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Spectrophotometric determination of thorium with the trisodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid and some properties of complexes involved

Carol H. Byrd
Iowa State College

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SPECTROPHOTOMETRIC DETERMINATION OF THORIUM WITH THE

TRISODIUM SALT OF 2-(2-HYDROXY-3,6-DISULFO-1-NAPHTHYLAZO)-

BENZENEARSONIC ACID AND SOME PROPERTIES OF COMPLEXES INVOLVED

by

Carol H. Byrd

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In Charge of Major Work

Head of Major Department

Dean of Graduate College

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I. INTRODUCTION

It has long been known that azo dyes substituted in positions ortho to the azo linkage combine with certain metallic ions to form characteristically colored complex compounds widely employed as mordant dyes. A number of workers (1,4,7,8,18,22,24,25,29,30,31,32,94) have studied these compounds and have presented evidence for the existence of relatively strong primary valence bonds between the metal and the orthofunctional groups and a somewhat weaker coordinate bond with the azo group.

In 1941 Kuznetsov (66) proposed that these dyes might be modified to produce selective, color-forming, analytical reagents by substituting in one of the ortho positions a functional group which reacts preferentially with a certain group of metals. Thus, an ortho-arsono-azo dye might be expected to react selectively with the tetravalent metals in group IV. Kuznetsov prepared such a compound (70). The compound, the sodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid, gave an orange color in acid solution and reacted with thorium to produce a raspberry red colored precipitate. Although the reagent could not be classified as specific, its selective nature was obviously superior to most of the other colorimetric reagents for thorium.

Kuznetsov confined his investigation to a detection scheme for thorium. By using an excess of reagent, a soluble, red colored complex is formed. Thomason, et al. (119) utilized this reaction to develop a spectrophotometric method for the determination of thorium. Because of the selective nature of the reagent, this method was a particularly significant contribution to the analytical chemistry of thorium and has been the basis of several papers on specific determinations of small quantities of thorium.

In the work reported here, further investigations into this method were made. The objective was two-fold: (1) a study of some properties of the reaction between the dye and thorium, (2) a study of the spectrophotometric method and its application in the determination of thorium in monazite sand.

Before proceeding further, it is pertinent to comment on the nomenclature to be used throughout the thesis. Most of the investigators who have worked with this reagent have named it as a naphthol derivative. The introduction to the 1945 Subject Index of Chemical Abstracts (23) and "The Definitive Report of the Committee on the Reform of the Nomenclature of Organic Chemistry" of the Commission and Council of the International Union of Chemistry (103) were used as guides in selecting a name. It seems more consistent with these recommendations to name the compound as an

arsonic acid derivative. Paragraphs 68 and 248 of the former are particularly pertinent to this argument since the principal functional group of the reagent is the selective arsonic acid group.

Functional prefixes were named according to I. U. C. Rules 52 and 59.1 and are listed in conformance with paragraph 77 of the Chemical Abstracts' report and I. U. C. Rule 7. These considerations led to the name the sodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid.

For the sake of brevity, a shorter common name is preferred. The most widely employed common name has been thoron. In view of the possible confusion with the radon isotope in the thorium decay scheme, the name thorin will be used throughout the thesis.

II. PART ONE: SOME PROPERTIES OF COMPLEXES
BETWEEN THORIUM AND THORIN

A. Review of Literature

1. General review of studies of metal-azo dye compounds

As mentioned in the introduction, a number of investigations of the nature of the complex mordant dyes have been made (1,4,7,8,18,22,24,25,29,30,31,32,94). For the most part these studies have dealt with azo dyes in which either hydroxy, carboxy, or amino groups occupy one or both of the positions ortho to the azo linkage. In a few cases, the chemically similar azomethine linkage has been substituted for the azo group. Compounds of nickel(II), cobalt(II), cobalt(III), zinc, chromium(III), aluminum, copper(II), and vanadium(IV) have been characterized. Although none of these compounds contain an arsono group, and although only one tetravalent metal, vanadium, was studied, it is relevant to mention some of the properties of these compounds.

Nearly all of the workers agree that the metal complexes with 2,2'-substituted azo dyes are more readily formed than those of the mono-substituted derivatives. This is attributed to the utilization of both groups as primary donors together with the azo or azomethine group as a secondary donor to form a fused ring system. Apparent exceptions to

this are found in the water-insoluble complex between
cobalt(III) and 2'-hydroxybenzal:2-hydroxy-5-chloroaniline,
having a dye to metal ratio of 3:1, in which only one
hydroxy group is involved (1) and in a neutral compound of
copper(II) and 1-(2-hydroxy-5-sulfo-1-benzeneazo)-2-naphthol,
having a dye to metal ratio of 2:3, in which the azo linkage
is said to furnish two secondary valence bonds (8).

Unsaturated coordination positions in the metal are
occupied by neutral donor groups such as water, ammonia,
pyridine, etc., or by covalent links with negatively charged
ions. Frequently these compounds exist as ions. Bailar and
Callis (1) describe an interesting example in which successive
additions of 2'-hydroxybenzal:2-hydroxy-5-chloroaniline to
hexaamminecobalt(III) chloride produce first a positively
charged 1:1 complex, then a negatively charged 2:1 complex
which reacts immediately to form a salt having a dye to
metal ratio of 3:2. Chromium(III) behaved similarly.

Introduction of sulfonic acid groups into the dye may
have some profound effects on the structure of the metal
complex. The work of Drew and Landquist (31) has shown that
with mono-o-hydroxy-azo-monosulfonic acids, copper(II) forms
salts with the sulfonic acid leaving the hydroxy group free.
However, on adding alkali or metallic acetates to a solution
of these salts, the copper associates with the oxygen of
the hydroxy group and the azo nitrogen atoms. These

so-called inner complex copper salts are readily decomposed by acids. When both o-positions were substituted, the inner complex compound was the stable form (8). In many cases, the metal reacts with both the sulfonic acid group and the o-substituted azo system.

Carboxy compounds give less stable metallic derivatives than do analogous hydroxy compounds (30,31). A single o-hydroxy group is insufficient to hold chromium(III) in stable combination with an azo group, but copper(II), nickel(II), and cobalt(III) form stable complexes with mono-o-substituted azo dyes (120). In the case of the di-substituted dyes, this order of stability is reversed. Drew and Dunton (29) showed that chromium(III) forms more stable complexes than vanadium(IV) with di-o-substituted azo dyes. Like chromium(III), vanadium(IV) does not react with mono-substituted dyes.

Ernsberger and Brode (33) studied the relationships between the absorption spectra of some o-substituted azo dyes and their metal complexes. They reported that the metal has little effect on the chromophore of the dye. Although a new band in the visible region was ascribed to the metal, it does not occur at the same wavelength as that for the simple metal salts. The band is, however, independent of the dye residue and therefore it appears that it is not associated with the electronic state of the entire

molecule. The general effect of adding metal ions to resonators is a decrease in frequency or a shift to longer wavelengths (15).

Very little experimental work evidencing the nature of the association in azo-arsonic acid-metal complexes has been reported. Kuznetsov (69) found that scandium, thorium, and titanium(IV) give a color test with the Schiff's base of 2-aminobenzenearsonic acid and salicylaldehyde. The interesting observation was that the isomers containing either the hydroxy or arsono group in the p-position do not yield the color test. This might indicate that both groups are implicated in the complex. However, Feigl (36) was able to obtain a brown zirconium salt with 4-(4-dimethylamino-1-benzeneazo)-benzenearsonic acid in which the dye to metal ratio was 2:1. Later this dye was used as a color-forming reagent for thorium (17).

Another interesting experiment involved the substitution of groups having highly varying electron affinities in the position para to the azo linkage in the benzene nucleus of thorin (68). Their effect on the color of the reaction product with thorium in acid solution was observed. Nitro, hydrogen, and amino groups in this position gave red-orange, strawberry pink, and bright violet colors respectively. Kuznetsov (72) also found that qualitatively thorin in concentrated sulfuric acid and the thorium-thorin complex in dilute hydrochloric acid solution have the same color.

2. Some selected chemical properties of thorium

Only those aspects of thorium chemistry of specific interest in this problem are to be reviewed. First some aspects of the aqueous chemistry will be discussed. According to Britton (14), thorium begins to precipitate as the hydroxide at a pH of about 3.57. In aqueous solution the tetravalent ion is said to be associated with twelve water molecules (13) although some say it is eight (60). The latter figure would be more consistent with its normal coordination number of eight (105). However, considerable latitude in this value is permitted by the electronic configuration of the thorium ion.

Very little work has been done on the hydrolytic behavior of thorium. Thorium is said to hydrolyze to give ThO^{++} as its first product (60) which then dimerizes to form Th_2O^{+6}. Dissociation constants have been evaluated by postulating such equilibria. In the case of the thorium concentrations used in the experiments subsequently described, hydrolysis first occurred at a pH of 3.0. Rydberg (112) reported no evidence for thorium hydrolysis below a pH of 2.0. In more concentrated solutions, thorium is said to exist as $Th_4O_4^{+8}$ (35).

Inasmuch as the arsonic acid is considered to be the principal functional group on the thorin molecule, it is of

interest to note that thorium forms two different arsenates
(3,21). In an excess of thorium, arsenic acid reacts as a
dibasic acid to form a product in which the acid to thorium
ratio is 2:1. A 4:1 precipitate separates from a large
excess of acid.

3. Some selected properties of azo dyes

The treatise of Venkataraman (120) is a particularly
fine source of information on the chemistry of the azo dyes.
Only those properties of peculiar significance to this
investigation (structure and absorption spectra) will be
surveyed.

Two geometrical isomers of azo dyes are possible, and
the configuration in which the substituents are situated in
the trans positions with respect to the azo linkage is much
more stable than the cis arrangement (16). The equilibrium
between the two forms is rapidly established and conversion
to the cis form is promoted photochemically.

The tautomeric equilibrium between the hydrazo and azo
forms of o-hydroxy-azo dyes (Figures 3 and 4) is of special
importance in this study. Lauer and Miller (78) were able
to carry out a Diels-Alder reaction with 4-(2,4-dinitro-1-
benzeneazo)-phenol, thus demonstrating the presence of a
hydrazo-azo equilibrium in this compound. Kuhn and Bär (65)
studied this phenomenon with 4-benzeneazo-1-naphthol, with

1-benzeneazo-2-naphthol, and with 2-benzeneazo-1-naphthol.
They found that the absorption spectra of the latter two
were characteristic of the hydrazo form and independent of
solvent. On the other hand, a benzene solution of the
p-compound contained approximately equal amounts of each
isomer; in pyridine and azo form predominated, and in
acetic acid and nitrobenzene the hydrazo form was preferred.
In phenol derivatives, the azo form prevailed.

Recently Ospenson (101,102) has worked with a number
of substituted benzene-azo-phenols, -naphthols, and -anthrols.
His findings support those of the preceding workers. In his
first work (101) he reported on the effects of various sub-
stituents in the benzene nucleus (2 and 4 positions) on the
position of the equilibrium in alcoholic solution. Naphthol
derivatives were predominantly hydrazo and phenols were
primarily azo forms. The effects of changing substituents
were relatively minor; however, it is notable that substitu-
tion of a carboxy group in the o-position of the naphthol
dyes forced the equilibrium even further toward the hydrazo
form. This was attributed to hydrogen bonding between the
protonated nitrogen and the carboxy oxygen.

In the absorption spectra, the position of the maximum
absorbance for the naphthols is in the vicinity of 480 mμ
for the hydrazo form and at 390 mμ for the azo configura-
tion (101,65). When appreciable amounts of both are present,

an inflection or slight maximum occurs at around 425 mμ .
In his second paper (102), Ospenson found that as the number
of linearly annulated rings in the auxochromic part of the
molecule was increased, the relative amount of the hydrazo
form increased.

B. Materials and Apparatus

1. Preparation and purification of thorin

The reagent was prepared according to a three-step
process: (1) diazotizing 2-nitroaniline and coupling it
with disodium hydrogen arsenite to form 2-nitrobenzenearsonic
acid, (2) reducing the nitro group with ferrous chloride,
and (3) diazotizing the resulting 2-amino-benzenearsonic
acid and reacting it with the disodium salt of 2-hydroxy-
3,6-disulfonapthalene (R-salt) to form the desired product.
The over-all yield was 33 per cent. The details of the
procedure are reported in a paper by Margerum, et al. (82).
The compound may be recrystallized from water or ten per
cent hydrochloric acid and may be dried by washing with
acetone or alcohol or in an oven at 105°C. The latter gives
an anhydrous, red-colored trisodium salt after recrystalli-
zation from water. Quantitative analysis of absorption
spectra proved that it did not decompose at 105°C. From
acid solution the orange-colored monosodium salt was isolated.

Since the compound decomposes without melting, it is necessary to test the purity by potentiometric titration with standard base. All standard thorin solutions used in the experimental work were standardized in this manner. The exact location of the midpoint of the second break in this titration is subject to considerable error; hence, the concentration of the reagent solutions is known only to within 2 or 3 per cent of the actual value.

2. Other materials

A 0.45 M thorium nitrate tetrahydrate solution which was 2 M in calcium nitrate and 3 M in nitric acid was extracted twice with an equal volume of methyl iso-butyl ketone which had been saturated by shaking with an equal volume of 4 N nitric acid for 5-10 minutes. The thorium was removed from the solvent by shaking with an equal volume of water. It was then precipitated from this aqueous solution as the oxalate and ignited to the oxide at 500°C. It was spectrographically free of significant quantities of rare earths and all common cations. Appropriate amounts of this oxide were then dissolved to make the stock solutions which were standardized by an oxalate precipitation.

All other chemicals used were reagent grade. The water used was distilled water which had been passed through a Barnstead Model BD deionizer. The Karl

Fischer reagent was prepared according to the method of Wernimont and Hopkinson (129). It was standardized against distilled water from a weight buret.

3. Apparatus

For most of the work, "Normax" volumetric ware manu-factured by Kimble Galss Division of Owens-Illinois Glass Company was used. In a few cases, where "Normax" was unavailable, the Standard "Pyrex" brand glassware of the Corning Glass Works was substituted. Both of these are manufactured to class A capacity tolerances.

All pH measurements were made with a Beckman Model G pH meter with general purpose glass electrodes. For pH values above 11.0 a type E indicator electrode was employed.

Absorbance measurements were made on the Beckman Model DU quartz spectrophotometer or the Cary Model 12 recording spectrophotometer. The latter was used with the slit control setting at 10, as recommended by the manufacturer.

The solutions used in the ion exchange experiment were agitated with the resin on a Burrell Wrist-Action shaker.

C. Experimental Procedures and Results

In this section the nomenclature and symbols used will be those recommended by the Joint Committee on Nomenclature

of the Society for Applied Spectroscopy and the American
Society for Testing Materials (47). The symbol R will be
used to denote thorin in subscripts. For example, M_R will
denote the molarity of thorin. Other symbols will be des-
cribed as they are used.

Although a constant temperature system was not employed,
all solutions were equilibrated at room temperature, $23 \pm 1^\circ C$,
during the course of these studies. All thorium and thorin
solutions were prepared and standardized as described in the
section on materials and apparatus. For all work described
in this section, a total solution volume of 200 ml was used.

1. Thorin

(a) <u>pH dependency of absorption spectrum</u>. A 10^{-4} M
thorin solution was prepared by dilution of a suitable stock
solution. Twenty-five ml aliquots of this solution diluted
to 200 ml were used in preparing the series for the investi-
gation of pH effects. In the neutral range, two different
buffer systems were employed to accurately control the pH
at uniform intervals. In one series an ammonia-ammonium
chloride system was used, and in the other a potassium di-
hydrogen phosphate-dipotassium hydrogen phosphate mixture
was employed. pH adjustments above 11.0 and below 5.0 were
effected with sodium hydroxide and hydrochloric acid. Ionic
strength was then adjusted to 0.5 ± 0.05 with sodium chloride
or ammonium chloride.

These solutions were scanned on the Cary instrument
against either a sodium chloride or water blank in 5.000-cm
absorption cells. The measurements were all taken within
three hours after solution preparation.

Figure 1 contains a few of these curves and demonstrates
some of the features of the spectral shift with changing pH.
Table I lists the absorbance values taken from these curves
at four selected wavelengths, and Figure 2 illustrates these
data graphically. The spread in the points at the second
break was not explained. It seems unlikely that time effects
could be responsible, for although the solutions are un-
stable in this pH range, as will be discussed later, their
rate of decomposition is slow.

Several points concerning Figure 1 are of some interest
in connection with the hydrazo-azo equilibria in hydroxy-
azo dyes. As the pH increases, the absorbance maximum of
the principal band shifts to somewhat longer wavelengths,
from 475 mμ to 490 mμ , and increases in intensity until a
pH of about 10 is reached. The plots in Figure 2 indicate
that the absorbance at 460 mμ is virtually independent of
the pH up to a value of 10.0. This, then, is an isosbestic
point, since the various species contributing to the
absorbance at this wavelength have identical molar absorp-
tivities. At the other wavelengths there is a stepwise
dependence indicating that the change in spectra is a
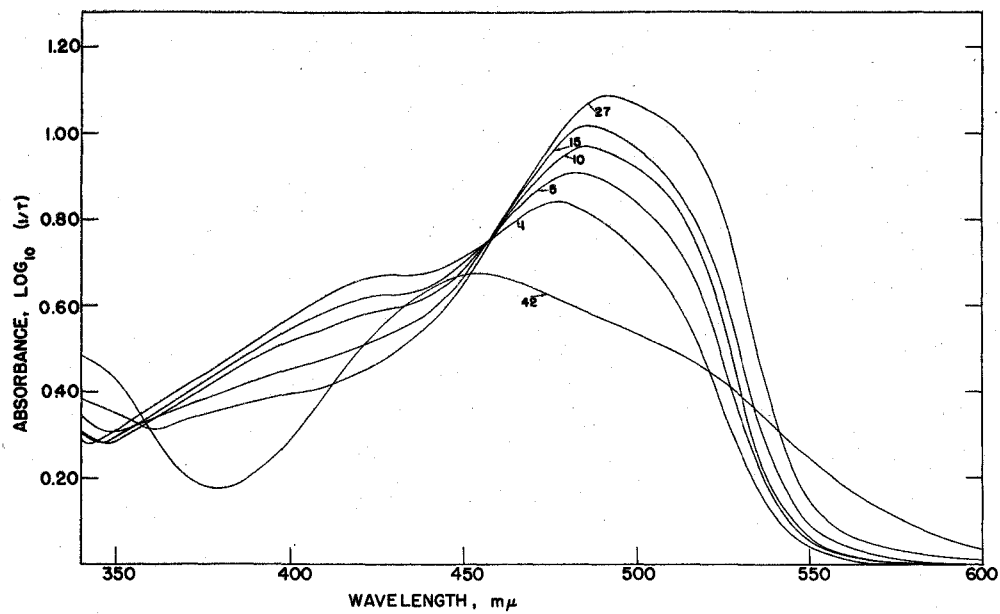
FIG. I— ABSORPTION CURVES ILLUSTRATING EFFECT OF VARYING pH
OF 1.25 x 10^{-5} M THORIN SOLUTIONS AT IONIC STRENGTH
OF 0.5.

NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN
TABLE I.

SCANNED IN 5.0 — cm CELLS VS WATER.

Table I

Absorbance of Thorin as a Function of pH[a]

Solution Number	pH	A_{480} mμ	A_{500} mμ	A_{510} mμ	A_{540} mμ
1	1.08	0.838	0.730	0.632	0.115
2	1.99	.848	.750	.653	.115
3	2.60	.860	.775	.690	.115
4	2.95	.898	.820	.740	.140
5	3.12	.908	.838	.760	.144
6	3.29	.918	.855	.780	.148
7	3.58	.933	.880	.805	.152
8	3.98	.948	.900	.828	.156
9	4.35	.955	.910	.840	.160
10	4.82	.955	.918	.852	.165
11	5.31	.955	.930	.842	.170
12*	6.87	.975	.920	.830	.180
13*	7.11	.970	.940	.878	.215
14*	7.23	.965	.950	.890	.220
15	7.42	.995	.965	.890	.220
16*	7.48	.965	1.000	.903	.250
17*	7.78	.975	1.020	.932	.275
18	7.78	1.005	1.030	.975	.285
19	8.12	1.020	1.060	.960	.280
20	8.12	1.015	1.050	.995	.300
21	8.30	1.015	1.060	1.012	.325
22	8.38	1.000	1.070	1.002	.330
23	8.43	1.045	1.095	1.052	.345
24	8.76	1.020	1.060	1.012	.350
25*	8.76	.995	1.050	.983	.335

[a]Each solution is 1.25×10^{-5} M in thorin. The ionic strength is 0.5 ± 0.05. Absorbance data are from the Cary spectrophotometer. Cell length = 5.000-cm.

*The pH of each solution marked in this way was adjusted with KH_2PO_4-K_2HPO_4 buffer. The pH's of all other solutions from 11 to 33 were adjusted with NH_4OH-NH_4Cl buffer. The pH's of solutions 1 to 10 were adjusted with HCl, while the pH's of solutions 34-42 were adjusted with NaOH.

Table I (Continued)

Solution Number	pH	A_{480} mμ	A_{500} mμ	A_{510} mμ	A_{540} mμ
26	9.00	1.020	1.065	1.012	.355
27	9.17	1.025	1.070	1.025	.355
28	9.36	1.025	1.065	1.025	.350
29	9.52	1.025	1.065	1.025	.350
30	9.72	1.025	1.065	1.010	.350
31	9.93	1.015	1.055	1.010	.350
32	10.28	1.005	1.030	.988	.350
33	10.92	.965	.965	.910	.335
34	10.97	.950	.960	.910	.320
35	11.18	.930	.925	.876	.315
36	11.40	0.890	0.875	.830	0.330
37	11.69	.805	.775	.678	.325
38	12.10	.715	.670	.628	.335
39	12.39	.675	.620	.600	.340
40	12.64	.650	.625	.576	.345
41	13.06	.630	.560	.522	.335
42	13.31	.610	.540	.500	.320
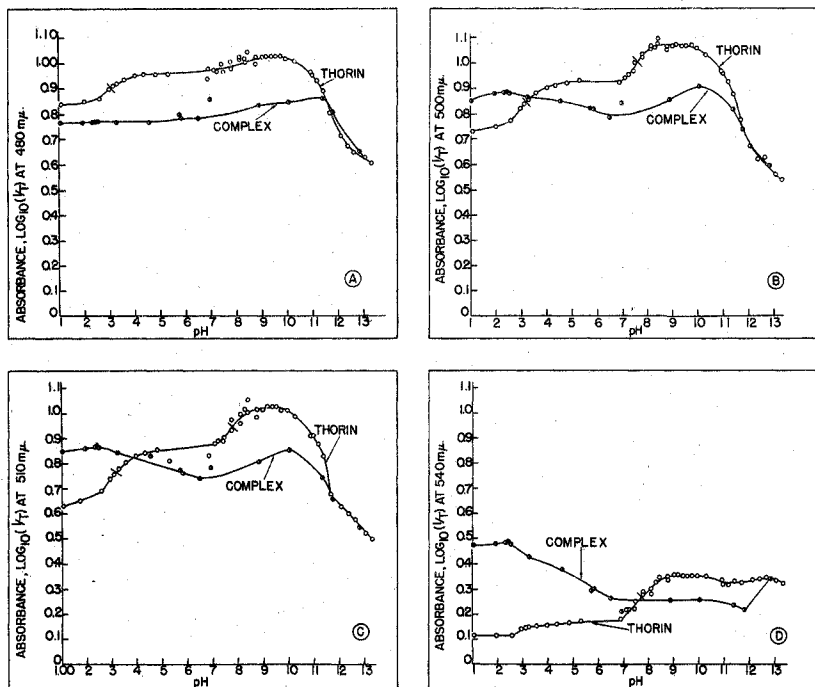
FIG.2 - EFFECT OF pH ON ABSORBANCE OF 1.25 x 10^{-5}M THORIN SOLUTIONS AT IONIC
STRENGTH OF 0.5 AND OF 1.25 x 10^{-5}M THORIN AND 0.5x10^{-5}M THORIUM
SOLUTIONS AT IONIC STRENGTH OF 0.1.
DATA FOR THORIN SOLUTIONS IN TABLE (I)
DATA FOR COMPLEX SOLUTIONS IN TABLE (III)

function of removal of the acid hydrogens on the molecule.
Above pH 10, the absorbance maximum at 490 mμ falls off to
a lower absorbance and shifts to 460 mμ. At the lowest
pH values, an inflection point occurs in the vicinity of
430 mμ, but as the pH increases, this vanishes.

According to the interpretations of Ospenson (101), as
discussed in the review of literature, this means that up
to a pH of 10, the hydrazo form of the dye, Figure 3, is
heavily predominant. The inflection point at 430 mμ
indicates that at lower pH values a significant amount of
the azo form, Figure 4, is also present, but that as pH
increases, its contribution decreases. Above a pH of 10.0
the system cannot be explained on this basis. Some further
considerations will be presented in the "Discussion" sec-
tion.

(b) Evaluation of pK's. Since isosbestic points are
present, it should be possible to determine the dissociation
constants for the several acid hydrogens which are removed
from the molecule over this pH range. A graphical modifica-
tion of the method of Stenström and Goldsmith (117) for the
spectrophotometric evaluation of pK values can be applied.
The plots of Figure 2 can be used for this purpose. Those
portions of the curve where the slope is near zero and is
virtually constant can be considered as representing pH
conditions in which only one species is contributing to the
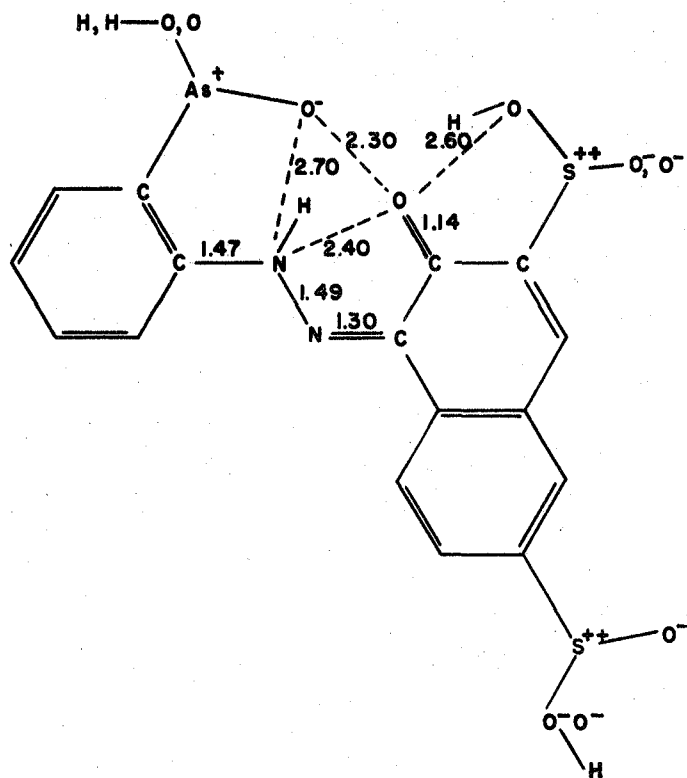
FIG. 3 CONFIGURATION OF HYDRAZONE FORM OF THORIN
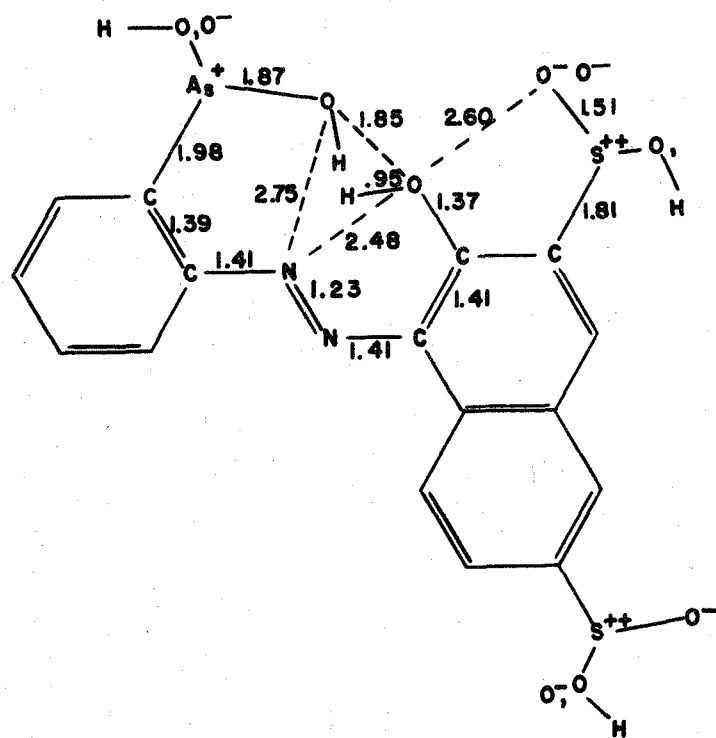
FIG. 4 CONFIGURATION OF AZO FORM OF THORIN

absorbance, providing the wavelength is not an isosbestic point. However, a sharp change in slope represents dissociation of the absorbing species into a new anion and proton. When this dissociation step is complete, the curve again levels off until another acid hydrogen begins to dissociate. The midpoint of this break represents the point at which equimolar quantities of acid and its salt are present; hence, the pH at this point is identical with the pK' value under the conditions of the experiment.

In some cases, this may be corrected to the thermodynamic pK using the extended Debye-Hückel theory if the ionic strength is constant (19). By making certain approximations, it can be shown that:

$$pK = pH + \log \frac{[HA^{-n}]}{[A^{-(n+1)}]} + \frac{0.509\mu^{\frac{1}{2}}}{1+\mu^{\frac{1}{2}}}$$

$$pK = pK' + \frac{0.509\mu^{\frac{1}{2}}}{1+\mu^{\frac{1}{2}}}$$

where: μ = ionic strength

pK' = experimentally determined value

pK = corrected thermodynamic value.

For an ionic strength of 0.5, this correction is + 0.21.

Over this pH range, the sulfonic acid hydrogens are undoubtedly completely dissociated. Consequently, the three breaks shown in Figure 2 represent the removal of the two

hydrogens from the arsonic acid and the naphtholic hydrogen. The fact that the naphtholic hydrogen is the weakest acid on the thorin molecule was established in the following way. The change in the ultraviolet absorption spectrum of 2-hydroxy-3,6-disulfo-naphthalene due to dissociation of the naphtholic hydrogen was experimentally determined. Qualitatively the change in the ultraviolet spectrum of thorin as the last proton was removed was the same as that for the case just described. Hence, this fifth hydrogen originated from the naphtholic group (82). The third and fourth acidic hydrogens are associated with the arsonic acid dissociation. In aqueous solution, the two strong sulfonic acids can be considered to be completely dissociated.

The two constants, pK_3 and pK_4, have been determined by adding an excess of standard acid to a thorin solution and back titrating potentiometrically with standard alkali (82). The work was done at an ionic strength of 0.1; therefore, only the corrected thermodynamic quantities can be compared as shown in Table II when varying ionic strengths are used. pK_5 has previously been evaluated spectrophotometrically in this laboratory (82).

It should be noted that, while changes in the ultraviolet spectrum were very sensitive to the removal of the naphtholic hydrogen, this was not the case for the dissociation of the arsonic acids.

Table II

Spectrophotometrically Determined Values of Acid Dissociation Constants of Thorin Compared with Potentiometrically Determined Values

Constant[a]	Corrected Potentiometric[b]	Graphical Spectrophoto-metric[c]	Corrected Graphical Spectrophoto-metric
pK_3	3.7	3.15	3.36
pK_4	8.3	7.71	7.92
pK_5	11.9	11.55[b]	11.76

[a]pK_3 = value for first arsonic acid hydrogen
pK_4 = value for second arsonic acid hydrogen
pK_5 = value for naphtholic hydrogen.

[b]Determined by Margerum, et al. (82).

[c]Each result is the average of determinations at three wavelengths.

(c) <u>Stability</u>. Thorin solutions below pH 6 appear to
be quite stable, and the absorbance does not seem to be time
dependent. In the pH range from 7 to 11, the absorbance of
the solutions decreases with time as does the pH in non-
buffered solutions. The pH drift may have been due to
absorption of carbon dioxide, to a decomposition of thorin,
or to a slow equilibrium. The fact that the absorbance also
decreased in buffered solutions in this pH interval might
suggest that the true effect here is one of decomposition.
On the other hand, this argument is weakened by the fact
that in one of the unbuffered solutions, the absorbance at
the isosbestic point (460 mμ) did not change significantly
after standing for 20 days. In the same interval the pH
changed from an original value of 8.87 to 7.35. The
absorbance at the maximum (490 mμ) changed from 1.102 to
1.010; at 540 mμ the absorbance increased from 0.215 to
0.235. From Figure 2 it can be seen that a decrease in
absorbance should accompany a decrease in pH at 540 mμ,
which is opposed to the observed effect. The ambiguous
nature of these results suggests that it would be at best
rather speculative to draw any conclusions concerning the
time effects in this pH interval without a more systematic
study.

At higher pH values, 12 to 13, a finely-divided,
crystalline, white suspension developed with time. Its

identity was not established, but it probably was sodium
carbonate. It is hard to see how a degradation of the thorin
could yield an insoluble solid. This formation precluded
a further study of time effects at these higher basicities.

The important thing to note in this study is the fact
that at low pH values, the range of interest in this work,
no appreciable time effects were observed. Studies at pH
1.0 showed no absorbance change over a two month interval.

2. Soluble complex

(a) pH dependency of solutions containing thorin and
thorium. A thorough study of the pH dependency of the
absorption spectrum of the complex was not attempted for
several reasons. In the first place, in order to form a
stable solution, it is necessary to use an excess of reagent.
As will be shown later, a precipitate develops very slowly
in solutions containing excess or equivalent amounts of
thorium. In the second place, the study is seriously
complicated by the hydrolytic behavior of thorium. There-
fore, the results presented in this section are to be
interpreted somewhat cautiously, and a much more thorough
study would be required to define the thorium-thorin system
at those pH values at which thorium is hydrolyzed.

A series of solutions was prepared in which the thorin
concentration was 1.25×10^{-5} M, the same concentration used

in the previous series for the study of the thorin pH dependency. These solutions were also 0.5×10^{-5} M in thorium perchlorate. In this experiment, it was necessary to use sodium perchlorate to control the ionic strength of the solutions since chloride ion complexes thorium (26,133). The pH was adjusted with perchloric acid and sodium hydroxide. The use of a buffer in the neutral region was precluded because thorium ion reacts with all common buffers to form complexes. The molar ratio of thorin to thorium in these solutions was 2.5:1. Hence, there is some excess reagent present, which complicates a study of the change in absorbance of the complex with changing pH.

There is no convenient way of separating the absorbance changes of the complex from those of the reagent when excess reagent is present. If the constitution of the complex were known and if it could be assumed that the reaction utilizes all of the thorium to form only one complex over the entire pH range, one could correct for the absorbance due to the uncomplexed thorin. This could be done by using a thorin blank of the same concentration as the calculated excess thorin in these solutions. Since the variation in the absorbance of the reagent with pH has been determined, the absorbance of the excess reagent could be subtracted from that of the complex in the solution. However, such a procedure is not possible since there is considerable uncertainty

concerning the identity of the soluble species. Moreover, above pH 3.0 there will certainly be competition between hydroxyl ion and thorin for the thorium.

The solutions were scanned on the Cary instrument in 5.000-cm cells and against a 0.1 M sodium perchlorate reference solution. The curves were taken immediately after preparation of the solutions. The pH values were read within two hours after solution preparation. The solutions were scanned intermittently thereafter to determine time effects, which will be discussed later.

A few of these curves are shown in Figure 5. Again it must be emphasized that these curves do not merely represent the change in the absorption spectra of the complex as the pH changes. Four limitations make the interpretation of these curves rather difficult: (1) the solutions were not at equilibrium, (2) more than one soluble thorium-thorin complex may exist and contribute to the pH effects observed, (3) some suspended hydrated thorium is probably present in the solutions of high pH, and (4) the absorbance of an unknown amount of uncomplexed reagent, which also changes with pH, is superimposed on that of the complex and any suspended material.

Despite these limitations, it is instructive to examine the curves. In the first place, it is noteworthy that at the lower pH values the absorption spectra of these solutions
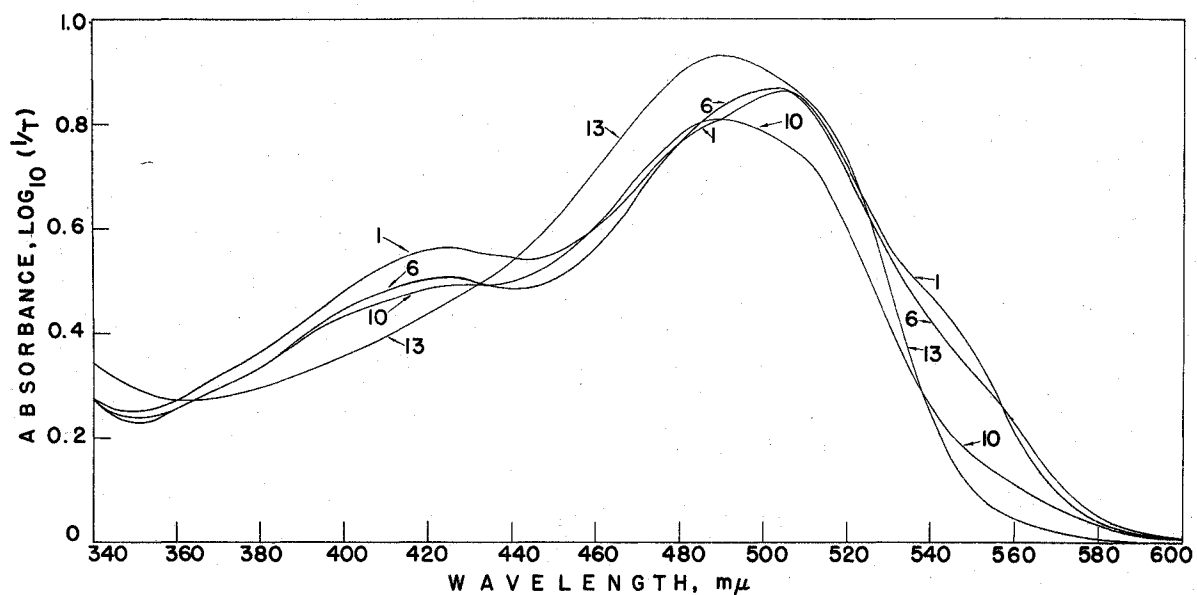
FIG. 5 ABSORPTION CURVES ILLUSTRATING THE EFFECT OF VARYING
pH OF 1.25×10^{-5} M THORIN AND 0.5×10^{-5} M THORIUM SOLUTIONS
AT IONIC STRENGTH OF 0.1 .

NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLE III
SCANNED IN 5.0- CM CELLS VS. 0.1 M Na Cl O$_4$

are different from those of the reagent (Figure 1) in several important respects. The absorbance maximum of the principal absorption band of these solutions is at a longer wavelength than that of the reagent alone. The inflection point in the thorin solutions has been replaced by a very definite maximum at 425 mμ. Perhaps the most important feature is the appearance of an inflection point in the spectra of the complex at about 535 mμ, a phenomenon totally absent in the thorin spectrum.

It is interesting to note that as the pH of the complex solutions is increased, the absorbance in the region of the inflection at 535 mμ drops sharply, which indicates that as the pH increases, less and less thorium reacts to form the complex. Moreover, the absorption spectra of these complex solutions at higher pH values are qualitatively identical with those of the reagent at similar pH, which indicates that no appreciable quantities of thorium are associated with the reagent at high pH.

A list of the absorbance values at various wavelengths as a function of pH for the series of solutions used in this experiment is presented in Table III. The values were obtained from the Cary data on these solutions immediately after the solutions were prepared. They are plotted in Figure 2 together with the previously discussed data on thorin alone. This gives a graphical picture of some important

Table III

Absorbance of Complex Plus Excess Thorin as a Function of pH[a]

Solution Number	pH	A_{480} mμ	A_{500} mμ	A_{510} mμ	A_{540} mμ
1	1.05	0.765	0.853	0.847	0.475
2	1.93	.768	.880	.860	.480
3	2.33	.770	.885	.865	.485
4	2.43	.770	.885	.870	.485
5	2.53	.768	.880	.862	.475
6	3.25	.768	.867	.843	.427
7	4.56	.768	.853	.830	.377
8	5.73	.800	.820	.772	.293
9	5.82	.785	.820	.762	.303
10	6.48	.785	.787	.738	.262
11	6.97	.860	.842	.782	.205
12	8.87	.835	.852	.808	.255
13	10.05	.897	.905	.852	.255
14	11.38	.863	.816	.742	.235
15	11.78	.814	.740	.660	.218
16	12.83	.653	.622	.595	.340

[a]Each solution is 1.25×10^{-5} M in thorin, 0.5×10^{-5} in thorium. pH was adjusted with $HClO_4$ and ionic strength is 0.10. Cell length = 5.000-cm.

differences between the absorption spectra of the thorin and
of the thorin-thorium reaction product. This difference is
only qualitative because of the restrictions outlined above.

The results at low pH, specifically below pH 3.0, are
of particular value. In this region the solutions are
fairly stable with time, and complications due to hydrolysis
of thorium are not likely (60). From Figure 9 it may be
seen that at 540 mμ, the absorbance of the thorin alone
at low pH values is slight compared to that of the complex.
Although considerable differences between the absorbances
of the complex-containing solution and the thorin solution
are exhibited at other wavelength intervals, this is the
only wavelength range at which the absorbance of the thorin
is small compared to that of the complex solutions. Further-
more, the absolute magnitude of the difference is larger
in this region than in any other (Figure 9). This condition
is favorable for studying the nature of the soluble species
spectrophotometrically since the magnitude of corrective
terms for the unreacted thorin absorbance would be small.
This is especially important because of the fairly large
uncertainty in the concentration of the reagent. At each
wavelength in Figure 2 the absorbance of the complex
increases slightly up to about pH 2.5, and then falls off,
eventually crossing the corresponding curve for the thorin
absorbance. Finally at a pH of near 11, the curves become

virtually coincident. This latter phenomenon suggests that
at this high pH the thorium is completely hydrolyzed and
the absorbance is due to the liberated reagent plus any
suspended thorium hydroxide which may have formed.

As might be expected, the majority of these solutions
were not stable and underwent considerable change with
time. Solutions from this series at original pH values of
1.05, 2.53, 4.56, 8.87, and 12.88 were examined for time
effects. The absorbance changes in these solutions were
measured as a function of time. At high pH, the formation
of suspended thoria obscured the study. For some reason
the data obtained were erratic, and a quantitative report
of the results is not considered to be of any value. How-
ever, qualitatively, it can be said that as pH is increased,
the instability of the complex is increased. At a pH of
1.05 the change with time was small. In all other solutions
a very definite change was noted. The absorbance of the
solutions at original pH values of 2.53 and 4.56 decreased
with time, and the solutions at pH 8.87 and 12.88 exhibited
an increase in absorbance on standing.

It seems probable that several factors contribute to
these changes: (1) the reagent alone decomposes on standing
at some pH values, as previously described, and (2) the
thorium may be slowly hydrolyzing to form a suspension which
would produce absorbance changes. The latter circumstance

might lead to either an increase or decrease in absorbance.
The increase could be due to suspended thoria, and a decrease
could be associated with adsorption of colored ions on a
hydrolyzed thorium ion or to surrender of the thorium bound
with the highly colored complex to hydroxyl ion to form
colorless bodies.

Because of the many complicating factors mentioned, a
far more detailed and systematic investigation would be
necessary to completely depict the effects of varying pH
on the absorption spectra of solutions of the type just con-
sidered. However, these results, when combined with those
on the reagent, are adequate for the further considerations
in this study. The most important observation was the
relative stability of the solution at pH 1.05.

In order to avoid undesirable time effects and side
reactions with hydroxyl ion, it appears necessary to confine
the investigation of the complex to a low pH. Later in the
thesis it will be shown that the optimum pH in the analytical
work is in the region of pH 1.0. A pH of 1.00 was chosen
for the work described subsequently in this section. At
this pH the free thorium is in the hydrated tetrapositive
state, and the free thorin is probably the dinegative ion
which results from the loss of the sulfonic acid hydrogens.

(b) Effect of time and formation of precipitate. It
seemed desirable to observe time effects on a series of

solutions in which the molar ratio of reactants varied over
a considerable range. This was most conveniently done by
preparing a series of solutions according to the scheme
in Job's method of continuous variations (51,128). Data
from these solutions were used to get information concerning
the ratio of ligand to central atom in the complex, as
described in the next section.

The constitution of these solutions is presented in
Table IV. The solutions were prepared by dilution of
appropriate aliquots of 2.5×10^{-4} M thorin and thorium
perchlorate solutions to 200 ml. The pH was adjusted to
1.00 ± .02 by the addition of perchloric acid. The concen-
tration of acid necessary to achieve this pH is very large
compared to the concentration of other ions in the solution
and serves to control the ionic strength. Immediately after
each solution was mixed, it was scanned on the Cary spectro-
photometer against a water blank. The solutions were
scanned frequently during the next day and then at more
extended intervals.

The variation in absorbance of these solutions with
time at two different wavelengths is shown in Tables V and
VI. The data are taken from the scanning curves. It will
be noted, especially in the data of Table VI, that the
absorbance increases rather sharply between the first and
second measurements, a period of 1 to 1.7 hours, tapers off,

Table IV

Solutions Used for the Determination of Ratio of Thorin to Thorium by Job's Method[a]

Solution Number	$M_R \times 10^5$	$M_{Th} \times 10^5$
J-1	0.625	5.625
J-2	1.250	5.000
J-3	1.875	4.375
J-4	2.500	3.750
J-5	3.125	3.125
J-6	3.750	2.500
J-7	4.375	1.875
J-8	5.000	1.250
J-9	5.625	0.625
J-10	6.250	0.000

[a]pH of each solution adjusted to 1.00 $\pm$ 0.02 with $HClO_4$.

Table V

Effect of Time on the Solutions Used for Analysis by
Job's Method at 510 mμ, Cary Data[a]

Solution Number	A_0[b]	A (min)	$A_{4.5}$ hr.	A_{51} hr.	A_{13} days	A_{22} days	A_{32} days
J-1	0.200	0.215 (104)	0.220	0.220	0.150*	0.095*	0.075*
J-2	0.400	0.430 (104)	0.440	0.443	0.273*	0.180*	0.120*
J-3	0.610	0.645 (101)	0.650	0.655	0.352*	-	-
J-4	0.825	0.860 (93)	0.870	0.890	0.400*	0.335*	0.320*
J-5	1.060	1.090 (87)	1.095	1.100	0.342*	0.370*	0.355*
J-6	1.250	1.255 (80)	1.250	1.245	0.470*	0.430*	0.375*
J-7	1.245	1.255 (72)	1.265	1.270	0.930*	0.835*	0.845*
J-8	1.200	1.215 (69)	1.235	1.235	1.190	1.165	1.230
J-9	1.195	1.205 (66)	1.220	1.225	1.220	1.220	1.225
J-10	1.210	1.205 (60)	1.225	1.230	1.220	1.220	1.235

[a]All readings were made on the Cary spectrophotometer using 2.000-cm cells and a water reference solution. The solutions are described in Table IV.

[b]Readings in this column were made immediately following the preparation of the solution.

*A visible, red-colored precipitate in these solutions was filtered off before the solutions were scanned.

Table VI

Effect of Time on the Solutions Used for Analysis by Job's
Method at 540 mμ , Cary Data[a]

Solution Number	A_0[b]	A (min)	$A_{4.5\ hr.}$	$A_{51\ hr.}$	$A_{13\ days}$	$A_{22\ days}$	$A_{32\ days}$
J-1	0.148	0.160 (104)	0.162	0.162	0.110*	0.070	0.060*
J-2	0.298	0.318 (104)	0.322	0.324	0.200*	0.130*	0.090*
J-3	0.453	0.473 (101)	0.480	0.485	0.255*	-	-
J-4	0.602	0.622 (93)	0.635	0.640	0.290*	0.235*	0.235*
J-5	0.753	0.777 (87)	0.787	0.785	0.225*	0.255*	0.240*
J-6	0.857	0.868 (80)	0.873	0.870	0.310*	0.280*	0.205*
J-7	0.764	0.780 (72)	0.790	0.790	0.540*	0.465*	0.475*
J-8	0.570	0.590 (69)	0.605	0.605	0.570	0.565	0.605
J-9	0.380	0.390 (66)	0.398	0.400	0.400	0.405	0.405
J-10	0.190	0.195 (65)	0.207	0.200	0.200	0.205	0.220

[a]All readings were made on the Cary spectrophotometer using 2.000-cm cells and a water reference solution. Solutions are described in Table IV.

[b]Readings in this column were made immediately following preparation of the solution.

*A visible, red-colored precipitate in these solutions was filtered off before the solutions were scanned.

and eventually reaches a stable state after 4.5 hours have elapsed. This static state prevails through a 51 hour interval. Between this time and the next readings, a red-colored precipitate develops in some of the solutions.

Absorbance changes in the same solutions were also checked on the Beckman spectrophotometer at several wave-lengths. The Beckman data supplement those presented in Tables V and VI in the time interval during which precipitation occured. The Beckman measurements at 540 $m\mu$ are shown in Table VII. They show that precipitation first occurred in solution J-5 in which the molar quantities of reactants were equal. This precipitate was detected visually 105 hours after solution preparation. Precipitation was observed in solutions J-2 through J-6 at the end of six days. After 13 days, precipitates could be seen in all solutions up to and including J-7.

The properties of the precipitate will be discussed in a subsequent section of the thesis. The color of the precipitate leaves little doubt that it is a product of the thorium-thorin reaction.

It is important to note that in the time interval following the sharp initial increase in absorbance and preceding precipitation, the solutions appear to be in a metastable equilibrium state for several days. Apparently the precipitate is very slow to form; however, once it does

Table VII

Effect of Time on the Absorbance of Solutions Prepared for Analysis by Job's Method at 540 mμ, Beckman Data[a]

Solution Number	$A_{1\text{ hr.}}$	$A_{9.5\text{ hr.}}$	$A_{57.5\text{ hr.}}$	$A_{105\text{ hr.}}$	$A_{149\text{ hr.}}$	$A_{195\text{ hr.}}$
J-1	0.081	0.085	0.086	0.085	0.083	0.082
J-2	0.159	0.165	0.165	0.163	0.161*	0.157
J-3	0.236	0.241	0.241	0.240	0.231*	0.229
J-4	0.313	0.319	0.321	0.319	0.314*	0.265
J-5	0.391	0.396	0.397	0.369*	0.258	0.217
J-6	0.437	0.446	0.435	0.434	0.412*	0.269
J-7	0.398	0.398	0.397	0.398	0.388	0.378
J-8	0.300	0.302	0.302	0.304	0.297	0.299
J-9	0.206	0.206	0.200	0.206	0.205	0.200
J-10	0.108	0.108	0.104	0.110	0.109	0.106

[a]All solutions were read on the Beckman spectrophotometer using 1.000-cm cells and a water reference solution. The red sensitive phototube was used and the slit width was 0.17 mm. The solutions are described in Table IV.

*This symbol denotes visual perception of the precipitate. The precipitate was not isolated from solution.

form, the absorbance of the solution falls off fairly rapidly. Although the absorbance never reaches a constant value, the rate of decrease does become quite small after several weeks. It is significant that the precipitation first occurred in the solution in which the total analytical concentration of thorin was equal to that of the thorium. A precipitate also separated from all solutions containing a molar excess of thorium and from two solutions, J-6 and J-7, containing a small molar excess of thorin. When a large molar excess of dye was in solution, there was no evidence of precipitation, and, after the initial increase, no significant changes in absorbance were noted.

The reagent itself is apparently quite stable at this pH, in confirmation of the earlier observations. The slight increase observed at 540 mμ (Table V) was probably due to contamination. The maximum absorbance value changed negligibly throughout the period of observation. The absorbance of a 3.125×10^{-5} M thorin solution was measured intermittently over a period of 135 days. There was some evidence of slight deterioration at the end of this period, but the solutions appeared to be stable for at least a month.

The fact that these solutions do achieve a steady state for several days suggests that it might be possible to utilize measurements taken during this time interval for

the determination of some of the properties of the soluble
reaction products. It appears that in this range of con-
centrations at a pH of 1.00, the steady state persists for
a period extending from four hours to at least 57.5 hours
after the solutions are mixed. However, in interpreting
any data taken under these circumstances, it is necessary
to consider the fact that the solutions do undergo modifi-
cation with time and that the apparent equilibrium is
definitely a metastable state. In the work described in
subsequent sections on the soluble complex, all measurements
were made during the time interval in which the metastable
state prevails.

It seemed possible that by working in more dilute
solution, the formation of a precipitate might be avoided
and a continuing steady state might be reached. The
absorbance at 540 mμ of solutions 1/10 as concentrated as
those in the preceding series is shown in Table VIII as a
function of time. It can be seen from this table that a
continuing equilibrium state is not reached in these solu-
tions. No visually detectable amount of precipitate was
formed, but the steady decrease in absorbance suggests
that it might be forming in such small quantities that it
cannot be observed visually.

Table VIII

Effect of Time on the Absorbance of Very Dilute Solutions of Thorin and Thorium at 540 mμ [a]

Solution Number	$M_R \times 10^6$	$M_{Th} \times 10^6$	A_0 hr.	A_2 hr.	A_{87} hr.	A_{32} days
JD-1	0.625	5.625	0.035	0.037	0.034	0.029
JD-2	1.875	4.375	0.114	0.118	0.110	0.100
JD-3	3.125	3.125	0.205	0.206	0.202	0.194
JD-4	4.375	1.875	0.186	0.191	0.182	0.173
JD-5	5.625	0.625	0.151	0.159	0.157	0.150

[a]All absorbance measurements were made with the Beckman spectrophotometer using 10.000-cm cells and a water reference solution. The slit width was 0.25 mm. pH of solutions was 1.00.

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(c) <u>Ratio of ligand to central atom.</u>

(1) <u>Job's method of continuous variations.</u> Job's
method of continuous variations (51,128) has been so widely
employed that a detailed treatment of the theory of this
procedure for determining the ratio of ligand to metal is
not necessary in this report. For this work, absorbance
data from the solutions described in Table IV were used.
In employing Job's method spectrophotometrically, it is
necessary to correct for the absorbance due to either react-
ant. Thorium perchlorate does not absorb at the wavelength
used. Thorin absorbs significantly at those wavelengths
at which the complex absorbs; therefore, corrections were
made in the usual manner. The absorbance of the dye added
to each solution was subtracted from the absorbance of the
complex solution. The absorbance of the reagent at any con-
centration can be obtained by taking the appropriate fraction
of the absorbance of solution number J-10 since thorin solu-
tions obey Beer's law upon dilution. This corrected
absorbance value is commonly denoted as "Y", the symbol used
in this report.

The corrected absorbance values are listed in Tables
IX and X. Table IX was prepared from data taken with the
Beckman spectrophotometer using 1.000-cm cells and water as
a reference solution. With the exception of the data at
240 mμ , the measurements were made 57.5 hours after the

Table IX

Corrected Absorbance Values, Y, for Job's
Method Plot, Beckman Data[a]

Solution Number[b]	$Y_{240 \, m\mu}$	$Y_{475 \, m\mu}$	$Y_{510 \, m\mu}$	$Y_{540 \, m\mu}$
J-1	-0.030	-0.015	0.053	0.076
J-2	-0.081	-0.033	0.102	0.144
J-3	-0.131	-0.050	0.147	0.210
J-4	-0.159	-0.065	0.202	0.279
J-5	-0.198	-0.077	0.248	0.345
J-6	-0.245	-0.087	0.264	0.373
J-7	-0.233	-0.085	0.203	0.324
J-8	-0.190	-0.060	0.121	0.219
J-9	-0.095	-0.034	0.061	0.106
J-10	0.000	0.000	0.000	0.000

[a]The readings at 240 mμ were made 71 hours after the solutions were prepared; all other readings were made after 57.5 hours. See Table VII for measurement conditions. The slit widths were: 0.600 mm at 240 mμ, 0.252 mm at 475 mμ, 0.200 mm at 510 mμ, and 0.170 mm at 540 mμ.

[b]Solutions are described in Table IV.

Table X

Corrected Absorbance Values, Y, for Job's
Method Plot, Cary Data[a]

Solution Number[b]	$Y_{420\ m\mu}$	$Y_{520\ m\mu}$	$Y_{530\ m\mu}$
J-1	-0.019	0.055	0.063
J-2	-0.038	0.110	0.129
J-3	-0.054	0.169	0.190
J-4	-0.070	0.224	0.252
J-5	-0.084	0.278	0.310
J-6	-0.095	0.284	0.334
J-7	-0.080	0.241	0.283
J-8	-0.053	0.160	0.192
J-9	-0.024	0.073	0.090
J-10	0.000	0.000	0.000

[a]Absorbance measurements were taken 24 hours after the solutions were prepared.

[b]Solutions are described in Table IV.

solutions were prepared. The ultraviolet data were taken 71 hours after the solutions were mixed, prior to the formation of any detectable precipitate. The data in Table X were obtained from absorbance measurements taken from the spectra of these solutions, Figure 6. These curves were made 23 hours after the solutions were prepared. The Cary measurements, which were made in 2.000-cm cells, have been halved in order that they may be compared with the Beckman measurements of Table IX, which were made in 1.000-cm cells. In those instances in which the thorin has a greater molar absorptivity than does the complex, the Y values are negative.

These data are plotted in Figure 7. It can be seen that, with the exception of the 240 mμ plot, the peaks in the Y values appear to cluster around the position which represents a thorin to thorium ratio of 1.5. This would suggest that in the soluble complex two thorium atoms are associated with three thorin molecules. However, the results are not conclusive. The exception in the 240 mμ plot suggests that possibly more than one complex exists. A shift in the peak position of Y with wavelength indicates such a situation. However, the fairly close agreement on the 3:2 ratio at all other wavelengths certainly presents a strong argument in favor of the existence of such a complex. The argument that perhaps only one complex forms is strengthened
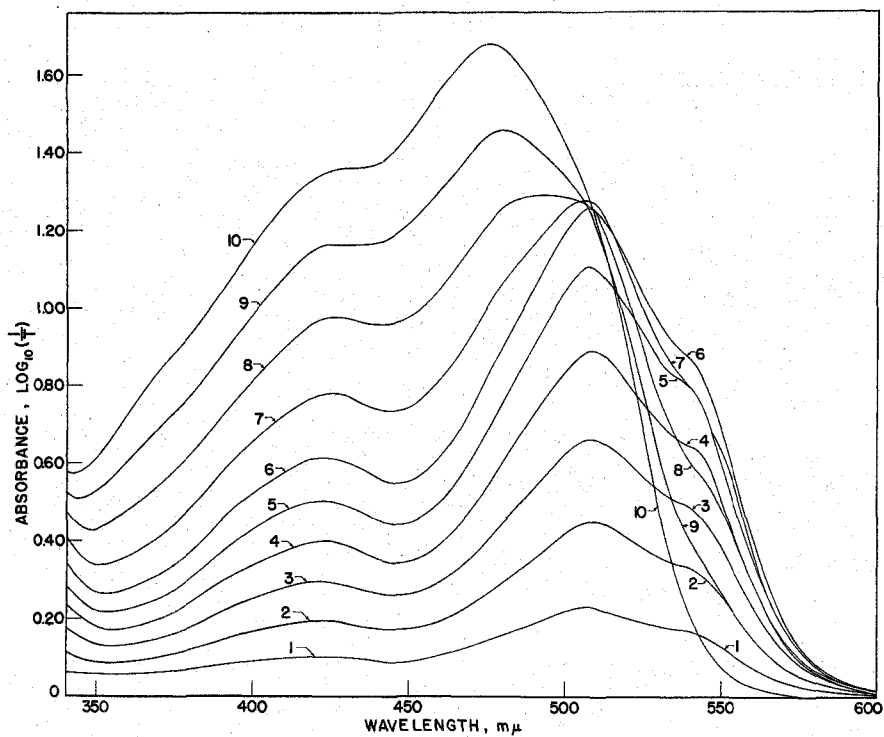
FIG. 6   ABSORPTION SPECTRA OF JOB'S SOLUTIONS OF COMPLEX.
SCANNED IN 2.0 CM. CELLS VS. WATER.
NUMBERS CORRESPOND TO SOLUTIONS DESCRIBED IN TABLE IV
23 HOURS AFTER PREPARATION.
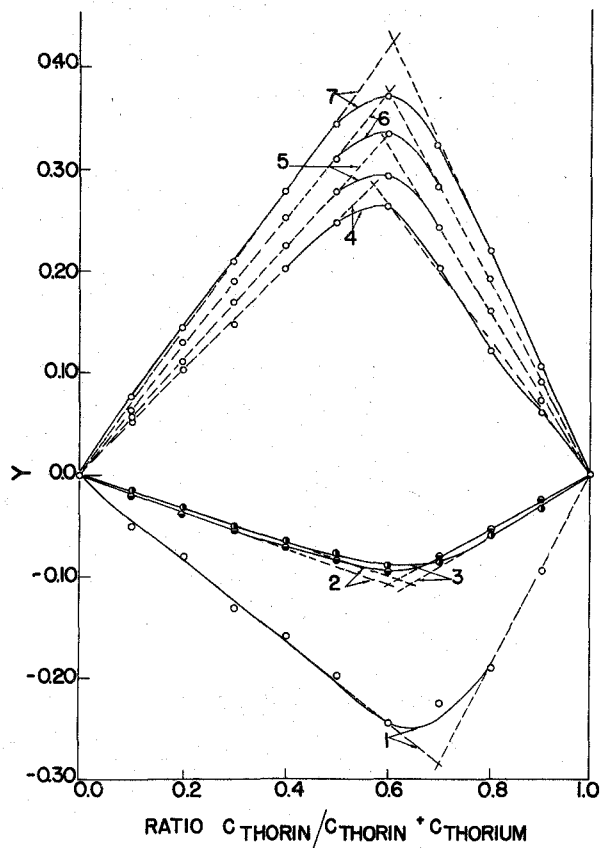
FIG.7 DETERMINATION OF RATIO OF
       LIGAND TO CENTRAL ATOM BY
       JOB'S METHOD.

CURVE I: AT 240mμ.   CURVE 5: AT 520mμ.
CURVE 2:AT 420mμ.   CURVE 6:AT 530mμ.
CURVE 3:AT 475mμ.   CURVE 7:AT 540mμ.
CURVE 4:AT 510mμ.

DATA FOR CURVES 2,5,AND6 ARE
FROM CARY CURVES OF FIG. 6.

DATA FOR CURVES I,3,4, AND7 ARE
FROM BECKMAN MEASUREMENTS.

by the fact that considerable inaccuracy may be associated
with the 240 mμ readings. Those readings were made after
71 hours had elapsed, and precipitation may have started
even though it was not noted. Also, both the reagent and
the complex have very high molar absorptivities at 240 mμ,
and it was difficult to get precise readings at the high
absorbance values obtained.

In summary, it can be stated that these data indicate
that the molar ratio of thorin to thorium in the soluble
complex is 3:2. However, there is definite evidence for
presuming that more than one complex exists, and it is
entirely possible that in such a case, none of the complexes
would correspond to the one just described.

(2) Molar ratio method. In this method of study-
ing a complex ion, the concentration of one of the reactants
is held constant in a series of solutions while that of the
other constituent is varied over a wide range (43). If the
absorbances of these solutions are plotted against the con-
centration of the varying species, a break might be observed
at that point representing the molar ratio of thorin to
thorium in the complex. If more than one complex is present,
or if the complex is weak, no such break is likely to occur.
Instead, a smooth curve is usually observed.

In this investigation two series of solutions were
prepared. In one series, the concentration of thorium was

kept constant at 0.625×10^{-5} M while that of the thorin was varied from 0.312×10^{-5} to 12.50×10^{-5} M. In the other series the concentration of thorin was held at 1.25×10^{-5} M while that of the metal was varied from 0.312×10^{-5} to 12.50×10^{-5} M. The absorbances of these solutions were measured on the Beckman spectrophotometer against a water blank at 540 mμ . Two-cm cells were used for the measurements on the solutions of varying dye concentration and 5.000-cm cells were employed in the other series. The readings were made ten hours after the solutions were prepared except in the few cases noted in Table XII. The absorbance measurements and the compositions of the solutions are tabulated in Tables XI and XII.

It should be pointed out that the lower numbered solutions in these tables are slightly less concentrated than those described in Tables IV to VII. Therefore, the results of the stability studies are not strictly applicable to these solutions. Since the time variation in these solutions was not checked, it is not possible to say definitely that the more dilute solutions had attained the metastable equilibrium state at the time of the measurements. This does not alter the qualitative conclusions presented below, but it might contribute some error to any quantitative interpretations.

The data in Tables XI and XII are plotted in Figure 8. It is readily seen from the curves that the break is a smooth

Table XI

Absorbance of Solutions Used for the Molar Ratio Method with Varying Thorium[a]

Solution Number	$M_{Th} \times 10^5$	$A_{540\ m\mu}$ [b]
1	0.000	0.121
2	0.312	0.338
3	0.625	0.522
4	0.937	0.652
5	1.250	0.714
6	1.875	0.765
7	2.500	0.792
8	3.125	0.817
9	3.750	0.828
10	5.000	0.838
11	6.250	0.850
12	7.500	0.850
13	10.000	0.850
14	12.500	0.858

[a] Each solution was 1.25×10^{-5} M in thorin, and the pH was adjusted to 1.00 ± 0.02 with $HClO_4$.

[b] Absorbance measurements were made on the Beckman spectrophotometer in 5.000-cm cells 10 hours after solution preparation with a reference solution of $HClO_4$, pH 1.00. The red-sensitive phototube was used and the slit width was 0.200 mm.

Table XII

Absorbance of Solutions Used for the Molar Ratio Method with Varying Thorin[a]

Solution Number	$M_R \times 10^5$	$A_{540 \ m\mu}$ [b]
1	0.312	0.060
2	0.625	0.123
3*	0.937	0.183
4	1.125	0.202
5	1.250	0.228
6*	1.500	0.244
7*	1.750	0.260
8	1.875	0.320
9*	2.000	0.274
10*	2.250	0.286
11	2.500	0.302
12	3.125	0.321
13	3.750	0.341
14	5.000	0.383
15	6.250	0.424
16	7.500	0.462
17	10.000	0.541
18	12.500	0.630

[a] Each solution contains 0.625×10^{-5} M thorium. pH was adjusted to 1.00 ± 0.02 with $HClO_4$.

[b] Absorbance measurements were made on the Beckman spectrophotometer in 2.000-cm cells with a reference solution of $HClO_4$, pH 1.00. The red-sensitive phototube was used and the slit width was 0.200 mm.

* These readings were made 8 hours after solutions were prepared. All other readings were made 10 hours after solution preparation.
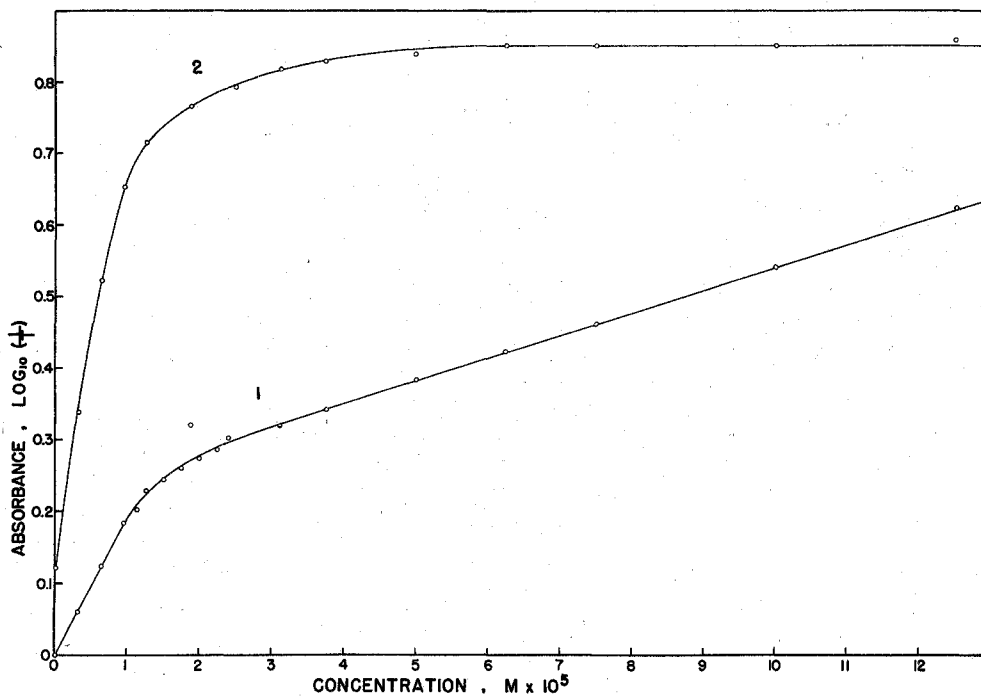
FIG. 8 – MOLAR RATIO CURVES FOR COMPLEX AT 540 mμ.– DATA FROM TABLES XI-XII

CURVE I : VARYING THORIN ; $C_{th} = 0.625 \times 10^{-5}$ M, SCANNED IN 2-cm. CELLS.
CURVE 2 : VARYING THORIUM; $C_R = 1.25 \times 10^{-5}$ M, SCANNED IN 5-cm. CELLS.
BLANK : WATER AT pH 1.00 WITH HClO$_4$

one. The fact that the break is not sharp indicates that
it is impossible to use this approach to obtain reliable
values of the constitution of the complex. Harvey and
Manning (43) have shown that extrapolations of the straight
portions of such curves to an intersection point do not
give reliable results. They recommend that in such cases,
it is advisable to increase the ionic strength of the solu-
tions. This modification was not tried and might very well
be a good extension to the investigation. However, such
an increase in ionic strength might affect the stability of
the soluble complex with respect to formation of a precipi-
tate.

These curves do present very substantial evidence
either that there are two or more complexes involved in
these solutions or that if only one complex is present, it
is rather weak. Data from curves of this type are of value
in estimating dissociation constants for the complexes.

(3) <u>Potentiometric and conductometric methods</u>.
The low pH conditions of the experiments were such as to
exclude the use of potentiometric and conductometric methods
to determine the ratio of ligand to central atom.

(4) <u>Titration to solution of precipitate</u>. It was
found that when a thorin solution, about 10^{-2} M and at a pH
of 1.0, is added to a thorium solution of the same order of
concentration at the same pH, the following events occur.

With the first addition of thorin, a bright red precipitate forms immediately. This precipitate remains suspended in solution with further addition of thorin until a point is reached at which it dissolves. This chain of events is not surprising since it has been shown in previous work that a precipitate develops even in quite dilute solutions unless a moderately large molar excess of thorin is present. At this higher concentration, the rate of formation of the precipitate is much faster. It seemed that some stoichiometric interpretation of these observations might be possible.

The stoichiometry was investigated in the following manner. Two 10-ml aliquots of a 1.864×10^{-2} M thorium solution at a pH of 1.00 were measured into Erlenmeyer flasks which were placed over a magnetic stirrer. The first aliquot was titrated with a 1.002×10^{-2} M thorin solution, pH 0.88, and the second aliquot was titrated with a 1.014×10^{-2} M thorin solution, pH 1.00. The thorin was added quite slowly with continuous stirring until the precipitate that was initially formed went into solution. The solution of the precipitate was observed visually and was found to occur fairly sharply. In the first titration, the precipitate dissolved at that point at which the molar ratio of thorin to thorium in the solution was equal to 1.58. In the second titration, solution occurred when the ratio of thorin to

thorium was 1.60. Each solution was then back-titrated with the standard thorium solution until turbidity appeared. This point was not as easily seen as in the reverse case and did not appear to occur as sharply. In the first solution, the turbidity reappeared after the addition of sufficient thorium to make the molar ratio of thorin to thorium 1.44. In the second solution, solution occurred at a thorin to thorium ratio of 1.41.

These results are indicative of a slow reaction around the equivalence point. If the system were reversible, only a few drops of standard thorium solution should be required to effect the reprecipitation. It is likely that a small excess of thorin over that necessary to form the soluble complex is required in order to stabilize the soluble complex, and that once this complex is formed, it is slow to react with thorium to re-form the precipitate.

If the results of the forward- and back-titrations are averaged, it is found that in this pH range 1.5 moles of reagent combine with one mole of thorium to produce a soluble complex. This is in very good agreement with the previous results obtained by Job's method.

(d) Ionic charge on complex. It was felt that some information concerning the nature of the metastable solutions might be obtained from a study of the sign of the charge on the colored species. If more than one complex is formed, the complex of lowest thorin to thorium ratio would be

favored in excess thorium and that of highest ligand to metal ratio would be preferred in excess reagent. Furthermore, it would not be unreasonable to suppose that the sign of the electrical charge on two such complexes might be opposite or that one species might be neutral, whereas the other might be charged. Consequently, if a reversal of charge accompanies a change from an excess of one reagent to an excess of the other, it would be very strong evidence that more than one complex is participating in the equilibrium.

Two approaches to this problem were used. In the first a migration experiment was employed, and in the second an ion exchange technique was used.

(1) Migration experiments. In these experiments various mixtures of thorium and thorin were prepared, and the pH of the solutions was adjusted with perchloric acid. An inert salt, sodium chloride, potassium chloride, or sodium perchlorate, was added to each solution to increase the density. The complex solution was placed in the bottom of a U-tube. A pH 1.0 perchloric acid solution was placed on top in such a manner that well defined interfaces were formed between the colored complex solution and the clear perchloric acid solution. The latter solution was connected by means of agar-potassium chloride bridges to dilute sulfuric acid solutions which contained two platinum

electrodes. These were connected to a battery and a current of 2 to 5 ma was passed through the system. The migration at the interface was observed for several days.

These experiments, when carried out on the reagent alone, showed that it is negatively charged. The study in the presence of an excess of reagent was considerably complicated by the fact that the surplus of the colored reagent moves toward the positive pole and tends to obscure the observation of the movement of complex species in that direction. However, in this situation a net migration always occurred toward the positive pole. When carefully extracted portions of the migrated solution were scanned on the Cary spectrophotometer, the curve was characteristic of that for the complex plus excess reagent. In addition, the migrated solution near the boundary was the characteristic pink color of the complex. These results indicate that in solutions containing an excess of reagent, the soluble complex formed is negatively charged.

The results on those solutions which contained an excess of thorium were not too definite. In one of these experiments, the preceding setup was modified to include an agar-potassium chloride gel in the bottom of the U-tube. Migration of color into the gel was observed. With excess thorium, a precipitate formed on the gel-solution interface nearest the negative electrode, which might indicate that

the complex was moving away from the negative pole and was negatively charged. From the migration experiments, it is concluded that probably a negatively charged complex predominates in solutions containing an excess of either reactant.

(2) Ion exchange experiments. In this work the sodium salt of Nalcite HCR was used as the cation exchange resin, and the perchlorate salt of Amberlite IRA 410 was used as the anion exchanger. Solutions were prepared by mixing various proportions of thorin and thorium. The absorption spectra of these solutions were measured on the Cary spectrophotometer. Then weighed quantities of the appropriate resin were added, and the mixtures were shaken on a Burrell Wrist-Action Shaker. A portion of the solution phase of each mixture was withdrawn periodically, and its spectrum was examined.

When 100 ml volumes of solutions containing a ten-fold molar excess of thorium, $M_{Th} = 12.5 \times 10^{-5}$ and $M_R = 1.25 \times 10^{-5}$, were shaken with 1, 5, and 10 gram portions of the anion exchanger, a precipitate developed. Presumably the shaking accelerated the precipitation reaction, which is normally very slow at this concentration. The same phenomenon occurred on shaking a similar solution containing no resin for a comparable length of time. The precipitation excluded the possibility of quantitatively following the change in the solution spectrophotometrically. However,

the absorbance was decreased to a greater extent by an increasing amount of resin, which suggests that possibly some exchange did occur.

Similar solutions were shaken with the same quantities of cation exchanger for 18 hours and were scanned on the Cary spectrophotometer. The resulting spectrum was quantitatively similar to that of the same amount of free thorin in the solution which contained 1 g of the resin. It was concluded that the cation exchanger had removed all of the free and complexed thorium in the solution. In solutions that were shaken with 5 g and 10 g quantities of exchanger, the absorbance of the solutions dropped slightly from that which could be attributed to the amount of thorin used to prepare the solution. However, qualitatively the spectra were identical with that for the reagent, and it was assumed that the difference was due to adsorption rather than exchange effects.

A number of similar experiments were run to determine the charge on the complex which exists in the presence of an excess of reagent. Only two of these experiments will be described. In the first, 50 ml of a solution which was 1.25×10^{-5} M in thorium and 7.5×10^{-5} M in thorin was shaken with 5 g of the anion exchanger for 18.5 hours. The excess reagent exchanges, and the complex should exchange also if it is negatively charged. The absorbance decreased greatly on shaking, but the spectrum remained unchanged

qualitatively. The resin was filtered off, and the filtrate was analyzed spectrophotometrically for thorium after the destruction of the organic residue. The concentration of thorium in solution had decreased, which indicates that some of the complex did exchange with the anion exchanger.

In the second experiment, two types of solutions were used. One contained only thorin, 12.80×10^{-5} M, and the other contained the same concentration of thorin and in addition was 2.33×10^{-5} M in thorium. Fifty-ml aliquots of each solution were agitated with 5-g portions of either the cation or the anion exchanger for several hours. With the cation resin, all of the thorium exchanged, and the spectrum of the solution was identical with that of the free reagent. The reagent did not exchange. With the anion exchanger, both the reagent and the complex solution appeared to exchange. The absorbance decreased in both the solutions, but the absorption curves were qualitatively undisturbed by the exchange.

From the migration and ion exchange experiments, it seems likely that the complex formed in an excess of thorin is negatively charged. Although the results are not conclusive, they indicate that the complex predominating in an excess of thorium is similarly charged. If these indications are correct, and if several complexes are contributing to the equilibrium, they are all negatively charged.

However, the author does not feel that very much dependence should be placed on these results.

(e) Dissociation constants for complexes. Calculations of the dissociation constants of assumed complexes were not particularly conclusive. The absorbance data from the molar ratio plot of Figure 8 were used in all calculations. Mention of curve 1 and curve 2 in the following discussion refers to this figure.

It can be seen from curve 2, in which the thorium concentration is varied, that the plot levels off to a constant absorbance value at the higher thorium concentrations. This part of the curve can be used to obtain a first approximation to the molar absorptivity of the assumed lowest complex. Data from the part of curve 2 immediately preceding the horizontal portion can be used to calculate a dissociation constant for the complex, since the lower complex should predominate in an excess of thorium. Adjustments in the estimated value of the molar absorptivity are made until precise values of the dissociation constant are obtained. For an assumed 1:1 complex, an instability constant of $1.0 \pm 0.1 \times 10^{-6}$ was calculated for an interval of the curve in which the ratio of the total analytical concentrations of thorium to thorin were 1.5:1 to 4:1. It was not necessary to adjust the value of the calculated molar absorptivity of the complex, 13,600 liter/mole-cm, to improve the precision in this particular case.

In curve 1, in which the thorin concentration is varied, it was assumed that the data over the linear portion of the curve were from solutions in which all of the available thorium had reacted to form the complex having the highest possible ratio of ligand to central atom. A value for this ratio was assumed and permitted a calculation of the absorbance due to the excess reagent. This absorbance was subtracted from the observed absorbance to give the absorbance due to the complex. From this value and the concentration of the complex, the molar absorptivity of the assumed complex can be calculated. As in the preceding case, the solutions represented in the portion of the curve just preceding the linear part of the plot were presumed to be those in which the highest complex predominated.

It was assumed that the highest complex was one in which the molar ratio of ligand to central atom was 2:1. The instability constant was calculated to be $2.0 \pm 0.3 \times 10^{-12}$ from data on solutions in which the ratio of the total analytical concentrations of thorin to thorium varied from 2.4:1 to 4:1. The calculated molar absorptivity was 20,500 liter/mole-cm, and the value which gave a minimum deviation in the dissociation constants was 20,700 liter/mole-cm.

Next it was decided to make calculations on the assumption that the predominating soluble complex in all of

the solutions was one in which the molar ratio of ligand to central atom was 3:2. The molar absorptivity was estimated from the flat portion of curve 2 to be 40,800 liter/mole-cm. The constant was calculated for the dissociation into two thorium and three thorin ions. An adjusted value of the molar absorptivity equal to 43,000 liter/mole-cm gave a value for the dissociation constant of $2.7 \pm 0.1 \times 10^{-22}$. Although the precision is excellent, there is some reason for believing that it may be fortuitous.

The data from the horizontal portion of curve 2 should give a calculated molar absorptivity having an accuracy of the same relative magnitude as that for the reagent concentration. The uncertainty in the latter is no greater than two to three per cent. It was necessary to change the calculated value of the molar absorptivity by more than five per cent to obtain precise values of the constant. No change in the calculated molar absorptivity was required when a 1:1 complex was assumed to predominate as the lowest complex. Next the data of curve 1 were used to calculate a dissociation constant for a 3:2 complex. Again a molar absorptivity of 43,000 liter/mole-cm was used, and the calculated value of the dissociation constant was $1.9 \pm 1.4 \times 10^{-22}$, which is in good agreement with the previous result. The precision of the constant is quite poor. If a value of 39,500 liter/mole-cm was used for the molar absorptivity, the calculated dissociation constant from the

data of curve 1 was $3.9 \pm 0.6 \times 10^{-23}$. Here the precision is improved, but the agreement with the previous data is very poor. These results seem very inconclusive to the author.

Thus far it has been shown that if a complex having a molar ratio of thorin to thorium of 1:1 is the major complex formed in an excess of thorium, its dissociation constant can be estimated as $1.0 \pm 0.1 \times 10^{-6}$. If a 2:1 complex predominates in an excess of reagent, its instability constant is $2.0 \pm 0.3 \times 10^{-12}$. If a 3:2 complex is the predominant species at all ratios of metal to reagent concentrations, the dissociation constant is approximately 2×10^{-22}. The existence of a single complex is very improbable, however, since the calculated molar absorptivity of any assumed complex is different in an excess of one reactant than it is in an excess of the other reactant, as described in the "Discussion" section.

From these results it would appear that reasonably precise dissociation constants can be calculated for an assumption of several different equilibria. Sufficient evidence has not been obtained to permit definite conclusions as to which of the assumptions are correct. The indications are that all three of the postulated complexes are formed. Other complexes not considered above might also be present.

Calculations of absorbance values of the various solutions in the molar ratio series in which both complexes might be present were made from the estimated instability constants for a 2:1 and 1:1 complexes. These did not correspond to the observed values, even on further adjustment of the constants, and the implication was that the system could not be described using just these two complexes. Attempts to do the same thing for additional complexes were not made. Such computations are very time consuming, and it was felt that more precise data should be obtained before extending the calculations. Some ideas on this subject are presented in the "Suggestions for Future Work" section.

It is of particular interest to be able to establish a maximum value for the dissociation constant that is predominant for those solutions used in the analytical work. Since this is done in an excess of reagent, a higher complex is assumed to prevail. It is shown in the second part of this thesis that a solution containing 0.004% thorin conforms to Beer's law in its reaction with 20 to 100 micrograms of thorium per 50 ml. At the lower thorium concentration, a gross dissociation of the complex would certainly lead to a departure from Beer's law. If it is assumed that the postulated complex at this concentration can be at most ten per cent dissociated and still conform to Beer's law, a maximum value for the instability constant can be estimated.

For a complex in which the molar ratio of thorin to thorium is 3:2, the constant would have to be less than 10^{-20} to satisfy this requirement. For a 2:1 complex, a value less than about 5×10^{-10} is necessary.

3. Solid compound

(a) Preparation. All preparations were carried out in solutions at a pH of 1.0. Numerous attempts to prepare fairly pure samples of the precipitate by slow addition of either reagent to the other in warm solution followed by digestion were not particularly successful. This appeared to be due to a great tendency of the reagent to coprecipitate. This problem was eventually resolved by rapidly mixing approximately equimolar amounts of fairly concentrated solutions, about 10^{-2} M, of the reactants in the cold to give an extremely finely-divided precipitate. Such small particle sizes greatly increase the effectiveness of the extended digestion period of four to eight days which followed. The precipitate was separated from the solution phase with the centrifuge and was washed several times with a pH 1.0 hydrochloric acid solution containing a trace of thorium. This procedure had the distinct advantage of being easily adapted to preparation of large samples. By using this technique, it was possible to prepare successive batches of product which gave check analyses for thorium.

Some precipitations were effected from a perchlorate
environment, but all washings were made with chloride
solutions. Most of the analytical work was done on product
precipitated from hydrochloric acid. The Dumas nitrogen
analysis was carried out on one of the purer precipitates
which had been prepared by a slow addition method before
the technique just described had been developed.

(b) Properties. The solid separates from the solution
as a rather brilliant-red compound which turns to a very
dark red on loss of water. When the first few samples of
the solid were isolated, attempts were made to dry them to
constant weight in a vacuum desiccator. However, the
precipitates continuously lost weight, and even after 35
days, equilibrium had not been attained in one sample. The
vacuum-dried product possessed a black luster. Although
the particles may not have been truly crystalline, they were
needle-shaped. When these black needles are pulverized to
smaller particles in a mortar, the precipitate takes on the
very dark red hue described above. These particles do not
gain weight on the balance and presumably are not hygrosopic.
It should be noted that these experiments were run on some
of the less pure precipitates prepared by the slow addition,
and they did contain some coprecipitated thorin. It may be
that the purer precipitates might dry to constant weight in
a vacuum, but it is doubtful.

When these vacuum-dried samples were placed in a drying
oven at 105°C, they lost considerable weight. The analytical
results described in the next section and the known stability
of thorin at this temperature indicate that the weight loss
was not due to decomposition, but instead probably to loss
of water. The oven-dried samples retained the deep-red hue
of the vacuum-dried samples and rapidly gained weight on
exposure to the atmosphere. The latter observation is true
of both the pure precipitates prepared as described previous-
ly and of those which are known to contain coprecipitated
thorin. All of the analytical work was done with samples
dried at this temperature. When water is added to these
dark-hued particles, they immediately assume the bright red
color characteristic of the freshly-formed precipitate.

Qualitative solubility studies showed that the oven-
dried precipitate is insoluble in carbon tetrachloride,
diethyl ether, acetone, butylamine, pyridine, methanol,
ethanol, and glycerol. It is slightly soluble in water and
is insoluble in dilute acids. It dissolves readily in both
ammonium hydroxide and sodium hydroxide solutions to give
a dark red solution.

This latter phenomenon suggests that the precipitate
retains one or more of the acidic hydrogens of the thorin
molecule. Several attempts to titrate a suspension of the
precipitate potentiometrically with standard base were made.

It seemed likely that if a break could be obtained and associated with the solution of the suspension, the stoichiometry of the reaction with base might be ascertained. In one of these experiments .03832 g of precipitate was suspended in 50 ml water. However, it was found that the reaction was too slow to be followed potentiometrically. Even heating to $72^{\circ}C$ did not improve the kinetics sufficiently to use such a technique. After adding approximately 2.5 moles of sodium hydroxide per mole of suspended precipitate, it dissolved.

It seemed that it might be possible to back-titrate the solution thus formed and make a potentiometric plot. However, stable pH readings were not obtained. Some slow hydrolytic equilibria with thorium may have been the source of trouble. It was assumed that actually only one mole of sodium hydroxide per mole of precipitate was consumed in the salt formation. An amount of standard hydrochloric acid slightly greater than needed to neutralize the excess base was added. The solution was stirred for five hours at room temperature. No precipitate had formed at the end of this time. The pH reading was 4.75. The pH was then reduced to 2.25 and still no precipitation occurred. However, when the pH was adjusted to 1.00, the precipitate separated from solution almost immediately. This would seem to indicate that although the oven-dried product is quite

insoluble in everything but moderately strong bases, its solution is not easily reprecipitated except at very low pH values. This is believed to be at least partially a kinetic effect.

Apparently the oven-dried precipitate is quite resistant to chemical reactions. Whereas the freshly precipitated product readily goes into solution on addition of further reagent, a water suspension of the oven-dried solid is impervious to reagent attack even when heated or cooled.

The fact that the precipitate is not readily reprecipitated from its solution even at quite low pH values was used in a semiquantitative study of the absorbance of a solution of the precipitate as a function of pH. A small amount of oven-dried precipitate was dissolved in sodium hydroxide and was scanned on the Cary spectrophotometer in 2.000-cm cells against a water reference solution. The actual concentration of the material in solution was unknown, but it was sufficiently low that it was possible to acidify the solution to pH 0.85 without initiating immediate precipitation. The resulting solution was scanned on the Cary, the contents of the cell were returned to the original solution, and the pH was raised by the addition of a concentrated sodium hydroxide solution. Another absorption curve was made, and the process was repeated for several more pH values. The addition of the base diluted the solution to

a very minor extent, and these experiments are therefore semiquantitative. Just as in the preceding pH studies, it was found that the maximum complex formation occurred at the lowest pH value, 0.85. As the pH was increased, the absorbance at the maximum characteristic of the complex, 509 mμ , dropped off sharply, and the curves acquired to a greater extent the characteristics of the reagent. At pH 10.8 there was evidence of some suspended hydrated thoria, and the curve was virtually identical with that for the reagent. This change is completely analogous to the changes noted in the solutions of Table III, which contained an excess of thorin.

The precipitate is also readily soluble in concentrated sulfuric acid. Its absorption spectrum in this environment appears to be identical with that of the reagent alone in the same medium. It is interesting that the peak in the principal absorption band of the complex at a pH of 1.00 is virtually identical with that for the thorin in concentrated sulfuric acid. Other portions of these two curves differ greatly, however. The precipitate also dissolves in 72% perchloric acid, but the absorption spectrum of the dissolved complex in this medium is quite different from that of the thorin alone. In perchloric acid the maximum for the complex occurs at 500 mμ instead of the usual position of 509 mμ . The peak for the reagent is

shifted from 475 mμ at pH 1.0 to 518 mμ in 72% perchloric acid.

(c) Analysis.

(1) Qualitative. It seemed possible that the precipitation might be the result of salt formation with a supposedly inert anion in the solution. This might be either hydroxyl or chloride ion in those instances in which the precipitate was prepared in chloride solution. The fact that the formation of the precipitate is promoted by decreasing pH would seem to discredit the possibility that hydroxyl ion might be involved. A qualitative test for chloride was run on a sample of one of the precipitates. The usual sodium fusion technique was employed to decompose the sample. The solution was acidified with nitric acid and boiled to expel the hydrogen cyanide and hydrogen sulfide. The addition of silver nitrate did give a slight turbidity, but this precipitate darkened at a much slower rate than the normal silver chloride precipitate. This indicated that most of the turbidity was due to reaction with residual cyanide ion. It was concluded that the formation of the precipitate did not involve a diverse anion in the solution.

(2) Thorium. Two different methods for analyzing the precipitate for thorium were used. In the one most often used, the oven-dried product was weighed out, the organic

matter was destroyed by treatment with nitric and perchloric
acids, the residue was dissolved, and the thorium was
determined spectrophotometrically with thorin. This method
gave fair accuracy, but the precision was not too good.
Its chief advantages are its convenience, rapidity, and
adaptability for small samples. Consequently, this was the
only procedure used until a precipitate of good purity was
obtained. Once the technique for preparing a fairly pure
precipitate was perfected, the final thorium determinations
were carried out by the following procedure. As before,
the organic material in the weighed samples was destroyed
by fuming with a mixture of nitric and perchloric acids.
The thorium was then precipitated from the dissolved residue
as the oxalate and ignited to the oxide. The results
obtained on triplicate analysis of the final products
prepared were 32.82 $\pm$ 0.02% thoria.

(3) <u>Nitrogen</u>. The percentage of nitrogen was
determined by the micro-Dumas method. The combustion tube
was packed according to the procedure described by Johns (52).
Standard acetanilide samples from the National Bureau of
Standards were analyzed on the Dumas apparatus until accurate
results were obtained consistently. Standard samples were
analyzed between analyses of the unknown compound to maintain
a check on the accuracy of the apparatus. There was one
important source of error. In weighing on the micro-balance,

sufficient time was expended for the hygroscopic oven-dried product to gain some moisture. This should lead to results which would be lower than the theoretical value. It should be noted that these samples did contain a small amount of coprecipitated thorin since the analyses were run before the method for preparing a fairly pure product had been developed. The presence of coprecipitated thorin would lead to higher results than those calculated for a probable ratio of thorin to thorium in the precipitate. Analysis of three samples gave a nitrogen content of 3.19 $\pm$ 0.06%.

The differences in the calculated nitrogen contents in the various postulated ligand to metal ratios are great enough that the small errors contributed by these considerations may be neglected. Therefore, no additional analyses were made.

(4) <u>Water</u>. For the water determination, the Karl Fischer reaction was used (89,90,129). The sample was suspended in methanol, and an excess of Karl Fischer reagent was added. The excess was back-titrated with a standard water solution, and the dead-stop technique was used to detect the end point. Analysis of three samples gave results of 5.20 $\pm$ 0.04%.

In Table XIII a list of some compounds that might represent the oven-dried precipitate and their compositions is presented. The theoretical values are compared with the observed results in the same table.

Table XIII

Compositions of Some Possible Compounds Compared
with the Analysis Obtained on the Oven-Dried Precipitate

Compound[a]	% ThO_2	% N	% H_2O
$Th(RH_3)_2$	20.43	4.33	0
$(ThRH_2)_2RH_3$	29.01	4.62	0
ThRH	34.73	3.68	0
$ThRH \cdot 2H_2O$	33.16	3.52	4.53
$ThRH \cdot 2.5H_2O$	32.79	3.48	5.59
$ThRH \cdot 3H_2O$	32.43	3.44	6.64
Found	32.82±0.02	3.19±0.06	5.20±0.04

[a]RH_5 is the neutral thorin molecule.

From the table it can be seen that the precipitate is definitely one in which the molar ratio of thorin to thorium is unity. From the results on the water and thoria, it appears that the precipitate is either the 2-hydrate, the 3-hydrate, or the 2.5-hydrate. Of these three possibilities, the 2-hydrate is favored for several reasons. The results from the Karl Fischer titration are much more likely to be high than low. For one thing, water is easily introduced during the weighing, and for another, there is a good possibility that some absorbed water may not have been removed during the drying process. The results of the thorium analysis would be expected to be a little lower than the calculated value if the samples contained some absorbed water. Any coprecipitated thorin would also lead to low thorium results. The results of the nitrogen analysis were expected to be high since the product which was analyzed was known to contain some coprecipitated dye.

D. Discussion and Summary

1. Effect of pH

It is of interest to correlate the pH dependency of the absorption spectrum of thorin with the work on the azo-hydrazo equilibrium in 2-hydroxy azo dyes. In his work,

Ospenson (101,102) showed that as the percentage of the hydrazo form in the equilibrium increases, the maximum in the principal absorption band moves toward slightly longer wavelengths, and the inflection or slight maximum in the neighborhood of 425 mμ becomes virtually indistinguishable. This is precisely the effect that occurs with removal of the acidic hydrogens on the arsonic acid.

In Figures 3 and 4, the bond distances and angles are taken from the values given by Branch and Calvin (12) or from Ospenson (101). The structures in Figures 3 and 4 are drawn so that the ring systems are coplanar, and the arsenic and sulfur atoms are tetrahedral. It will be noted that the distance of closest approach between the oxygen of the arsono group and the azo nitrogen, as well as that between the hydroxy oxygen and the azo nitrogen, is such as to permit hydrogen bonding with very little distortion from coplanarity in either of the tautomeric forms. The normal hydrogen bond distance is 2.5 to 2.9 angstroms. Hydrogen bonding between the arsono and hydroxy oxygens would require a considerable departure from the resonance favored coplanar configuration in the azo form and a somewhat smaller deviation in the hydrazo structure. It would appear that the closest oxygen-oxygen distance between the 3-sulfo group and the hydroxy group is favorable for hydrogen bonding in either tautomeric form.

The proposed explanation for the increased preference for the hydrazo form as acid hydrogens are removed from the arsono group is that this group becomes more negative and leads to a stabilization of the hydrogen bond between the azo nitrogen and the group. A change in spectrum might also be attributed to a shift of the hydrogen bonding within the hydrazo form rather than a shift toward that form in the tautomeric equilibrium. A change in the hydrogen bonding of the hydrazo hydrogen from the hydroxy group to the arsono group would be expected to produce a hyposochromic shift. The removal of the hydrogen from the proximity to the hydroxy group would decrease the relative contribution of the C^+-O^- form to the resonance of the quinoid system.

After the removal of the naphtholic hydrogen, these interpretations are no longer applicable for the tautomeric equilibrium ceases to exist.

There is some concern over the failure of the spectrophotometrically determined pK values to check those determined potentiometrically as well as was expected. At first it seemed that this difference might be due to the difference in the ionic strength values employed in the two experiments. This would imply that the correction equations are inadequate. However, a spectrophotometric determination of pK_3 at an ionic strength of 0.1, the same value used in the potentiometric work, checked the absorptiometric value

at the higher ionic strength. It was also shown that
ion-pair formation does not explain the differences, since
an exchange of ammonium chloride for sodium chloride
produced no change in the results.

Because the work on the pH dependency of the absorbance
of the complex was not very exhaustive, it would be
inappropriate to attach too much significance to minor
details. In Figure 2 at 540 mμ it can be noted that the
positive differences between the absorbances of the reagent
and of the complex are at a maximum at a pH of about 1.00
and that an increase in pH results in a continual decrease
in this difference until it finally becomes negative. If
this decrease in the absorbance of the complex could be
attributed to the formation of hydrolyzed thorium species
and liberated reagent, the curve of Figure 2 for the complex
would be expected to become coincident with that for the
reagent but never to fall below it at this wavelength. The
fact that the reagent absorbance does exceed that of the
complex between certain pH values indicates that the change
which occurs is associated with the formation of hydroxy or
oxy coordination with the thorium in the complex and not to
a removal of the metal from the dye. There might also be
a change in the thorin-thorium bonding. At the higher pH
values where the reagent and complex spectra become

coincident, it is likely that a hydrated thorium species
and liberated reagent are present.

2. Configurations of complex reaction products

The amount of crystal structure data on thorium compounds
is not sufficient to enable one to draw definite conclusions
about its bonding preferences. It seems generally accepted
that thorium most often has a coordination number of
eight (105). According to Kimball (56), the most favored
bonding for an octacoordinated atom is either one in which
the bonds are directed toward the corners of a dodecahedron
with triangular faces or one in which the bonds are projected
toward the corners of an Archimedean antiprism. Less stable
arrangements are the prismatic structure, in which two of
the bonds are directed to the centers of two of the prism
faces, and the cubic structure. The crystal structures of
thorium hydroxy chromate and thorium hydroxy sulfate have
been determined (80,81) and are such that the thorium bonds
are of the antiprismatic type. It is not valid to extend
these observations to a generalization. However, this might
be considered strong evidence that thorium accommodates this
orientation comfortably. There would appear to be no clear
reason against thorium forming tetrahedral, octahedral, or
dodecahedral bonding if that geometry were preferred. The
dye has a number of reactive centers any of which might be

united to the thorium under certain conditions. Union with thorium may take place through the formation of bonds with the arsono, the sulfo, the hydroxy, or the azo groups. The necessity of coplanarity for high resonance energy makes it unlikely that the reagent is present as the non-coplanar cis-form.

It seems impossible to draw any conclusions concerning the participation of the naphtholic group in the formation of the complex. The generally accepted theory that both of the groups ortho to the azo linkage are associated with the metal in this type of complex suggests that the naphtholic hydrogen is replaced. Kuznetsov's failure to obtain a color reaction between thorium and a 2'-arsono-4-hydroxyazomethine dye further supports this view (69). In this work it was found that the ultraviolet absorption spectrum of a basic solution of the oven-dried thorin-thorium precipitate was different from that of the thorin after the removal of the naphtholic proton. The ready solubility of the precipitate in base was thought to be due to the retention of an acidic hydrogen of the thorin in the precipitate. If this hydrogen were the one on the naphthol group, one might expect that a basic solution of the precipitate would have qualitatively the same ultraviolet absorption spectrum as thorin with the naphtholic hydrogen removed. However, the fact that it does not is no proof that the naphtholic oxygen

is associated with the thorium. It might mean that as base
is added, the removable hydrogen is replaced by a thorium
bond. In this case the characteristic spectrum of the ion
would not be observed. It is very possible that the solu-
tion of the precipitate in base does not involve salt forma-
tion but is instead a reaction to produce a soluble, mixed
hydroxy and thorin complex with thorium. Such complexes
were indicated in the pH studies.

The sulfonic acids might satisfy primary valence bond-
ing in the thorium. This is probably the case with the
precipitate, since no diverse anions appear to be present.
It is doubtful that these groups contribute much to the
bonding in the soluble species, unless polymerized complexes
are formed, because of their distance from the central atom.

Since it confers the selectivity to the reagent, the
arsono group is very likely bound to the thorium in the
complex. The arsono group contains two replaceable hydrogens
and one or both of these might be replaced in the reaction
with thorium. Because the arsenic atom is tetrahedral, it
is very unlikely that all three arsono oxygen atoms are in
union with the same thorium atom. If two oxygen atoms from
the same arsono group are attached to the same thorium, a
four-membered ring would be formed. This would involve a
prohibitive strain if the thorium bonds were oriented either
tetrahedrally or octahedrally. The calculated values of

the smallest bonding angles in either the antiprismatic or the dodecahedral forms show that there also would be considerable distortion if the four-membered rings were formed. However, the strain would be quite a bit smaller than in the case of the tetrahedral or octahedral bonding. It might be that each of the protons on the arsono group is replaced by a different thorium atom.

It was shown in the experimental section that there is considerable reason for believing that the predominant complex under the conditions of these experiments might be one in which the ratio of ligand to central atom is 3:2. Some speculation on the possible structure of such a complex might be of interest. Two geometrical configurations are to be proposed here for the 3:2 complex.

Emphasis will be placed on the bonds formed when a thorium atom replaces a hydrogen on the arsono group. It will be presumed in this argument that both of the hydrogens are removed. This postulate is open to some challenge, since thorium does form a water insoluble compound with arsenic acid in which only one hydrogen is replaced (3,21). No assumptions concerning the replacement of the naphtholic hydrogens or the coordination with the azo linkage are implied. It may be supposed that whether or not such bonds occur depends on the configuration resulting from the

restrictions imposed by the foregoing assumptions about the bonding between the arsono oxygens and thorium.

In the first proposed structure, one thorium atom is considered to have substituted both of the arsono hydrogens, and two such groups are connected by sharing the arsono group of a third thorin molecule. Two thorium-arsono four-membered rings are required; hence, it might be supposed that the octacoordinated bond types would be utilized in the thorium in order to minimize the strain. With the aid of Fisher-Taylor-Hirschfelder atomic models, it was possible to show that such a structure should be permitted sterically. However, octacoordinated metal atoms were not available, and the possibility of utilizing the other nucleophilic groups on thorin for filling thorium bonding positions was not studied. It does appear that the angular distribution of the bonds permits at least one of the remaining donor groups, hydroxy or azo, to occupy vacant thorium orbitals.

The second proposed structure is one in which each arsono group is bonded to two thorium atoms by elimination of the two protons. Each thorium is connected to three of these arsono groups. In this case all of the thorium-arsono oxygen bonds are equivalent and the configuration is such that the groups are situated at the corners of a trigonal

bipyramid. The three arsenic atoms would lie at the corners
of the base, and the thorium atoms would be at the apexes
of the bipyramid.

Here again there is no intention to convey any impres-
sions concerning bonding with other donor groups in the
dye. It appears clear, from the models, that in either
of the proposed configurations, the geometry is such as to
afford adequate space for the three thorin molecules.

With the models it was possible to show that the thorium
atoms would probably not be bonded octahedrally in this
second arrangement, since such bonding would require a
thorium-thorium bond. A tetrahedral thorium atom would
satisfy the geometrical requirements of such a pattern, but
this makes bonding with other parts of the dye molecule
impossible. It is probable therefore that such a structure
would employ an octacoordinated thorium atom.

Which, if either, of these two proposed structures is
more likely to be correct is not certain. The fact that
there are no strained four-membered rings in the bipyramidal
arrangement is the strong argument in its favor. It is also
significant that in thorium hydroxy sulfate, the sulfates
are shared by different thorium atoms. The less symmetrical
first structure is favored from entropy considerations.
However, the energy involved in the strained configuration
probably more than offsets the entropy effects. The

availability of the remainder of the thorin molecule for
bonding with thorium will have an important effect on the
actual configuration.

The configurations discussed above are not the only
ones that might be considered. It might be supposed that
only one hydrogen is replaced on the arsono group. In
this case, the naphtholic oxygen might be expected to be
bonded to the thorium. The experimental observations do
not offer sufficient evidence to justify a choice between
the various possibilities. However, these arguments do
indicate that it is not unreasonable to suppose that two
thorium ions combine with three thorin ions to form a
stable product.

There are undoubtedly other products formed in the
reaction. However, pertinent experimental evidence would
be needed to properly orient a further discussion of
structural features.

3. Ratio of ligand to central atom in solution

From a first consideration of the experimental work,
it might appear that the only complex in solution to any
great extent is the one in which the ratio of ligand to
central atom is 3:2. However, certain other considerations
make this presumption untenable. If there are no signifi-
cant quantities of complexes other than the 3:2 species

formed in these solutions, the calculated molar absorptivity
should be independent of which of the reactants is in excess.
This is based on the assumption that if a considerable
excess of one reagent is present, the amount of complex
formed is very nearly controlled by the total analytical
concentration of the minor species. This implies very
little dissociation. When the reagent is in excess, it
is necessary to correct for the absorbance of the excess
before calculating molar absorptivity. Table XIV compares
the calculated values in an excess of either reactant for
postulated complexes in which the molar ratio of ligand to
metal is 1:1, 3:2, and 2:1. From the table, it would
appear that a single complex species does not predominate
over the entire concentration range.

The calculated molar absorptivities in Table XIV have
an uncertainty of two to three per cent in the case of
solutions containing a large excess of thorium. This
follows from the fact that the concentration of the assumed
complex is a function of the total analytical concentration
of the reagent which may be in error by this amount. How-
ever, the differences in the table are much larger than
this and can be presumed to be significant if the assumption
of complete reaction is valid.

Therefore, it is not possible to describe the system
by a single predominant equilibrium. The experimental

Table XIV

Calculated Molar Absorptivities of Several Possible Complexes
in an Excess of Either Reactant[a]

Wavelength, $m\mu$	Postulated Ratio, Ligand to Metal	ϵ_R	$\epsilon_{\text{Excess Thorin}}$[b]	$\epsilon_{\text{Excess Thorium}}$[c]
475	1:1	13,150	7,840	10,720
510	1:1	9,760	19,520	18,240
540	1:1	1,730	19,200	13,600
475	3:2		28,850	32,210
510	3:2		48,720	54,810
540	3:2		40,060	40,870
475	2:1		20,960	21,470
510	2:1		29,280	36,540
540	2:1		20,800	27,240

[a]These values were calculated from the absorbance data on solutions described in Table IV. Measurements were made on the Beckman spectrophotometer with a slit width of 0.170 mm at 540 $m\mu$, 0.200 mm at 510 $m\mu$, and 0.252 mm at 475 $m\mu$ with red-sensitive phototube.

[b]$C_R = 5.625 \times 10^{-5}$; $C_{Th} = 0.625 \times 10^{-5}$ M.

[c]$C_R = 0.625 \times 10^{-5}$; $C_{Th} = 5.625 \times 10^{-5}$ M.

results indicate that there are several complexes contributing to the absorbance. There is a good possibility that the complex having a ligand to metal ratio of 3:2 is an important contributor to the equilibrium. The molar ratio of thorium to thorin in the precipitate was shown to be 1:1. It appears that the nucleation rate for the precipitation is slow. If this is so, significant quantities of the normally insoluble product might be found in the equilibrium mixture prior to the precipitation. It will be impossible to more completely describe the nature and the number of the reaction products with any certainty without some further experimental work. Some suggestions are offered later as to what approach might be successful.

III. PART TWO: SPECTROPHOTOMETRIC DETERMINATION

OF THORIUM WITH THORIN

A. Review of Literature

1. Colorimetric and spectrophotometric reagents for thorium

Most of the color-forming reagents for thorium have been
utilized as qualitative reagents. A number of organic com-
plexing agents have been proposed for this use. No attempt
will be made to present a complete list of these, but a
few typical examples will be given.

Kaserer (54) described the yellow color formed when
thorium reacts with pyrogallolaldehyde. 1,2-Dihydroxy-
anthraquinone (alizarin) and the sodium salt of 1,2-di-
hydroxy-3-sulfoanthraquinone (sodium alizarin sulfonate)
give characteristic colors with thorium which are quite pH
dependent (6,38,84,104). The pink dye Solochrome Brilliant
Blue BS (C.I. 723) reacts with thorium to give a blue color
in a monochloroacetic acid buffer (88). A yellowish-orange
color results when the purple ammonium purpurate (murexide)
is added to a thorium-containing solution (5). In alkaline
solution 1,2,5,8-tetrahydroxyanthraquinone (quinalizarin)
gives a blue color or precipitate with thorium (59).
Middleton (87) reported that thorium forms a bright red
lake with aurintricarboxylic acid.

Kuznetsov (67) described colors formed between thorium and 4-nitrocatechol, 4-nitrosocatechol, alizarin, 4-(4-sulfo-1-benzeneazo)-catechol, and 4-(4-sulfo-1-benzeneazo)-1,2-dihydroxynaphthalene in acid solution. When thorium, 2-aminobenzenearsonic acid, and 2-furylaldehyde are mixed in acid solution, a colored product is formed (73). With the pyridine or triethanolamine salt of 4,4'-bis-(2-hydroxy-1-naphthylazo)-2,2'-stilbenedisulfonic acid, thorium forms an orange-red color (71).

In neutral solution, 2-(2-hydroxy-5-methyl-1-benzeneazo)-benzenearsonic acid produces a brown color with thorium, and in weakly acid solution a yellow color is formed (66). 2-(1,8-Dihydroxy-3,6-disulfo-2-naphthylazo)-benzenearsonic acid gives a violet color with thorium in acid solution, but the 4-substituted arsonic acid does not give a color (66). The pink color of the thorium compound with 2-(2-hydroxy-6,8-disulfo-1-naphthylazo)-benzenearsonic acid, the violet color with 2-(2-carboxy-1-benzeneazo)-1,8-dihydroxy-3,6-disulfonaphthalene, and the reaction with thorin are described in the same paper. Later, the reaction with thorin was covered in greater detail (70).

With the exception of the arsonic acids, these reagents are not very selective, and a preliminary separation from many common metals is required. The selectivity of the arsonic acids has been referred to earlier in the thesis.

The number of quantitative spectrophotometric methods developed has been relatively small. In one method, the thorium iodate precipitate is reduced with hypophosphorous acid. The free iodine is then extracted into chloroform to form a bluish-red color. The chloroform solution is then analyzed spectrophotometrically at 520 mμ (34). Rider and Mellon precipitated thorium with an excess of standard oxalate. They determined the excess oxalate in the filtrate spectrophotometrically by measuring the decrease in color of a standard permanganate solution (108).

The blue color formed when thorium is reacted with carminic acid at a pH of 3.0 has been utilized in a spectro-photometric method (42). However, the method appears to have many common interferences. Byerly, et al., described a procedure wherein the highly insoluble thorium derivative of p-dimethylaminoazobenzenearsonic acid is dissolved in 4% sodium hydroxide and measured spectrophotometrically at 460 mμ (17). As mentioned earlier, Kuznetsov's qualitative method (70) has been extended to a quantitative scheme (119). Recently a method for estimation of thorium with alizarin has been described (98).

2. Determination of thorium in monazite sands

Because of its limited supply, particular emphasis has been placed on the determination of thorium in its ores.

In this section, the analytical chemistry pertinent to the analysis of thorium in its principal ore, monazite sand, is surveyed.

A number of excellent reviews (10,37,46,53,85,93,109, 110,111,113) of the analytical chemistry of thorium have been published. The paper by Bonardi (10) is a very good summary of the better methods of monazite sand analysis up to 1923, and the pamphlet by Rodden (110) contains good outlines of three methods that have proved successful in his work. Rodden and Warf (111) have made an extensive survey of recent work done on the analysis of thorium. A comprehensive survey of this field up to 1948 was the subject of the review paper of Moeller, Schweitzer, and Starr (93).

The analytical chemistry of thorium has been adequately reviewed in these last two reports. Therefore, only the more prominent classical methods will be mentioned here together with recent work and papers of particular significance to the method proposed in this report.

Two points in the procedure for the assay of thoria in monazite sands present the most difficult. As in the analysis of most ores, decomposition and solution of the sample constitute the first problem.

One of the most widely employed methods for decomposing monazite sands has been to fume the sample with concentrated

sulfuric acid and then to dissolve the resulting sulfates
in cold water (37). This method is more time consuming
than most of the procedures subsequently described and
has the additional disadvantage of leaving an acid insoluble
residue. Some authors (28,41) prefer fusion with sodium
peroxide followed by a nitric acid leach. Williams (132)
has used a potassium hydroxide fusion in a nickel crucible
with considerable success, but this method, like the
previous one, introduces fairly large quantities of alkali
salts into the solution to be analyzed. Willard and
Gordon (130) used fuming perchloric acid, but this also
leaves an insoluble residue.

Some investigators have used fusion with various
mixtures such as sodium fluoride and potassium pyrosulfate
(46) to effect decomposition. The thorium and rare earths
are converted to insoluble fluorides which, in turn, are
ordinarily decomposed by fuming with sulfuric acid. In
recent years Rodden (110) has fused the sands with potassium
hydrogen fluoride with considerable success. One author
recently combined the use of hydrofluoric acid with a
sodium peroxide fusion of the residue for this purpose (48).

The second problem in this analysis, the separation
of thorium from the rare earths, has received considerable
attention. In its natural state, thorium is nearly always
associated with the rare earths. The chemical similarity

between thorium and the rare earths presents somewhat of a challenge to the analytical chemist who wishes to separate them. Despite the difficulties, many reasonably good methods have been developed for this purpose. For the most part these separations have been gravimetric; accordingly, these procedures will be considered first.

For many years the procedure for precipitation of thorium as the iodate from 30% nitric acid solutions has been pre-eminently popular (86). Separation in such a highly acid medium affords greater selectivity and an easily filterable precipitate. A recent paper suggests the use of iodic acid instead of potassium iodate as the precipitating reagent (123). The pyrophosphate (20) and hypophosphate (45) separations are also carried out in a highly acid environment and have been widely employed.

Since 1902, the precipitation of thorium with hydrogen peroxide in a neutral nitrate solution has been fairly popular (9). Rodden and Warf (111) describe several modifications of this procedure. Hexamethylenetetramine (hexamine) will precipitate thorium and leave the rare earths in solution (49). Rodden presents a good outline of this procedure. In neutral solution, sodium thiosulfate will selectively precipitate thorium (44).

James and his co-workers are responsible for two more methods which are of considerable interest historically.

The sebacic acid procedure is an early example of the use
of weak organic acids to effect this separation (115).
The selectivity of the arsonic acids for tetravalent ions
was used in the benzenearsonic acid precipitation (107).

In recent years many more papers have been published
on the use of organic acids for precipitating thorium in
the presence of rare earths. Raghava Rao and his co-workers
at Andhra University of India have carried on an extensive
investigation along this line. The following reagents have
been studied: anisic acid (62), o-chlorobenzoic acid (74,95),
o-toluic and acetylsalicylic acids (75), o- and p-aminobenzoic
acids (96), adipic and succinic acids (118), cinnamic acid
(63,126,127), benzoic acid (121), naphthoic acid (122),
trimethylgallic, phenoxyacetic, and tannic acids (125),
ammonium picrate and 2,4-dinitrophenol (76), camphoric
acid (97), m-cresoxyacetic acid (124), ammonium furoate
and sodium sulfanilate (77), and vanillic acid (61). Nearly
all of these have been tested and proved useful in monazite
sand analyses.

Osborn (100) and Williams (132) have adapted uses for
the m-nitrobenzoic acid separation of Neish (99) to monazite
sand analyses. Willard and Gordon (130) used the basic
formate precipitation for this purpose. Later they suggested
tetrachlorophthalic acid (40) as a precipitating agent.

Ammonium benzoate has been used to effect this separation (50). Dickson and Kaufman (28) precipitated thorium hydroxide at a controlled pH. The rare earths do not precipitate below a pH of 6 while thorium precipitates from sulfate solution at a pH of 3.91 (11).

Some of the gravimetric methods have been modified and adapted to volumetric determinations. In general these methods have not been as accurate as their gravimetric counterparts. The iodate precipitates can be dissolved in an acid potassium iodide solution and the liberated iodine titrated with thiosulfate (91,116). According to Banks and Diehl (2), the precipitate of thorium molybdate can be dissolved in hydrochloric acid and the molybdate reduced in a Jones reductor and titrated with cerium(IV) sulfate.

Thorium may be separated from 50 per cent ethyl alcohol solution with selenious acid and then dissolved in hydrochloric acid (27). When potassium iodide is added to the solution, iodine is liberated and titrated with thio-sulfate. Trivalent cerium does not interfere, but the other rare earths are not mentioned. Amperometric methods for the direct titration of thorium chloride with ammonium molybdate have been described recently (39,114). They are accurate in the presence of a rare earth to thorium ratio of ten to one. None of the other volumetric methods were adjudged satisfactory in the presence of rare earths.

A limited amount of work has been done on the separation of thorium from the rare earths by solvent extraction. Recent work on the extraction of thorium into mesityl oxide from a saturated aluminum nitrate solution has shown very fine promise (48,79).

Another interesting approach has been the use of chromatographic and ion exchange procedures for this separation. Cellulose (55,57) and cellulose plus alumina (131) have been suggested as absorbents. Amberlite IR 100 has been used in the ion exchange work (106). In another physical method, the thorium is precipitated with an excess of radioactive pyrophosphate, and the excess is determined from the radioactivity of the filtrate (92). Komárek (58) has developed a procedure wherein the thorium is precipitated as the iodate, transformed to the hydroxide with sodium hydroxide, and the resulting sodium iodate determined polarographically.

Many methods for effecting a separation of thorium from rare earths have been omitted, but most of the more important classical procedures as well as all of the additions to the literature since the publication of Moeller, et al. (93) have been discussed.

Aside from the problems of dissolving the sample and separating thorium from the rare earths, the analysis of monazite sands for thorium seems relatively free of difficulties.

Thorium is easily separated from the alkali and alkaline earth metals by precipitation with ammonia, and from all other metals excepting the rare earths by oxalic acid precipitation.

B. Materials and Apparatus

1. Materials

The thorium and thorin are from the same sources as those used in the work described previously. The thorin solutions were prepared by weighing air-dried samples of the trisodium salt, dissolving them, and diluting the solution to volume. In most cases, one gram of the dye was dissolved in one liter of water to make a 0.1% thorin solution.

Technical grade mesityl oxide from Distillation Products Industries, catalog number T-582, was purified by distillation, and the fraction boiling at 129° to 130°C was reserved for this work. Later work showed that the purified grade, catalog number 582, marketed by this company was suitable.

All other chemicals were reagent grade except for the potassium hydrogen fluoride, which was the technical grade produced by the City Chemical Company, New York, New York.

2. Equipment

All volumetric ware used was either the Standard "Pyrex" brand manufactured by the Corning Glass Works or the "Normax" brand produced by the Kimble Glass Division of Owens-Illinois Glass Company. All pH measurements were made with a Beckman Model G pH meter. Absorbance measurements were made on a Beckman Model DU spectrophotometer. An International Clinical Centrifuge with 50-ml Lusteroid tubes was used for centrifugal separations.

C. Experimental Procedures and Results

1. Spectrophotometric analysis

(a) Absorption spectra. Figure 9 shows the absorption spectrum of a 0.005% solution of the air-dried trisodium salt of thorin at pH 1.00 and that of a similar solution containing 4 micrograms of thoria per ml and the same amount of reagent at the same pH, measured against a water blank. In curve 3 the complex-containing solution was scanned against the reagent solution. These curves indicate that in the wavelength range shown, the reagent has a higher molar absorptivity than does the complex at many wavelengths. Maxima in the positive differences are exhibited at 545, 332, 282, and 248 mμ. The greatest of these is at
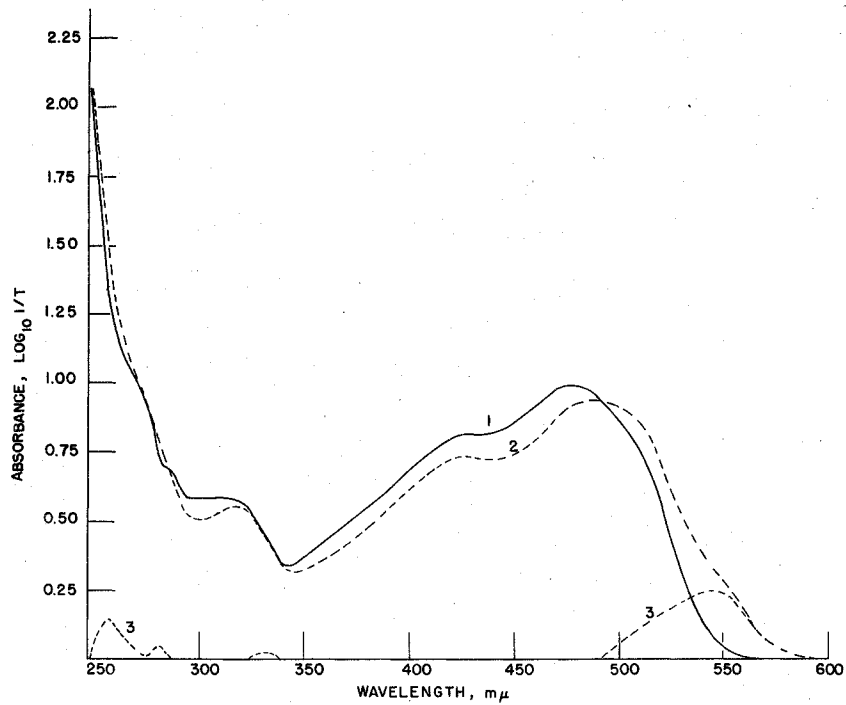
FIG.9-ABSORPTION SPECTRA OF THORIN
AND COMPLEX WITH THORIUM
CURVE I- .005% THORIN VS. WATER
CURVE 2- 4μg THO$_2$ PER ML IN .005%
THORIN VS. WATER
CURVE 3- SOLN. OF CURVE 2 VS .005%
THORIN

545 mμ. Consequently, this particular wavelength is
the most favorable to use for the spectrophotometric
analysis. The relatively low absorbance of the thorin at
this wavelength is also advantageous, for if the reagent
blank has a high absorbance, it becomes difficult to
balance the spectrophotometer at low slit widths.

(b) <u>Effect of pH</u>. The pH studies were carried out
in the following manner. A series of solution was prepared
in which the thorin concentration was 0.01% and the thoria
concentration was five micrograms per ml in a total volume
of 200 ml. The pH of these solutions was varied over a
range from 0.27 to 5.06, as shown in Table XV. The pH
was adjusted with perchloric acid and sodium hydroxide.
The pH study was confined to this range because it had been
shown earlier that at higher pH values, the reagent
absorbance exceeds that of the complex at this wavelength.
The absorbance of each solution was measured at 545 mμ
against a blank of the reagent at the same concentration
and at very nearly the same pH. Over this pH range, the
variation in the absorbance of the reagent in this wave-
length interval is relatively small; hence, a small difference
in pH between the sample and its blank should not contribute
a significant error. These data are shown in Table XV.

It can be seen from this table that the absorbance
remains reasonably constant between pH 0.27 and 1.50. The

Table XV

Optimum pH for Analysis

Solution Number	pH	$A_{545\ m\mu}$ [a]
1	0.27	0.313
2	0.59	0.315
3	0.67	0.317
4	0.73	0.313
5	0.88	0.314
6	1.08	0.314
7	1.26	0.314
8	1.50	0.314
9	1.98	0.302
10	3.04	0.276
11	4.06	0.253
12	4.92	0.191

[a]The absorbance of each solution was measured on the Beckman spectrophotometer against a reagent blank at approximately the same pH. The slit width was 0.17 mm, and the red-sensitive phototube was used. Cell length was 1.000-cm.

first definite change occurs with the decrease in absorbance at a pH of 1.98. From this point on, the absorbance decreases more sharply with increased pH. This effect is also illustrated in Figure 2.

To check the effect of higher acidities, another series of solutions was run in which known quantities of perchloric acid were added to a sample solution and its blank. The absorbance decreases with the increase in hydrogen ion activity. Apparently the constant interval shown in the table represents the optimum pH condition. A pH value of 1.00 was chosen for subsequent work.

These solutions were stable with time. No significant changes were recorded for either the pH or the absorbance over a three day period.

(c) <u>Optimum amount of reagent</u>. The optimum amount of reagent for use in the analysis was determined by preparing a series of solutions of identical thorium concentration, 2 mg thoria per 200 ml, and varying amounts of thorin. These solutions are listed in Table XVI. The absorbance of each solution was measured against a reference solution of identical reagent concentration. The results show that the choice of the amount of reagent to be used is fairly arbitrary since the effect of changing thorin concentration is small over this range. In the work to be described next, 20-ml aliquots of a 0.1% thorin solution were used. This is an

Table XVI

Optimum Amount of Reagent for Analytical Method[a]

Solution Number	ml 0.1% thorin	$A_{545 \ m\mu}$
1	10.00	0.635
2	12.50	0.642
3	15.00	0.639
4	17.50	0.634
5	20.00	0.629
6	22.50	0.624
7	25.00	0.619

[a]Each solution contained 2 mg ThO_2 in a total volume of 200 ml. Measurements were made with the Beckman spectrophotometer against a reference solution containing a similar amount of reagent in 1.000-cm cells. Slit width was 0.130 mm. The red-sensitive phototube was used.

amount greater than needed for maximum absorbance, but it was chosen because the reagent purity is not reproducible and because this higher concentration should serve to ensure essentially complete reaction at lower thorium concentrations.

The optimum amount of reagent found necessary here is smaller than that found by Thomason, et al. (119). This is probably due to the lower pH conditions used in their work.

(d) Effect of time. These solutions undergo no appreciable changes during a period of at least several weeks. The stability of the solutions containing an excess of reagent and of the reagent alone at a pH of 1.00 was demonstrated earlier in the thesis.

(e) Effect of diverse ions.

(1) Cations. The effect of diverse cations was investigated in the following manner. Solutions of the ions were prepared to contain one mg of the ion or its oxide per ml. Reagent-grade commercial chemicals were used in most instances. The rare earth solutions were prepared from the oxides of rare earths that had been purified by ion exchange and were known to be thorium free. In most cases, perchlorate solutions were employed to minimize errors arising from anion effects. In those cases in which it was necessary to use other salts, the concentrations of the

diverse anions were small enough that their effect could be neglected.

A series of solutions that contained one mg of thoria, five mg of the diverse ion or oxide, and 20 ml of 0.1% thorin in 200-ml total volume was prepared. The absorbances of these solutions were measured against a reagent reference solution on the Beckman spectrophotometer. These absorbances were compared with those of a solution containing no diverse ion. The results are shown in Table XVII.

Most common cations do not interfere. The major interferences are iron(III), bismuth(III), chromium(III), uranium(VI), zirconium, titanium(IV), and the rare earths. The iron interference can be minimized by reduction to the divalent state with hydroxylammonium chloride. The fluoride precipitation serves to separate thorium from zirconium, titanium(IV), and uranium(VI), as shown in the section on monazite sand analysis. A preliminary oxalate separation from acid solution would eliminate all interferences except the rare earths. The latter may be separated from thorium conveniently by the mesityl oxide extraction procedure. These results do not agree with the findings of Thomason, et al. (119), for they found a positive interference from titanium(IV). These workers reported that uranium(VI) ion does not interfere at pH 0.5, but they

Table XVII

Effect of Diverse Cations[a]

Diverse Ion	A_{545} mμ	Error, μg ThO$_2$/5 mg div. ion[b]		Remarks
None	0.315			
None	0.318			
Sodium	0.321			
Potassium	0.319			
Ammonium	0.320			
Copper(II)	0.321			
Beryllium	0.318			
Magnesium	0.318			
Calcium	0.319			
Strontium	0.318			
Barium	0.319			
Zinc	0.319			
Cadmium	0.319			
Aluminum	0.319			
*Lanthanum	0.323	+	19	
*Cerium(III)	0.336	+	60	
Praseodymium	0.330	+	41	
Neodymium	0.330	+	41	
Samarium	0.326	+	28	
Tin(II/IV)	0.316			Mixed valence states present
Zirconium	-			Precipitated with thorin
Titanium(IV)	0.296	-	66	
Lead(II)	0.321			
Vanadium(IV)	0.318			Present as vanadyl ion
Arsenic(III)	0.317			

[a]Five mg of each listed ion, 1 mg of thoria, and 20 ml of 0.1% thorin were present in a total volume of 200 ml. Absorbance measurements were made on a Beckman spectrophotometer against a reagent reference solution. The slit width was 0.045 mm and the blue-sensitive phototube was used. pH was adjusted to 1.00 with HClO$_4$.

[b]If no number is recorded, the error is considered insignificant.

*Weights taken as the oxide.

Table XVII (Continued)

Diverse Ion	$A_{545\ m\mu}$	Error, $\mu g\ ThO_2/5\ mg$ div. ion[b]	Remarks
Antimony(III)	0.316		
Bismuth(III)	1.176	+2,710	
Chromium(III)	0.364	+ 148	Absorbance appeared to increase with time.
Manganese(II)	0.318		
Iron(III)	0.502	+ 583	
Iron(II)	0.323	+ 19	Reduced with $NH_2OH \cdot HCl$
Cobalt(II)	0.319		
Nickel(II)	0.320		
Uranium(VI)	0.331	+ 44	Present as uranyl ion

did find that as the pH was raised to 1.00, the uranium interference became very important. Hence, when working with uranium(VI) solutions, it would be advisable to select a pH of 0.5 for the analysis. Uranium(IV) was found to be a very serious interference by these workers. Its chief effect was a reduction of the thorin. Oxidation to the hexavalent state by fuming with perchloric acid minimized this difficulty.

The interferences from rare earth ions were also found to be quite pH dependent. The absorbance of solutions containing 0.1 mg cerium(III) per ml and 0.004% in thorin increased tenfold as the pH was raised from 0.5 to 2.1. A similar effect was noted with lanthanum. For these ions, the change in absorbance with pH is fairly small at first but begins to increase very sharply between pH 1 and 2.

The pH effects with uranium(VI) and rare earth ions are interesting because they point out one of the major advantages of this method for thorium analysis. The stability of the thorium complex with thorin at a low pH confers a much greater selectivity on the procedure than would normally be expected. The difference in optimum pH conditions for the thorium and the rare earth reactions with thorin is probably due to the differences in the basicities of these ions.

It should be noted that the zirconium interference was checked with a one mg quantity since the 5 mg sample precipitated. As expected, a large positive interference was observed. It may be that zirconium has a greater affinity for the reagent than does thorium.

The fact that a cation is not shown as an interference in Table XVII does not imply that the ion in question will not interfere at higher concentrations. According to these data, there is no reason to suspect that beryllium might interfere in the method. Yet at a concentration 400 times greater than that tested, beryllium was definitely an offender. The object of this study was to provide an indication to the effect of diverse ions of the same order of concentration as the thorium. Therefore, the usefulness of these data are limited to such conditions.

(2) Anions. Only the very common anions were investigated. Thorium has a great tendency to form complex ions with a large number of organic complexing agents. Hence, most of these would be expected to interfere by producing a negative interference. In carrying out these tests, one ml quantities of the concentrated acid of the anion to be tested were used in each solution. In the case of phosphate and sulfate ions, 0.1-ml portions were also employed since the larger quantities interfered greatly.

The same procedure as that outlined in the preceding cation work was followed. The results are shown in Table XVIII.

From these data it can be seen that only very small quantities of phosphate and sulfate can be tolerated. On standing, the absorbance of the nitrate solution decreased due to oxidation of the reagent. The usefulness of the data is restricted again to conditions under which amounts of the anion in question do not exceed these concentrations.

(f) Conformance to Beer's law. The results of the test for the conformance to Beer's law are shown in Table XIX. From an inspection of the data, it can be seen that by using a 0.01% reagent solution, the system conforms to Beer's law over a thoria concentration range of 0.4 to 2.0 mg per 200 ml. There is a slight deviation at the highest concentration, but it is well within the range of the expected experimental error.

In earlier work on this problem it was desirable to develop a procedure for the determination of very small amounts of thorium. The method used was applicable to a thorium concentration range of 20 to 100 micrograms of thorium per 50 ml total volume. By using 5.000-cm cells and a 0.004% thorin solution, it was possible to develop a sensitive method which followed Beer's law over this concentration range as shown in Table XX. These results indicate that the method is applicable to the determination

Table XVIII

Effect of Diverse Anions[a]

Diverse Ion	Ml Conc. Acid	$A_{545\ m\mu}$	Error, μg ThO_2[b]
None	-	0.315	
None	-	0.318	
Acetate	1.0	0.316	
Chloride	1.0	0.316	
Nitrate	1.0	0.315	
Phosphate	0.1	0.226	-287
Phosphate	1.0	0.025	-921
Sulfate	0.1	0.286	- 98
Sulfate	1.0	0.035	-890

[a]Each solution contained 1 mg thoria and 20 ml 0.1% thorin in a total volume of 200 ml. Absorbance measurements were made with the Beckman spectrophotometer against a reagent reference solution. A slit width of 0.045 mm and the blue-sensitive phototube were used. pH was adjusted to 1.00 with $HClO_4$.

[b]If no number is recorded, the error is considered insignificant.

Table XIX

Thorium Recovery in the Extraction and Conformance to Beer's Law[a]

ThO_2 mg/200 ml	Absorbance, $A_{545 m\mu}$ (extracted)	Absorbance, $A_{545 m\mu}$ (unextracted)
0.4	0.128	0.127
0.8	0.255	0.254
1.2	0.382	0.379
1.6	0.507	0.505
2.0	0.632	0.630

[a]The pH of each solution was 1.00 ± 0.04 and 20 ml of 0.1% thorin were added to each solution. Total solution volume was 200 ml. Absorbance measurements were made with the Beckman spectrophotometer against a reagent reference solution in 1.00-cm cells at a slit width of 0.17 mm.

Table XX

Conformance to Beer's Law at Dilute
Thorium Concentrations[a]

Th g/50 ml	Absorbance, $A_{545 \, m\mu}$
20	0.144
40	0.286
60	0.432
80	0.572
100	0.712

[a]Each solution contained 10 ml of 0.02% thorin in 50 ml
total volume. Absorbance measurements were made with
the Beckman spectrophotometer against a reagent reference
solution in 5.000-cm cells. The slit width was 0.17 mm.
pH was adjusted to 1.00 with $HClO_4$.

of widely varying quantities of thorium by suitable
modifications in amount of reagent, total volume, and
cell length.

2. Analysis of thorium in monazite sands

(a) Outline of procedure. The primary aim of this
particular project has been to develop a method for the
determination of thorium in monazite sands which is both
rapid and accurate. Levine and Grimaldi (79), Kronstadt
and Eberle (64), and Rodden (110, p. 193) have developed
methods which appear to approach this goal. The procedure
proposed in this report further simplifies the determina-
tion without any significant loss of accuracy. The mesityl
oxide extraction of Grimaldi and Levine (79) has been
modified and combined with the spectrophotometric method
of Thomason, et al. (119) in the procedure proposed. The
method is outlined as follows:

1. The sand is decomposed by a potassium hydrogen
   fluoride fusion, the insoluble fluorides contain-
   ing all of the rare earths and thorium are digested
   in dilute hydrofluoric acid and finally separated
   by centrifugal action.

2. These fluorides are dissolved in a saturated
   aluminum nitrate solution acidified with nitric acid.

3. The thorium is separated from this solution by extraction into mesityl oxide. The thorium is then stripped from the solvent with water.

4. Appropriate aliquots of this aqueous solution are reacted with thorin to produce the colored complex ion which is the basis for the spectrophotometric determination.

(b) _Completeness of extraction and conformance to Beer's law_. In order to determine if the extraction was complete and whether aliquots of the thorium solution stripped from the solvent after the extraction could be analyzed directly without further treatment, the following experiment was carried out. An amount of the standard stock solution of thorium equivalent to 40 mg thoria was measured out, and to this were added 1.5 ml of concentrated nitric acid and 19 grams of aluminum nitrate 9-hydrate. This solution was then extracted according to the method discussed in the preceding section. The aqueous thorium extract was diluted to 1-1 to give a solution which should contain 40 micrograms of thoria per ml if all the thorium was recovered in the extraction. A second thorium solution having the same concentration as that one just described was prepared by dilution of the standard stock solution. Aliquots of these two solutions were taken to prepare two

identical sets of solutions which had varying amounts of thorium as shown in Table XIX.

The absorbances of these solutions were measured on the Beckman spectrophotometer at a wavelength of 545 mμ using 1-cm cells and a slit width of 0.17 mm with the red-sensitive phototube. The reference solution contained the same amount of reagent at the same pH as the sample solutions. The agreement between the absorbances of the extracted solutions and the standard solutions indicates that the thorium recovery from the extraction is complete. Secondly, it shows that the reaction is not affected by the presence of foreign material introduced during the extraction. This latter conclusion definitely contradicts the findings of Ingles (48) who stated that the thorium must be separated from the aluminum nitrate which contaminates the extract before reaction with the reagent.

An inspection of these data would indicate a very slight departure from Beer's law at higher concentrations. However, this departure is well within the range of the expected experimental errors and the assumption of a first order dependency between absorbance and thorium concentration seems justified in this concentration range.

(c) Optimum conditions for spectrophotometric analysis.

(1) Effect of pH. One of the extracted thorium solutions from the analysis of one of the monazite sands was

used for the study of the effect of pH on the absorbance of the complex. The concentrations of the thorium and the thorin remain constant in this series with pH being the only variable. Spectrophotometric measurements were made as previously described. Each reagent reference solution was at the same pH as the sample solution.

This investigation was limited to a particular pH range because earlier work described previously as well as that of Thomason, et al (119), had shown this to be the optimum range for the reaction. These data prove that the pH dependency of the reaction remains unaltered by any contaminants introduced by the extraction. Also, it can be seen that the effects of pH changes are very small over this range. For the subsequent work, a pH of 1.00 was used. However, any pH value in this range would appear to be suitable, see Table XXI.

(2) Stability. It has already been shown that in the absence of diverse ions, the colored solutions remain stable for at least several weeks. However, some nitric acid will be present as a contaminant in the extracted solutions and might slowly oxidize the reagent, which would cause a gradual decrease in absorbance with time. Studies show that the absorbance remains unaltered over the first few hours and very slowly falls off afterward. It seems advisable to make the spectrophotometric measurements within

Table XXI

Optimum pH for Spectrophotometric Analysis of the Thorium Extract[a]

pH	$A_{545\ m\mu}$	pH	$A_{545\ m\mu}$	pH	$A_{545\ m\mu}$
0.38	0.388	0.58	0.388	0.78	0.387
0.48	0.388	0.71	0.388	0.92	0.388
0.49	0.391	0.71	0.387	1.02	0.386
0.57	0.389	0.71	0.386	1.18	0.383
				1.38	0.384

[a]Measurements were made on the Beckman spectrophotometer against a reagent reference at the same pH. 1.00-cm cells were used, and the slit width was 0.17 mm.

a two hour interval after solution preparation to minimize
this source of error. It should be noted that the use of
hydrochloric acid to adjust pH would probably lead to a
rapid deterioration of the color due to the strong oxidizing
power of the mixture of hydrochloric and nitric acids.
The stability here refers to the constancy of the absorbance
of the sample solutions using a corresponding reagent solu-
tion as the reference.

(3) <u>Optimum amount of reagent</u>. The optimum amount
of reagent to be used in the reaction over the thorium con-
centration range indicated in Table XVI was established in
the following manner. Once again, one of the thorium solu-
tions extracted from a monazite sand was used as the source
of thorium. Table XXII contains the data. The thorium
concentration represented by these aliquots was 2.035 mg
thoria per 200 ml.

These data would indicate that the 15 ml aliquot is
the optimum level. However, a 20 ml aliquot was chosen
since the reagent purity is not always reproducible and
certainly no significant loss in sensitivity is thus
incurred.

(d) <u>Interferences</u>. A detailed study of interferences
has been discussed in a preceding portion of the thesis.
The complete recovery of thorium as evidenced in Table XIX
indicates that the aluminum and nitrate contaminants in

Table XXII

Optimum Amount of Reagent for the Analysis
of the Thorium Extract[a]

Solution Number	ml 0.1% Thorin	$A_{545\ m\mu}$	pH
1	10	0.633	0.98
2	15	0.656	1.02
3	20	0.647	0.98
4	25	0.639	0.98
5	30	0.631	0.98

[a]Each reference solution for the spectrophotometric measurements contained the same concentration of reagent as the solution with which it was compared. The pH of the reagent reference was the same as that of the complex solution. Measurements were made on the Beckman spectrophotometer at a slit width of 0.17 mm in 1.00-cm cells.

the extracted solution do not exhibit any deleterious
effects. Levine and Grimaldi (79) presented a rather
complete study of those ions which accompany thorium in
the extraction process. Several cations that are normally
present in monazite sand, especially zirconium and uranium,
do so, but they are previously eliminated by the fluoride
separation.

An amount of cerous chloride equivalent to 400 mg of
ceria was extracted, and the extract was analyzed by the
usual spectrophotometric method with no interference indicated.
The same results were obtained from 800 mg of lanthanum
oxide, indicating the high efficiency of the separation
of thorium from these rare earths. The possibility of
interferences from other rare earths seems very remote.

(e) Recommended procedure.

(1) Preparation and decomposition of the sample.
The samples should be ground to 200 mesh in order to ensure
homogeneity of small samples and to increase the efficiency
of the fusion. Accurately weigh approximately 0.2 gram
samples into 50 ml platinum crucibles and add 3 grams of
technical grade potassium hydrogen fluoride. (Note:
potassium hydrogen fluoride is very hygroscopic, and the
user is cautioned to keep the container tightly sealed at
all times when not in use). Cover the crucible and place
it over a low flame to drive off any moisture. Gradually

increase the temperature until the full heat of the Meker
burner is applied. If the full heat is applied directly,
excessive spattering occurs. Keep the crucible at a red
heat for 3 to 5 minutes and no longer. Excessive heating
may result in partial conversion of some of the thorium
to a highly refractory oxide. Transfer the cooled melt
to 300 ml platinum dishes with the aid of approximately
100 ml of hot water. (Note: smaller platinum dishes may
be used if these larger ones are not available, since the
300-ml size is recommended for convenience only). Add 20
ml of 48% hydrofluoric acid and digest under infrared
heating lamps (or on a steam bath) for 30 minutes. Pulverize
the melt and allow it to cool.

(2) Separation and solution of the fluorides.
Transfer the fluorides to 50-ml "Lusteroid" centrifuge tubes
and separate at the full speed of the centrifuge for 5 to
10 minutes. Carefully pour off the supernatant liquid.
After the last of the soluble fluorides have been discarded,
wash the insoluble ones with dilute hydrofluoric acid. This
may be done by nearly filling the tube with water and add-
ing a few ml of 48% hydrofluoric acid. Transfer these
fluorides with a minimum amount of water to a 150-ml beaker
containing 19 grams of aluminum nitrate 9-hydrate and 2.5
ml of nitric acid. Place on a hot plate. As the mixture
is warmed, the fluorides will dissolve through the formation

of the stable fluoaluminate ion. Reduce the volume to 20 ml by evaporation and allow the solution to cool.

(3) <u>Extraction with mesityl oxide.</u> CAUTION: Carry out the extraction in a hood since excessive inhalation of mesityl oxide may cause serious respiratory difficulties.

Prepare a scrub solution by dissolving 380 grams of aluminum nitrate 9-hydrate in 170 ml of water and 30 ml of nitric acid. Heat if necessary. Cool to room temperature before using.

Pour the sample solution from the beaker into a 125-ml separatory funnel. Measure 20 ml of mesityl oxide (B.P. 128-130°C) into the beaker, swirl, and add to the separatory funnel. Shake for 20 seconds. Drain off the aqueous phase into a second separatory funnel. (Frequently a white suspension or emulsion forms at the interface during the extraction. Usually this will not be excessive, but if it is, the effect can usually be minimized by adding an additional 1 ml of nitric acid. Since nitric acid will oxidize the reagent, further addition of the acid is not recommended. The exact nature of this effect is not known; however, it does not appear to affect the results in any way.) Add 10 ml of solvent to the second separatory funnel. Shake the system for 20 seconds and discard the aqueous phase.

Combine the solvent with the original portion and add 20 ml of the scrub solution. Again shake for 20 seconds and discard the aqueous phase. Repeat this operation twice more. Strip the thorium from the solvent by agitation for 20 seconds with 20 ml of water. Drain the water layer into a 200-ml volumetric flask and repeat the procedure once more. Dilute the contents of the flask to volume.

It should be noted that the solvent turns brown during the extraction apparently due to some oxidation by nitric acid. Occasionally, this effect will cause a yellow tinge in the strip solution. However, this will not affect the subsequent spectrophotometric work since the color is slight. This oxidation can be minimized by working with maximum expediency and by avoiding the use of warm solutions.

(4) <u>Spectrophotometric determination of thorium.</u> Usually the analyst will have only the roughest estimation of the thoria assay to be expected in the sample. In this case, a fairly reliable first approximation is 5 per cent thoria. For the spectrophotometric work, it is best to take a portion representing 1 to 2 mg of thoria. For a 0.2 gram sample containing 5 per cent thoria dissolved in 200 ml, a 25-ml aliquot is suggested as a first approximation. Pipet the aliquot into a 250-ml beaker. Dilute to 140 ml and add 20 ml of a 0.1% thorin solution. Adjust the pH with a pH meter to 0.8 $\pm$ 0.1 using perchloric acid, and

transfer to a 200-ml volumetric flask. This procedure has been found to give a final pH of 0.9 $\pm$ 0.1. The solutions are ready for measurement immediately after dilution and mixing.

A solution containing the same concentration of reagent at the same pH is used as a reference in the spectrophotometric measurement. Using the Beckman Model DU spectrophotometer with the wavelength set at 545 mμ and 1.000-cm cuvettes, measure the absorbance of the solutions within two hours after they are prepared.

(5) <u>Calculations</u>. As has been noted previously, the system conforms to Beer's law at least up to a concentration of two mg thoria per 200 ml. Because of some variation in the purity of the thorin, the analyst should determine the factor for converting absorbance to thorium concentration for his particular reagent. To do this, prepare a series of solutions similar to those described in Table XIX and plot the absorbance against the thoria concentration. From the slope of the best straight line through these points, one can relate absorbance to the thoria content. If absorbance is plotted as the ordinate and mg thoria per 200 ml as the abscissa, the mg thoria per 200 ml corresponding to a given absorbance value may be obtained by multiplying that value by the inverse of the slope.

The following formula will then give the percentage of thoria in the sample:

$$\%ThO_2 = \frac{(mg\ ThO_2/200\ ml)\ (200\ ml/aliquot,\ ml)\ (100)}{wt.\ sample,\ mg}$$

(f) <u>Results</u>. A fairly wide variety of monazite sands have been analyzed by this method. These sands were provided by the following laboratories: The New Brunswick Laboratory of the Atomic Energy Commission, New Brunswick, New Jersey; United States Bureau of Mines, Raleigh, North Carolina; and Lindsay Light and Chemical Company, West Chicago, Illinois. The results are tabulated in Table XXIII. The column labeled "$\%ThO_2$ reported" contains the results obtained by the laboratories furnishing the samples with the exception of the sand numbered NBS 2601 which was a National Bureau of Standards sample issued by the New Brunswick Laboratory.

With the exception of NBL 8412, these results would seem to be quite satisfactory. The reason for the disagreement in that sample could not be ascertained.

(g) <u>Discussion</u>. The chief advantages of this method are its simplicity and rapidity. This analysis contains a minimum number of separations, and thus reduces the errors due to this factor as well as the time involved. With proper planning and some experience, the entire analysis

Table XXIII

Results of the Analyses for Thorium
in Several Monazite Sands[a]

Sample Number	% ThO_2 found	Number of analyses[b]	%ThO_2 reported	Difference
NBL 8412	6.39±0.02	5	6.05	+0.34
NBS 2601	9.53±0.03	3	9.65	-0.12
Florida	4.86±0.02	2	4.9	
Idaho	3.89±0.02	4	3.8	
AN 516032	3.52±0.05	4	3.60	+0.08
AN 4236	9.20±0.02	3	9.19	+0.01
SMI 187	6.37±0.01	4	6.54	-0.17

[a]The first two sands were obtained from New Brunswick, the next two from Lindsay Light and Chemical, and the last three from the Bureau of Mines.

[b]The number of analyses run by the proposed method.

can be accomplished in about four hours. The procedure is readily adaptable to the simultaneous analyses of several samples.

D. Summary

1. A literature survey of some colorimetric and spectrophotometric methods for the detection and determination of thorium has been presented, and the analytical chemistry of thorium of particular importance in the analysis of thorium in monazite sand has been reviewed.

2. Optimum conditions for the spectrophotometric determination of thorium with thorin have been established. In a 200-ml volume of 0.01% thorin at a pH of 1.00, Beer's law is followed from 0.4 to 2 mg thoria. A modification using 0.004% thorin for thorium concentrations from 20 to 100 micrograms per 50 ml has been described. Interferences have been studied and their elimination discussed.

3. A rapid method for the determination of thoria in monazite sand has been described. The sand is fused with potassium hydrogen fluoride, the insoluble fluorides are separated and dissolved in a saturated aluminum nitrate solution which has been acidified with nitric acid, the thorium is extracted from this solution into mesityl oxide, stripped with water, and determined spectrophotometrically with thorin.

IV. SUGGESTIONS FOR FUTURE WORK

1. It appears to this writer that there is a definite need for further studies on the hydrolytic behavior of thorium. However, it must be admitted that such an investigation may be greatly complicated by various side reactions such as polymerization. To understand the pH dependency of reactions of thorium in aqueous solution it is essential to know more about the part the solvent plays in the equilibria involved.

2. A more exact idea of the nature of the reaction between thorium and the arsono group is of great importance to this study. One method of approach would be to investigate the thorium complexes formed with less complicated arsonic acids. If pure samples of sulfonated aliphatic or aromatic arsonic acids could be obtained, they might be excellent to use for this purpose.

3. A clearer understanding of the role of the 2-hydroxy group on the naphthalene system in the complex is of considerable interest. The ability of the 4-hydroxy isomer of thorin to form a colored product would aid in this study. However, such a compound might not be easily prepared. The preparation of the O-methyl ether of the thorin has been considered for an investigation of the function of the naphtholic group in these complexes. However, failure to

obtain a reaction between the methylated thorin and thorium might be due to steric effects rather than the loss of replaceable hydrogen.

4. An X-ray study of the thorium-thorin precipitate would be of great interest. Such a study would require the production of well-defined crystals, which appears to be a difficult problem.

5. A more complete knowledge of the number and nature of predominating complexes in the metastable equilibrium state is needed. It would appear, on the basis of the experiments reported in this thesis, that the best way to approach this problem would be to further extend the molar ratio method to more accurately determine equilibrium constants. To do this, several uncertainties in the data presented in this work should be reduced. In the first place, it would seem to be more advantageous to conduct the investigation at a somewhat higher pH. From Figure 2 it may be seen that the maximum absorbance in the complex solutions occurs at a pH between 2.2 and 2.5, which might suggest that hydrolytic effects were not yet occurring at these pH values. On the other hand, it was found that the solid 1:1 complex which had been dissolved in base did not reprecipitate on reducing the pH to 2.25 in approximately 10^{-2} M solution. It might be that at a pH of 2 to 2.5, one could obtain a very stable equilibrium state. In the second

place it would be advisable to carefully follow the time dependent changes in any such studies to ensure attainment of equilibrium.

A series of solutions similar to those described in Tables XI and XII could be prepared at this higher pH. This pH should be very carefully regulated since the acid dependency of these reactions is not known, and the calculated constant intrinsically contains the activity of the hydrogen ion to an appropriate power. Absorbance readings should be made against a reference solution containing the same thorin concentration as the sample with which it is compared. This would avoid the relatively large reading errors associated with the steep slopes of the absorption curves of the reagent and complex compared with distilled water (see Figure 9). It can be seen that over those regions in which a maximum difference between the molar absorptivities of the complex and reagent occurs, the curve of the complex solution scanned against the reagent is relatively flat, thus minimizing reading errors.

Once equilibrium has been reached, plots similar to those in Figure 8 can be made at suitable wavelengths. Equilibrium constants might be fitted to these curves by the usual methods of approximations according to the general approach discussed in Part One of the thesis.

One other important feature in this work would be the reduction of error due to the uncertainty in the thorin

concentration. This could be minimized by using larger aliquots of a more concentrated reagent solution for the potentiometric titration with standard base. More base would thus be required, and the relative error due to uncertainty in the midpoint of the second break in the titration curve would be reduced.

6. The possibility of developing a good spectrophotometric method for bismuth with thorin is indicated by the interference studies. Some preliminary work has indicated that the pH conditions will have to be altered to obtain a sensitive procedure.

7. Mesityl oxide has a disagreeable odor and may cause considerable respiratory difficulty if not used in a hood. It would be advantageous to find another extraction solvent which does not possess these disadvantages.

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VI. ACKNOWLEDGMENTS