

was dissolved through the filter paper into an iodine flask with 50 ml.

of warm 4.0 M HCl, the filter paper and funnel washed with 50 ml. of water, and the oxine content of the product then determined by bromination. The data are summarized in Table VII.

Assuming that the solubility loss is negligible, about 62 per cent of the 1:4 thorium oxinate is converted to the 1:5 compound under the experimental conditions. The per cent addition of oxine is essentially constant as a function of time, which indicates that the reaction has reached equilibrium.

The preponderance of data in Table VII relating to one hour was necessary in order to obtain a reliable average result, needed for work concerned with the structural nature of 1:5 thorium oxinate in the following section.

(d) Structural Nature of 1:5 Thorium Oxinate: The studies described below involve molecular weight determinations of 1:5 thorium oxinate in benzene, the recovery and analysis of precipitates obtained from the dissolution of 1:5 thorium oxinate in benzene and nitrobenzene, radioactive analysis of thorium oxinate compounds derived from the reaction of oxine, labelled with carbon-14, with inactive 1:4 thorium oxinate, and the preparation of thorium chelates of 2-, 3-, and 4-methyl-oxine.

The molecular weight of 1:5 thorium oxinate was determined cryoscopically using the apparatus and method to which reference has been made. The 1:5 compound was prepared and dried as described earlier.

The molecular weight of the 1:5 compound was calculated from the equation: $M.W. = \frac{1000K_f w}{W \Delta T_f}$, where K_f (5.12) is the cryoscopic constant for benzene (50), ΔT_f is the measured freezing-point depression, w is

the weight, in grams, of the 1:5 compound, and W is the weight, in grams, of benzene. The data from these experiments are summarized in Table VIII.

Table VIII

CRYOSCOPIC MOLECULAR WEIGHT OF 1:5 THORIUM OXINATE

w (g. x 10^3)	W (g.)	ΔT_f (°C.)	M.W.
20.0	17.4	0.013	453
20.1	17.4	0.015	394
21.0	17.4	0.013	475
17.1	17.4	0.010	503

The average of the molecular weight determinations is 456, with poor precision. The wide deviation in the results is due to the low solubility of the 1:5 compound in benzene, resulting in very small freezing-point depressions. Poor precision has also been reported (62) by investigators who determined the cryoscopic molecular weight of the scandium oxinate which contains an "extra" molecule of oxine. Here, too, the difficulty was likely due to the low solubility of the scandium chelate in benzene. The only solvents in which the 1:5 thorium oxinate appeared to be appreciably soluble were basic ones such as pyridine and quinoline. These could not be used because of the strong possibility of chemical interaction with the chelate compound.

The theoretical molecular weight of 1:5 thorium oxinate is 954. However crude the results are, they do nevertheless indicate that the 1:5 compound has dissociated into two substances, probably 1:4 thorium oxinate and oxine. The significance of this will be discussed in a later

section. A similar observation has been reported for scandium oxinate (62).

Since the presence of a small amount of impurity (such as less than a milligram of water) could account for, say, half of the depression observed, the conclusion that a molecule of 1:5 thorium oxinate dissociates into two molecules in benzene cannot be drawn with certainty without further supporting evidence. Such evidence is given next.

Quantities (50-100 mg.) of the 1:5 compound were put in a vessel containing either 25 ml. of benzene or 25 ml. of nitrobenzene, and the mixtures were gently heated to 55-60°C. Dissolution occurred at the elevated temperature. The 1:5 compound appeared to be more soluble in benzene than in nitrobenzene. When the solutions cooled, yellow precipitates formed. The precipitates were filtered and washed with the solvent. Those washed with benzene were dried at 110°C. for two hours, whereas those washed with nitrobenzene were dried at 200°C. for 1½ hours. Samples of the dried compounds were then analyzed bromometrically for oxine. The data are shown in Table IX.

Table IX

BROMOMETRIC ANALYSIS OF PRECIPITATES FROM
BENZENE AND NITROBENZENE

Solvent	Yellow Compd. Taken (mg.)	Oxine Found (mg.)	Oxine Expected for 1:4 Compd. (mg.)
Benzene	80.3	57.5	57.6
Benzene	69.4	49.2	49.8
Benzene	43.7	31.4	31.4
Benzene	35.0	24.8	25.1
Nitrobenzene	45.7	32.5	32.8
Nitrobenzene	36.1	25.7	25.9
Nitrobenzene	34.3	24.4	24.6

There seems to be no doubt, from the data of Table IX, that the compound recovered from the dissolution of the 1:5 compound in benzene or nitrobenzene is 1:4 thorium oxinate. When dissolved in solvents such as benzene and nitrobenzene, then, 1:5 thorium oxinate dissociates into 1:4 thorium oxinate and oxine.

In these experiments, one would have liked to have dried the precipitates at a low temperature (e.g., 60-70°C.) to prevent any loss of oxine in the event that the precipitates were 1:5 thorium oxinate. Unfortunately, higher temperatures were needed to free the precipitates of solvent. For the precipitate obtained in benzene, a temperature of 110°C. was required. Since a much higher temperature is necessary to completely convert 1:5 thorium oxinate to 1:4 thorium oxinate (EXPERIMENTAL AND RESULTS, PART A (b)), it is certain that the precipitate obtained in benzene, at least, is the 1:4 compound.

Information about the structure of 1:5 thorium oxinate was sought in experiments involving the reaction of oxine, labelled with carbon-14, with 1:4 thorium oxinate in which the oxine ligands were inactive. The rationale of the experiments will be given in the Discussion.

The synthesis of carbon-14 labelled oxine has already been described. The inactive 1:4 thorium oxinate required for these experiments was prepared thermally from 1:5 thorium oxinate by the procedure set forth earlier.

The reaction of active oxine with inactive 1:4 thorium oxinate was carried out as described in a previous section. The reaction was stopped at the end of one hour, after which time, as has been shown

earlier, about 62 per cent conversion to the 1:5 compound has occurred. The composition of the product of the reaction can be conveniently represented by $Th(ON)_4 \cdot 0.62HON$. The product was dried at $60^{\circ}C$. for 6 hours prior to measurements of its activity.

The activity of the product, $Th(ON)_4 \cdot 0.62HON$, was determined using the apparatus and method to which reference has been made. The $Th(ON)_4 \cdot 0.62HON$ was thermally converted to the 1:4 compound, $Th(ON)_4$, as described earlier, and the activity of the resultant $Th(ON)_4$ was measured. The results of these experiments are shown in Tables X and XI. In the two tables, samples with corresponding numbers contain equal amounts of thorium.

The data of Tables X and XI show that the $Th(ON)_4$, derived thermally from the $Th(ON)_4 \cdot 0.62HON$, is highly active, and that its specific activity is equal to that of the $Th(ON)_4 \cdot 0.62HON$. The same observation,

Table X

ACTIVITY OF $Th(ON)_4 \cdot 0.62HON$

Sample No.	Wt. of $Th(ON)_4 \cdot 0.62HON$ Taken (mg.)	Measured C^{14} Activity* (mv./sec.)	Calculated Wt. of Oxine in $Th(ON)_4 \cdot 0.62HON$ (mg.)	Specific Activity (mv./sec./ mg. oxine)
1	32.0	54.3	23.7	2.29
2	23.7	40.0	17.6	2.27
3	13.8	23.3	10.2	2.28
4	11.4	19.0	8.5	2.24
5	7.7	13.1	5.7	2.30

Av. 2.28

* corrected for background

Table XI

ACTIVITY OF $Th(ON)_4$ DERIVED FROM $Th(ON)_4 \cdot 0.62HON$

Sample No.	Wt. of $Th(ON)_4$ Taken (mg.)	Measured C^{14} Activity* (mv./sec.)	Calculated Wt. of Oxine in $Th(ON)_4$ (mg.)	Specific Activity (mv./sec./ mg. oxine)	Relative Activity** $Th(ON)_4/$ $Th(ON)_4 \cdot 0.62HON$
1	28.8	47.1	20.5	2.30	0.87
2	21.3	34.9	15.2	2.30	0.87
3	12.4	20.2	8.8	2.30	0.87
4	10.3	16.5	7.3	2.26	0.87
5	6.9	11.1	4.9	2.27	0.85
				Av. 2.29	Av. 0.87

* corrected for background

** column #3 of Table XI divided by column #3 of Table X

put in a different way, is illustrated by the relative activity of $Th(ON)_4/$ $Th(ON)_4 \cdot 0.62HON$ given in the last column of Table XI. The relative activity (0.87) is equal to the relative oxine content ($\frac{4.00}{4.62} = 0.87$) of the $Th(ON)_4$ and $Th(ON)_4 \cdot 0.62HON$ species, i.e., on heating, 13 per cent of the oxine and 13 per cent of the activity in $Th(ON)_4 \cdot 0.62HON$ has been lost. The significance of this observation is left for later discussion.

Thorium chelates of 2-, 3-, and 4-methyloxine were prepared and analyzed. The preparation and analysis of the thorium chelate of 2-methyl-oxine are given later (EXPERIMENTAL AND RESULTS, PART B (b)). With 2-methyloxine, thorium forms the normal 1:4 chelate. No evidence for the formation of a 1:5 thorium chelate was obtained.

The 3- and 4-methyloxinates of thorium were prepared as follows: 25.00 ml. of a thorium solution (containing 1.37 mg. Th/ml., standardized gravimetrically using 2-methyloxine as described in EXPERIMENTAL AND RESULTS, PART B (b)) were pipetted into a 150-ml. beaker and heated to

70°C. To this solution were added slowly 8.0 ml. of a 1.80 per cent solution of the organic precipitant (3- or 4-methyloxine). Then 20 ml. of an aqueous solution containing 2.0 g. of ammonium acetate and previously warmed to 70°C., were added dropwise with stirring. This was followed by the dropwise addition (with stirring) of about 25 ml. of 1.0 M aqueous ammonia, the pH being 8.0 ± 0.5. In each case the yellow-orange precipitate that was obtained was allowed to digest for one hour at 70°C. before it was filtered and washed with 100 ml. of hot water adjusted to pH about 8.5 with dilute aqueous ammonia. Precipitates which were to be dried at 70°C. or heated to 165°C. were filtered into fritted-glass crucibles (medium porosity); those to be ignited to thorium dioxide were filtered into Selas porcelain filtering crucibles; and those to be taken for bromometric determination of 3- or 4-methyloxine were collected on Whatman No. 40 filter paper. The analytical data are given in Table XII.

The data in the last column of Table XII show that the precipitation of thorium in these experiments was almost quantitative, being short of it by only 0.5%. When allowance is made for this, the average weight of oxinate found is very close (-0.4 per cent) to that expected for the 1:5 thorium 4-methyloxinate and somewhat higher (1.7 per cent) than that expected for the 1:5 thorium 3-methyloxinate - but for both oxinates, the weight is about 18 per cent higher than that which would correspond to oxinates of 1:4 stoichiometry. The slightly high results with the 3-methyl compound are probably due in part to adsorbed water, for during weighing the compound increased in weight.

The bromometric determinations provide similar evidence that the

Table XII

COMPOSITION OF 3- AND 4-METHYLOXINATES OF THORIUM

Th taken: 34.3$\pm$0.1 mg. (equivalent to 39.0$\pm$0.1 mg. ThO$_2$)

For 1:5 compd.: expected wt. of chelate is 151.3$\pm$0.4 mg.
 expected wt. of 3- or 4-methyloxine is 117.6$\pm$0.3 mg.

For 1:4 compd.: expected wt. of chelate is 127.8$\pm$0.4 mg.
 expected wt. of 3- or 4-methyloxine is 94.1$\pm$0.3 mg.

Wt. of Compd. after Drying 5 hr. at 70°C. (mg.)	3- or 4- methyloxine Found (mg.)	ThO$_2$ Found (mg.)
Thorium 3-methyloxinate*:		
153.4	116.2	38.9
155.0	115.9	38.8
152.4	116.2	38.7
152.9	116.4	38.9
153.1	116.2	
152.4	116.0	
	116.0	
	116.1	
	116.0	
Thorium 4-methyloxinate*:		
148.4	117.2	38.9
151.1	115.9	38.7
150.6	116.7	38.6
149.4	116.2	38.9

* Each determination involves a separate 25.00 ml.
  volume of the standard thorium solution.

thorium compounds precipitated by 3- and 4-methyloxine are of 1:5 and

not 1:4 stoichiometry: in each instance the methyloxine found is within

one per cent of that expected for 1:5 compounds, but about 24 per cent

higher than that expected for 1:4 compounds.

Additional evidence for the 1:5 compounds is seen in the fact

that when the precipitates, which are yellowish-orange in colour, are heated at 165°C. for a few hours, a decrease in weight occurs and the colour of the residue is the yellow colour characteristic of 1:4 thorium oxinate and of 1:4 thorium 2-methyloxinate. Indeed, when samples of the 3-methyloxinate were heated at 165°C. for a total of 13 hours, the weights of the residues corresponded very closely to those expected for the 1:4 compound. The rate of decrease in weight was at first rapid and then much slower as the weight appropriate to the 1:4 compound was approached.

PART B   Thorium and 2-Methyloxine

Stock solutions of thorium were standardized gravimetrically by precipitation with ammonia and ignition to thorium dioxide (63), or gravimetrically with oxine. Standardization by means of oxine was done as follows: a 50.00-ml. portion of the stock solution containing thorium at a concentration of about 0.7 mg./ml. was pipetted into a beaker and warmed to 50°C. To this solution were added 8.0 ml. of a 1.6 per cent solution of oxine and then, very slowly with stirring, 10 ml. of a warm solution containing 2.0 g. of sodium acetate, followed by the dropwise addition, with stirring, of 1.0 M sodium hydroxide to a pH of 7.0 ± 0.5. The precipitate was digested for one hour at 70°C., collected in a fritted-glass crucible (medium porosity), and washed with about 75 ml. of hot water. The precipitate was dried in air for about 5 hours and then to constant weight at 70°C. It was weighed as 1:5 thorium oxinate.

The average result of three determinations of thorium made by this method was 34.5 ± 0.1 mg. Th/50.00 ml. of solution. Three determinations of thorium in the same solution made by ignition of the hydrous

oxide to thorium dioxide yielded 34.3 ± 0.1 mg. Th/50.00 ml., while (twelve) determinations made by the gravimetric method using 2-methyl-oxine (described below) gave 34.4 ± 0.1 mg. Th/50.00 ml. Thus, with care in the drying of the 1:5 thorium oxinate precipitate, suitable determinations of thorium can be made by precipitation with oxine.

(a) Precipitation of Thorium as the 1:4 2-Methyloxinate: The procedure developed for precipitating thorium quantitatively as 1:4 thorium 2-methyloxinate follows*. A 50.00-ml. portion of the solution containing thorium at a concentration not higher than 0.7 mg./ml. $(3 \times 10^{-3}$ M) is pipetted into a beaker and warmed to about 70°C. To this solution are added 8.0 ml. of a 2.0 per cent solution of 2-methyloxine and then, slowly with stirring, 2.0 g. of ammonium acetate dissolved in 10 ml. of hot (70°C.) water. The pH is then adjusted to within the range 8.0 - 9.0 (making use of narrow-range pH paper) with 1.0 M aqueous ammonia, added drop by drop with vigorous stirring. (This should bring the volume to about 90 ml.) The precipitate is digested for one hour at about 70°C. (Some of the excess 2-methyloxine may volatilize during the digestion and condense on the underside of the covering watch glass; this should not be washed down.)

The concentration of reagent, adjustment of pH, and pH control are variables that affect the precipitation of thorium as the 2-methyl-oxinate. Each of these was investigated.

Concentration of reagent: Precipitations were done as just described except that the amount of excess 2-methyloxine was varied.

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*It is convenient to give here the procedure that finally was developed. The experiments that led to this procedure are given on the pages that follow.

The precipitates were subsequently treated as set forth later in the procedure for the gravimetric determination of thorium by 2-methyloxine, except for the use of low-porosity Selas crucibles instead of fritted-glass ones. The results are in the first two columns of Table XIII; comment is made on these later.

Table XIII

EFFECT OF EXCESS 2-METHYLOXINE ON THE PRECIPITATION OF THORIUM AS $Th(C_{10}H_8ON)_4$

pH of precipitation (determined on filtrate at room temp.): 8.1 ± 0.1

Th taken: 34.5 ± 0.1 mg.: equiv. to 128.6 ± 0.4 mg. of $Th(C_{10}H_8ON)_4$ and to 39.3 ± 0.1 mg. of ThO_2

Excess Reagent (%)	Wt. of Ppte. (mg.)	Wt. of ThO_2 (mg.)
90	128.5	
65	128.4*	39.3
60	128.4	
50	124.2	39.2
35	120.5	39.4
20	108.5	39.0
10	98.4	

*This value is an average of 10 determinations (average deviation: 0.2); the other values represent, for the most part, a single determination.

Adjustment of pH: The concentration of the aqueous ammonia used to raise the pH to within the desired range, and the way in which the ammonia is added, were varied and their effect on the precipitation of thorium as the pure 1:4 chelate was determined.

Curve A of Fig. 1 summarizes data from precipitations carried out as described earlier except that the concentration of the ammonia, which was added dropwise with stirring, was varied. The precipitates

Curve A - Molarity of ammonia
Curve B - Time of digestion (hours)
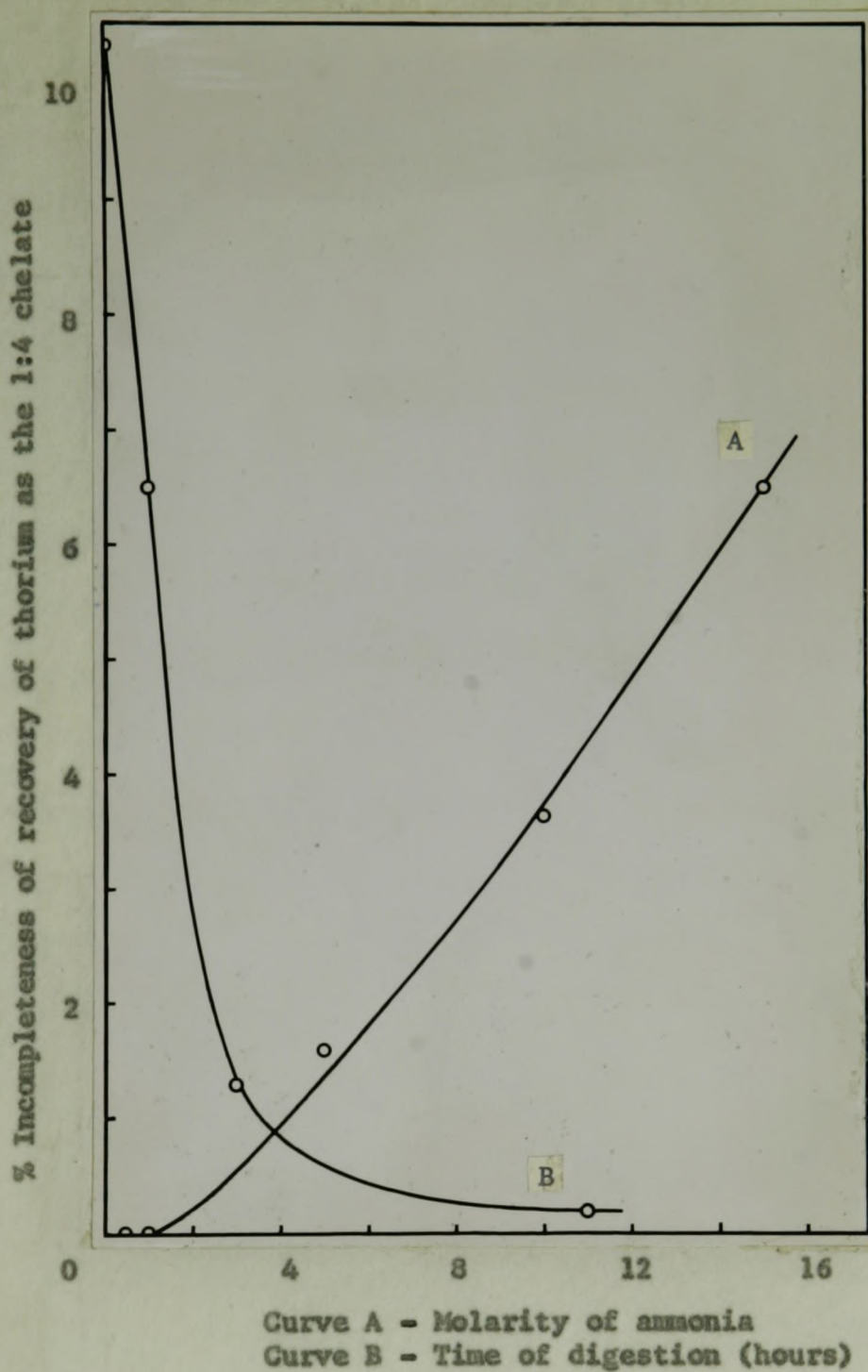
Fig. 1

Effect on recovery of thorium as $Th(C_{10}H_8ON)_4$, of: (A) Molarity of ammonia used to adjust pH; (B) Time of digestion after pH adjustment by rapid addition of 15 M ammonia. In all experiments, the concentration of thorium was 0.7 mg./ml., the pH of precipitation was 8.0 - 8.5, the excess of precipitant was 70 per cent. Each point is the average of at least two determinations; the two lowest points of Curve A summarize 15 determinations.

were analyzed bromometrically according to the procedure (given later) for the bromometric determination of thorium through 2-methyloxine.

Curve B of Fig. 1 summarizes data from precipitations in which the pH was adjusted with 15 M ammonia, added rapidly with little regard for stirring, and in which the precipitates were digested at 70°C. for varying periods of time, and then analyzed bromometrically.

pH control: Experiments were performed to determine the pH range in which thorium can be precipitated quantitatively as the 1:4 chelate. For these experiments, which are summarized in Fig. 2, the thorium was precipitated by 2-methyloxine as already described except that the pH of precipitation was varied over a wide range, with consequent variation in the buffer medium. The solutions were buffered in the acid range by ammonium acetate and acetic acid, and in the alkaline range (to pH 9) by ammonium acetate and ammonia. For pH values above 9, appropriate volumes of 1.0 M and 2.0 M sodium hydroxide were added after the solution had been brought to pH 9 with ammonium acetate and ammonia. Accordingly, the portion of the curve in Fig. 2 for pH values above 9 was not established in properly buffered solutions and the "break-point", shown at pH 11.5, may be a bit in error. Since the flat portion of the pH-precipitation curve is broad, a small uncertainty at the "break-point" is of little practical significance. The precipitates from these experiments were analyzed bromometrically.

The foregoing experiments established appropriate conditions for the quantitative precipitation of thorium by 2-methyloxine as the 1:4 chelate and led to the procedure set forth at the beginning of this section.

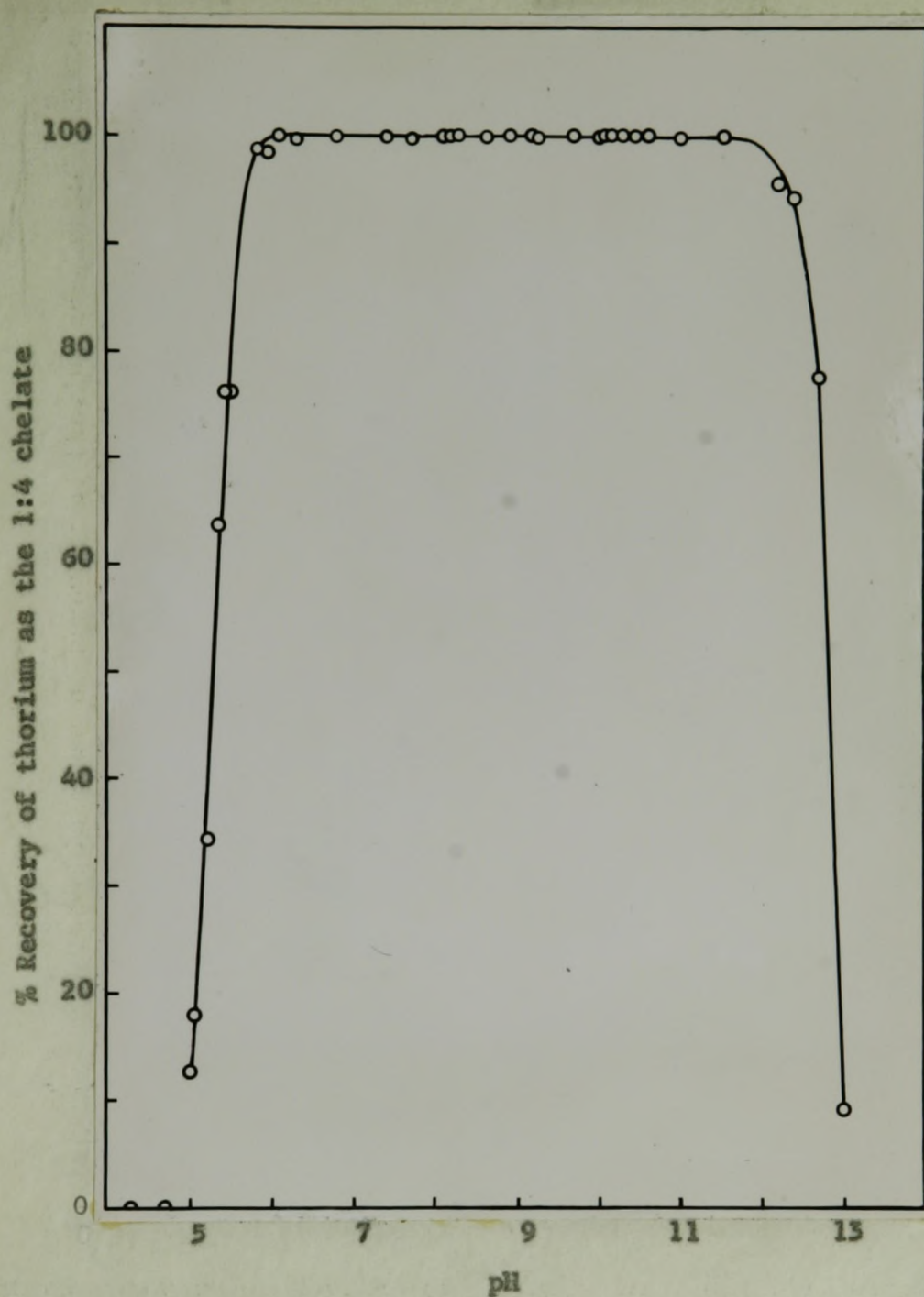The work which is now to be described was done to test the claim

Fig. 2

pH Range for precipitation of thorium as $Th(C_{10}H_8ON)_4$. The concentration of thorium was 0.7 mg./ml., the excess of precipitant was 70 per cent.

of Van Tassel and Wendlandt (42) that they prepared 1:5 thorium 2-methyl-
oxinate. All evidence prior to this was that thorium is precipitated by
2-methyloxine only as a compound of 1:4 stoichiometry.

Precipitations were carried out using, as far as could be
determined, the procedure of Van Tassel and Wendlandt. The amounts of
reagents, concentrations and volumes of solutions, and the manner in
which all the reactants were brought together were exactly those given
by the authors. Although they specified the time of digestion (5 minutes),
the authors did not give the temperature of digestion. A reasonable
assumption is that they used a temperature of 70°C. since they refer to
work (39) in which a temperature 70°C. was used, and since this tempera-
ture is commonly used in the precipitation of metal oxinates. Accordingly,
in this work, the precipitates were digested at 70°C.

After digestion, the precipitates were filtered and washed 15
times with water (about 250 ml. in all) adjusted to pH 7.5 - 8.0 with
dilute ammonia. Air was passed through the precipitates for $2\frac{1}{2}$ hours,
they were allowed to stand overnight at room temperature, and then
dried further for one hour at 50°C. These drying conditions are milder
than those used by Van Tassel and Wendlandt and afford less opportunity
than theirs for 2-methyloxine to be lost.

Accurately weighed samples of the dry precipitates were taken for
bromometric analysis of 2-methyloxine and for ignition to thorium dioxide.
The findings are in Table XIV.

According to Van Tassel and Wendlandt, the presumed "extra"
molecule of 2-methyloxine begins to sublime at 70°C., the process being
complete at 155°C. To test this observation, samples of the precipitates

Table XIV

ANALYSIS OF A THORIUM OXINATE COMPOUND

For 1:5 compd.: Theor. 2-methyloxine anion: 77.31%
Theor. Th: 22.66%

For 1:4 compd.: Theor. 2-methyloxine anion: 73.17%
Theor. Th: 26.83%

Wt. of Sample Taken (mg.)	2-Methyloxine Anion Found (mg.)	2-Methyloxine Anion Found (%)	ThO$_2$ Found (mg.)	Th Found (mg.)	Th Found (%)
75.1	54.9	73.1			
62.9	46.2	73.4			
64.9	47.7	73.5			
98.9			30.1	26.5	26.8
95.4			29.1	25.6	26.8
94.6			28.9	25.4	26.8

were accurately weighed and heated at 155°C. for 75 minutes, and then reweighed. The data of the previous workers were obtained thermogravimetrically. No heating rate is given for their experiments, but if a reasonable heating rate (4°/min.) is assumed, only about 40 minutes would have been required for their furnace to reach 155°C. - thermal conditions far milder than those used in obtaining the data of Table XV.

Table XV

THERMAL TREATMENT OF A THORIUM OXINATE COMPOUND

Heating at 155°C. for 75 min.

Wt. of Sample Taken (mg.)	Wt. of Sample after Heating (mg.)	Wt. Loss (mg.)	Wt. Loss Expected for 1:5 Compd. (mg.)
96.5	96.3	0.2	15.0
94.0	93.8	0.2	14.6
96.0	95.7	0.3	14.9

The data in this section are discussed later.

(b) Gravimetric Determination of Thorium: Gravimetric determinations of thorium by means of 2-methyloxine are possible, making use of the precipitation procedure developed earlier and the favourable thermal stability of 1:4 thorium 2-methyloxinate.

After the precipitation and digestion of the precipitate as directed in the previous section, the solution is cooled somewhat, filtered through a medium-porosity fritted-glass crucible, and the precipitate washed, using for the transferring and washing about 75 ml. of hot 0.15 M aqueous ammonia. The precipitate is dried for one hour at 110°C. $\pm$ 5°C. and weighed as $Th(C_{10}H_8ON)_4$.

Results of gravimetric determinations made in this way over a wide range of thorium concentrations are given in the third column of Table XVI.

Table XVI

DETERMINATIONS OF THORIUM AS $Th(C_{10}H_8ON)_4$

Approx. Concn. of Th (mg./l. or p.p.m.)	Th Taken (mg.)	Th Recovered (mg.)*	
		Gravimetrically	Bromometrically
690	34.5_1	$34.4_5 \pm 0.0_5$	$34.5_5 \pm 0.0_2$
680	34.1	$34.1_0 \pm 0.0_6$	$34.1_4 \pm 0.0_4$
410	20.4	$20.4_7 \pm 0.0_2$	$20.4_3 \pm 0.0_5$
140	6.81	$6.7_9 \pm 0.0_3$	$6.8_0 \pm 0.0_3$
27	1.36	$1.3_4 \pm 0.0_4$	
13	0.68	$0.6_7 \pm 0.0_3$	$0.6_5 \pm 0.0_2$**

*Each value is an average of 7-13 determinations; the precision measure is the average deviation.

**Precipitates were dried for one hour at 110°C., before dissolution in acid, to avoid interference from contaminating reagent.

Experiments showed that detectable losses (0.1 - 0.2 mg.) of the
precipitate, due to its solubility in the hot wash liquid, occurred
only after 200 ml., at least, of the wash liquid had been used. The
recommended volume, adequate for washing, is 75 ml.

Thermogravimetric experiments showed that this 1:4 thorium che-
late can withstand 110°C., without detectable volatilization or decompo-
sition, for at least three hours. The thermolysis curve, identical to
that obtained by Wendlandt (41) and so not reproduced here, showed that
the compound has no water of crystallization and is thermally stable to
about 180°C. For the thermogravimetric experiments, the thorium 2-methyl-
oxinate was precipitated, filtered, and washed as directed earlier, and
then dried under suction for 5 hours and in the room for 8 days.

(c) Bromometric Determination of Thorium: This is made by the
following procedure, which involves some modifications and improvements
in the standard bromometric procedure. After precipitation and digestion
of the precipitate as already directed, the solution is allowed to cool
somewhat, then filtered through No. 40 Whatman paper, and the precipitate
washed carefully, about 100 ml. of hot 0.15 M aqueous ammonia being used
for transferring and washing. The precipitate is dissolved through the
paper, using 50 ml. of warm 4.0 M hydrochloric acid, and the solution is
caught in an iodine flask. The acid is followed by 50 ml. of water and
to the solution of 2-methyloxine, now 2.0 M in hydrochloric acid, are
added 2.0 g. of potassium bromide (dissolved in 10 ml. of water) and
three drops of a 0.1 per cent aqueous solution of the sodium salt of
methyl red. Standard potassium bromate solution (about 0.02 M) is

added carefully from a buret until the solution becomes yellow, and then are added, rapidly, 1.0 to 1.5 ml. of the bromate solution. The flask is quickly stoppered and a few millilitres of a solution of potassium iodide (1.0 g. per 10 ml. of water) are poured around the lip of the flask. After five minutes, the iodide solution is allowed to run into the flask and more is added, bringing the total volume added to 10 ml. The liberated iodine is immediately titrated with a standard thiosulphate solution (about 0.1 M, standardized against potassium bromate). The content of 2-methyloxine, and hence of thorium, is calculated from the titers involved, allowing for the indicator blank.

When less than five milligrams of thorium are present, the washed precipitate is dried, while still on the paper, for one hour at $110^{\circ}C$., to volatilize any 2-methyloxine that may be contaminating the precipitate. The precipitate and paper are then put into an iodine flask, treated with 50 ml. of warm 4.0 M hydrochloric acid and 50 ml. of water, and the bromination and back-titration are done as indicated above.

The results of bromometric determinations over a wide range of thorium concentrations are shown in Table XVI (set forth earlier). Not shown in this table are some 22 bromometric determinations of thorium (at a concentration of 0.7 mg./ml.) which gave 33.2_1 mg. Th, with an average deviation of 0.0_3 mg. Also, the average of 15 bromometric determinations on a solution that contained 33.6 ± 0.1 mg. of thorium was 33.7_6 mg., with an average deviation of 0.0_5 mg.

The brown precipitate which sometimes forms when the iodide is added and which obscures the end-point is related to the amount of excess potassium bromate. In the bromination procedure recommended

above, the brown precipitate, which is discussed later, is entirely
avoided by restricting the excess bromate to 1.5 ml.

In the course of this work it was desirable to gain information
about the rate at which 2-methyloxine and certain related compounds
undergo dibromination. In these investigations, the brominations were
done as set forth in the preceding section, except that the time
between the addition of the standard bromate solution and of the
iodide-ion was varied. For each oxine compound, except 6-methyloxine,
100.0 ml. of 2.0 M hydrochloric acid containing a known amount (about
0.1 g.) of the oxine compound were taken for each determination. Because
of the limited amount of 6-methyloxine available, only about 10 mg. of
this oxine compound were used for each determination.

The standard bromate solution (about 0.02 M) was added from a
buret at a rate of about 10 ml. per minute. About 30 ml. of the
solution were added in the bromination of each oxine compound, except
6-methyloxine, in which instance about 3 ml. were added. Zero time was
taken as that moment when the chosen volume of bromate solution had
been added. After a measured time interval, the bromination reaction
was stopped by the addition of the iodide-ion. After titration with
standard thiosulphate solution, the per cent of oxine compound which
had been brominated was calculated. The results of the experiments are
summarized in Table XVII. All determinations were made at room tempera-
ture (25-27°C.), under conditions corresponding to those of an analytical
bromometric titration.

The anomalous results with 4-methyloxine will be discussed later.

The following experiments have to do with the brown precipitate

Table XVII

PER CENT DIBROMINATION OF OXINE COMPOUNDS
AS A FUNCTION OF TIME

Compd. \ Time (min.)	0	1	3	5	7	10	15	20	30
oxine	100.1	100.1	100.0	100.1		100.1		100.2	
2-phenyloxine*	99.6	100.0	99.8	99.7	100.1				
2-methyloxine	99.9	99.9	100.0	100.1				100.1	100.2
4-methyloxine	75.2	94.5	97.8	98.0		99.3	99.7**	99.9***	100.0
6-methyloxine	100.0			100.0			100.0		

*2-phenyloxine was used as the hydrochloride salt; the dibrominated derivative precipitated and caused some interference at the end-point.

**average of 7 results   ***average of 13 results   For the most part, other values are the average of 3 or 4 results.

that can form, on the addition of iodide-ion, during the bromometric determination of 2-methyloxine and related compounds.

It was found that this brown precipitate is obtained no matter whether the compound that is brominated is oxine, 2-phenyloxine, or 2-, 4-, or 6-methyloxine. The experiments described below, concerned with the nature of the brown precipitate, were carried out mainly with the brown precipitate obtained in the bromometric determination of oxine. A summary of these experiments, many of which are only qualitative, follows.

In one set of experiments, the amount of oxine taken for bromination (the solvent was 100 ml. of 2.0 M hydrochloric acid) was varied from about 50 to 200 mg., and the volume of excess bromate solution (0.02 M) was kept approximately constant. It was observed that, on the addition of 1.0 g. of potassium iodide, the amount of the brown precipitate increased as the amount of oxine increased. When, in other experiments,

the amount of oxine (about 50 mg.) was kept constant and the volume of excess bromate solution was varied (from one to 10 ml.), the amount of the precipitate increased as the volume of bromate solution increased.

In a further experiment, about 100 mg. of 5,7-dibromo-oxine were dissolved in 100 ml. of 2 M hydrochloric acid and to this solution were added 1.0 gram of potassium bromide and then 10 ml. of the bromate solution. Bromine was produced but the solution remained clear. On the addition of 1.0 g. of potassium iodide, however, the brown precipitate formed. When the experiment was repeated without the 5,7-dibromo-oxine, the addition of iodide-ion gave only the familiar reddish colour of iodine and polyiodide-ion in aqueous solution.

In other experiments, the brown precipitate was filtered, washed liberally with warm water, and dried in air. When a few milligrams of the compound were placed in a flame, purple vapours and the odour of iodine were detected. Samples of the original dried compound were weighed into crucibles and heated at 110°C. for $7\frac{1}{2}$ hours. Assuming that the weight loss was due to volatilization of iodine and that the tan-coloured residue was 5,7-dibromo-oxine, the ratio I_2/5,7-dibromo-oxine from these experiments was 1.1 $\pm$ 0.1 (1.0, 1.1, 1.1). The tan residue was recrystallized from aqueous acetic acid. The melting point of the product, in agreement with the melting point of 5,7-dibromo-oxine, was 196-197°C. (lit., 195-196°C. (64)).

In a series of experiments, in which the amount of oxine was about 100 mg., the excess of bromate solution was 10 ml., and the amount of potassium iodide, added to precipitate the brown compound, was 1.0 g., the following observations were made: the brown precipitate disappears

when there are added 2-3 g. of potassium iodide, or a few millilitres

of thiosulphate solution, or 10 ml. of concentrated hydrochloric acid,

or 25 ml. of nitrobenzene, carbon disulphide, chloroform or carbon

tetrachloride, the colour of iodine appearing in the organic-liquid

phase. When these experiments were repeated with 2-phenyl, 2-methyl,

and 4-methyloxine, the observations were essentially the same, although

the brown precipitates derived from the 2-phenyl and 2-methyl compounds

were not as rapidly affected by the treatments.

In another experiment, 0.1 g. of iodine were dissolved in 10 ml.

of pyridine (yielding a dark brown solution). On the addition of 50 ml.

of water a brown precipitate, very similar in appearance to that derived

from oxine, was obtained. When excess iodide-ion, concentrated hydro-

chloric acid, or thiosulphate-ion were added, this precipitate disappeared,

behaving remarkably like the brown precipitate derived from oxine. When

0.1 g. of iodine were dissolved in 10 ml. of benzene rather than in

pyridine, no trace of a precipitate was observed on the addition of

50 ml. of water.

Finally, 0.1 g. of α-naphthol, structurally identical to oxine

except for the presence of a carbon atom in place of the nitrogen atom,

were dissolved in 100 ml. of 2.0 M hydrochloric acid and brominated, using

a large excess of bromate solution. (Some of the bromination product

precipitated.) On the addition of iodide-ion, no brown precipitate

appeared.

Comment on these experiments, and on the nature of the brown

precipitate, is in the Discussion.

Experiments were done to determine the effect of the brown pre-

cipitate on the detection of the end-point in the bromometric deter-
mination of oxine and 2-methyloxine. In the bromometric determination
of oxine, the brown precipitate decomposed very readily during the
titration with thiosulphate-ion, and did not seriously interfere with
the end-point detection. For example, the average of five results from
experiments in which 100.1 mg. of oxine were taken for bromination was
100.2 mg. $\pm$ 0.1 mg. In the bromometric determination of 2-methyloxine,
however, the brown precipitate did not decompose readily (even after 20 g.
of potassium iodide had been added) during the titration with thiosul-
phate-ion, and it interfered with the detection of the end-point. The
precipitate decreases the accuracy and precision of the bromometric
determination, as is shown by the last 12 results of Table XVIII.

To avoid interference at the end-point in the bromometric deter-
mination of 2-methyloxine, it is best to prevent the precipitation of the
brown compound. For 0.1 g. or less of 2-methyloxine (in 100 ml. of
2.0 M hydrochloric acid) and with 0.02 M bromate solution, precipitation
of the brown substance does not occur when the excess of bromate solution
is 1.5 ml. or less. Accurate and precise determinations of 2-methyl-
oxine can then be made, as shown by the first five results of Table XVIII.

(d) Polarographic Determination of Thorium: The quantitative
precipitation of thorium as the stoichiometric 1:4 2-methyloxinate, and
the reduction of 2-methyloxine at the dropping-mercury electrode yielding
a polarographic wave suitable for analytical purposes, make possible a
polarographic method for the determination of thorium.

After the quantitative precipitation and digestion of the thorium
2-methyloxinate, and filtration and washing of the precipitate as directed

Table XVIII

EFFECT OF EXCESS BROMATE ON
BROMOMETRIC DETERMINATIONS OF 2-METHYLOXINE

2-Methyloxine taken: 100.0 mg.

Excess KBrO$_3$* Soln. (ml.)	2-Methyloxine Found (mg.)
1.2	100.0, 100.0
1.4	100.0
1.5	99.8, 100.0
4.0	99.6, 100.1, 99.8 99.7, 99.6, 99.9
4.2	100.3, 99.6, 100.0
4.3	99.5, 100.1, 99.8

*Brown precipitate is present for
excesses of bromate (0.02 M) of
4 ml. or more.

for the bromometric determination of thorium, polarographic determinations of the thorium may be made by the following procedure. This was developed after numerous preliminary experiments.

The washed precipitate is treated on the filter paper with 100 ml. of a hot (80°C.) solution of 1.0 M sodium hydroxide. The precipitate is decomposed by the sodium hydroxide solution, leaving hydrous thoria on the filter paper. The 2-methyloxine anion, which is equivalent to the thorium, passes through the filter paper in the sodium hydroxide solution. This solution is caught in a 100-ml. volumetric flask, cooled to 25°C., and then made up to volume with 1.0 M sodium hydroxide (yielding a solution of pH 14). The polarographic cell is rinsed three times with portions of this solution and then filled. The solution is de-aerated for 15 minutes by slowly passing through it nitrogen (purified by passage

through a train of chromium(II) chloride solutions). The diffusion

current due to the reduction of 2-methyloxine in the solution is then

measured (five waves being recorded) and the concentration of thorium

is assessed by reference to a calibration curve.

For small amounts of thorium (5 mg. or less), the precipitates,

before dissolution in 1.0 M sodium hydroxide, are dried for one hour at

$110^{o}C.$ to volatilize any 2-methyloxine that may be present.

A calibration curve is shown in Fig. 3, in which the lengths of

the plotted "points" show the spread in the eight measurements of the

diffusion current that were made for each thorium concentration. In Fig. 3,

the range of concentration of thorium (in the original solution) is from

5.86×10^{-5} M to 2.94×10^{-3} M, corresponding to concentrations of

2-methyloxine (in the final solution) of from 1.17×10^{-4} M to $5.88 \times$

10^{-3} M. The diffusion current of 2-methyloxine is certainly linear with

respect to this 50-fold range of concentration, and may well be linear

over a wider range.

The preliminary investigations on which the foregoing method is

based concerned the suitability of several possible supporting electro-

lytes, the polarographic purity of buffer components present in solutions

of 2-methyloxine, the stability of these solutions, and the effect of pH

on the shape of the polarographic wave and on the diffusion current due

to 2-methyloxine.

It was found that polarographic determinations of 2-methyloxine

are best made in solutions which are 1.0 M in sodium hydroxide. The

polarographic wave ($E_{\frac{1}{2}}$ = -1.82 volts vs. S.C.E.) from the reduction of

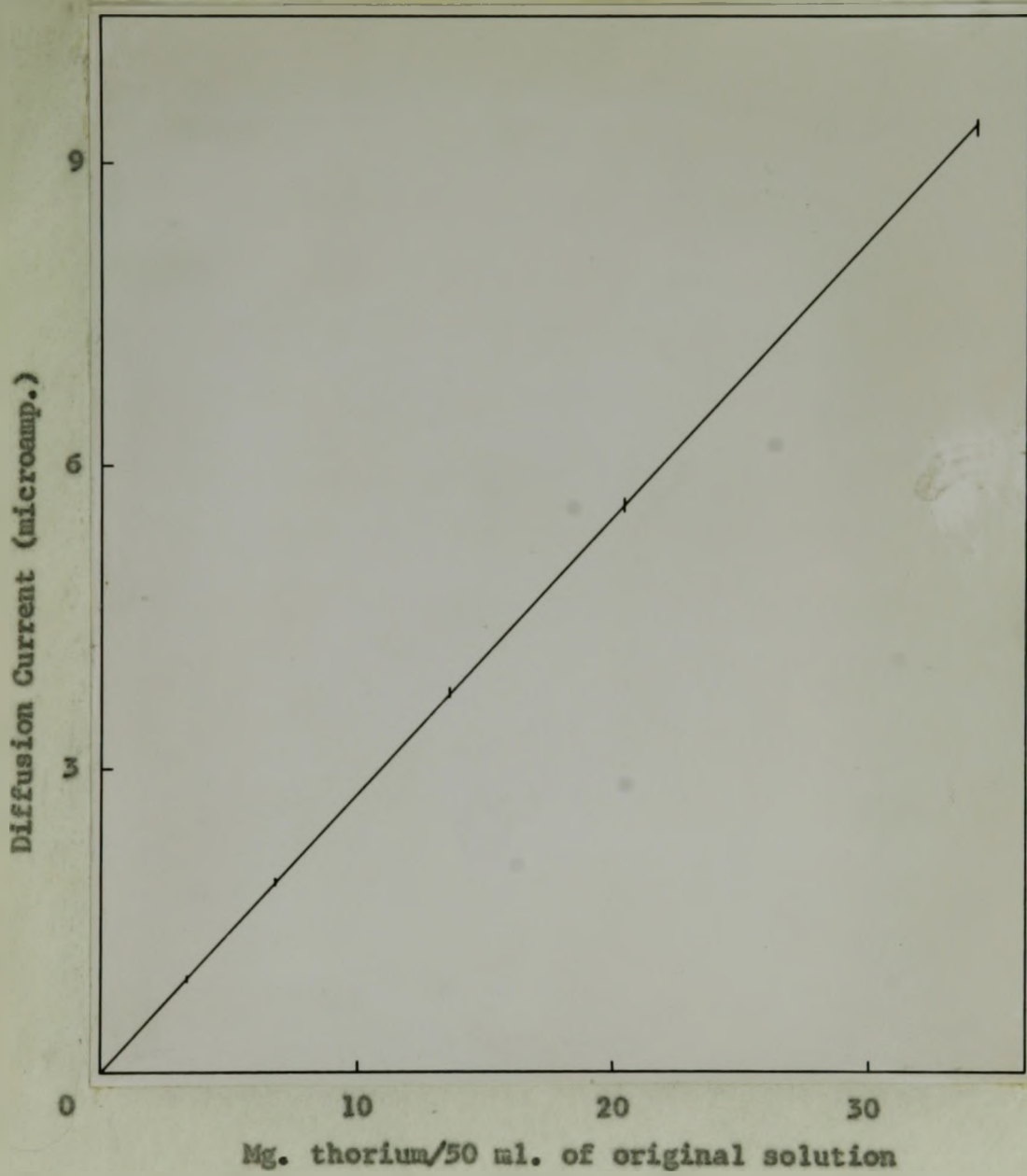2-methyloxine in these solutions (pH 14.0) is well formed (Fig. 4) and

Fig. 3

Calibration curve for polarographic determination of thorium by
2-methyloxine.

Fig. 4

Polarographic wave of 2-methyloxine in 1.0 M sodium hydroxide

thus easily measured. This is not so at lower pH values, where the waves

are of poor form, similar to those found by Fernando and Phillips (43).

In addition, 2-methyloxine is stable in 1.0 M sodium hydroxide for at

least 45 hours, as shown by the constancy of the diffusion current over

this period. Furthermore, no significant variation in the diffusion

current occurs when the concentration of sodium hydroxide is varied from

0.5 to 1.5 M.

(e) Polarography of 2-Methyloxine: The experiments described

below are concerned firstly, with whether the current from the polaro-

graphic reduction of 2-methyloxine is diffusion controlled and secondly,

with the determination of the number of electrons involved in the reduction

of a molecule of 2-methyloxine at the dropping-mercury electrode. In these

experiments the polarographic reduction of 2-methyloxine in solutions of

pH 7.6 to 14.2 was studied.

Table XIX lists the composition of the 2-methyloxine solutions with regard to buffer components (which also served as supporting electrolytes). In these solutions, the concentration of 2-methyloxine was 7.0×10^{-4} M. Also given in Table XIX are data from the experiments done to determine whether the current observed in each solution is governed by the rate of diffusion of 2-methyloxine to the surface of the dropping-mercury electrode. For each solution of 2-methyloxine tested, measurements of the current, i, measured on the "plateau" of the wave and corrected for the residual current, were made over a wide range (about 20-65 cm.) of "effective" pressures of mercury, h_e, and values of $i/h_e^{\frac{1}{2}}$ were determined. In Table XIX, the value of $i/h_e^{\frac{1}{2}}$ represents the average value for each solution tested, the precision measure being the overall deviation. The small deviations indicate the constancy, within experimental error, of values of $i/h_e^{\frac{1}{2}}$ over the wide range of mercury pressures.

Included in Table XIX are the values of the capillary characteristics: m (milligrams of mercury dropping per second), and t (life-time of the drop, in seconds), and also the value of the half-wave potential $(E_{\frac{1}{2}})$ of the polarographic waves obtained in solutions having pH values above 11. The m and t values were determined using techniques recommended by Meites (65).

When the $E_{\frac{1}{2}}$ values are plotted against pH (for the pH values between 11.2 and 14.2), a straight line is obtained with slope 0.061 and intercept 0.98, giving the relationship:

$$-E_{\frac{1}{2}} = 0.98 + 0.061 \text{ pH}$$

For a polarographic wave arising from a reversible reaction at

Table XIX

BUFFER COMPOSITION AND POLAROGRAPHIC DATA FOR 2-METHYLOXINE SOLUTIONS

Buffer Compn./100 ml. of 2-Methyloxine Soln.	pH	$i/h_e^{\frac{1}{2}}$*	m (mg. Hg/sec.)	t (sec.)	$E_{\frac{1}{2}}$(vs. S.C.E.) (volts)
23 ml. 0.2 M NaOH 25 ml. 0.2 M KH$_2$PO$_4$	7.6	0.76 ±0.02	1.63	3.41	
8.1 ml. 0.2 M NaOH 25 ml. 0.2 M H$_3$BO$_3$ in 0.2 M KCl	8.7	0.70 ±0.02	1.63	3.41	
22 ml. 0.2 M NaOH 25 ml. 0.2 M H$_3$BO$_3$ in 0.2 M KCl	10.0	0.43 ±0.01	1.62	3.70	
6 ml. 0.2 M NaOH 25 ml. 0.2 M Na$_2$HPO$_4$	11.2	0.34 ±0.01	1.62	3.66	−1.66
46 ml. 0.2 M NaOH 25 ml. 0.2 M Na$_2$HPO$_4$	12.6	0.33 ±0.02	1.61	3.45	−1.75
0.5 M NaOH	13.7				−1.80
1.0 M NaOH	14.0	0.21 ±0.00	1.62	3.05	−1.82
1.5 M NaOH	14.2				−1.85

*For each solution, h_e was varied from about 20-65 cm. of mercury pressure.

the dropping-mercury electrode, at 25°C., the equation

$$E_{de} = E_{\frac{1}{2}} - \frac{0.059}{n} \log \frac{i}{i_d - i}$$

holds (66), where E_{de} is the potential of the dropping-mercury electrode, i is the current at a potential E_{de}, i_d is the diffusion current, $E_{\frac{1}{2}}$ is the half-wave potential (the value of E_{de} when i = i_d/2), and n is the number of electrons acquired at the cathode by a molecule or ion of the substance being reduced. When values of E_{de} are plotted against values

of $\log(i/i_d-i)$, a straight line is obtained (for reversible reactions)
with slope $0.059/n$, from which the value of n can be estimated.

Values of E_{de} and $\log(i/i_d-i)$ obtained from polarograms recorded
from strongly alkaline solutions of 2-methyloxine were plotted, and
straight lines were obtained. The values of n, calculated from the
slopes of the lines, and the data for the plots, are given in Table XX.

Table XX

POLAROGRAPHIC n VALUES FOR 2-METHYLOXINE AT HIGH pH VALUES

pH	i_d (μa)	$-E_{de}$ (volts vs. S.C.E.)	i (μa)	$\log(i/i_d-i)$	n
11.2	1.84	1.62	0.30	-0.710	1.05
		1.64	0.50	-0.428	
		1.65	0.70	-0.212	
		1.66	0.90	-0.019	
		1.67	1.10	+0.173	
		1.68	1.30	+0.382	
12.6	1.75	1.72	0.40	-0.529	1.03
		1.73	0.60	-0.282	
		1.74	0.80	-0.074	
		1.75	1.00	+0.124	
		1.77	1.20	+0.339	
		1.78	1.40	+0.602	
13.7	1.29	1.76	0.20	-0.737	1.11
		1.78	0.40	-0.347	
		1.80	0.60	-0.060	
		1.81	0.80	+0.212	
		1.83	1.00	+0.538	
14.0	1.29	1.78	0.20	-0.737	1.09
		1.80	0.40	-0.347	
		1.82	0.60	-0.060	
		1.83	0.80	+0.212	
		1.85	1.00	+0.538	
14.2	1.28	1.81	0.20	-0.733	1.13
		1.83	0.40	-0.342	
		1.84	0.60	-0.053	
		1.86	0.80	+0.223	
		1.87	1.00	+0.553	

From these plots, the value of the half-wave potential, $E_{\frac{1}{2}}$, can
also be obtained for, when $i = i_d/2$, $\log(i/i_d-i) = 0$, and $E_{de} = E_{\frac{1}{2}}$. The

values of $E_{\frac{1}{2}}$ in the previous table (Table XIX) were obtained in this way.

The polarograms recorded for pH values of 7.6, 8.7, and 10.0 were such that useful plots of potential and current data could not be made. In order to obtain at least approximate values of n for the electrode reaction at these pH values, it was necessary to make use of the Ilkovic equation (67):

$$i_d = 607n \; D^{1/2} \; m^{2/3} \; t^{1/6} \; C$$

where the terms, other than those already defined, are $D(cm^2 sec^{-1})$, the diffusion coefficient of the species being reduced, and C (millimoles/l.), its concentration.

The values of m and t have already been given (Table XIX). Values of the diffusion current at the pH values 7.6, 8.7, and 10.0 were obtained using solutions of 2-methyloxine of known concentration (7.0×10^{-4} M). The diffusion coefficient, D, of 2-methyloxine is not known. This was calculated, however, by measuring the diffusion current (for the known concentration of 2-methyloxine) in solutions at pH 11.2 and 12.6* (Table XXI), and using these values in the Ilkovic equation with the appropriate values of m and t (Table XIX) and the value of n, known now to be unity for the electrode process at pH values above 11. The average of the two such calculations of the diffusion coefficient was $0.62 \pm 0.02 \times 10^{-5} \; cm^2 sec^{-1}$

In Table XXI are the values of n, calculated from the Ilkovic

---

*Among other things, the diffusion coefficient depends on the viscosity and ionic strength of the solution. Because the viscosity and ionic strength of the solutions in the pH range 13.7 - 14.2 (0.5 - 1.5 M sodium hydroxide) are substantially different from those of the solutions in the pH range 7.6 - 12.6, the diffusion coefficient for 2-methyloxine in the sodium hydroxide solutions would not be useful and so was not calculated.

equation, for the electrode reactions at pH 7.6, 8.7, and 10.0. For purposes of comparison, values of n (from Table XX) for the electrode reaction at higher pH values are also given.

Table XXI

n VALUES FOR POLAROGRAPHIC REDUCTION OF 2-METHYLOXINE

$(C = 7.0 \times 10^{-4} M; D = 0.62 \times 10^{-5} cm^2 sec^{-1})$

pH	i_d (μa)	$m^{2/3} t^{1/6}$ $(mg^{2/3} sec^{-1/2})$	$D^{1/2} \times 10^3$ $(cm.sec^{-1/2})$	n
7.6	3.72	1.70	2.5	2.06
8.7	3.33	1.70	2.5	1.84
10.0	2.70	1.72	2.5	1.48
11.2	1.84			1.05
12.6	1.77			1.03

In the Discussion, an attempt will be made to interpret these n values in terms of plausible mechanisms for the polarographic reduction processes of 2-methyloxine in alkaline solution.

DISCUSSION

PART A   Thorium and Oxine

(a) Composition of Thorium Oxinate Precipitated from Cold Solution:
The data of Table III, together with the recovery of oxine by appropriate
heating of the compound under investigation, show convincingly that the
yellow compound precipitated in the cold is $Th(C_9H_6ON)_4 \cdot C_9H_7ON$, and not
$Th(C_9H_6ON)_4$, as is so widely thought. It is apparently identical in
composition to the orange-red thorium oxinate precipitated from hot
solution. The difference in colour is not due to a difference in stoichio-
metry, but is in some way related to the temperature of precipitation and
digestion.

The colour changes are reversible. When the yellow compound, at
0°C. with the supernatant liquid, is warmed to and held at 70°C., it
becomes orange-red in about half an hour. Similarly, the orange-red
compound changes colour when it is cooled from 70°C. to 0°C., although
this colour change is not as rapid as the reverse one.

The difference in colour of the two 1:5 thorium oxinates may be
due to a difference in a physical property such as state of aggregation
or crystal structure.

(b) Thermal Stability of 1:5 Thorium Oxinate: The thermal insta-
bility of 1:5 thorium oxinate lessens considerably its significance as
an analytically useful compound. When used for gravimetric purposes,
the 1:5 compound must be dried at a temperature certainly below 80°C.
(Table I). This not only requires a tediously long drying time, but

also prevents the removal of oxine (significantly volatile only at temperatures above about 85°C. (28)) that may be contaminating the precipitate. Furthermore, the 1:5 compound has only limited use in bromometric determinations. In these determinations, it may often be necessary to heat the metal oxinate (e.g., Table XVI), before its dissolution, to above 100°C. to remove traces of contaminating reagent.

This work shows (Tables V and VI) that it is possible to quantitatively convert by thermal means the 1:5 compound to the 1:4. The tediousness of the conversion and the careful control it requires are such, however, that 1:4 thorium oxinate is not a convenient weighing form.

Several factors probably account for the disagreement among workers concerning the thermal behaviour of 1:5 thorium oxinate. Firstly, thorium hydrolyses very readily to form hydroxo complexes, even in acid solution. Only under carefully controlled conditions (DISCUSSION, PART B, (a)) is it possible to prepare thorium derivatives of organic reagents which are non-basic and free of hydrous thoria. Examination of the literature shows that carefully controlled conditions were not used by workers who prepared 1:5 thorium oxinate and investigated its thermal stability. It is distinctly possible that the precipitates used in these investigations were contaminated with varying amounts of basic thorium compounds. Secondly, the limited solubility of oxine in water and the ease with which it can precipitate from aqueous solution leads to the further possibility that the 1:5 thorium oxinate used by some workers may have been contaminated with the precipitant. Thirdly, the temperature and time required for quantitatively removing the "extra"

molecule of oxine might reasonably be expected to depend, to some extent, on the state of aggregation and particle size of the compound. It is impossible to tell from the work of others whether the thorium oxinate taken for thermal studies was in the form of a cake, large particles, or fine powder. Fourthly, in thermogravimetric experiments, the rate of heating, which has a bearing on the shape of the pyrolysis curve, was not constant among the various workers. Lastly, the investigators have often drawn their conclusions from only one experiment.

All in all, it is not surprising that their agreement is limited to the observation that the 1:5 compound begins to decompose at some temperature below $100^{\circ}C.$, probably at about $80^{\circ}C.$

(c) Reaction of Oxine with 1:4 Thorium Oxinate: The solubility of 1:4 thorium oxinate appears to be so slight in 95 per cent ethanol that the addition of the "extra" molecule of oxine most likely proceeds by interaction between oxine molecules in solution and molecules of 1:4 thorium oxinate in the solid state:

$$1:4_{solid} + oxine_{solution} = 1:5_{solid}$$

The data of Table VII indicate that the addition reaction has reached equilibrium by 45 minutes. This reaction was studied under only one set of experimental conditions. Studies at other oxine concentrations and other temperatures would undoubtedly alter the extent to which the reaction proceeds.

The main importance of the addition reaction in this thesis is its use in the investigation of the structural nature of 1:5 thorium oxinate.

(d) Structural Nature of 1:5 Thorium Oxinate: The rationale
of the carbon-14 experiments is as follows. From the reaction of
oxine with 1:4 thorium oxinate, a mixture of the 1:4 and 1:5 compounds
results. The composition of the mixture at chemical equilibrium (under
the conditions of temperature and concentration used in this work) is
conveniently described by Th(ON)$_4$·0.62HON. The use of active oxine in
the chemical reaction is potentially useful in deciding whether one of
the oxine groups in 1:5 thorium oxinate is a component of the crystal
lattice, or whether all five oxine groups are bonded to the central
thorium atom and are equivalent or approximately so.

In the absence of any complicating reactions, the reaction of
active oxine with inactive 1:4 thorium oxinate ought to, in the case
of the "lattice compound", lead to a specific activity in the product,
Th(ON)$_4$·0.62HON, of $\frac{0.62}{4.62}$ x 4.40 = 0.59 mv./sec./mg. oxine, where 4.40
is the specific activity of the reacting oxine, and $\frac{0.62}{4.62}$ is in effect
the dilution factor. Furthermore, if the 1:5 compound contains the
"extra" oxine as a lattice component, heating the Th(ON)$_4$·0.62HON to
remove this oxine would be expected to yield an inactive product,
Th(ON)$_4$.

If, on the other hand, all five oxine groups are bonded to the
thorium atom and are approximately equivalent, the reaction of active
oxine with inactive 1:4 thorium oxinate should lead to activity not only
in the product, Th(ON)$_4$·0.62HON, but also in the Th(ON)$_4$ obtained after
heating the Th(ON)$_4$·0.62HON. The latter point follows since any one of
the five equivalent ligands (active or inactive) in the 1:5 compound
could be lost on heating. The specific activity expected in the

Th(ON)$_4$·0.62HON from the acquisition by a 1:4 molecule of only one molecule of oxine (of specific activity: 4.40 mv./sec./mg.) should be 0.59 mv./sec./mg. oxine. The total activity expected in the Th(ON)$_4$, obtained from the thermal treatment of the Th(ON)$_4$·0.62HON, should be 4/5 of the total activity of the latter.

The data of Table X show that the Th(ON)$_4$·0.62HON is active, as is expected for either of the two structures proposed for 1:5 thorium oxinate. The data of Table XI show, however, that the Th(ON)$_4$ is also active. This, at first sight, suggests that all five oxine groups are bonded to the thorium atom.

However, on closer inspection of the data it is seen that the specific activity of the Th(ON)$_4$·0.62HON (and of the Th(ON)$_4$; the two, incidentally, being equal: 2.3 mv./sec./mg. oxine) is much greater than the specific activity expected (0.59) from the acquisition of only one molecule of oxine (of specific activity: 4.40 mv./sec./mg.). The high specific activity of the Th(ON)$_4$·0.62HON (and of the Th(ON)$_4$) means that an exchange between inactive ligands associated with the thorium, and active ligands in solution, is accompanying the addition reaction. The extent to which the exchange occurs can be approximated. At the completion of the exchange process, the activity in the Th(ON)$_4$·0.62HON will be equilibrated with the activity of the oxine in solution, and the specific activity of each will be equal. In the addition reaction, 200 mg. of oxine (specific activity, 4.40 mv./sec./mg.) were reacted with 60 mg. of 1:4 thorium oxinate containing 43 mg. of inactive oxine. When the activity has equilibrated, the specific activity of oxine in solution, and therefore of Th(ON)$_4$·0.62HON, would be $\frac{200}{243}$ x 4.40 = 3.6 mv./sec./mg.

oxine. Since the specific activity of the $Th(ON)_4 \cdot 0.62HON$ was found to be 2.3 (for a reaction time of one hour), the exchange of ligands has proceeded towards equilibrium to an extent of $\frac{2.3}{3.6} \times 100\% = 64$ per cent.

Clearly, with the occurrence of an exchange reaction, the data provided by the carbon-14 experiments are difficult to interpret in terms of either of the two structures proposed for 1:5 thorium oxinate for, even if one of the oxine groups were a lattice component, the $Th(ON)_4$ left after thermal treatment of the $Th(ON)_4 \cdot 0.62HON$ would be active due to the exchange process.

However, despite the complicating exchange reaction, the data of Tables X and XI do allow some basis for a choice between the two structures. These data show that the specific activity of the mixture, $Th(ON)_4 \cdot 0.62HON$, and of the $Th(ON)_4$ left after the thermal treatment of the mixture, are equal; or, in other words, that the relative activity of the two species is equal to their relative oxine content (0.87).

The data are examined below assuming first that one of the oxine groups is a lattice component, and that exchange is occurring between active oxine molecules in solution and the four ligands bonded to the thorium atom. If, at the time the product of the addition reaction was isolated, the exchange reaction had proceeded towards equilibrium to an extent of 64 per cent, the specific activity of.the oxine in solution and therefore of the oxine in the lattice would be 4.4 - $\left[(4.4-3.6) \times 0.64\right]$ = 3.9 mv./sec./mg. oxine. This specific activity of the "lattice oxine" is substantially higher than the experimental value of the specific activity (2.3) of the four ligands associated with the

thorium atom. When, then, the "lattice oxine" is removed from the
Th(ON)$_4$·0.62HON by heating, the specific activity of the product,
Th(ON)$_4$, should be lower than the specific activity of the Th(ON)$_4$·0.62HON,
and not equal to it as was found experimentally. Put in other words,
the relative activity of Th(ON)$_4$ to Th(ON)$_4$·0.62HON should not be 0.87
(the relative ligand content), as was experimentally determined
(Table XI), but should be somewhat lower. Although 13 per cent of the
ligand content in the Th(ON)$_4$·0.62HON is lost on heating, more than
13 per cent of the activity in it would be lost, since the oxine vola-
tilized would be of higher specific activity than the oxine bound to the
thorium atom. Indeed, the expected relative activity of Th(ON)$_4$ to
Th(ON)$_4$·0.62HON can be calculated.

In the first column of Table XXII (below) are the (calculated)
amounts of oxine (based on the weights of the Th(ON)$_4$·0.62HON samples
in Table X) that would be present in the lattice. The (calculated)
activity in the Th(ON)$_4$·0.62HON due to the "lattice oxine" is given in
the second column. For the calculations, the value used for the
specific activity of the lattice oxine was 3.9 mv./sec./mg. This value,
as noted earlier, takes into account a correction made necessary by the
occurrence of the exchange reaction. In the fourth column is the
activity expected in the Th(ON)$_4$ after removal of the "lattice oxine" by
heating. The figures in this column were obtained by subtracting the
figures of the second from those of the third column. The expected
relative activity (fifth column) was obtained by dividing the figures in
the fourth column by those of the third.

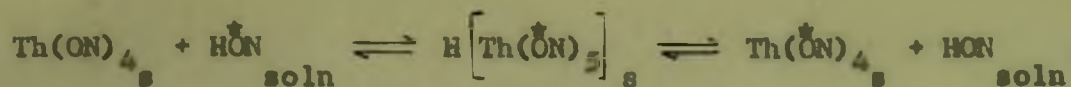The value of the expected relative activity (0.77) is considerably

Table XXII

EXPECTED RELATIVE ACTIVITY $Th(ON)_4/Th(ON)_4 \cdot 0.62HON$ FOR OXINE HELD IN LATTICE

(Specific Activity of HON is taken as 3.9 mv./sec./mg.)

Calc. Amt. of Oxine in Lattice (mg.)	Calc. Activity due to Oxine in Lattice (mv./sec.)	Measured Activity in $Th(ON)_4 \cdot 0.62HON$ (mv./sec.)	Expected Activity in $Th(ON)_4$ (mv./sec.)	Relative Activity $Th(ON)_4/$ $Th(ON)_4 \cdot 0.62HON$
3.20	12.5	54.3	41.8	0.77
2.37	9.2	40.0	30.8	0.77
1.38	5.4	23.3	17.9	0.77
1.14	4.4	19.0	14.6	0.77
0.77	3.0	13.1	10.1	0.77

lower than the value (0.87) found experimentally (Table XI). This suggests that in 1:5 thorium oxinate, the "extra" molecule of oxine is not a lattice component - unless, of course, the value 0.87 came about through randomization of the oxine groups in the lattice with those bonded to the thorium atom during the thermal treatment of the $Th(ON)_4 \cdot 0.62HON$. The likelihood of randomization having occurred during the heating stage, however, seems remote: the "extra" molecule is not tightly bound and begins to volatilize at about $80^{\circ}C$. (18,28). A significant proportion of the "extra" molecules will have been volatilized at temperatures probably too low to allow randomization.

A plausible process is set forth below to explain the experimental fact that the specific activity of the $Th(ON)_4 \cdot 0.62HON$ is equal to that of the $Th(ON)_4$ (or, in other words, that the ratio of the activity of the $Th(ON)_4$ to that of the $Th(ON)_4 \cdot 0.62HON$ is the ratio of their oxine contents, 0.87):

$$\text{Th(ON)}_{4_s} + \text{H}\overset{*}{\text{O}}\text{N}_{\text{soln}} \;\rightleftharpoons\; \text{H}\left[\text{Th(}\overset{*}{\text{O}}\text{N)}_5\right]_s \;\rightleftharpoons\; \text{Th(}\overset{*}{\text{O}}\text{N)}_{4_s} + \text{HON}_{\text{soln}}$$

The subscripts "s" and "soln" denote solid and solution, res-
pectively, and the asterisks denote active species. In this process,
it is postulated that in 1:5 thorium oxinate the five oxine ligands are
bonded to the thorium atom; further, it is postulated that the exchange
reaction occurs through this 1:5 complex. Since the five oxine ligands
are considered to be equivalent, the release of an inactive ligand by an
active 1:5 molecule is statistically more probable than the release of
an active ligand. Given sufficient time, the specific activity of the
1:4 compound would become equal to that of the 1:5 compound.

A curious aspect of the experimental data is that they suggest
that the chemical reaction has attained equilibrium (Table VII) but that
the exchange reaction has not. When the exchange reaction has attained
equilibrium, the specific activity of the oxine in the solid and of the
oxine in solution should be equal - about 3.6 mv./sec./mg., as calculated
earlier. The specific activity of the oxine in the solid was found,
however, to be 2.3 mv./sec./mg. That chemical equilibrium but not
exchange equilibrium has been attained is likely due to an inherent
difference between the chemical and exchange reactions. The chemical
reaction is involved with the transfer back and forth of one oxine ligand,
whereas the exchange reaction must proceed to involve, eventually, all
the oxine ligands associated with the central thorium atom.

The occurrence of the exchange reaction was not anticipated at
the time of the experiments. Had it so been, it would have not been
difficult to determine whether or not the specific activity of the

Th(ON)$_4 \cdot$0.62HON increased with time (after chemical equilibrium had been established) to a value of about 3.6 mv./sec./mg. oxine. Such an experiment would have provided an immediate test for statements just made above.

The mechanism by which the oxine molecules in solution react with molecules of 1:4 thorium oxinate in the solid state is not understood. This mechanism, likely a complicated one, may involve reaction at and slightly within the surface of small particles of 1:4 thorium oxinate, with subsequent transfer of the added ligand to molecules of 1:4 thorium oxinate which are more deeply buried in the particle. The fact that the specific activity of the Th(ON)$_4 \cdot$0.62HON and of the Th(ON)$_4$ are equal implies that molecules of 1:4 thorium oxinate even in the centre of particles have had opportunity to react with oxine, and to exchange inactive ligands for active ones.

Bonding of the five oxine groups to the thorium atom is further suggested by a comparison of the thorium chelates obtained with 2-, 3-, and 4-methyloxine. Both 3- and 4-methyloxine, like the parent compound oxine, give thorium compounds of 1:5 stoichiometry (Table XII), but the 2-methyl derivative yields only the normal 1:4 chelate. This behaviour is readily explained if the ligands are all associated with the thorium atom. In 2-methyloxine, the methyl group, which is in the alpha position with respect to the coordinating nitrogen atom, sterically inhibits the grouping of five 2-methyloxine ligands around the thorium atom, permitting only four ligands to chelate to it. This is not unreasonable when it is considered firstly, that five oxine ligands around the thorium atom must be near to exhibiting some steric repulsion

towards one another, and secondly, that the methyl group in the 2-position
has already been claimed to sterically destabilize chelates of 2-methyl-
oxine (8,9). Indeed, with aluminium 2-methyloxine even fails to give a
precipitate. This, as previously mentioned, has been attributed (3,4,5,
6,7) to steric interference due to the 2-methyl group. When the methyl
group is moved to positions beta or gamma with respect to the nitrogen
atom, the steric inhibition is relieved sufficiently to allow once again
formation of 1:5 compounds with thorium. The difference in behaviour
towards thorium between 2-methyloxine on the one hand, and oxine, 3-,
and 4-methyloxine on the other, is not so readily accounted for by a
structure in which one of the organic groups is merely a component of
the crystal lattice.

As mentioned earlier, scandium, uranium(VI), and plutonium(VI)
form compounds with oxine that also contain an "extra" molecule of the
organic reagent. The structural nature of the scandium and plutonium(VI)
oxinates has received little or no attention but that of uranium(VI)
oxinate has been studied to some extent. In the light of the evidence
given above, which supports the view that all five oxine ligands are
bonded to the thorium atom, it is interesting to note the results of
recent work (68) concerning the nature of the 1:3 uranium(VI) complex.
This compound until recently was formulated as $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$ (16),
the "extra" molecule being considered (e.g., (29)) to be a lattice com-
ponent. In a careful study (68) by Bullwinkel and Noble, however,
convincing evidence is given to show that the "extra" molecule of oxine
is coordinated to the central uranium atom and that the compound is
better formulated as $H\left[UO_2(C_9H_6ON)_3\right]$. Among the evidence which led the

investigators to this conclusion was the fact that they found it possible to titrate the acidic proton and to prepare the salts $MUO_2(C_9H_6ON)_3$, where $M = Na^+$, $(C_2H_5)_4N^+$, or $(C_6H_5)_4As^+$. Other workers (69) have noted that a band at 14.1 μ in the absorption spectrum of oxine is absent in the spectrum of the 1:3 uranyl complex, suggesting that the "extra" molecule of oxine is not existing as such in the crystal lattice.

It would be interesting to attempt experiments with 1:5 thorium oxinate similar to those done with 1:3 uranium(VI) oxinate. During the course of this present work, one such experiment was done, in which an attempt was made to prepare the sodium salt of 1:5 thorium oxinate, but the experiment was not successful. In 0.001 M sodium hydroxide, the 1:5 compound was apparently unaffected. In 0.01 to 0.1 M sodium hydroxide, decomposition of the 1:5 compound to a mixture of apparently the 1:4 compound and hydrous thoria occurred. In more concentrated solutions of sodium hydroxide, decomposition to hydrous thoria was complete. Complete decomposition of the uranyl oxinate also occurs at very high concentrations of hydroxyl-ion (68).

A comparison of the 1:5 thorium and the 1:3 uranyl oxinates is not entirely valid because of the obvious difference between the thorium and uranyl ions and between the number of oxine groups associated with each. But the facts that each oxinate contains an "extra" molecule of oxine (16), that each loses this molecule of oxine on heating to give the normal lower oxinate (16), and that each lower oxinate reacts with oxine to yield the higher one (16), cannot be overlooked.

The data of Tables VIII and IX show that, in organic solvents

such as benzene and nitrobenzene, 1:5 thorium oxinate dissociates into 1:4 thorium oxinate and oxine. Although this dissociation is very easily explained if oxine is held in the crystal lattice, it is not inconsistent with five oxine groups being bonded to the thorium atom. The 1:5 molecule would be a bulky one and in solution may readily lose a ligand to form the less-strained 1:4 molecule. It is not unreasonable, however, that the 1:5 compound is stabilized in an environment containing an excess of oxine. This, for example, would be the reason for the formation of some 1:5 compound when the 1:4 compound is put into an ethanolic solution of oxine. But, if the 1:5 compound is placed in a solution containing no oxine, an oxine group is lost and the more stable 1:4 compound formed. This would account for the dissociation of 1:5 thorium oxinate into two particles in either benzene or nitrobenzene.

In the absence of further evidence, the view must be taken that in 1:5 thorium oxinate the five oxine groups are bonded to the central thorium atom. A more accurate representation of the structure of 1:5 thorium oxinate would then be given by the formulation $H\left[Th(ON)_5\right]$, than by the formulation $Th(ON)_4 \cdot HON$. A reasonable diagrammatic representation is shown below, in which hydrogen bonding is postulated to contribute somewhat to the stability of the molecule.
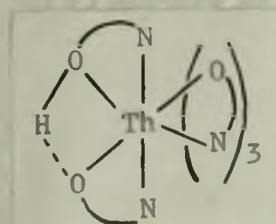
Bonding of all five oxine groups implies that thorium, which usually exhibits a coordination number of eight in its chelate compounds, is in this instance exhibiting a coordination number of ten. This is a high and very rare coordination number and indeed, may not yet have been observed. There are, however, no theoretical reasons against unusually high coordination numbers. The number of ligands associated with a central metal atom is limited by steric interference of the ligand groups and by the directional properties of available orbitals (70). In 1:5 thorium oxinate, the oxine groups are admittedly large, but steric interference of these may be somewhat compensated by the large covalent radius that thorium would have in such a compound. The ionic radius of thorium is 1.10Å (71), but the covalent radius would be appreciably larger than this, probably more comparable to the radius of the atom, which is 1.65Å (71). A sufficient number of orbitals (e.g., the 5f and 6d orbitals) for a coordination number of ten are available in the Th(IV) ion. Whether, however, a combination of some of these orbitals can be made, leading to ten suitably directed orbitals, is another matter.

The structural nature of the interesting 1:5 thorium oxinate certainly merits further study, preferably by spectroscopic and X-ray methods.

PART B   Thorium and 2-Methyloxine

(a) Precipitation of Thorium as the 1:4 2-Methyloxinate:

Concentration of reagent: The experiments summarized in Table XIII show that, although thorium can be quantitatively precipitated with only a modest excess of 2-methyloxine present, the precipitation is not quantita-

tive as the 1:4 chelate unless there is present a substantial excess of 2-methyloxine. The addition of the precipitant "in slight excess" (39) is not a sufficient direction. Under the conditions of the experiments of Table XIII (concentration of thorium: 0.7 mg./ml.; pH of precipitation: 8.1), when the excess of reagent is less than 60 per cent some of the thorium precipitates in a form other than the 1:4 chelate. With an excess of 60 per cent or greater, however, the precipitation of thorium as the 1:4 chelate is not less than 99.8 per cent complete from solutions of concentration 0.7 mg. Th/ml. For such solutions, the recommended procedure for the quantitative precipitation of thorium as the 1:4 chelate allows a nearly 70 per cent excess of reagent.

Other experiments showed that a 70 per cent excess of reagent is insufficient, however, to precipitate thorium quantitatively as the 1:4 chelate from solutions with less than about 0.7 mg. Th/ml. (when the pH after precipitation is 8.0 - 8.5). From solutions only one-fiftieth as concentrated as this, thorium can nevertheless be precipitated quantitatively (Table XVI) if the concentration of 2-methyloxine corresponds to 65-70 per cent excess for a solution containing 0.7 mg. Th/ml.

These effects are related to the ease with which thorium hydrolyzes. To prepare pure thorium chelates uncontaminated by basic thorium compounds a large excess of the chelating agent is required.

Adjustment of pH: The concentration of the aqueous ammonia used to raise the pH to within the desired range, and the way in which the ammonia is added, are important factors in obtaining a precipitate of the pure thorium chelate. If the ammonia is concentrated, the results can be low by as much as 7 per cent, even when the base is added drop by

drop, with rapid stirring (Fig. 1, Curve A). In fact, with the ammonia
as dilute as 0.5 M the results can be low if the base is added rapidly
without stirring*. On the other hand, base as concentrated as 1.0 M
may be used if added drop by drop, with efficient stirring. Under these
conditions, and with a 70 per cent excess of precipitant and the pH
adjusted to 8.0 - 8.5, thorium is quantitatively precipitated solely as
the chelate. The average of 15 determinations (the two lowest points
on Curve A of Fig. 1) on a solution that contained 33.6 ± 0.1 mg. of
thorium (concentration 0.7 mg./ml.) was 33.7_6 mg., with an average
deviation of 0.0_5 mg.

The low results - that is, low as the chelate - induced by adjust-
ing the pH with concentrated ammonia, or even with relatively dilute
ammonia added rapidly, are likely due to the precipitation of some of
the thorium as hydroxo complexes, occasioned by local excesses of
hydroxyl-ion. When local excesses were encouraged by using 5 M and 15 M
ammonia without care in stirring, and when (by eliminating the digestion)
the metathesis of any hydroxo complexes to the chelate was hindered, the
error rose to over 10 per cent. The error was greater the higher the
concentration of the added ammonia, being 4 per cent (3.4, 4.5) with 5 M
ammonia and 10 per cent (10.0, 10.1) with 15 M ammonia. Ignition, to
thorium dioxide, of precipitates formed under the same conditions showed
that the thorium was being precipitated quantitatively: concentration

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*In two experiments in which 0.5 M ammonia was added rapidly
without stirring, the recovery of thorium as the 1:4 thorium 2-methyl-
oxinate was low by 1.2 per cent (1.1, 1.3), while in two other experi-
ments in which 1.0 M ammonia was added in the same way, the recovery of
thorium as the 2-methyloxinate was low by 1.4 per cent (1.3, 1.4).

of ammonia, stirring, and digestion affect the nature of the precipitate that is first formed but not (provided the pH is appropriate) the completeness of precipitation.

If local excesses of hydroxyl-ion initially induce precipitation of some hydroxo complexes when the chelate is the stable form for the precipitate under the conditions existing in the solution, then the hydroxo compounds should in time metathesize to the chelate. The data of Curve B of Fig. 1 show that this occurs. This metathesis was also observed in thermogravimetric experiments. A thermogram for a precipitate digested for only two minutes indicated that the precipitate was not all thorium chelate, whereas the thermogram for a similarly induced precipitate that had been digested for 11 hours was identical with the thermogram of pure chelate.

Provided, then, that the pH be chosen properly (Fig. 2), the thorium will finally be present solely (and quantitatively) as the chelate, even though initially some of it precipitates in another form. Under other precipitation conditions (i.e., careful addition of 0.5 and 1.0 M aqueous ammonia) the thorium can be initially obtained quantitatively as the chelate.

pH Control: The data of Fig. 2 show that thorium can be precipitated quantitatively as the 1:4 chelate in the pH range 6.1 to 11.5, at least with the concentrations of thorium and reagent used in this work. This pH range for quantitative precipitation - fully 5 pH units - is broader than that reported for any other organic precipitant for thorium, insofar as is known (14).

Between the pH values of 5 and 6, the pH-precipitation curve

rises very sharply. From the expression below (in which Ox⁻ represents the chelating anion of 2-methyloxine) for the K_{sp} of thorium 2-methyl-oxinate:

$$K_{sp} = \left[Th^{+4}\right] \left[Ox^-\right]^4$$

it can be seen that a small increase in the concentration of Ox⁻ due to a small increase in pH reduces the concentration of thorium in solution through a fourth-power effect. Therefore, the extent of precipitation increases very rapidly with a small increase in pH. If thorium existed in solution solely as a simple hydrated ion, one could (making use of the dissociation constants, K_{OH} and K_{NH}, of 2-methyloxine) calculate the K_{sp} for this 1:4 chelate from any point on the rising portion of the pH-precipitation curve. Calculations made on this unwarranted assumption show the K_{sp} to be of the order of 10^{-33} and give, as a matter of fact, rather surprisingly consistent results throughout the rise of the curve.

Beginning at a pH of 11.5, precipitation (though complete) is partly as, say, hydrous thoria; by a pH of 13.0, the precipitate is almost entirely hydrous thoria. With increasing pH, the concentration of hydroxyl-ion of course increases, but (for a given stoichiometric concentration of 2-methyloxine) the concentration of the chelating anion approaches a maximum, corresponding to complete dissociation of the reagent. This leads to the eventual dominance of hydroxyl-ion in controlling the concentration of metal-ion in solution, through the precipitation of hydroxo complexes of thorium ("hydrous thoria") rather than the chelate. The pK_{OH} of 2-methyloxine is such (pK_{OH} = 10 (72)) that it is largely dissociated by a pH of 11.

The pH of incipient precipitation of thorium by 2-methyloxine is

substantially higher than the corresponding value found in this work

and elsewhere (73)*, under not greatly different experimental conditions,

for the precipitation of thorium by oxine. This is in accord with what

has been found (4,39,74) for the precipitation of other metal-ions by

these two related reagents. Such comparisons are not really proper,

however, unless among other conditions of the experiments, the concen-

trations (both of metal-ion and reagent) are the same, for these influence

the pH of precipitation. With all conditions comparable, the difference

in the pH of precipitation for the chelates of a given metal with two

related reagents should reflect differences in the intrinsic solubility

(75) and the stability of the chelates in solution, and in the acidity

of the reagents. The latter two of these are ordinarily related, in that

a given metal commonly forms the more stable chelate with the weaker

acid (77). When this is so, two opposing effects (4,75) bear on the pH

of precipitation of the chelate: the more stable of the two chelates

does not require as high a concentration of the chelating anion to bring

about its precipitation (which argues for a lower pH of precipitation)

but, on the other hand, the weaker of the two acids holds protons more

firmly and so, to compare with the stronger acid as a provider of the

---

*The pH values of incipient and of quantitative precipitation
of thorium by oxine reported by Gotô (73) are about 4.0 and 4.4, res-
pectively. These pH values were established in an acetate buffer
medium, as was the work in this thesis with 2-methyloxine. At higher
pH values (7.9 and higher), however, tartrate in substantial concen-
tration was used by Gotô as a buffer component. It is difficult to
understand why tartrate did not interfere with the quantitative pre-
cipitation of thorium at these higher pH values, since, firstly, other
workers (15) have reported that tartrate prevents the quantitative
precipitation of thorium by oxine and, secondly, tartrate was found in
the present work to interfere in the precipitation of thorium by
2-methyloxine. A more critical discussion of Gotô's work has been
given elsewhere (76).

chelating anion, requires a higher pH. A given metal-ion would be expected to form a more stable chelate with 2-methyloxine than with oxine, for the former is the weaker acid (both its pK_{NH} and pK_{OH} are higher). In point of fact, however, the 2-methyloxine chelates are somewhat less stable, at least in 50 per cent aqueous dioxane (8,9), than the corresponding oxine chelates. (The lesser stability of the 2-methyloxine chelates is attributed to a steric hindrance to their formation, due to the methyl group in the 2-position.) Thus, with respect to the precipitation of the chelates of a given metal with these particular reagents, the two factors - chelate stability and reagent anion concentration - should operate, not in opposition but in concert, to favour the precipitation of the oxine chelate at a lower pH than the 2-methyloxine chelate. These considerations could account for the experimental observation that oxine precipitates thorium at a lower pH than does 2-methyloxine.

Strictly, however, these considerations apply only when the chelates being compared are of the same stoichiometry. The difference in stoichiometry between 1:5 thorium oxinate and 1:4 thorium 2-methyloxinate makes it more difficult to assess the effect of the relative stability and intrinsic solubility of the two thorium chelates on the pH of their incipient precipitation.

The remainder of the discussion in this section is concerned with the experimental work done to test the claim (42) that 1:5 thorium 2-methyloxinate had been prepared.

As the analytical data of Table XIV clearly show, the compound obtained under the conditions which are reported to yield the 1:5

compound, is, without any doubt, 1:4 thorium 2-methyloxinate. Moreover, when the compound is heated to 155°C., its weight remains essentially constant (Table XV); 2-methyloxine is not lost, as would be expected for a 1:5 compound. Again, even when extremely large excesses of 2-methyloxine are used (e.g., the last results in Table XVI were obtained using several thousand per cent excess of the reagent) in the precipitation of thorium, the thorium compound obtained is the 1:4 and not the 1:5 2-methyloxinate, despite the fact that the use of large excesses of 2-methyloxine would very much favour the formation of a 1:5 compound. Lastly, throughout all the investigations concerned with thorium and 2-methyloxine, no evidence for any compound of thorium and 2-methyloxine other than that represented by $Th(C_{10}H_8ON)_4$, was obtained.

This claim for the preparation of 1:5 thorium 2-methyloxinate is rejected.

(b) Gravimetric Determination of Thorium: The very good accuracy and precision of the gravimetric method that was developed are shown in Table XVI. The method is sensitive, too: the precipitation of the thorium chelate can be quantitative from solutions that contain the metal at concentrations as low as 0.013 mg./ml. This value, about 6 x 10^{-5} M, is the lowest concentration at which experiments were done. For quantitative precipitation from solutions with less than about 0.7 mg. Th/ml., an excess of reagent greater than 70 per cent is required. This is provided for in the recommended procedure.

The wash liquid is hot and alkaline to aid in the removal of any 2-methyloxine that may be contaminating the precipitate. Even so, when less than about 5 mg. of thorium are precipitated (in which event

the excess of precipitant is large), the precipitate may retain a
significant amount of 2-methyloxine. This is of no consequence, for
any that remains is volatilized during drying at 110°C., as several
experiments proved.

The thermogravimetric experiments showed that thorium 2-methyl-
oxinate has excellent thermal stability insofar as its use for analytical
purposes is concerned. The thermolysis curve obtained in this work con-
firms the one found concurrently by Wendlandt (41). The chelate is
stable up to about 180°C.

The excellent thermal stability of thorium 2-methyloxinate and
the ease with which this chelate may be freed of excess 2-methyloxine
gives 2-methyloxine a distinct advantage over oxine as a reagent for
thorium. Because 1:5 thorium oxinate is not stable above about 80°C.
(18,28), the determination of thorium by weighing this compound not only
is inconvenient (a long drying time at low temperature being required)
but also is exposed to error (particularly in the determination of small
amounts of thorium) from contamination by oxine, which is not appreciably
volatile below 85°C. (28).

(c) Bromometric Determination of Thorium: The recommended
bromometric method for the determination of thorium is fully as accurate
and precise as the gravimetric method, as results over a wide range of
concentrations show (Table XVI).

When small amounts of thorium are precipitated, it is desirable
in the bromometric determination to dry the precipitate at 110°C., prior
to its dissolution, to remove any excess reagent. Since 1:5 thorium
oxinate cannot be safely heated at a temperature sufficiently high to

remove excess oxine, the bromometric determination of small amounts of thorium is more satisfactorily done with 2-methyloxine.

The usefulness of 2-methyloxine for the bromometric determination (and, of course, also for the gravimetric determination, and for the polarographic determination which is discussed later) of thorium in the presence of other metals is restricted by the unselective character of this reagent. Ironically, the inability of 2-methyloxine to precipitate aluminium does not of itself give this reagent an immediate advantage over oxine, which does precipitate aluminium. Experiments showed that aluminium (Al to Th molar ratio: 1:1 - 5:1) interferes in the bromometric determination of thorium even though the reagent does not precipitate aluminium. Low results (from 3 to 10 per cent) for thorium were obtained. The pH used for the precipitation of thorium (about 8.0 to 8.5) is such that hydrous alumina precipitates with the thorium chelate. The low results for thorium may be due to occlusion of thorium ions by the aluminium precipitate.

To prevent the precipitation of hydrous alumina, complexing agents such as tartrate and fluoride were added to the solution but both of these form complexes with thorium that are sufficiently stable to interfere with its precipitation by 2-methyloxine. The gravimetric and polarographic determinations of thorium by means of 2-methyloxine would be similarly affected by aluminium unless, of course, a suitable complexing agent were found.

Because the thorium precipitate yielded by 2-methyloxine is stoichiometric and thermally stable, the bromometric and gravimetric methods based on this precipitate have advantages over such methods

involving other organic reagents (14) for the standardization of thorium solutions. In comparison with the common gravimetric method involving precipitation as the hydrous oxide and ignition to thorium dioxide, the gravimetric method using 2-methyloxine is preferable because of the more favourable gravimetric factor (factor for ThO_2: 0.8788; for $Th(C_{10}H_8ON)_4$: 0.2683).

Discussion concerned with the rate of dibromination of 2-methyloxine and of some related compounds follows. From the data of Table XVII it is seen that, with the exception of 4-methyloxine, the oxine compounds rapidly dibrominate quantitatively, in fact by the time the addition of the bromate solution is complete. There is no need in the bromometric determination of these compounds to allow any time, before the addition of the iodide-ion, for the dibromination to proceed quantitatively.

The rate of dibromination of 4-methyloxine is interesting because it is, anomalously, slow. The relatively slow rate of bromination is thought due to the 4-methyl group sterically hindering the entry of a bromine atom in position-5 of the quinoline ring. Construction of a model of the 5,7-dibromo-4-methyloxine molecule (using Stuart and Briegleb atom models) supports this view by demonstrating that the rotation of the 4-methyl group is completely restricted when a bromine atom is occupying the 5-position. Thus, accurate bromometric determinations of 4-methyloxine cannot be made unless about 20 minutes, at least, are allowed for the dibromination to become quantitative.

In contrast to 4-methyloxine, 6-methyloxine is quantitatively dibrominated by "zero time". Construction of a model of 5,7-dibromo-6-methyloxine showed that the 6-methyl group is, somewhat surprisingly, free

to rotate between the large bromine atoms in the adjacent 5- and 7-
positions.

Although other workers (39) have reported that the bromination
of 2-phenyloxine is not quantitative, the data of Table XVII show that
it is - and at "zero time". The quantitative dibromination of 2-phenyl-
oxine is of some analytical significance, as this compound is potentially
a useful one. The non-quantitative dibromination found by the previous
workers was ascribed by them to deactivation towards bromination in the
molecule due to the electron-withdrawing phenyl group. The most likely
valence-bond structure, however, to cause deactivation to bromination is:
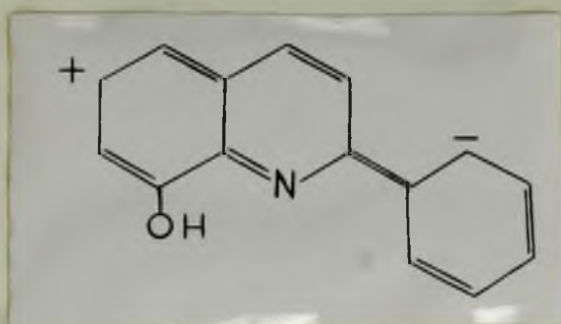
Because of the charge separation, this structure would not be expected
to contribute significantly to the overall structure of the 2-phenyloxine
molecule. (The same is true, of course, for the related structures
obtained by moving the negative charge around the phenyl group.)

2-Phenyloxine is a difficult compound to prepare in high purity.
It is possible that the low bromination results of the previous workers
were due to impurities. The hydrochloride of 2-phenyloxine, on the
other hand, is easily prepared in pure form; this was used in the present
work.

The experiments having to do with the brown precipitate that can
form in the bromometric determination of oxine, 2-methyloxine, and other

related compounds are now discussed.

The observation that the amount of the brown precipitate formed on the addition of the iodide-ion increases with either increasing amount of oxine (or, of course, 2-methyloxine) taken for bromination, or increasing amount of excess bromate, suggests that the precipitate is related both to the 5,7-dibromo-oxine and iodine (or species such as I_3^-).

That 5,7-dibromo-oxine is involved in the brown precipitate is indicated further by the appearance of the brown precipitate on the addition of potassium iodide to a solution containing bromine and added 5,7-dibromo-oxine, and the failure of the precipitate to form in the absence of 5,7-dibromo-oxine. The agreement of the melting point of the residue (obtained by heating the brown precipitate at 110°C.) with that of 5,7-dibromo-oxine leaves little doubt that 5,7-dibromo-oxine is a component of the brown precipitate.

The analytical data, although somewhat crude, indicate the molar ratio of iodine to the dibromo derivative (I_2/5,7-dibromo-oxine) to be 1:1.

The facts that oxine can yield a brown precipitate but α-naphthol apparently cannot, and that a solution of iodine in pyridine, but not a solution of iodine in benzene, gives, on the addition of water, a brown precipitate similar in appearance to the one obtained in a bromometric determination, indicate that a heterocyclic nitrogen atom also plays a role in the formation of this precipitate.

On the basis of this evidence a provisional structure can be advanced for the brown precipitate, showing a molecule of iodine bonded

to a molecule of 5,7-dibromo-oxine through the nitrogen atom:
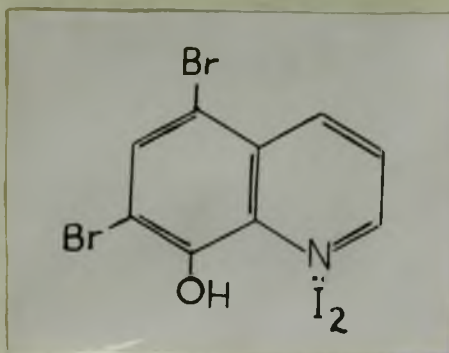
A structure such as this readily explains why the precipitate decomposes on the addition of: excess iodide-ion (by formation of I_3^-); or concentrated hydrochloric acid (by formation of the hydrochloride of 5,7-dibromo-oxine); or thiosulphate-ion (by reduction of iodine to iodide-ion); or solvents such as nitrobenzene, carbon disulphide, chloroform, and carbon tetrachloride (by extraction of iodine into the organic-liquid phase).

Theoretically, the formation of a bond between the heterocyclic nitrogen atom in 5,7-dibromo-oxine and molecular iodine is possible.   In the iodine molecule, a vacant antibonding molecular orbital is available to accept the unshared pair of electrons of the nitrogen atom.

Evidence in the literature indirectly supports the suggestion that, in the brown precipitate, iodine is bonded to the nitrogen atom of 5,7-dibromo-oxine.   It has been observed (78) that when iodine dissolves to give brown solutions, it is chemically combined with solvent molecules, the latter being capable of furnishing a pair of electrons for the formation of a coordinate covalent bond.   The best-known example of iodine-solvent complexes of this kind is the iodine-pyridine complex ($C_5H_5N-I_2$).   This complex has been widely studied (e.g., 79,80) and it is now established that in this stable complex a molecule of iodine is

bonded to a molecule of pyridine through the nitrogen atom.

As previously described, the addition of water to a solution of iodine in pyridine causes precipitation of a brown compound, strikingly similar in both appearance and chemical behaviour to the brown precipitates that can be obtained in bromometric determinations. This has also been observed by Mulliken and Reid (79), who thought the precipitate to be the aforementioned iodine-pyridine complex in the solid state.

The experimental work in this thesis and evidence in the literature thus strongly indicate that the brown compound that often forms in the bromometric determination of oxine, 2-methyloxine, and other related compounds, is a complex in which molecular iodine is bonded to the nitrogen atom of the dibrominated oxine compound.

In the bromometric determination of oxine, the brown precipitate was not found to interfere with the detection of the end-point (although other workers (46) have claimed that it does), and accurate and precise determinations of oxine can be made (at least under the experimental conditions described earlier). In the bromometric determination of 2-methyloxine, however, the brown precipitate decomposes slowly during titration with thiosulphate-ion and interferes with the end-point detection, with resultant decrease in accuracy and precision (Table XVIII). When, however, the excess volume of standard bromate solution is restricted under the given experimental conditions to 1.5 ml. or less, the precipitate does not form and accurate and precise determinations of 2-methyloxine can then be made (Table XVIII).

(d) Polarographic Determination of Thorium: The diffusion current due to the polarographic reduction of 2-methyloxine in 1.0 M

sodium hydroxide is linearly proportional (Fig. 3) to the concentration of 2-methyloxine (at least over a concentration range of about 1×10^{-4} M to 60×10^{-4} M). The form of the polarographic wave (Fig. 4) permits easy measurement of the diffusion current and is distinctly better, for analytical purposes, than the one reported (43) by previous workers to give a diffusion current linearly proportional to the concentration of 2-methyloxine. The latter wave form is really not very suitable for analytical use.

The magnitude of the diffusion current obtained in strongly alkaline solution is not significantly affected by changes in the concentration of the sodium hydroxide over the range 0.5 M to 1.5 M. In addition, 2-methyloxine is stable in 1.0 M sodium hydroxide for at least 45 hours, a time much longer than that (less than an hour) required for the polarographic measurements.

The procedure for the polarographic determination of thorium by 2-methyloxine involves treatment of the 1:4 thorium 2-methyloxinate precipitate with hot 1.0 M sodium hydroxide. By such treatment, the precipitate is decomposed: hydrous thoria is left on the filter paper and the 2-methyloxine anion passes through with the sodium hydroxide solution. The separation of the organic anion from the hydrous thoria is strictly quantitative. This was shown by the fact that on dissolution of the hydrous thoria in 2.0 M hydrochloric acid, no 2-methyloxine could be found in the acid solution by bromometric analysis.

Although the form of the polarographic wave is indeed good, the polarographic method for the determination of thorium is not as precise as the gravimetric and bromometric methods. The precision varies from

about $\pm$ 1 per cent (for thorium concentrations of about 3×10^{-3} M in the original solution) to about $\pm$ 7 per cent (for thorium concentrations of about 6×10^{-5} M). This precision is, however, satisfactory for a polarographic method. The method is equally as sensitive as the gravimetric and bromometric methods: polarographic determinations of thorium can be made at concentrations of the metal ion at least as low as 0.013 mg./ml. (13 p.p.m.). In the polarographic determination of small amounts of thorium (5 mg. or less), the thorium 2-methyloxinate precipitate should be dried at 110°C. to free it of any contaminating 2-methyloxine.

The polarographic method is really one for determining the concentration of 2-methyloxine, and is, of course, applicable to any metal ion that can be precipitated by this reagent, provided the precipitation is quantitative and the precipitate is of reproduceable stoichiometry.

(e) Polarography of 2-Methyloxine: The polarography of organic substances is in general much more complicated than that of inorganic substances. For relatively few of the many organic compounds which have been studied have the polarographic processes been fully elucidated over a wide range of pH. More specifically, for heterocyclic nitrogen compounds the polarographic processes are generally complex and incompletely understood (81,82). For example, the behaviour of oxine is known to be complicated (83) (and there is apparently disagreement about the experimental facts (84)).

The present study of the polarography of 2-methyloxine is not a comprehensive one, and so the conclusions reached are to be regarded as tentative ones.

For 2-methyloxine, the half-wave potential ($E_{\frac{1}{2}}$) is pronouncedly dependent on pH, becoming increasingly negative with increasing pH (Table XIX). This indicates that in the reduction, hydrogen ions are involved, which is commonly so in the polarographic reduction of organic compounds (85). The relationship between $E_{\frac{1}{2}}$ and pH should, then, be linear, and it was found to be so (at least over the pH range 11.2 - 14.2):

$$-E_{\frac{1}{2}} = 0.98 + 0.061 \text{ pH}$$

The slope of the line represented by this equation is in good agreement with that (0.059) which would be expected (44) for an electrode reaction involving hydrogen ions and electrons in equal numbers.

The plots of E_{de} vs. $\log(i/i_d-i)$ for the polarographic waves that permitted respectable measurements of potential and current to be made (those obtained from solutions of pH 11.2 - 14.2) are linear, with slopes close to those expected for a reversible electrode reaction involving one electron (n = 1). The conclusion that the electrode process for the reduction of 2-methyloxine at high pH values involves one electron (and one hydrogen ion) is consistent with the data.

At pH values below 11.2, the polarographic waves are not well defined, and cannot be analyzed as can those obtained from solutions of pH above 11. Throughout the entire pH range studied (7.6 - 14.2), however, the current is apparently diffusion controlled; strong evidence for this (86) is found in the fact that, all other conditions being constant, the current is proportional to the square root of the "effective" pressure of mercury in the capillary - i.e., $i/h_e^{\frac{1}{2}}$ is constant. (Table XIX shows the constancy of this quantity, within experimental error, for each set of conditions.) Further evidence that the current

is diffusion controlled is found in its linear dependence on the concen-
tration of 2-methyloxine (Fig. 3).

Because the current is diffusion controlled, the Ilkovic equation
($i_d = 607$ n $D^{1/2}$ $m^{2/3}$ $t^{1/6}$ C) may be used with some confidence to obtain
n values for the electrode reaction in the solutions of pH 7.6, 8.7 and
10.0 This involves, as pointed out earlier (EXPERIMENTAL AND RESULTS,
PART B (e)), calculating the diffusion coefficient, D, of 2-methyloxine
from the diffusion current at pH values 11.2 and 12.6 (where n is known
to be unity), and using appropriate, experimentally determined, values
of $m^{2/3}t^{1/6}$. The n values obtained by this method (Table XXI) for the
reaction at pH values 7.6 to 10.0 suggest that a two-electron process is
occurring at pH 7.6.

Plausible mechanisms for a two-electron reduction at pH 7.6 and
for a one-electron reduction at pH values above 11 are now considered.
(An accounting for the processes that may be occurring in the inter-
mediate pH range (8-11) is deferred for the moment.) The mechanisms
take into account the evidence - variation of $E_{\frac{1}{2}}$ with pH - that hydrogen
ions are involved in the processes.

It is proposed that the two-electron process occurring at pH 7.6
is the reduction of 2-methyloxine to a dihydro derivative, such as
3,4-dihydro-2-methyloxine*:

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*The 1,2- or 1,4-dihydro derivatives are equally reasonable.
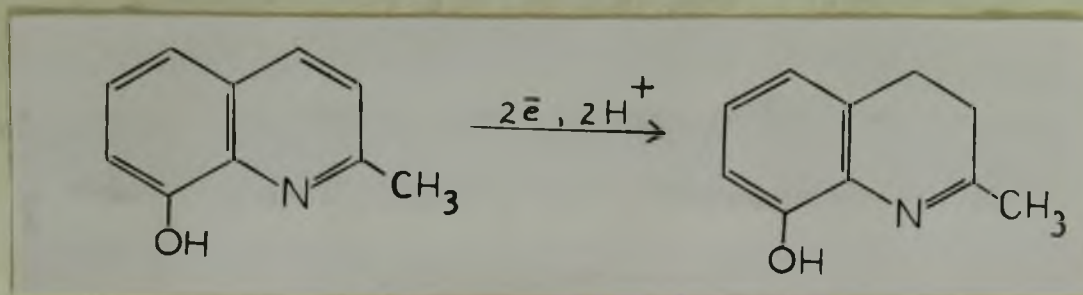
The reduction is shown as occurring in the pyridine ring for two reasons. Firstly, because of the electron-releasing tendency of the phenol group, the electron density is likely to be higher, and there-fore reduction more difficult, in the benzene ring than in the pyridine ring. Secondly, chemical reduction of quinoline and related compounds has been reported (87) in the pyridine ring, the product being a dihydro derivative. In earlier work (83) concerned with the polarography of the parent compound, oxine, reduction in the pyridine ring was also suggested.

It is proposed that the one-electron process occurring in solutions at pH values above 11 is the reduction of the 2-methyloxine anion (2-methyloxine being essentially fully dissociated into its anionic form (I) at these high pH values) to a free radical (II).

dimer or products
from
disproportionation

I   II
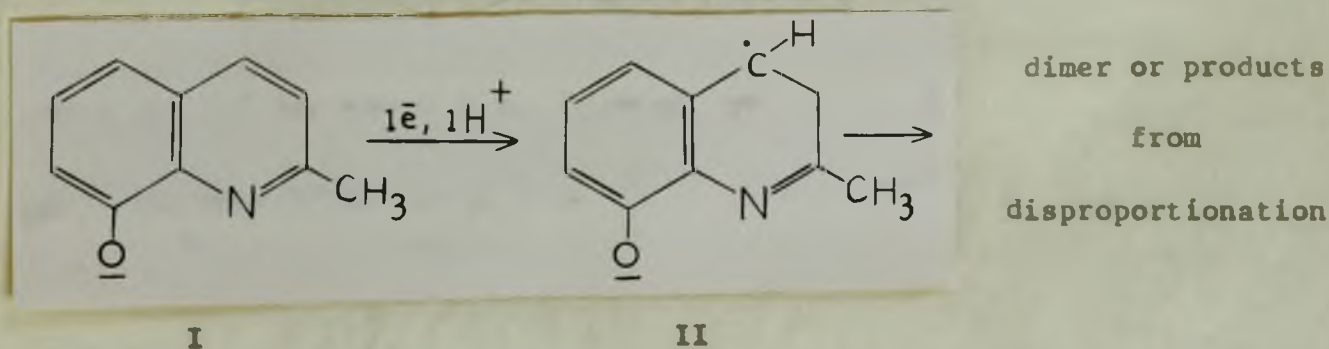
(Other formulations of the free radical, involving reduction in the pyridine ring are, of course, possible.) The free radical, not likely

to remain as such for long, probably undergoes dimerization or dis-
proportionation. This reduction process is similar to one (83)
proposed for oxine in solutions of high pH, although in this instance,
the investigator apparently considered the species undergoing reduction
to be the neutral molecule.

In solutions of pH values between 7.6 and 11.2, the apparent
number of electrons taking part in the electrode process is non-integral.
(At pH 8.7, n = 1.84; at pH 10.0, n = 1.48 (Table XXI).) Clearly, an
electrode process cannot involve a non-integral number of electrons. An
attempt to account for these anomalous values of n follows.

Using the values pK_{OH} = 10.0 and pK_{NH} = 5.7 for the dissociation
constants of 2-methyloxine*, one can, of course, calculate for any pH
value the percentage of 2-methyloxine in the form of the quinolinium-ion
(H_2Ox^+), the neutral molecule (HOx), and the anion (Ox^-) resulting from
dissociation of the phenolic hydrogen. The results of these calculations
for the pH range 7.6 to 12.6 are given in Table XXIII.

In Fig. 5, a comparison is made of the plot of per cent dissociation
of the phenolic hydrogen vs. pH with a plot of n values vs. pH. It is
seen that the pH range over which dissociation of the phenolic hydrogen
varies from substantially 0 to 100 per cent coincides closely with the pH
range over which the value of n varies from two electrons to one electron.

This suggests that the two-electron reduction at pH 7.6 involves
the neutral molecule (HOx), that the one-electron reduction at pH values

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*Näsänen (72), in very careful and precise work, has determined
the dissociation constants of 2-methyloxine as a function of the ionic
strength of the solution. The values given above are those given by
Näsänen for solutions with ionic strength corresponding to the ionic
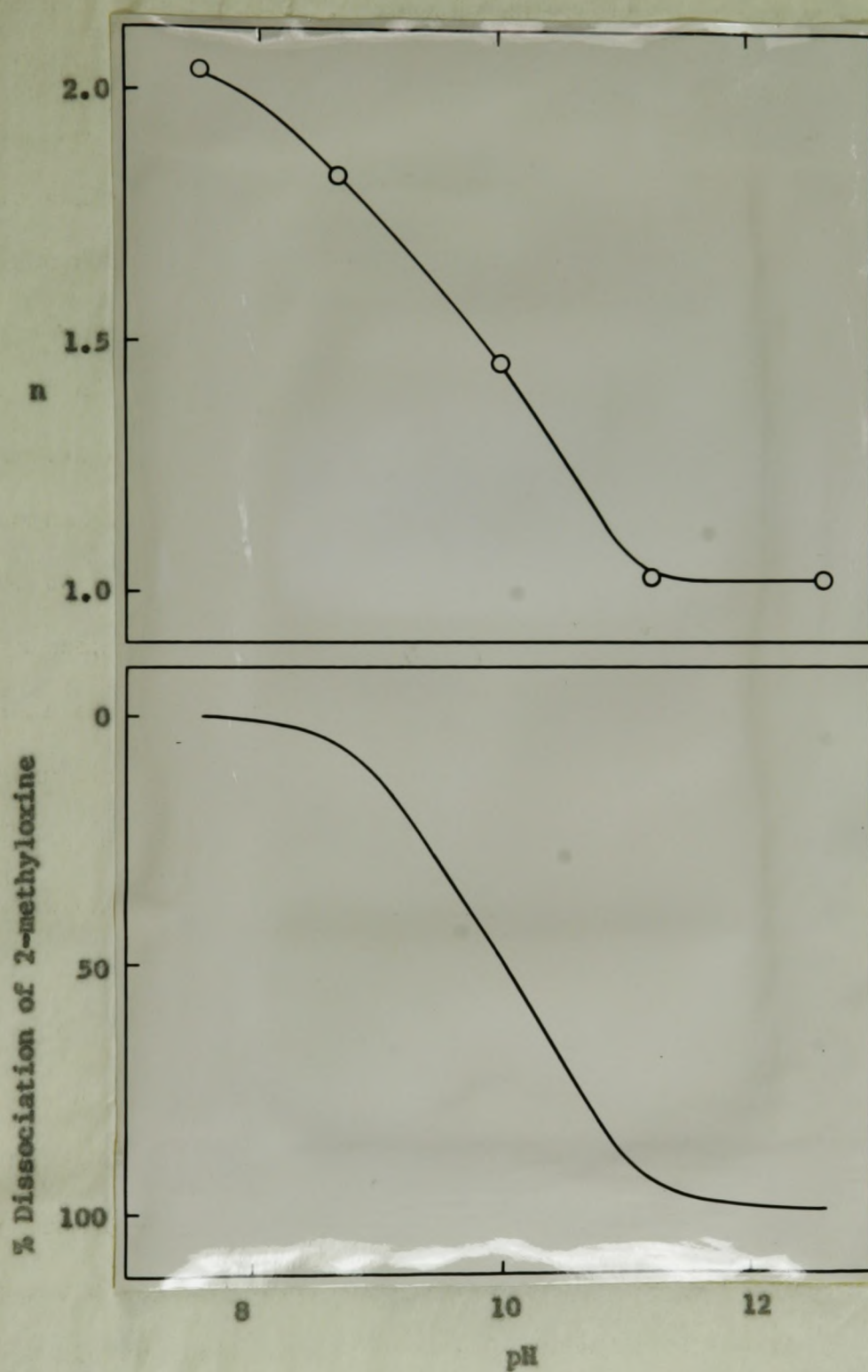strength of the solutions used in the present work.

Fig. 5

Upper-Variation in n values with pH; Lower-Variation in per cent
dissociation of phenolic hydrogen of 2-methyloxine with pH.

Table XXIII

DISTRIBUTION OF 2-METHYLOXINE AMONG THE
SPECIES H_2Ox^+, HOx and Ox^-

pH	H_2Ox (%)	HOx (%)	Ox^- (%)
7.6	1.2	98.5	0.3
8.7	0.1	95.1	4.8
10.0	-	50.0	50.0
11.2	-	6.0	94.0
12.6	-	0.1	99.9

above 11 involves the anion (Ox^-), and that at intermediate pH values
the reduction involves both species, leading to "overall" values of n
between two and one.

The foregoing can be put in more quantitative terms. In
Table XXIV are given, as a function of pH, the number of neutral mole-
cules (HOx), and of anions (Ox^-), per 1000 of the 2-methyloxine species.
Assuming that a neutral molecule consumes two electrons in its
reduction and an anion one electron, the total number of electrons

Table XXIV

COMPARISON OF n VALUES

pH	No. of HOx Molecules/ 1000 Species	No. of Ox^- Ions/1000 Species	"Apparent" n Values	n Values from Table XXI
7.6	985	3	2.00	2.06
8.7	951	48	1.95	1.84
10.0	500	500	1.50	1.48
11.2	60	940	1.06	1.05
12.6	1	999	1.00	1.03

involved in the reduction of both the 2-methyloxine species can be cal-
culated very simply. Thus an average number of electrons, or an
"apparent" n value, involved in the reduction of one species can be
obtained. These "apparent" n values are compared in Table XXIV to the
n values found through the use of $\log(i/i_d-i)$ vs. $E_\frac{1}{2}$ plots or the
Ilkovic equation (as given in Table XXI).

The agreement between the last two columns of Table XXIV is
indeed very satisfactory, and lends support to the ideas advanced above.

The discussion which follows is an attempt to account for the
difference between the polarographic reduction of the anion (a one-
electron process) and of the neutral molecule (a two-electron process).

In the anionic free radical (II), suggested as the reduction
product of the anion (I), a distribution of negative charge would exist
in the pyridine ring. This is illustrated by the valence-bond form (III)
which contributes to the overall structure of the free radical. The

II   III
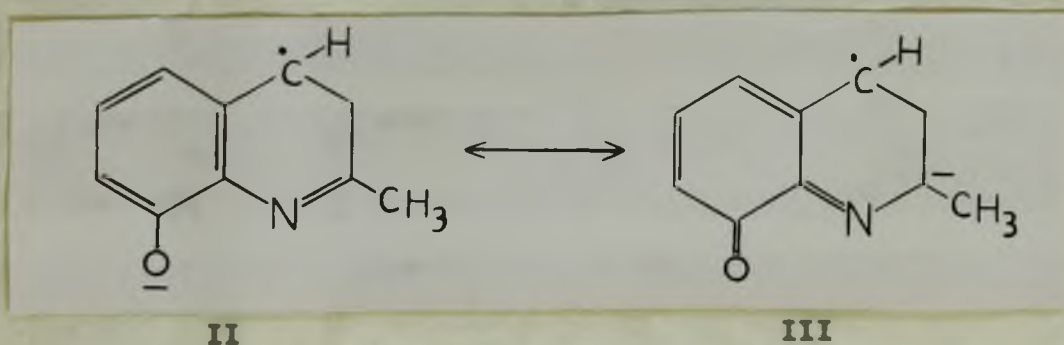
presence of negative charge in the pyridine ring would hinder the
acquisition of a second electron and, therefore, reduction of the free
radical to the dihydro derivative. As a result, dimerization or dispro-
portionation of the free radical is more likely to occur. On the other
hand, the two-electron reduction of the neutral molecule to the dihydro
derivative proceeds in the absence of the negative charge.

That the foregoing explanation is plausible gains some support from observations made in a study of the polarographic reduction of oxine-5-sulphonic acid (88). The diffusion current arising from the reduction of oxine-5-sulphonic acid in alkaline solution decreases as the pH increases. At a pH of about 12, polarographic reduction ceases altogether. It was considered by the investigators that the double negative charge on the ionic species, $C_9H_5ONOSO_2^=$, which would predominate in solutions of high pH, may prevent its acquisition of electrons (i.e., its reduction) at the dropping-mercury cathode.

The reduction mechanisms proposed above are considered plausible, but are not regarded as established. That the reduction process at high pH values involves one electron and one hydrogen ion does, however, appear to be well supported. There is no doubt at all that the reduction process at high pH values is the one most suitable for exploitation for analytical purposes. At pH about 14, the polarographic wave is very well formed (Fig. 4), enabling the diffusion current to be readily measured; the diffusion current is not sensitive to modest changes in pH; and it is linearly proportional (Fig. 3) to the concentration of 2-methyloxine.

SUMMARY

1.   The first detailed study has been made of the reaction of
2-methyloxine with thorium. Under controlled conditions, thorium can be
precipitated quantitatively from aqueous solution solely as the 1:4
thorium 2-methyloxinate. No evidence was found for the formation of a
1:5 thorium 2-methyloxinate, and a recent claim for its preparation is
refuted.

2.   Gravimetric, bromometric and polarographic determinations of
thorium through 2-methyloxine have been made. These methods are accurate
and precise, as shown by well over 100 determinations, and hold for concen-
trations of thorium even as low as a few parts per million. The excellent
thermal stability of 1:4 thorium 2-methyloxinate gives 2-methyloxine an
important advantage over oxine as a reagent for thorium.

3.   In the polarographic reduction of 2-methyloxine, it is proposed
that in mildly alkaline solution the neutral 2-methyloxine molecule is
reduced by a two-electron process to a dihydro-2-methyloxine, and that in
strongly alkaline solution a one-electron reduction of the 2-methyloxine
anion occurs, the product being a free radical which likely undergoes
dimerization or disproportionation. In moderately alkaline solution,
both the neutral and anionic species are thought to undergo reduction.

4.   Oxine, 2-phenyl, 2-methyl and 6-methyloxine rapidly dibrominate
quantitatively, but the dibromination of 4-methyloxine is slow. The
decrease in the rate of dibromination of 4-methyloxine is attributed
to a steric factor.

5.   Evidence is advanced to show that the brown precipitate which can form in the bromometric determination of oxine compounds is a complex of molecular iodine and the 5,7-dibromo derivative of the oxine compound. It is postulated that bonding occurs between the iodine molecule and the nitrogen atom of the quinoline ring.

6.   Pure 1:4 thorium oxinate has been prepared thermally from 1:5 thorium oxinate. This claim, unlike earlier ones, is adequately supported by chemical analysis.

7.   Oxine in solution reacts with 1:4 thorium oxinate to form 1:5 thorium oxinate but the conversion to the 1:5 compound is not complete, at least under the conditions studied. An equilibrium is attained.

8.   Experiments involving radioactive oxine, and the establishment of the stoichiometry of the 2-, 3- and 4-methyloxinates of thorium, lead to the view that all five ligands in 1:5 thorium oxinate are bonded to the thorium atom.

9.   The thorium oxinate precipitated from cold aqueous solution is 1:5 thorium oxinate, and not the 1:4 compound as has been widely thought.

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