STUDIES ON
THORIUM 3-METHYL-8-HYDROXYQUINOLATE

By

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University
October 1965

MASTER OF SCIENCE (1965)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Studies on Thorium 3-Methyl-8-hydroxyquinolate

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NUMBER OF PAGES: vii, 76

SCOPE AND CONTENTS:

Thorium is shown to react with 3-methyl-8-hydroxyquinoline in the molar ratio 1:5, but isolation of the pure anhydrous compound requires special precautions. Thermogravimetry and differential thermal analysis of the compound indicate, amongst other things, the existence of a thorium 3-methyl-8-hydroxyquinolate of 1:4 stoichiometry.

The pH dependence of the precipitation of thorium 3-methyl-8-hydroxyquinolate is determined, and correlated theoretically, with data for thorium 2-methyl-8-hydroxyquinolate.

Thermal and other studies on thorium 8-hydroxyquinolate emphasize its anticipated similarity to the 3-methyl-8-hydroxyquinolate, and its differences from the 2-methyl compound. The precipitation of at least two compounds of thorium and 8-hydroxyquinoline is demonstrated.

3-Methyl-8-hydroxyquinoline is established as a sensitive reagent for determining thorium by both bromometric and polarographic methods with good precision and accuracy.

ACKNOWLEDGMENTS

The author wishes to express his appreciation for the help and advice of Dr. R. P. Graham during the course of this research.

The author is indebted also to Mr. R. F. Lane and Mr. R. S. Lane, who assisted with experiments during the summer months.

Financial assistance from the Government of Ontario in the form of Ontario Graduate Fellowships is gratefully acknowledged.

TABLE OF CONTENTS

DISCUSSION

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

No organic reagent for the determination of inorganic ions has received more attention that 8-hydroxyquinoline (8-quinolinol, oxine). A review of the chemistry of this compound and its derivatives (1), published about ten years ago, comprises four substantial volumes and researches on this compound continue to be reported regularly in the literature. There are two main reasons for this interest: 8-hydroxyquinoline forms stable chelate compounds with a great number of metal ions, and this reagent may be used in a great variety of analytical methods.

In its reaction with metal ions, M^{n+}, 8-hydroxyquinoline, HOx, usually forms compounds of the type MOx_n, where Ox^- represents the 8-hydroxyquinolate anion. However, scandium(III) (2), plutonium(VI) (3), uranium(VI) (4), uranium(IV) (5), and thorium(IV) (6), have been reported to form compounds of the type $MOx_n \cdot HOx$, containing one molecule of reagent more than required from valence considerations. Since these metals have high valence states, the possibility of very large coördination numbers in their chelate compounds makes the composition and structure of this type of compound very interesting.

Of these compounds, perhaps thorium 8-hydroxyquinolate has received the most attention. This complex has been investigated in several different ways, including work concerned mainly with precipitation and composition (4, 6-13) with its thermal properties (6, 7, 9, 14-19) or with its behaviour in other studies, such as ultraviolet, visible and infrared spectroscopy (10,20), X-ray analysis (21,22,23), thermodynamic studies (19,24), solvent extraction and radioisotope techniques (25,26), and non-aqueous titrations (21). Although this list is lengthy, the chemistry of thorium 8-hydroxyquinolate remains in a confused state: critical reading of the literature reveals many deficiencies and erroneous statements, some of which are likely due to accumulated misquotations and uncritical acceptance of the published work. Detailed examples have been noted elsewhere (11,27).

There are many differences in opinion on the behaviour and nature of thorium 8-hydroxyquinolate. Although most workers agree to a general pattern of thermal decomposition, there is little agreement on the conditions of time and temperature for these thermal reactions (11). The interesting question of the structure of the thorium complex is unsettled. Two points of view have found support: in one, the so-called "extra" molecule of reagent is thought to be held by weak lattice forces, while the other four molecules form a chelate with the thorium atom in the normal manner (9,19); in the other, the "extra" molecule is regarded as an integral part of the complex, bonded to the thorium atom in some manner (10,11,20). So far, the structure has not been unambiguously determined.

Furthermore, there have been fluctuations in thinking concerning the composition of the thorium chelate. Thorium 8-hydroxyquinolate was first thought to have 1:4 stoichiometry and to exist in two forms; an orange hydrate and an anhydrous yellow form (4). The hydrate was thought to be contaminated slightly with excess reagent. Further work (6,7), however, led to the view that the stoichiometry of this compound was actually 1:5, but that the 1:4 thorium chelate could be prepared by heating the compound. The composition of thorium 8-hydroxyquinolate was then thought to have been established, and for many years studies and determinations were done on this assumption. Recently, however, a molar ratio, HOx/Th, of about 4.8 was found (12,13) and water was collected on heating the compound (13). Moreover, there have been conflicting claims (4,10,11,28-30) about whether or not, under certain conditions, a thorium 8-hydroxyquinolate of 1:4 stoichiometry can be precipitated. Obviously, the composition of thorium 8-hydroxyquinolate is not yet settled.

A derivative of 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline (8-hydroxyquinaldine, 2-methyl-8-quinolinol, 2-methyloxine) has attracted some attention as an analytical reagent (e.g., 31-35), and has particularly been used in solvent extraction systems (36-41). The physical and chemical properties of 2-methyl-8-hydroxyquinoline and many of its chelates have been investigated (21-24, 42-51). This interest probably arose from the fact that 2-methyl-8-hydroxyquinoline does not precipitate aluminium (31), while 8-hydroxyquinoline does; this fact has been attributed to steric hindrance caused by the methyl group in the 2-position, close to the coördinating nitrogen (31,42,52-54).

2-Methyl-8-hydroxyquinoline also differs from 8-hydroxyquinoline in its reaction with thorium. Instead of forming a 1:5 complex, 2-methyl-8-hydroxyquinoline forms with thorium only a 1:4 complex, ThQ_4, (32,33,55), where Q^- represents a substituted 8-hydroxyquinolate anion, in this case the 2-methyl derivative. The steric effect mentioned above is presumably the reason for the difference in the behaviour of the two reagents (11). A claim that a 1:5 thorium 2-methyl-8-hydroxyquinolate can be formed (45,21) has been refuted with strong evidence (33,55) and indeed, a retraction of the claim has been made (22,56). The thorium-2-methyl-8-hydroxyquinoline system has been fairly thoroughly studied, and the reagent has been recommended for the determination of thorium (33): thorium 2-methyl-8-hydroxyquinolate has better thermal stability than thorium 8-hydroxyquinolate (16,57,33), the 2-methyl compound can be quantitatively precipitated, and 2-methyl-8-hydroxyquinoline can be dibrominated quantitatively. Therefore, both gravimetric and bromometric methods are feasible. Moreover, the polarography of 2-methyl-8-hydroxyquinoline permits an indirect determination of thorium (11,58). A method for the homogeneous precipitation of the thorium chelate by the hydrolysis of 8-acetoxyquinaldine has been developed (55). Thermochemical, X-ray, and differential thermal analysis studies on thorium 2-methyl-8-hydroxyquinolate have also been reported (22,23,45).

In contrast to the vast literature on 8-hydroxyquinoline and the considerable number of references concerning 2-methyl-8-hydroxyquinoline, 3-methyl-8-hydroxyquinoline (3-methyl-8-quinolinol, 3-methyloxine) has received very little attention. In fact, all references to this potential analytical reagent have been included in broad studies concerned only in part with 3-methyl-8-hydroxyquinoline. Some of these studies had to do with the possible antibacterial and antifungal action of 3-methyl-8-hydroxyquinoline (59,60,61). (It is thought that the ability to chelate with trace elements in the cell accounts for some antifungal activity.) Two methods for the determination in pharmaceutical products of substituted 8-hydroxyquinolines, among them 3-methyl-8-hydroxyquinoline, have been proposed (62): the zinc chelate was formed and the excess of the known amount of zinc determined by complexometric titration or, alternatively, the free bases were titrated in acetic anhydride with perchloric acid.

3-Methyl-8-hydroxyquinoline has been most used in studies relating the position of the substituted group in 8-hydroxyquinoline to the ability to form metal chelates. It was in this context that its preparation was first reported (63): o-aminophenol hydrochloride and methacrolein were reacted in the presence of an oxidizing agent, arsenic(V) oxide, with 4% yield. The yield has been increased to about 30% by using o-aminophenol as the oxidizing agent (64). Some properties of 3-methyl-8-hydroxyquinoline have been studied: quantitative dibromination of the compound was inferred (63) and supporting results were given in another paper (32); the thiocyanic acid salt of 3-methyl-8-hydroxyquinoline is readily formed and has been recommended as a characterization derivative (65); the indophenol of 3-methyl-8-hydroxyquinoline was prepared in a study of derivatives with oxidation-reduction and indicator properties, while also containing chelating groups (66); the ultraviolet spectra of 3-methyl-8-hydroxyquinoline in acidic and basic solution was determined and Beer's law found to be obeyed over the concentration range studied (63); the acid and base ionization constants of this compound were determined spectrophotometrically (63); the chromatography of divalent and trivalent cations on paper impregnated with 3-methyl-8-hydroxyquinoline has been investigated (67); polarographic studies on 3-methyl-8-hydroxyquinoline showed the height of the wave to be proportional to concentration between pH 10 and 12, the half-wave potential to be dependent on pH, and complexes of 3-methyl-8-hydroxyquinoline to be formed with aluminum (68,69); and precipitation studies showed 3-methyl-8-hydroxyquinoline formed insoluble chelates with aluminium, copper(II), zinc, and iron(III) ions in acetate buffers, and magnesium ions in alkaline solution (63).

There is no mention of thorium 3-methyl-8-hydroxyquinolate in the published literature. Some work on this compound has, however, been done in this laboratory (11). A yellow-orange compound was precipitated from an acetate buffer at pH about 8.0 by dropwise addition of 1.0 M aqueous ammonia, followed by digestion, washing and filtering. Data obtained from ignition to thorium dioxide, bromination of the 3-methyl-8-hydroxyquinoline, and weighing the compound after drying in the air at 70°C. for 5 hr., indicated the compound may have 1:5 stoichiometry and contain some water. The four thorium analyses indicated that precipitation of thorium was almost quantitative (low by 0.5%) and the gravimetric data was 1.3% higher than that expected from the titer of the thorium solution. This was thought due to water since the compound had shown some hygroscopic character. The results of the bromometric analyses showed that the amount of 3-methyl-8-hydroxyquinoline was close to within 1% of that required for 1:5 stoichiometry. From the few thorium and 3-methyl-8-hydroxyquinoline analyses that were done, a HQ/Th ratio of 4.9_6 may be calculated. A 1:5 stoichiometry for thorium 3-methyl-8-hydroxyquinolate was assumed, and this was then used in an argument concerned with the structure of thorium 8-hydroxyquinolate.

The composition of thorium 8-hydroxyquinolate, however, has been questioned since that time, on the basis of evidence that the HOx/Th ratio was 4.8, not 5.0 (12,13). Because of this, and the very modest amount of data relating to thorium 3-methyl-8-hydroxyquinolate, it must be considered that the composition of this compound has not been established with certainty. To establish this, and to increase knowledge about this little-studied compound (but one which may be useful in correlating data on other substituted 8-hydroxyquinolines), the work reported in this thesis was undertaken.

This thesis is primarily concerned with the composition of thorium 3-methyl-8-hydroxyquinolate, its thermal properties, and its analytical significance. The dependence of precipitation on pH is determined, and compared on theoretical grounds with the pH-precipitation curve of thorium 2-methyl-8-hydroxyquinolate (33). In order to permit other comparisons, some investigations of thorium 2-methyl-8-hydroxyquinolate and thorium 8-hydroxyquinolate were made: these include precipitation, composition, and thermal studies.

EXPERIMENTAL AND RESULTS

Reagents and Standard Solutions

The 3-methyl-8-hydroxyquinoline was synthesized by a procedure based on the Doebner-von Miller reaction as modified by Corsini (64), using o-aminophenol and methacrolein (2-methyl-propenal) as starting materials and o-nitrophenol as an oxidizing agent. The crude product was steam distilled and recrystallized from aqueous ethanol: m.p. 112.5-113°C. (uncorr.); literature (63,64): 112-113°C. The purity of the product, after it was dried for 30 min. at 95°C., was established by bromination, 3-methyl-8-hydroxyquinoline being known (32) to dibrominate quantitatively in the 5,7 positions. The brominations were done using standard bromate solution, back-titrating the iodine (from the excess bromine) with standard thiosulfate solution. The results showed a purity of 99.6_8%, with an average deviation (five determinations) of 0.0_4%. After re-crystallization of a small portion of the product from aqueous ethanol, drying the crystals for 30 min. at 95°C., grinding them to a fine powder in an agate mortar, and drying for a further 60 min. at 95°C., the purity was 99.9_2%, with an average deviation (three determinations) of 0.0_3%.

The 2-methyl-8-hydroxyquinoline was a commercial product (Aldrich Chemical Co., Inc., Milwaukee, Wisconsin, U.S.A.) that was further purified by crystallization from aqueous ethanol: m.p. 72-74°C. (uncorr.); the values in the literature range from 71.5° to 75°C. (33,70).

The 8-hydroxyquinoline was Analar reagent (British Drug Houses, Ltd., Poole, England) that was twice recrystallized from ethanol: m.p. 72-73°C. (uncorr.); the values in the literature are many, in the range 72-76°C. (71).

The stock solutions of thorium(IV) were prepared from thorium nitrate tetrahydrate (Code 103, Lindsay Chemical Division, American Potash and Chemical Corporation, West Chicago, Illinois, U.S.A.). The purity of this salt was tested by spectrographic analysis in the Research and Development Laboratories, Canadian Westinghouse Company Limited, Hamilton, after its conversion to thorium dioxide by ignition in a platinum crucible at 800°C. The purity was found to be equal to or greater than that of standard sample JM 490 thorium dioxide (Johnson Matthey and Co., Ltd., London, England) certified to be 99.98% ThO_2. Potentially serious contaminants (for a technique employing 8-hydroxyquinoline or its derivatives) were found to be negligible.* The acidity of the two thorium stock solutions was kept below pH 2 with freshly boiled nitric acid. The stock solutions (of concentration ∼ 1.3 mg. Th/ml.) were standardized by direct titration of aliquot portions, to an Alizarin Red S end point, with standard disodium ethylenediaminetetraacetate (72). The tetraacetate was standardized by titration to the Eriochrome Black T end point with standard zinc solution (73) prepared from zinc of 99.999%

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*In the ThO_2 prepared from the hydrated nitrate, Ca, Cu, and Mg were detected, at concentrations 0.01%, 0.001%, and 0.001%, respectively. Thirteen rare-earth elements were sought, but none detected. The sensitivity of the spectrographic method was such that the following upper limits were established for 13 other elements (none of which were detected): 0.1% - P; 0.01% - Al, Fe, Mo, Na, Si; 0.003% - Mn, Ni, Pb, Ti, Zr; 0.001% - Cr, Sn.

purity (Johnson Matthey and Co., Ltd., London, England) or zinc meeting A.C.S. specifications (Mallinckrodt Chemical Works, Montreal, P.Q.). Earlier work in this laboratory has shown these standards to be equivalent.

The organic chemicals for the synthesis of the 3-methyl-8-hydroxyquinoline were technical products (Matheson, Coleman and Bell Division, Matheson Company, Inc., Norwood, Ohio, U.S.A.), and the Alizarin Red S and Eriochrome Black T for the complexometric titrations were indicator quality (British Drug Houses, Ltd., Poole, England).

All other chemicals were analyzed reagent grade. The water used in all experiments was distilled and then passed through a mixed-bed ion exchanger.

Apparatus

All weights and volumetric glassware were calibrated.

Measurements of pH were made using a Radiometer Model PHM4 pH meter (Radiometer, Copenhagen, Denmark) equipped with Radiometer G 202 B glass and K 401 saturated calomel electrodes. Before use, the meter was standardized with a buffer solution of suitable pH (Beckman Instruments, Inc., Fullerton, California, U.S.A.).

The thermobalance was a Chevenard-type photographically recording instrument (TBP No. 27, S.A.D.A.M.E.L., La Chaux de Fonds, Switzerland). The rate of heating was 2.6°/min., and the sensitivity was 0.87 mm./mg. Temperature readings were made with a platinum-platinum(87%),rhodium(13%) thermocouple in association with a potentiometer (No. 8662, Leeds and Northrup Co., Philadelphia, Pennsylvania, U.S.A.) standardized against the internal standard cell.

The apparatus for differential thermal analysis was a Du Pont 900

Differential Thermal Analyzer (E.I. du Pont de Nemours and Company, Inc., Wilmington, Delaware, U.S.A.). The rate of heating was 10°C./min., and the sensitivity settings on the ΔT and T axes were 0.5°C./in. and 50°C./in., respectively. Temperature readings were made with chromel-alumel thermocouples. Glass beads, in a quantity approximately the weight of the sample, were used as the reference material.

All polarographic measurements were made at 25.0°C. ± 0.1°C. using a pen-recording Tinsley polarograph, Type 14/3 (Tinsley Industrial Instruments, Ltd., London, England). The capillary for the dropping mercury electrode was a 4.9-cm. length of marine barometer tubing, (S-29417, E. H. Sargent and Co., Chicago, U.S.A.), with a drop time of about 3.5 sec. under the conditions in which it was used. The polarographic cell was the conventional H-type, electrolytic contact to the saturated calomel reference cell being made through a potassium chloride-agar bridge. When different sensitivity settings were used, corrections to the diffusion currents were made using a calibration of these settings: the current through a resistor (instead of the polarographic cell) at a constant applied potential was measured for the different settings and the factors relating these values to an arbitrary reference were determined.

Composition of Thorium 3-Methyl-8-hydroxyquinolate

Precipitation of thorium 3-methyl-8-hydroxyquinolate: A 25-ml. aliquot portion of thorium stock solution (1.358 mg.Th/ml.) was pipetted into a 150-ml. beaker and diluted with 25 ml. of water. (In some experiments, 50 ml. of water were used, as indicated in a footnote to Table I.) To this solution were added 8.0 ml. of an aqueous solution containing 160 mg. of 3-methyl-8-hydroxyquinoline which had been dissolved in 1.3 ml.

of glacial acetic acid. The resulting solution was placed on a hot plate (about 80°C.) and precipitation was induced by the dropwise addition to the hot solution, with rapid stirring, of 15 ml. of a solution of ammonium acetate (2 g. per 15 ml. of solution). The acidity of the solution was further adjusted to give final pH values in the range 5.0-7.2 by the slow addition, with rapid stirring, of either 5 ml. or 10 ml. of 3 M aqueous ammonia, or 10 ml. of water. The precipitate was digested at about 80°C. for 3½ hr. to 22 hr., then filtered hot onto a medium-porosity fritted-glass crucible and washed with 75-200 ml. of hot water (about 65°C.).

The filtrate was allowed to cool to room temperature, and the pH was determined and recorded as the "pH of precipitation".

Conditions for drying the precipitate were varied, as indicated in Tables I, II, and V. The precipitate was stored in a desiccator over phosphorus pentoxide. The precipitate was weighed either directly in a normal manner (Table I data), or by the dry-box technique to be described presently (Table II data), or after heating to elevated temperatures (Table V data) and then its content of 3-methyl-8-hydroxyquinoline was determined bromometrically (as described below).

Bromometric analysis procedure: A carefully weighed sample (45-195 mg.) of the compound was transferred to an iodine flask, dissolved in 100 ml. of 2 M hydrochloric acid, and titrated essentially by the procedure of Corsini and Graham (33). In instances when the volume of standard bromate solution would be beyond the calibrated portion of the buret, 10 ml. of the bromate solution were priorly added by means of a calibrated pipet and then the rest of the required bromate solution was added from the buret.

Results of direct-weighing procedure: The results, calculated as a percentage of 3-methyl-8-hydroxyquinoline, are summarized in Table I.

As indicated in a footnote to Table I, a significant increase in weight during the weighing of the precipitate was noticed in some instances. This suggested absorption of moisture from the air, and led to the following more rigid procedure.

Dry-box transfer procedure and results: Two kinds of capped containers, of polypropylene and polyethylene, both large enough to hold the crucible and its contents, were tested for air-tightness. A small quantity of phosphorus pentoxide was placed in a crucible, which was then put into a container, and this was weighed at intervals for 2.3 hr. Little increase in weight of the polyethylene container occurred, but the polypropylene container gained weight significantly. The containers with their phosphorus pentoxide were allowed to stand for 12 days; inspection for metaphosphoric acid clearly indicated the superiority of the polyethylene container. In another similar experiment, two polyethylene containers remained at constant weight (within 0.1 mg.) for 4 hr., while containing phosphorus pentoxide.

The polyethylene container was 3.2 cm. in diameter and 8.3 cm. in height, with a friction-fitting cap. The container, crucible, and precipitate weighed about 25 g.

The dry box was prepared as follows: at least 20 hr. (and usually longer) before use, the desiccant trays, which held phosphorus pentoxide, were scraped to remove the metaphosphoric acid, or else the desiccant was replaced. Dry nitrogen was swept through the box at a rate sufficient to create a small positive pressure (with respect to atmospheric)

TABLE I

COMPOSITION OF THORIUM 3-METHYL-8-HYDROXYQUINOLATE: DIRECT-WEIGHING PROCEDURE

Detn. No.*	pH of Pptn.	Time of Drying (hr.)	Temp. of Drying (°C.)	Weight of Dried Sample Obtained (mg.)	3-Methyl-8-Hydroxy-Quinoline Found (%)
1	5.92	96	Room	-	74.0_9
2	5.95	96	Room	-	74.0_7
3	5.99	23	60	155.2	74.3_0
4	6.28	3.5	60	154.9	74.3_5
5	5.96	1.0	110	154.6	74.2_5
6	5.82	1.0	110	153.6	74.3_8
7	-	168	Room	-	74.5_4
8	5.81	2.5	60	153.8	***
9	6.16	2.5	60	154.9	***
10	5.14	3.3	60	153.3	***
11	5.08	3.3	60	154.2	***
12	5.12	3.3	60	154.1	-
13	5.13	3.3	60	154.0	74.5_1
14	5.13	3.3	60	151.0	74.6_7
15	5.17	3.3	60	154.5	74.6_5
16	5.04	3.3	60	154.8	74.4_4
17	5.11	3.3	60	153.0	74.6_8
18	5.08	3.3	60	154.2	74.4_2
			Averages:	154.2** ± 0.5 (av. dev.)	$74.4_1 \pm 0.1_6$ (av. dev.)
Theoretical, for $Th(C_{10}H_8ON)_4 \cdot C_{10}H_9ON$:				149.7 ± 0.2 (av. dev.)	77.73

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* In the nine separately prepared samples for determinations Nos. 1-9 inclusive, the 25-ml. aliquot portion of thorium stock solution was diluted with 50 ml., rather than 25 ml., of water. With the nine separately prepared samples for determinations Nos. 10-18 inclusive, a significant increase in the weight of the precipitate was noticed during weighing.

** Omitting Detn. No. 14.

*** These samples correspond to Preparations Nos. 1-4 in Table V, which were analyzed for 3-methyl-8-hydroxyquinoline only after being heated at 200-220°C., with the results given in Table V.

inside the box. (The nitrogen was dried by passing it through columns of coarse-mesh calcium chloride, fine-mesh calcium chloride, and phosphorus pentoxide on glass wool.) The flushing with dry nitrogen was begun 1½ to 4 hours before the dry box was used. The polyethylene container was placed in the dry box shortly after it and the empty crucible had been weighed.

The precipitate, which had been dried for 3½ to 4 hours at 60°C. after precipitation as described above, had been kept in a small desiccator over phosphorus pentoxide. When the dry box was ready, this desiccator was placed in it, and the crucible transferred to the polyethylene container, and the top fitted. Then the container was removed from the dry box and weighed.

After this weighing, the precipitate was dissolved through the fritted-glass crucible with 60 ml. of approximately 3 M hydrochloric acid and the resulting solution diluted to give about 100 ml. of 2 M acid. The 3-methyl-8-hydroxyquinoline content of the solution was determined bromometrically (*vide supra*). The results are recorded in Table II.

Vacuum-drying and weighing procedure and results: The data in Tables I and II indicated that even more rigid drying conditions and greater precautions to exclude moisture during weighing might lead to still higher results for the 3-methyl-8-hydroxyquinoline content of the compound. Accordingly, samples of the compound were dried in a vacuum line and weighed while still *in vacuo*, in the manner set forth below. The samples of compound for these experiments were prepared in larger batches than in the earlier experiments, and separate determinations were done on samples from each batch.

TABLE II

COMPOSITION OF THORIUM 3-METHYL-8-HYDROXYQUINOLATE: DRY-BOX TRANSFER PROCEDURE

pH of Pptn.	Time of Drying (hr.)	Temp. of Drying (°C.)	Weight of Dried Sample Obtained (mg.)	3-Methyl-8-Hydroxy-Quinoline Found (%)
5.71	3.5	60	151.3	76.2_0
5.73	3.5	60	150.6	77.0_0
5.60	3.8	65	150.4	76.6_2
5.72	3.8	65	150.6	76.7_9
5.78	3.8	65	150.1	76.8_0
7.12	4.0	60	152.2	76.0_1
		Averages:	150.9 ± 0.6 (av. dev.)	$76.5_7 \pm 0.3_1$ (av. dev.)
Theoretical, for $Th(C_{10}H_8ON)_4 \cdot C_{10}H_9ON$:			149.7 ± 0.2 (av. dev.)	77.73

An 100-ml. aliquot portion of thorium stock solution (1.349 mg. Th/ml.) was used for each preparation. The procedure was that set forth earlier, but with all quantities four times larger; concentrations were the same. After the addition of the ammonium acetate, 40 ml. of water were ordinarily added (to give a volume of about 330 ml.), but in one instance 40 ml. of 3 M aqueous ammonia, added dropwise with rapid stirring, were used to adjust the solution to pH $\sim$ 8. The precipitates were digested for 4-4½ hr. at about 80°C., washed with 600 ml. of hot water, and were dried for 2 1/3 - 3 1/3 hr. at 60°C. before being stored in a desiccator over phosphorus pentoxide.

Fig. 1 is a schematic representation of the simple vacuum line used for the thorough drying of the compound. A tilting McLeod gauge, (a), with a scale graduated from 10 mm. to 0.01 mm. of mercury served to measure the pressure. At the controllable air inlet, (b), the line was protected from moisture by a cylindrical drying tube, 2 cm. x 10 cm., containing 8-mesh Drierite mixed with a small amount of the indicating type. Condensation traps, (f,g), were cooled by Dry Ice in acetone, contained in Dewar flasks.

The weighing container, (e), for the compound, depicted in detail in the lower portion of Fig. 1, consisted of two parts: the upper part was a vacuum stopcock, (j), attached to outer and inner standard tapered ground-glass joints, as shown in A. The assembly was fitted with a wire harness, (h), for ease in weighing. The lower part of the container was of either design B or C, each of which fitted into the upper part A by means of an inner B10 ground-glass joint. Design B was used in early experiments. Experience with it dictated modification to design C, which resembled a small Erlenmeyer flask with an elongated neck. The parts were held together by a steel spring. Experiments showed that the separating and re-assembling of the parts of the container could be done without significant weight change (within 0.1 mg.) after manipulative experience had been gained.

The parts of the weighing container, (e), were thoroughly cleaned (including the steel spring and wire harness) and, after careful lubrication of the ground-glass joints with Apiezon N stopcock lubricant, were assembled and fitted to the vacuum line at (d). Evacuation of the entire system was begun and a pressure of $\leqslant 0.01$ mm. attained. The system was

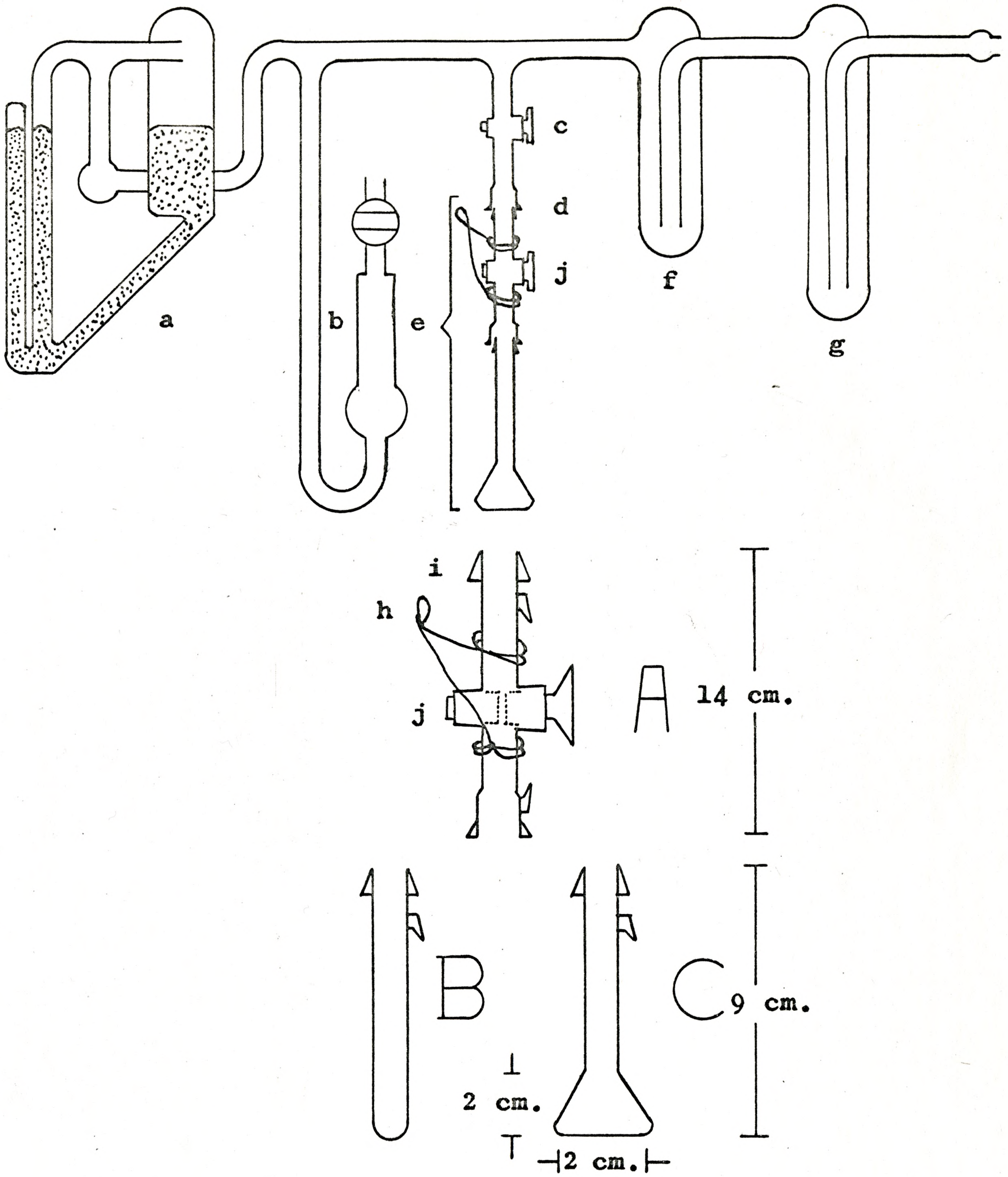

Figure 1

The Vacuum Apparatus with
Detail of Weighing Container

(a) Tilting McLeod gauge;(b) Drying tube, with controllable air inlet;(c) Vacuum stopcock(3 mm.);(d) Ground glass B10 outer joint;(e) Container, see detail below;(f),(g) Condensation traps;(h) Weighing harness of Nichrome wire; (i) Attachment to vacuum line, B10 inner joint;(j) Vacuum stopcock(3 mm.)

then flamed, and evacuation continued for about one hour at this pressure. Stopcocks (j) and (c) were then closed, and the container, (e) detached from the line at (d). The exposed inner ground-glass joint, (i), was thoroughly cleaned with carbon tetrachloride and the evacuated container very carefully weighed. Joint (i) was then lubricated and the container fitted to the vacuum line again. Stopcock (c) and then (j) were re-opened and evacuation of the system continued. This cycle of evacuation and weighing was repeated until the weight of the container became constant. This usually required two, perhaps three, weighings, 30 min. apart.

Approximately 150 mg. of the compound, previously dried in air at 60°C., were transferred to the lower part of the container by means of a small glass funnel to avoid contaminating the exposed greased surfaces. The container was carefully re-assembled and evacuated by a water aspirator for one hour, after which the container was removed from the aspirator and placed in position, (d), on the vacuum line. The container was not, however, at this stage opened to the vacuum line. The line pressure was adjusted by means of the air leak, (b), to a value approximating that attained by the water aspirator. (This pressure was not sufficiently low to register on the McLeod gauge.) Then, stopcock (c) and then (j) were opened and the pressure of the entire system slowly reduced, in stages, by the gradual closing of the air leak, (b), until a pressure $\leqslant 0.01$ mm. was attained. An air jacket was then mounted about the lower part of the container and, by rapidly refluxing acetone through the outer portion of this jacket, the container was kept at approximately 53°C. for an hour or more. Then the container and its contents were removed from the line, and very carefully weighed after joint (i) had been cleaned. Thereafter the compound was transferred to an iodine flask with 100 ml. of 2 M hydrochloric acid. The 3-methyl-8-hydroxyquinoline content of the product was determined by bromination in the usual manner (vide supra). The results are given in Table III.

TABLE III

COMPOSITION OF THORIUM 3-METHYL-8-HYDROXYQUINOLATE:

VACUUM-DRYING PROCEDURE

pH of Pptn.*	Time of Drying in Vacuo at 53°C. (hr.)**	Weight of Vacuum-Dried Sample (mg.)	3-Methyl-8-Hydroxy-Quinoline Found (%)
4.62	1.0	195.0	77.3_3***
-	1.1	144.7	77.7_3
4.83	1.1	132.4	77.7_6
4.83	1.1	141.9	77.7_6
8.05	2.5	143.2	77.4_1
		Average:	$77.6_0 \pm 0.1_8$ (av. dev.)
Theoretical, for $Th(C_{10}H_8ON)_4 \cdot C_{10}H_9ON$:			77.73

---

*The five determinations involved four separate preparations of the compound, as distinguished in this column. The one marked with a dash (-) was a mixed sample consisting largely of material precipitated at pH 4.66 together with some from the preparation at pH 8.05. As before, "pH of Precipitation" refers to the pH of the filtrate, after it had cooled to room temperature.

**Prior to being put into the vacuum line, the samples were dried in air at 60°C. for 2 1/3 - 3 1/3 hr. The step-wise reduction in pressure to $\leq$ 0.01 mm. required about 3/4 hr. Then the samples were in vacuo for times up to 20 min. while their temperature was being raised to 53°C. Thereafter, they were dried at 53°C. for the times given in this column.

***In this determination, the container of design B (Fig. 1) was used, and "bumping" was serious; all the other determinations were done using the container of design C (Fig. 1).

pH Dependence of Precipitation of Thorium 3-Methyl-8-hydroxyquinolate

Precipitations in the pH range 2.9-3.6 were done substantially in the manner described earlier (p.11), using 25 ml. of thorium stock solution (1.358 or 1.349 mg. Th/ml.) that had been diluted to 50 ml. with water. The differences were that only about 2 ml., rather than 15 ml., of the ammonium acetate solution were added, and no aqueous ammonia or water was subsequently added. The precipitates were digested at about 80°C. for 4 hr., filtered as before, and washed with 200 ml. of hot water. The precipitates were dried for 3.0-3.5 hr. at 60°C., weighed, and then dissolved through the fritted-glass crucible with 60 ml. of approximately 3 M hydrochloric acid and resulting solution diluted to give about 100 ml. of 2 M acid. The 3-methyl-8-hydroxyquinoline content of the solution was determined bromometrically (*vide supra*).

The results are recorded in Table IV, as Detns. 1B-7B inclusive, along with data for six other determinations (8A-13A inclusive) for precipitations in the pH range 5.6-7.1. These latter correspond to the determinations of Table II, which were analyzed in the same way: in all instances in Table IV, the entire precipitate was analyzed for 3-methyl-8-hydroxyquinoline and any differences in possible water pick-up occasioned by differences in drying techniques are irrelevant.

The data relating degree of precipitation to pH of precipitation are plotted in Fig. 7, given in the Discussion.

Preparation of 1:4 Thorium 3-Methyl-8-hydroxyquinolate

The preparation of a possible 1:4 thorium 3-methyl-8-hydroxyquinolate, $Th(C_{10}H_8ON)_4$, by the thermal decomposition of the "1:5" 3-methyl-8-hydroxyquinolate, was attempted.

TABLE IV

PRECIPITATION OF THORIUM 3-METHYL-8-HYDROXYQUINOLATE AS A FUNCTION OF pH

Detn. No.*	pH of Pptn.	3-Methyl-8-Hydroxy-Quinoline Found (mg.)	Completeness of Pptn. (%)**
1B	2.90	Trace	-
2A	3.20	47.8***	41.1
3A	3.43	86.5***	74.3
4A	3.43	88.7***	76.2
5B	3.52	100.1***	86.7
6B	3.53	104.3***	90.3
7B	3.60	94.6***	81.9
8A	5.60	115.2	99.0
9A	5.71	115.3	99.1
10A	5.72	115.6	99.4
11A	5.73	116.0	99.7
12A	5.78	115.3	99.1
13A	7.12	115.7	99.4
Averages, for Detns. 8A-13A:		115.5 ± 0.3 (av. dev.)	99.3 ± 0.2 (av. dev.)

---

*"B" indicates use of a thorium stock solution of titer 1.349 ± 0.001 mg. Th/ml.;
"A" indicates use of a thorium stock solution of titer 1.358 ± 0.001 mg. Th/ml.
Other data relevant to Detns. 8A-13A inclusive are given in Table II.

**Calculated from the data of the preceding column and the titers of the thorium solution given in the preceding footnote, assuming that one mole of thorium reacts with five moles of 3-methyl-8-hydroxyquinoline.

***The weights of the precipitates corresponding to these values, after the precipitates had been dried at 60°C. for 3.0-3.5 hr., were, respectively, in mg., 64.9, 117.6, 119.4, 134.8, 144.5, 129.3.

Preparation of the parent compound: Samples of the "1:5" 3-methyl-8-hydroxyquinolate were prepared as set forth earlier (p.11). The samples were those listed as Detn. Nos. 8-11 inclusive in Table I, details of their preparation being given in the body and first footnote of that table.

Heating procedure and results: The samples were heated at 200° or 220°C., then cooled in a desiccator over phosphorus pentoxide, weighed, and reheated. Eventually they were analyzed bromometrically for 3-methyl-8-hydroxyquinoline, by the method given earlier (p.12).

The results of these experiments are recorded in Table V.

TABLE V

THERMAL PREPARATION OF 1:4 THORIUM 3-METHYL-8-HYDROXYQUINOLATE

Prepn. No.	Weight of Dried Sample (mg.)*	Cumulative Time of Heating (hr.)	Temp. of Heating (°C.)	Weight of Heated Sample (mg.)	Total Weight Loss (%)	3-Methyl-8-Hydroxy-Quinoline Found (%)
1	153.8	1.0	220	124.9		
		1.8	220	124.3	19.2	72.7_3
2	154.9	1.0	220	125.3		
		1.8	220	125.1	19.2	72.5_1
3	153.3	0.7	200	124.5		
		1.1	200	124.2		
		1.7	200	124.2	19.0	73.0_6
4	154.2	0.7	200	125.2		
		1.1	200	124.8	19.1	73.5_3
		Averages:		124.6** ± 0.4 (av. dev.)		$72.9_6 \pm 0.3_4$ (av. dev.)
Theoretical, for $Th(C_{10}H_8ON)_4$:				126.4 ± 0.1 (av. dev.)		73.63

---

* The figures in this column are the weights after the samples had been dried at 60°C. for 2.5 hr. (Preparations 1 and 2) or 3.3 hr. (Preparations 3 and 4). These preparations correspond to Detn. Nos. 8-11 inclusive, in Table I.

** Average of the four "final" weights.

Thermal Studies with Thorium 3-Methyl-8-hydroxyquinolate

Thermal properties of thorium 3-methyl-8-hydroxyquinolate were studied using the complementary techniques of thermogravimetric analysis and differential thermal analysis. Some investigation of 3-methyl-8-hydroxyquinoline was also made.

Preparation of thorium 3-methyl-8-hydroxyquinolate: The samples for the thermogravimetric experiments were prepared in the manner set forth earlier (p.11) except that the thorium stock solution was diluted with 50 ml., rather than 25 ml., of water, and that no ammonia or water was added after the solution of ammonium acetate had been added. The pH of precipitation, measured on the filtrate in the usual manner, was 4.90. After filtering and washing, the precipitate was "dried" by allowing it to stand, loosely covered, for 144 hr. in air at room temperature and then placing it in a desiccator over phosphorus pentoxide.

The samples for the differential thermal analysis experiments were taken from a single batch of compound prepared substantially as set forth earlier (p.11) but with all quantities four times larger; concentrations were the same. The digestion time was 2 hr., and the precipitate was washed with 400 ml. of hot water; the pH of precipitation was 4.58. The precipitate was "dried" by drawing through it, for 18 hr., filtered air at room temperature, and then storing it in a desiccator over phosphorus pentoxide.

Thermogravimetric analysis: The thermogravimetric curve, or thermogram, for 3-methyl-8-hydroxyquinoline (a sample of about 125 mg.) in air and that for thorium 3-methyl-8-hydroxyquinolate (about 140 mg.) in air are shown in Fig. 2. Another thermogram for the latter compound, obtained with a sample that had been "dried" only by standing in the room

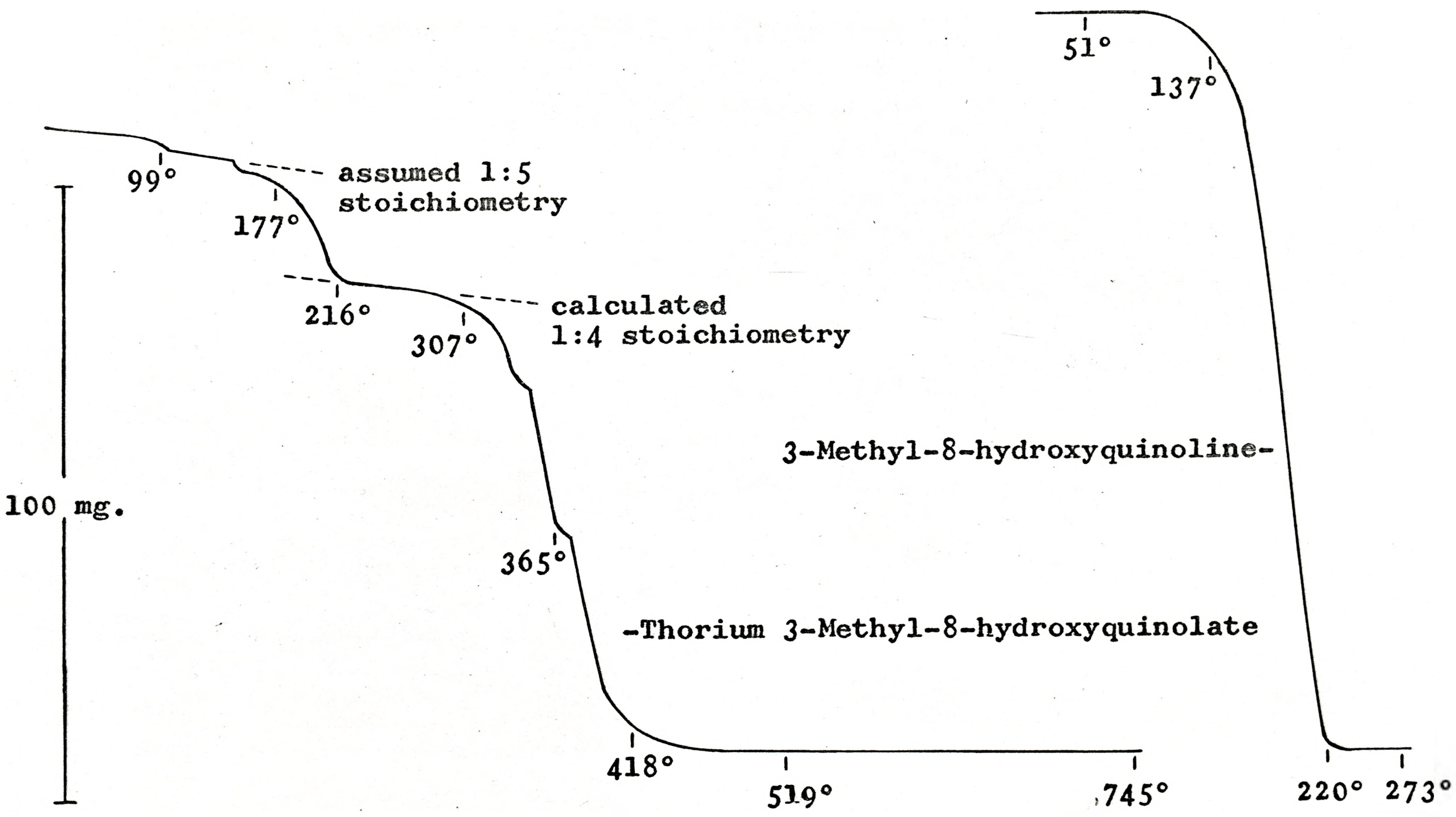

Figure 2

Thermogravimetric Curves for the Decomposition of 3-Methyl-8-hydroxyquinoline and its 1:5 Thorium Chelate

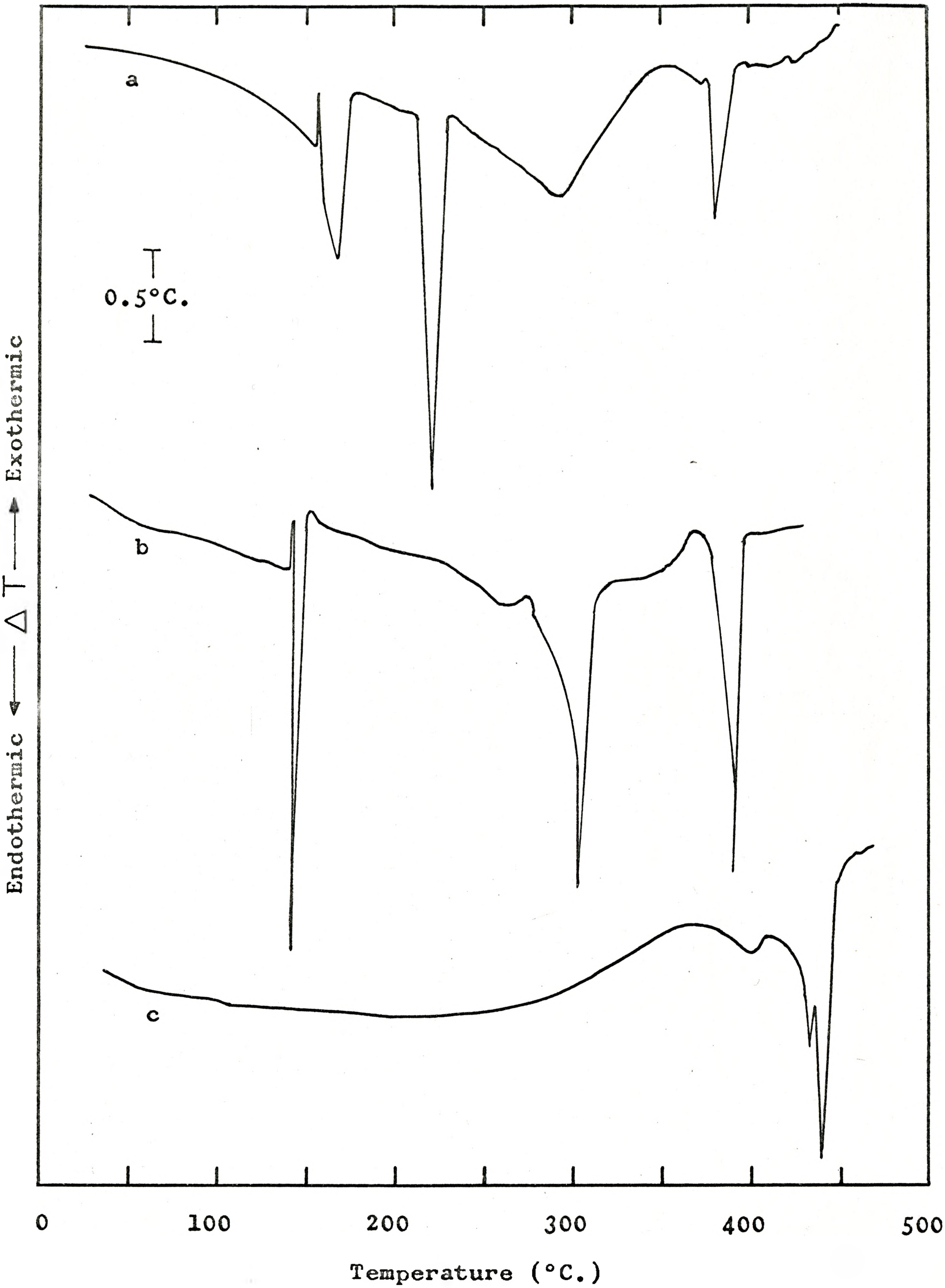

Figure 3

Differential Thermal Analysis Curves
for the Decomposition of
(a) Thorium 3-methyl-8-hydroxyquinolate
(b) Thorium 8-hydroxyquinolate
(c) Thorium 2-methyl-8-hydroxyquinolate

overnight was similar except for a rapid weight decrease at low temperatures due to the loss of a large quantity of adventitious water and the lack of any level plateau corresponding to a "1:5" compound; this plateau was likely concealed by the large weight loss.

Differential thermal analysis: The differential thermal analysis curve for thorium 3-methyl-8-hydroxyquinolate is shown in Fig. 3,a. A sample of about 40 mg. was used, and the curve for the compound was repeated, using a sample of about 5 mg., with good reproducibility.

Polarographic Determination of Thorium by means of 3-Methyl-8-hydroxyquinoline

Some preliminary experiments were done to ascertain whether 3-methyl-8-hydroxyquinoline could be conveniently determined polarographically, as some earlier work (68) had suggested.

The effect of pH on the shape of the polarographic wave was studied over the pH range 7.5-13.4. Buffer solutions, which also served as the supporting electrolyte, were prepared in the manner of Corsini (74); their polarographic purity was established. With a concentration of 3-methyl-8-hydroxyquinoline of 7.0×10^{-4} M, the compound gave easily measurable waves between pH 10.0 and 11.3, a pH of 11.3 being best for the measurement of diffusion current. A polarographic wave taken at this pH is reproduced in Fig. 4. At pH values less than 10.0, a steep slope in the limiting current occurred and, at 7.6, a pronounced maximum had developed. This behaviour is very similar to that reported by Fernando and Phillips (68). At pH values greater than 11.3 a maximum again developed and became more and more pronounced up to pH 13.4, the limit of the testing.

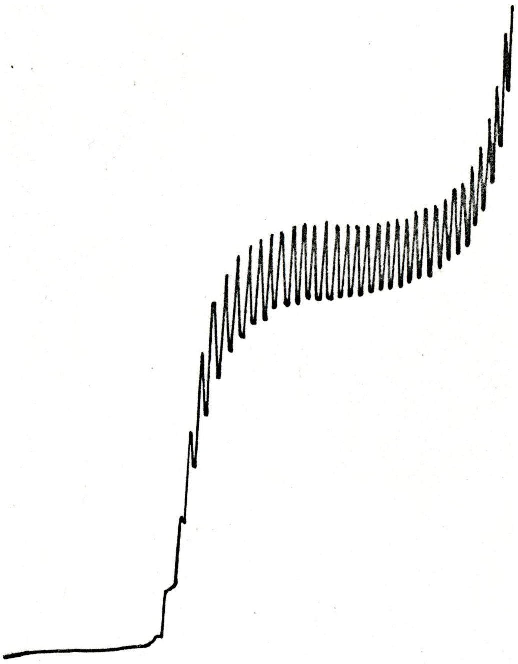

Figure 4

A Polarographic Wave of
3-Methyl-8-hydroxyquinoline
(at pH 11.3)

The half-wave potential of the reduction was dependent on the pH of the solution. Over pH range 10.0 - 12.2, the relationship was found to be $-E_{1/2}$(vs. S.C.E.) = 0.97 + 0.061 pH, in very respectable agreement with that found by Fernando and Phillips (68): $-E_{1/2}$(vs. S.C.E.) = 0.91 + 0.056 pH. It is reasonable to suppose, then, that the reduction involves hydrogen ions.

At pH 10.0 and 11.3, the height of the wave was shown to be diffusion controlled; this was demonstrated by varying the "effective" pressure of mercury, $h_{eff.}$, over a wide range (about 30 to 55 cm.) and observing constancy in the value of $i_d/h^{1/2}_{eff.}$ where i_d is the diffusion current.

It was found, also, that a solution of 3-methyl-8-hydroxyquinoline in the buffer solution used at pH 11.3 yielded a constant diffusion current over a period of at least 36 hr.

Many experiments preliminary to the actual polarographic method were concerned with dissolving the thorium 3-methyl-8-hydroxyquinolate. Attempts at decomposing the thorium chelate on the filter paper with either hot buffer solution or dilute base, or sequestering the thorium ion by complex formation with either ethylenediaminetetraacetic acid or acetylacetone, proved ineffectual. The method that was finally evolved is as follows:

The precipitation and digestion of the thorium 3-methyl-8-hydroxyquinolate is that which has been described on p. 11; the pH of precipitation is adjusted to about pH 5.25 with 3 M aqueous ammonia added dropwise with rapid stirring. The precipitate is then filtered, hot, onto No. 40 Whatman filter paper, and washed thoroughly with hot water until the filtrate is clear. The thorium chelate is then dissolved through the filter paper with about 1 ml. of 6 M hydrochloric acid, followed by a minimal amount of hot water to ensure quantitative transfer to the precipitation vessel. To this solution is added 200 ml. of a buffer solution of pH 11.3 (0.012 M in sodium hydroxide and 0.05 M in disodium hydrogen phosphate). The pH of the solution at this point is in the range 8-9. To complete the formation of a white gelatinous precipitate of thorium, sodium hydroxide (about 0.25 g.) is added to the solution, which brings the pH of solution to 10.0 - 10.5. The thorium precipitate (which probably consists of a mixture of the hydrous oxide and thorium phosphate) is immediately filtered onto No. 541 Whatman filter paper and washed with hot buffer solution (about 80°C.) until the precipitate is white. The filtrate is collected in a 500-ml. volumetric flask, cooled to 25°C., and then made up to volume with the buffer solution. The polarographic cell is rinsed three times with portions of this solution and then filled. The solution is de-aerated for 15 minutes by slowly passing through it nitrogen (purified by passage through a train of vanadium(II) chloride solutions). The diffusion current due to the reduction of 3-methyl-8-hydroxyquinoline in the solution is then measured (five waves being recorded), and the concentration of thorium is assessed by reference to a suitable calibration curve, such as that shown in Fig. 5.

In this calibration curve, obtained using the precipitation and treatment methods outlined just above, the error bars represent the precision (expressed as an average deviation) of ten measurements of the diffusion current for each concentration of thorium. The value of the diffusion current for the highest concentration of thorium involves two independent determinations. In Fig. 5, the range of concentration of thorium (in the original solution) is from 2×10^{-4} M to 2×10^{-3} M, corresponding to concentrations of 3-methyl-8-hydroxyquinoline (in the final solution) of from 1.5×10^{-4} M to 1.5×10^{-3} M. The curve is obviously linear over at least this ten-fold range of concentration.

Composition of Thorium 8-Hydroxyquinolate

The vacuum-drying and weighing technique developed for thorium 3-methyl-8-hydroxyquinolate was applied to the analysis of thorium-8-hydroxyquinolate. This compound was prepared as set forth below, and then vacuum-dried and analyzed bromometrically by the methods used with the 3-methyl derivative.

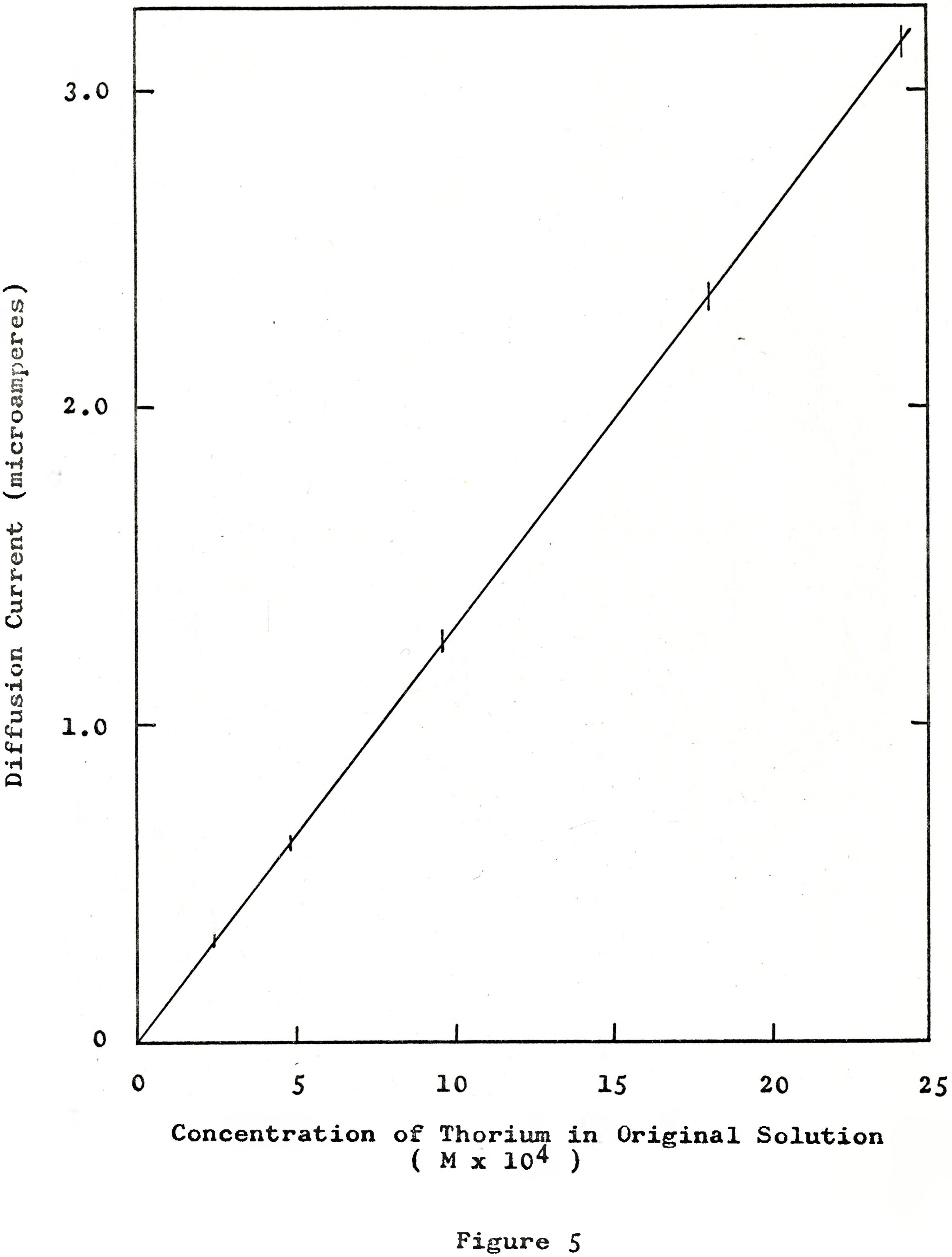

Figure 5

A Calibration Curve for
the Polarographic Determination of
Thorium by 3-Methyl-8-hydroxyquinoline

Precipitation of thorium 8-hydroxyquinolate: An 100-ml. aliquot portion of thorium stock solution (1.349 mg. Th/ml.) was diluted to 200 ml. with water. To this solution were added 32 ml. of an aqueous solution containing 720 mg. of 8-hydroxyquinoline which had been dissolved in 2.0 ml. of glacial acetic acid. The resulting solution was placed on a hot plate (about 80°C.), and precipitation was induced by the dropwise addition to the hot solution, with rapid stirring, of 60 ml. of a solution of ammonium acetate (2 g. per 15 ml. of solution). The precipitate was digested at about 80°C. for 3 hr., then filtered hot onto a medium-porosity fritted-glass crucible and washed with 200 ml. of hot water (about 65°C.).

The filtrate was allowed to cool to room temperature, and its pH measured; it was 5.64.

Drying procedure and results: The precipitate was dried in air for 3 hr. at 60°C., and then stored in a desiccator over phosphorus pentoxide.

The vacuum-drying and weighing procedure that was used was similar to that described earlier for thorium 3-methyl-8-hydroxyquinolate, using the container of design C (Fig. 1). During the first determination (which exactly duplicated the procedure used with thorium 3-methyl-8-hydroxyquinolate) it was observed that thorium 8-hydroxyquinolate showed a lesser tendency to "bump". Accordingly, in subsequent determinations, the partial evacuation of the container, using the water aspirator, was omitted, and the evacuation of the container was done on the vacuum line directly. Moreover, the step-wise reduction of the pressure to a value $\leqslant$ 0.01 mm. could be accomplished more rapidly than before.

Other procedures, including weighing the container, flaming the line, transferring the compound, and evacuation and heating the container, were as before.

The 8-hydroxyquinoline content of the product was determined by bromination in the usual manner (vide supra). The results are given in Table VI.

TABLE VI

COMPOSITION OF THORIUM 8-HYDROXYQUINOLATE:

VACUUM-DRYING PROCEDURE

Weight of Vacuum-Dried Sample (mg.)		8-Hydroxy-Quinoline Found (%)
117.8		76.09
122.9		76.00
122.3		76.35
	Average:	$76.1_5 \pm 0.1_4$ (av. dev.)
Theoretical, for $Th(C_9H_6ON)_4 \cdot C_9H_7ON$:		76.10

Some factors influencing the composition of thorium 8-hydroxyquinolate: During an investigation of the pH-dependence of the precipitation of thorium 8-hydroxyquinolate under conditions comparable to those which were used for thorium 3-methyl-8-hydroxyquinolate, unexpected results were obtained. These led to a number of experiments, the data of which are tabulated in summary form in Tables VII-X.

The general procedure was as follows: in most instances, a 25-ml. aliquot portion of thorium stock solution (1.349 or 1.350 mg. Th/ml.) was diluted to 50 ml. with water. To this solution were added 8.0 ml. of an aqueous solution containing a weighed amount of 8-hydroxyquinoline, which had been dissolved in 1.3 ml. of glacial acetic acid. The resulting solution was placed on a hot plate (about 80°C.) and precipitation was induced by the dropwise addition to the hot solution, with rapid stirring, of a solution of ammonium acetate (2 g. per 15 ml. of solution). If further adjustment of pH was required, 3 M aqueous ammonia was then added dropwise, with rapid stirring. The precipitate was digested at about 80°C., then filtered hot onto a medium-porosity fritted-glass crucible, and washed with about 200 ml. of hot water (about 65°C.). The filtrate was allowed to cool to room temperature, and its pH measured. The precipitate was dried for 3 hr. at about 60°C., and then placed in a desiccator over phosphorus pentoxide. (Some precipitates which were used for the determination of thorium, the data for which is summarized as Group A in Table VII, were dried for 3 hr. at 50°C. at a pressure of 40 mm., and then placed in a desiccator over phosphorus pentoxide.) The excess of precipitant, the final pH of the solution and the period of digestion used in the various experiments are given in Table VII.

Some precipitates (Group F in Table VII and the data in Table VIII, were prepared by a slightly different procedure, this being analogous to that given on p. 32 except that one-quarter of the quantities indicated there was used; these precipitates were digested for 3 hr. at about 80°C., filtered hot, washed with about 100 ml. of hot water (about 65°C.), dried at about 60°C. for 3 hr. and then placed in a desiccator over phosphorus pentoxide.

The samples were either analyzed bromometrically for 8-hydroxyquinoline in the usual manner (<u>vide supra</u>) or, for the determination of

TABLE VII

SOME FACTORS INFLUENCING THE COMPOSITION OF THORIUM 8-HYDROXYQUINOLATE

Group	Colour of Precipitate[1]	pH of Precipitation	Time of Digestion at 80°C. (hr.)	Excess of 8-Hydroxy-Quinoline (%)[2]	Weight of Dried Sample Obtained (mg.)[3]	8-Hydroxy-Quinoline Found (mg.)[3]	8-Hydroxy-Quinoline Found (%)[4]	Thorium Found (%)[4]
A[5]	Y	3.71-3.81 av.(6):3.77	4	40	101.0-103.6 av.(6):102.2	58.1-59.2 av.(3):58.8	57.4-58.5 av.(3):58.1	31.7-32.0 av.(3):31.9
B	O	4.21	4	40	109.9	76.2	69.3	-
C	O	4.62-4.65 av.(6):4.64	1	40	120.7-122.2 av.(3):121.7	88.0-89.0 av.(3):88.7	72.9-72.9 av.(3):72.9	24.1-25.3 av.(3):24.7
D	O	5.15-5.29 av.(3):5.22	1	40	137.4-140.0 av.(3):138.9	100.6-102.6 av.(3):101.2	73.1-73.5 av.(3):73.2	-
E	O	4.81-4.86 av.(2):4.84	1	143	140.6-141.3 av.(2):141.0	103.6-104.0 av.(2):103.8	73.6-73.7 av.(2):73.6	-
F[6]	O	5.02-5.05 av.(4):5.03	3	70	140.1-140.4 av.(4):140.2	103.2-103.7 av.(4):103.5	73.7-73.8 av.(4):73.8	-

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[1] Y = yellow; O = orange

[2] Based on the assumed formation of a 1:5 thorium chelate

[3] Based on the titer of the thorium solution, and assuming 100% precipitation, the expected weight of 1:5 chelate is 138.4 ± 0.1 mg. (for gp. F only, 138.6 ± 0.1 mg.), and the expected weight of 8-hydroxyquinoline is 105.3 ± 0.1 mg. (for gp. F only, 105.4 ± 0.1 mg.)

[4] Theoretical values for a 1:5 compound are: % HQ = 76.10; % Th = 24.33

[5] Samples for the thorium analyses of this group were dried at 50°C. for 3 hr. at 40 mm. of pressure

[6] Full details of data in this group are given in Table VIII

TABLE VIII

REPRODUCIBILITY OF THE PRECIPITATION PROCEDURE FOR THORIUM 8-HYDROXYQUINOLATE*

pH of Precipitation	Weight of Sample Obtained (mg.)	8-Hydroxy-Quinoline Found (mg.)	8-Hydroxy-Quinoline Found (%)
5.02	140.4	103.7	73.8_4
5.03	140.3	103.4	73.7_1
5.03	140.1	103.2	73.6_6
5.05	140.1	103.5	73.8_4
Averages:	140.2 ± 0.1 (av. dev.)	103.5 ± 0.2 (av. dev.)	$73.7_6 \pm 0.0_8$ (av. dev.)

*This Table gives the results which have been summarized as Group F in Table VII.

thorium, ignited in platinum crucibles at 800°C. under oxalic acid (9) to thorium dioxide.

One of the unexpected results mentioned above was the formation of a bright yellow precipitate instead of the usual orange one. Most often, when this occurred, the initial precipitate was orange in colour and changed to bright yellow on digestion. To investigate this phenomena further, the experiment outlined below was done.

The general procedure outlined on p.33 was used for the precipitation with conditions arranged to give an orange precipitate initially, but one that on digestion, would convert to a yellow precipitate. (The pH was adjusted to about 3.8-4.0). The orange precipitate was allowed to digest for 1/2 hr. and then a portion of it was collected on a medium-porosity fritted-glass crucible. The filtrate was returned to the precipitation vessel and the remainder of the sample was digested at about 80°C. until the conversion to yellow had occurred. The yellow compound was then filtered off, as above. The precipitates were each washed with about 100 ml. of hot water and dried for 3 hr. at about 60°C., then placed in a desiccator over phosphorus pentoxide. The samples were analyzed bromometrically in the usual manner (vide supra). The results are given in Table IX, and elemental analyses of the yellow compound are tabulated in Table X.

Thermal Studies with Other Thorium 8-Hydroxyquinolates

In the course of this work, some investigations with thorium 8-hydroxyquinolate and thorium 2-methyl-8-hydroxyquinolate were also made.

Preparation of thorium 8-hydroxyquinolate: The sample for the differential thermal analysis was prepared substantially by the method which was described earlier (p.32). Modifications were the addition, dropwise, of 40 ml. of 0.25 M aqueous ammonia after the 60 ml. of ammonium acetate solution had been added, a digestion period of 1½ hr. rather than 3 hr., and washing with 400 ml., rather than 200 ml., of hot water. The pH of precipitation was 5.10. The precipitation was "dried" by drawing through it, for 18 hr., filtered air at room temperature, and then storing it in a desiccator over phosphorus pentoxide.

Preparation of thorium 2-methyl-8-hydroxyquinolate: A sample of the compound for the differential thermal analysis experiments was prepared substantially by the method of Corsini and Graham (33), but with all quantities four times larger. Precipitation and digestion was done at 80° rather than 70°C., and the precipitate was washed with 400 ml. of hot water. The pH of precipitation was 6.90. The precipitate was "dried" by drawing through it, for 18 hr., filtered air at room temperature, and then storing

TABLE IX

EFFECT OF DIGESTION ON THE COMPOSITION OF A THORIUM 8-HYDROXYQUINOLATE

Detn. No.	Colour of Precipitate*	pH of Precipitation	Time of Digestion at 80°C. (hr.)	Excess of 8-Hydroxy-Quinoline (%)**	Weight of Dried Sample Obtained (mg.)	8-Hydroxy-Quinoline Found (mg.)	8-Hydroxy-Quinoline Found (%)***
1	O	-	0.5	40	31.6	22.2	70.3
2	O	-	0.5	40	33.3	23.4	70.4
1a.	Y	4.02	10.0	40	78.0	45.7	58.6
2a.	Y	3.82	4.5	40	75.2	43.4	47.7

* O = orange; Y = yellow

** Based on the assumed formation of a 1:5 thorium chelate

*** Theoretical value for a 1:5 compound: % HQ = 76.10

TABLE X

COMPOSITION OF A YELLOW THORIUM 8-HYDROXYQUINOLATE

Sample No.*	Carbon Found (%)	Nitrogen Found (%)	Hydrogen Found (%)	Oxygen Found (%)	Thorium Found (%)**	Total (%)	HQ Calc'd. From C detn. (%)***	HQ Calc'd. From N detn. (%)***
1	47.40	6.09	3.16	9.66	32.67	98.98	63.6_5	63.1_1
2	47.55	6.13	3.22	9.54	31.45	97.89	63.8_5	63.5_2
Averages:	47.48	6.11	3.19	9.60	32.06	98.44	63.5_3	
Calculated for ThQ_3OH:	47.58	6.17	2.81	9.39	34.05	100.00	Theoretical HQ:	63.90%
Calculated for ThQ_3OH, containing 0.5% H_2O:	47.35	6.14	2.85	9.79	33.88	100.00	Theoretical HQ:	63.56%

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*Samples for all determinations were dried at 60°C. at 2 mm. of pressure, except that for the nitrogen determination of sample No. 1, which was undried. The analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium im Max Planck-Institut fur Kohlenforschung, Mulheim (Ruhr), Germany.

**Calculated from the weight of a white residue remaining after ignition, presumed to be thorium dioxide.

***Comparison of the C/N ratio for 8-hydroxyquinoline with that experimentally determined indicates that all C and N in the compound is in the form of 8-hydroxyquinoline. Thus, the % HQ may be calculated from % C and % N data.

it in a desiccator over phosphorus pentoxide.

Differential thermal analysis: The differential thermal analysis curves for thorium 8-hydroxyquinolate and thorium 2-methyl-8-hydroxyquinolate are shown in Fig. 3, b and c, respectively. Samples of about 40 mg. were used and the curves for each compound were repeated, using samples of about 5 mg., with good reproducibility.

DISCUSSION

Composition of Thorium 3-Methyl-8-hydroxyquinolate

In this investigation, the precipitation conditions were chosen to minimize coprecipitation of 3-methyl-8-hydroxyquinoline and contamination by species containing the hydroxyl group. The pH of precipitation was generally kept as low as possible, in the region of pH 5-6; digestion times were long; and the volume of the wash water (hot) was large. Because of the low solubility of the organic reagent (63), however, a high excess of the precipitant could not be employed.

After its precipitation, the compound was treated in three different ways: by conventional (or direct) drying and weighing; or by transferring to air-tight containers in a dry-box and then weighing; or by drying and weighing in vacuo. These procedures will be referred to as different methods in that this treatment stage, only, is different. Finally all samples were analyzed bromometrically, by the same procedure.

The results of these bromometric analyses of the thorium chelate, as given in Tables I, II, and III, are summarized in Fig. 6. In this, both the ranges of the values and the means of the 3-methyl-8-hydroxyquinoline content of the compound as determined in the three different procedures are plotted both as percentage composition and as apparent deviation (in parts per thousand) from 1:5 stoichiometry, where the latter refers to the formulation $ThQ_4 \cdot HQ$ or $HThQ_5$, Q^- being the 3-methyl-8-hydroxyquinolate ion.

The effect of the treatment method on the apparent percentage con-

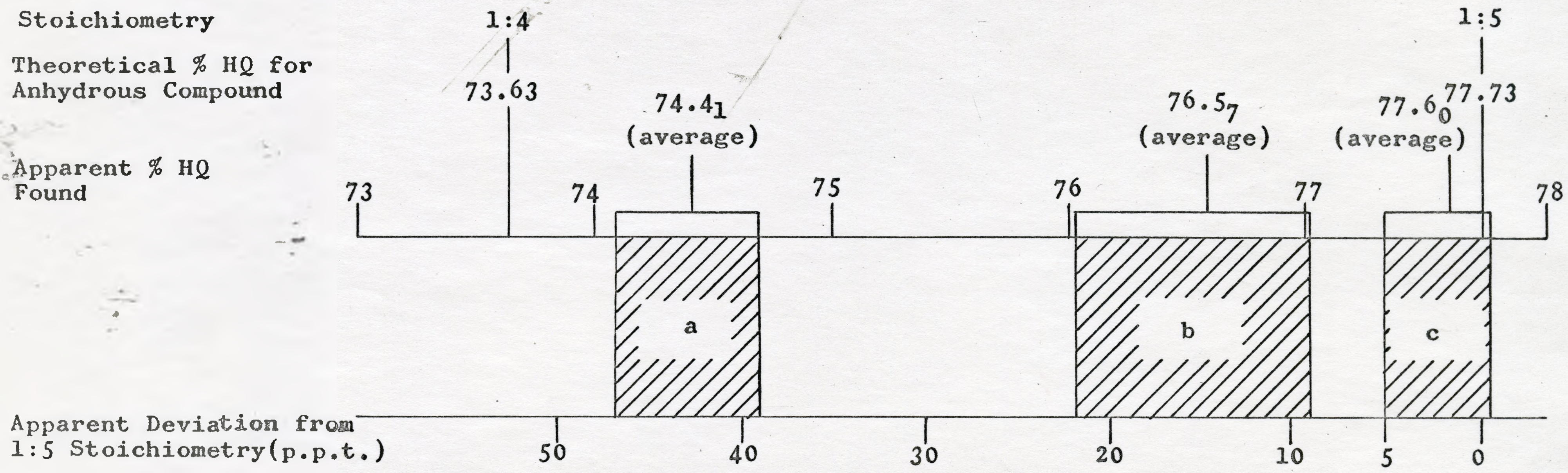

Figure 6

Apparent Composition of Thorium 3-Methyl-8-hydroxyquinolate: Ranges of Results by(a) Direct-Weighing Method;(b) Dry-box Method;(c) Vacuum-Drying Method tent of organic ligand in the compound is quite dramatic. By the so-called direct-weighing method, the average content of HQ is apparently only 11 parts per thousand removed from the value corresponding to a compound with 1:4 stoichiometry. Yet, with the vacuum-drying method, the results span the value corresponding to a 1:5 compound, and the mean value is within 2 parts per thousand of it.

The procedures employed may conceivably change the stoichiometry of the compound that is precipitated, but this is indeed unlikely. Under the severest condition of treatment, the vacuum-drying method, significant volatilization of the thorium chelate or HQ might occur (as well as the loss of water): the loss of 1:5 chelate or the loss of HQ itself cannot raise (as was found) the percentage of 3-methyl-8-hydroxyquinoline in the product that remains. In the vacuum system, there was no evidence of products of decomposition or volatilization (with the exception of water). Apparently, the conditions (pressure, temperature, time) of this treatment method were not sufficient to cause any significant degradation of the compound. The only difference in the treatment steps is the dryness of the atmosphere to which the precipitate was exposed, and in which it was weighed.

From the vacuum-drying data, it is apparent that thorium 3-methyl-8-hydroxyquinolate does exist as a compound of 1:5 stoichiometry.* This data was obtained with samples separately prepared (in the main) and with samples that were very extensively washed; accordingly, the possibility that the results arise from a fortuitous amount of co-precipitated reagent is very slight indeed.

In samples prepared under more ordinary conditions, apparent

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*Earlier work (11) had established that the compound had a thorium content appropriate for a compound of 1:5 stoichiometry.

variations from a 1:5 stoichiometry are due to the presence of water in the product. Both the gravimetric and bromometric results of the various methods exhibit the trend which is expected if the compound is hygroscopic, i.e., as the apparent HQ content of the product approaches the theoretical value, the gravimetric data tend toward the expected weight. The averages of the data drawn from Table I and II are summarized in Table XI. The absorption or holding of water by thorium 3-methyl-8-hydroxyquinolate also accounts for several observations:

TABLE XI

ANALYSES OF THORIUM 3-METHYL-8-HYDROXYQUINOLATE

Method	Apparent HQ Content (%)	Weight of Precipitate (mg.)
Direct Weighing*	$74.4_1 \pm 0.1_6$	154.2 ± 0.5
Dry-Box Transfer	$76.5_7 \pm 0.3_1$	150.9 ± 0.6
Theoretical	77.73	149.7 ± 0.2

*There is reason to believe, that, for the direct weighing procedure, a strict comparison of the bromometric data with the gravimetric data is not fair: the former data was obtained from a sample of the compound which yielded the latter data. Since the compound is hygroscopic, the material analyzed for HQ may be different material than was weighed for the gravimetric determination. The dry-box data does not suffer from this deficiency.

A footnote to Table I draws attention to the fact that about half the samples (Nos. 10-18 inclusive) in that table experienced a significant increase in their weight on the balance pan, which is consistent with the proposed explanation. The percentage HQ in the determinations Nos. 3 to 6 inclusive, in which the weight gain was not noticed, are generally even lower than those where the weight gain was noticed. This indicates that an appreciable amount of water had been absorbed before these samples were weighed.

In the experimental section concerned with the vacuum-drying method, it was mentioned that thorium 3-methyl-8-hydroxyquinolate had a pronounced tendency to "bump" at reduced pressure in a container of design B (Fig. 1). The compound would quite unpredictably "boil" and become distributed throughout the vacuum system, at pressures between 7 mm. and 1 mm. Water vapour apparently was trapped in the bed of the precipitate until sufficient pressure developed to release the trapped vapour. This release was violent enough to scatter the compound quite effectively. When design C (Fig. 1) was used, the depth of the bed of precipitate was greatly decreased and the water vapour could escape without the explosive bumping occurring, provided the reduction of the pressure was gradual.

As the pressure was reduced and the compound was heated, its colour changed slowly from orange-yellow to pure orange. This colour change was most marked at a pressure of about 0.2 mm. The colour change also occurred when the metal chelate was desiccated over phosphorus pentoxide. Gradually the orange-yellow colour would return on the surfaces of the precipitate when the orange compound was exposed to the air of the room. Almost certainly, this colour change is associated with the absorption of water by the metal chelate.

Moreover, in all probability, the spread of the gravimetric data in Tables I and II for the direct-weighing and dry-box transfer methods is largely a reflection of the hygroscopic nature of the compound: the extent of water absorption is related to the humidity, length of time which the compound is exposed to the air, and the particle size, all of which would vary from sample to sample. (These data in turn are incorporated in the apparent HQ content calculations and therefore, in part, are responsible for the spread of the data summarized in Fig. 6*). From the data of Table II, it is seen that the per cent average deviation of the gravimetric results is 0.4%, a value very close to that (0.5%) found by Corsini (75). Since the bromometric titrations are intrinsically precise and the bromometric results are independent of adventitious water, one would expect that, if indeed the compound is hygroscopic, the bromometric results would show significantly less scatter. This was in fact found by Corsini, whose bromometric results have per cent average deviation of only 0.09%. The per cent average deviation for the bromometric results in the present work (0.2_6%) is a little better than that of the gravimetric results, but not the equal of that obtained by Corsini. This is reasonable, however, in the view of the greater manipulations, with accompanying mechanical losses, in the method of the present work compared to the method of Corsini.

It should be mentioned that the only other work on thorium 3-methyl-8-hydroxyquinolate, that of Corsini (75), yielded data consistent with that of the present work. From this data, a percentage HQ of 75.7_8 may be calculated. This is lower than the average of the dry-box data (76.5_7%), which is to be expected by virtue of differences in the atmospheric conditions of the two procedures.

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*In the vacuum-drying method, the conditions are probably reproducible to a greater degree than in the other methods; such spread in the data as exists is most likely related to the technique of weighing by difference, in which the sample container was relatively heavy.

pH Dependence of the Precipitation of Thorium 3-Methyl-8-hydroxyquinolate and Related Compounds

The data of Table IV, relating pH of precipitation of thorium 3-methyl-8-hydroxyquinolate to the completeness of its precipitation (as a 1:5 chelate) are plotted in Fig. 7. Under the conditions (of concentration of reagents, buffer, temperature) used in this work, the pH of incipient precipitation is very close to 2.9, and precipitation is substantially complete below a pH of 5, very possibly at pH 4.2.

Bromometric analyses of precipitates formed at pH values in the range 5.6-7.1 give values for the completeness of precipitation up to 99.7%, with the mean value being 99.3%. The true value may well be higher than this, because significant solubility losses may have been incurred by the extensive washing these precipitates were given. (The washing was deliberately extensive because experiments were primarily designed to yield very pure products, for the study of their composition.) In any event, the precipitation of thorium from these solutions, containing the element at a concentration of only 2×10^{-3} M, is at least very close to being quantitative. The value of 99.3% for the 3-methyl-8-hydroxyquinoline compound may be compared with the value of 99.8% found (33) for the 2-methyl-8-hydroxyquinoline compound.

Another comparison with the 2-methyl-8-hydroxyquinoline compound is more interesting, *viz.*, a comparison of the positions of the precipitation curves along the pH axis. Such a comparison can properly be made, and possible reasons for differences can usefully be discussed, only if the concentration of reagents and the temperature are similar in the cases being compared, because such conditions affect the position (on the pH axis)

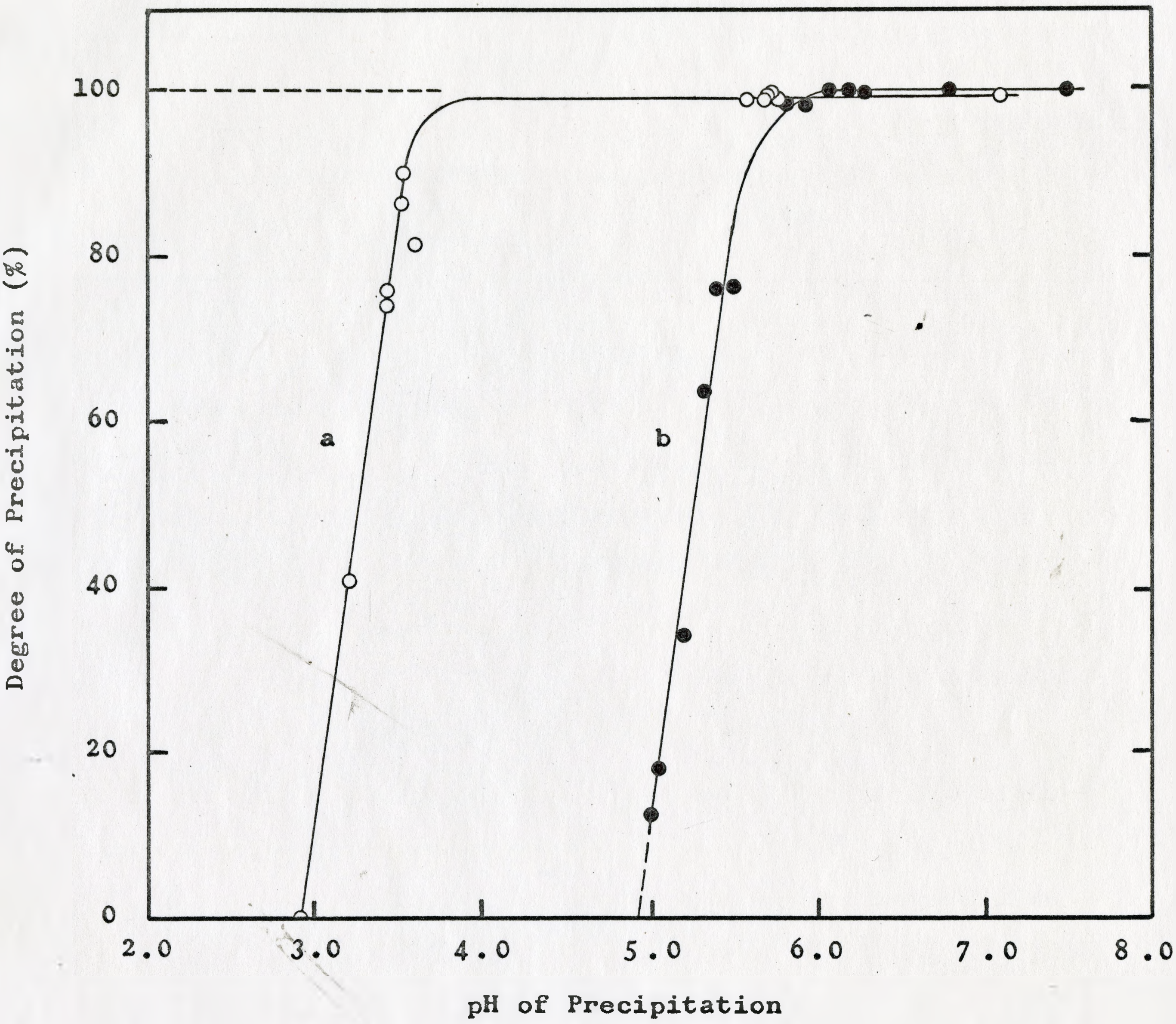

Figure 7

pH Dependence of Precipitation of
Thorium 3-Methyl-8-hydroxyquinolate (a)
in Comparison with that of
Thorium 2-Methyl-8-hydroxyquinolate (b)

of the precipitation curve for a given pair of reactants. In the comparison about to be made, that of the precipitation of thorium 3-methyl-8-hydroxyquinolate, as determined in the present study, with the precipitation of thorium 2-methyl-8-hydroxyquinolate, as determined earlier in this laboratory (33), the conditions are quite similar. In both sets of experiments, the concentration of thorium was 2 x 10^{-3} M, and in both sets of experiments, there were seven moles of precipitant for each mole of thorium. (it is true that, since the 2-methyl compound precipitates as a 1:4 chelate and the 3-methyl compound precipitates as a 1:5 chelate, the excess of reagent in the two instances is different - about 70% in one case and about 40% in the other - but an equalizing of the excesses could not eliminate but would in fact increase the difference that is to be accounted for.)

As has been pointed out (33), when all conditions are comparable, the difference in the pH of precipitation for the chelates of a given metal with two related reagents should reflect differences in the intrinsic solubility (76) and stability of the chelates, and the acidity of the reagents. Generally, the stability of the chelate and the acidity of the reagent are related, a given metal forming the more stable chelate with the weaker acid (77). When this is so (and assuming the intrinsic solubilities of the chelates to be the same), then the pH of precipitation should be the resultant of one effect that operates to lower it and another that operates to raise it (33). The nature of these effects will be discussed presently, but first it needs to be pointed out that what was just said above about a given metal forming the more stable chelate with the weaker acid is not always true, and in fact should not be true in the instance of

2-methyl-8-hydroxyquinoline and 3-methyl-8-hydroxyquinoline. The argument for this is as follows.

Although no measurements of the stabilities of the metal chelates of 3-methyl-8-hydroxyquinoline have as yet been made, it can be predicted that they are very close to those of the corresponding chelates of 8-hydroxyquinoline. This follows from the fact that these two reagents have essentially identical pK_{NH} and pK_{OH} values (Table XII). The two reagents have substantially the same affinity for protons; accordingly, they should have substantially the same affinity for a given metal-ion, there being no reason to suppose that a methyl group in the 3-position should affect chelation in the 1- and 8-positions.

TABLE XII

IONIZATION CONSTANTS FOR 8-HYDROXYQUINOLINE AND RELATED REAGENTS

Reagent	pK_{NH}	pK_{OH}	Method and Reference*
8-hydroxyquinoline	4.92	9.71	Spectrophotometric, Phillips and Merritt (78)
3-methyl-8-hydroxyquinoline	4.94	9.75	Spectrophotometric, Phillips (63)
2-methyl-8-hydroxyquinoline	5.55	10.31	Spectrophotometric, Phillips and Merritt (78)

*Based on the method of Stenstrom and Goldsmith (79)

On the other hand, 2-methyl-8-hydroxyquinoline is a distinctly weaker acid that either 8-hydroxyquinoline or its 3-methyl derivative (Table XII), and so one might expect that a given metal-ion would form the most stable chelate with the 2-methyl compound. Actually, however, stability measurements (in 50% aqueous dioxane) show that the chelates of 2-methyl-8-hydroxyquinoline are somewhat less stable than the corresponding 8-hydroxyquinoline chelates (48,49). This is attributed to a steric hindrance to chelate formation by virtue of the methyl group in the 2-position of the reagent, the steric effect outbalancing the otherwise more favourable disposition of the 2-methyl compound toward forming stable chelates. When the methyl group is in the 3-position, no steric hindrance to chelate formation is expected and, the acidities of 8-hydroxyquinoline and the 3-methyl compound being the same, one can expect that the chelates (with a given metal) of 2-methyl-8-hydroxyquinoline should be less stable than those of 3-methyl-8-hydroxyquinoline.

If this is accepted, then one can predict that, under comparable conditions of concentrations, etc., the precipitation curve for the 2-methyl-8-hydroxyquinoline chelate should be at a higher pH value than that for the 3-methyl-8-hydroxyquinoline chelate (of the same metal). This follows because the more stable of the two chelates, that of 3-methyl-8-hydroxyquinoline, does not require as high a concentration of the chelating anion to bring about its precipitation, i.e., if the two reagents had the same acidity, the 3-methyl chelate would precipitate at a lower pH. Actually, however, 3-methyl-8-hydroxyquinoline is the stronger of the two acids (Table XII), and so dissociates more readily, providing the required concentration of the chelating anion at a lower pH than the weaker acid, 2-methyl-8-hydroxyquinoline. Thus, for these two reagents, the two effects should work in concert to separate the positions of the precipitation curves along the pH axis, with the curve for the thorium 2-methyl-8-hydroxyquinolate being at the higher pH values.

The experiments with the thorium chelates of 3-methyl-8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline, summarized in Fig. 7, show this predicted displacement unambiguously, the curve for the 2-methyl compound being a full 2 pH units beyond that for the 3-methyl compound. This concurrence with prediction provides substantial support for the validity of the theoretical concepts that have been proposed as factors governing the precipitation of metal chelate compounds.*

A comparison has been made earlier (33) between the precipitation of thorium 2-methyl-8-hydroxyquinolate and thorium 8-hydroxyquinolate, and this comparison, supports the theory, too. But the work with 8-hydroxyquinoline (8) on which that comparison is based is open to question on more than one count. For example, in the early work of Gotô (8) the exact conditions of the precipitation are not clear. He states that the precipitation was done "by a method similar in every respect to that for uranium" as reported in the literature (4) and that the investigators referred to had shown this to be possible. In point of fact, these workers (4) reported two different procedures, one for thorium and one for uranium. Also, it is difficult to understand how Gotô could have precipitated thorium 8-hydroxyquinolate as an exact 1:4 chelate (which his data implies) throughout his entire pH range, in view of all the subsequent studies in which a compound of 1:5 or approximately 1:5 stoichiometry was precipitated, and the work in the com-

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*Only if large differences in intrinsic solubility and/or proneness to supersaturation existed, would a reversal of the positions of the curves of the 2-methyl-8-hydroxyquinolate and the 3-methyl-8-hydroxyquinolate chelates be expected; neither of these is probable, nor does either appear to be so, since the values for the pH of precipitation are so distinctly separated.

position of thorium 8-hydroxyquinolate to be discussed later in this thesis.* Even apart from this, one cannot make as proper a comparison of the precipitation curves for the thorium chelates of 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline as one would like because, although similar concentrations of thorium and acetate buffer were used in the studies with 8-hydroxyquinoline (8) and 2-methyl-8-hydroxyquinoline (33), the relative concentrations of reagents were somewhat different (ten moles of 8-hydroxyquinoline, per mole of thorium, compared to seven moles of 2-methyl-8-hydroxyquinoline).

Thermal Preparation of 1:4 Thorium 3-Methyl-8-hydroxyquinolate

In the thermogram of thorium 3-methyl-8-hydroxyquinolate (Fig. 2), two features are of particular interest at this point in the discussion: they are the small plateau between 110°C. and 150°C., which is assumed to be due to the anhydrous 1:5 metal chelate, and the large, gently sloping, plateau beginning at about 215°C. By equating the distance between the small plateau and the plateau for thorium dioxide (about 500°C. upwards) to the weight loss corresponding to the conversion of 1:5 thorium 3-methyl-8-hydroxyquinolate to thorium dioxide, one can calculate the position of a line on the thermogram corresponding to a 1:4 species. This line very closely corresponds to the large sloping plateau beginning at 215°C., as is

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*Another aspect of Gotō's work, although not directly related to a comparison of the initial portions of the precipitation curves, raises questions. Even though it had been reported earlier (4) that tartrate ion interferes in the precipitation of thorium, an observation that has had more recent support (80), the upper portion (pH 7.9 and above) of Gotô's precipitation curve was determined in the presence of a massive excess of tartrate (a molar ratio of tartrate to thorium of 64:1); yet he reports quantitative precipitation of thorium up to a pH of 8.8!

shown in Fig. 2. This strongly suggests the existence of a 1:4 compound.

Attempts at the thermal preparation of the 1:4 metal chelate were encouraging. As the data in Table V indicate, the bright yellow material which was the result of heating at elevated temperatures contained approximately the appropriate percentage of 3-methyl-8-hydroxyquinoline for a 1:4 chelate, but the results, on the average, were low by 10 parts per thousand. The percentage weight loss on heating was very constant, suggesting that a true compound had been formed. The less rigorous conditions for thermal conversion (1.1 or 1.7 hr. at 200°C., compared to 1.8 hr. at 220°C.) give the better results (i.e., 73.3 ± 0.2% compared to 72.6 ± 0.1%; theoretical; 73.63%). This behaviour might be expected, since the plateau on the thermogram is really a slope, not a flat level. Thus, critical control of time and temperature would be necessary for the thermal preparation of pure 1:4 thorium 3-methyl-8-hydroxyquinolate, but it almost certainly could be done, as Corsini (11) suggested.

Thermal Studies with Thorium 3-Methyl-8-hydroxyquinolate

Thorium 3-methyl-8-hydroxyquinolate was studied by thermogravimetric analysis (T.G.A.), differential thermal analysis (D.T.A.), and also, careful observation during a melting-point determination. (The heating rate in the melting-point determination was generally between 2° and 5°C. per minute.) The results of these methods may be profitably discussed together, but first a few precautionary remarks should be made.

None of the D.T.A. temperatures have been corrected for thermocouple errors. (At a scale reading of 400.0°C., the corrected temperature is 390.5°C.) Also, temperatures of the melting-point observations are uncorrected. In any event, temperature comparisons involving the three sets of data may not be very accurate, since the observed temperature of a thermal event is dependent on many uncontrolled variables: these include the sample characteristics (degree of packing, caking or pulverizing, etc.); the sample size; the furnace conditions (the size and design of both the furnace and sample holder); and, of great importance, the heating rate. Bearing these points in mind, there still is, however, much correlation in the data.

The observations at low temperatures in the thermal experiments are consistent with loss of water from the compound. As the sample was heated, the T.G.A. curve (Fig. 2) shows a significantly decreasing weight to about 110°C., and from this temperature to about 150°C. a slightly sloping plateau, which is most likely due to the 1:5 metal chelate. A colour change from yellow-orange to orange starting at about 70°C. was observed in the melting-point determination; this colour phenomena was earlier associated with the loss of water. The D.T.A. curve (Fig. 3,a) exhibits a gently curving endothermic trend in this temperature range, which is in agreement with loss of water.

From about 150°C. to about 215°C. on the T.G.A. curve, a large weight loss is recorded until the sloping plateau of the 1:4 chelate is reached. Visually, the sample's colour changed from orange to bright yellow; this occurred slowly from about 150°C. to about 200°C., but most rapidly at about 172°C.; the sample remained solid. The D.T.A. curve is very "active" in this temperature range. Its predominant feature is a sharp endothermic peak (max. temp.: 167°C.) with a shoulder endotherm (max. temp.: about 154°C.) and perhaps an exothermic peak (max. temp.: about 157°C.). Sharp peaks on a D.T.A. curve are diagnostic of phase or crystal transitions, while broader peaks generally are representative of pyrolysis or oxidation of the sample. The marked activity is undoubtedly connected with the thermal decomposition of the 1:5 compound to the 1:4 compound by the loss of 3-methyl-8-hydroxyquinoline.

At 212°C. in the determination of the melting point, the bright yellow sample was observed to shrink to a brownish-yellow "cake". The next sharp endotherm (max. temp.: about 221°C.) on the D.T.A. curve probably corresponds to this reaction but its exact nature is as yet undetermined. The T.G.A. method, which indicates only a small continuous weight loss in this temperature region, is insensitive to the loss of hydrogen or other light gases or vapours. A polymerization reaction similar to these postulated in the pyrolysis of other metal 8-hydroxyquinolates (81) may occur or, perhaps, there is a structure collapse or rearrangement following the removal of the 3-methyl-8-hydroxyquinoline.

The broad peak at about 290°C. on the D.T.A. curve is probably due to decomposition or volatilization of the 1:4 chelate, since the sample was still solid; the onset of an exothermic trend in the D.T.A. curve indicates that oxidation is playing an increasingly important rôle in the decomposition of the sample. The T.G.A. curve indicates a more rapid weight loss at about 280°C. which steadily becomes greater until, following 340°C., the curve falls very quickly. The rounded D.T.A. exotherm (max. temp.: about 355°C.) is probably due to this oxidative pyrolysis.

In each of the methods of observation, some event is recorded as occurring during the oxidative pyrolysis, but its nature is as yet undetermined: the first sharp break in the otherwise rapidly falling portion of the T.G.A. curve occurs, at about 341° to 348°C., and a small D.T.A. endotherm (max. temp.: about 372°C.) may be correlated with this break;

moreover, the colour darkened to a deeper brown, at about 340°C.

The last sharp endotherm (max. temp.: about 380°C.) on the D.T.A. curve corresponds closely to the start of the second break in the T.G.A. curve (365°-380°C.), and visually the compound melts at about 370°C. to a black tar. The oxidative pyrolysis to thoria is then completed, the T.G.A. curve drops to the large flat plateau (about 500°C. upwards) and the D.T.A. curve assumes an irregular behaviour with a slight exothermic trend.

Another technique, that of effluent gas analysis, may be used to investigate the gaseous products of decomposition; this knowledge could be very useful in assigning the origins of the peaks on the D.T.A. curve. This information together with values for thermodynamic functions (which may be obtained from quantitative D.T.A.) might be very useful in elucidating the bonding of the so-called "extra" molecule of reagent.

Analytical Properties of Thorium 3-Methyl-8-hydroxyquinolate

In this study, it has been shown that thorium may be precipitated by 3-methyl-8-hydroxyquinoline as a pure compound of strict 1:5 stoichiometry, but the precipitate is hygroscopic. Conditions have been established in which this precipitation is at least 99.3% complete. These results have some analytical significance.

The direct determination of thorium by means of 3-methyl-8-hydroxyquinoline cannot be recommended. In a gravimetric method in which the weighing form is a metal chelate, too many problems are encountered. The hygroscopic nature of thorium 3-methyl-8-hydroxyquinolate, under ordinary circumstances, will lead to inaccurate (high) results and poor precision may be expected. Also, the thermal characteristics of this compound are inappropriate; the sloping plateau on the T.G.A. curve of the 1:5 chelate indicates that some volatilization or decomposition may be occurring, and the conditions of the thermal conversion of the 1:5 compound to the 1:4 species are likely too critical for the latter to be a useful weighing form. Although ignition of the compound to thorium dioxide is possible, the favourable gravimetric factor would be lost.

On the other hand, since thorium 3-methyl-8-hydroxyquinolate can be quantitatively precipitated as a compound of strict stoichiometry, any method for the determination of 3-methyl-8-hydroxyquinoline can become the basis of an indirect method for the determination of thorium. For example, the bromometric determination (Table IV, Detn. Nos. 8A-13A, inclusive) of thorium was done with a precision of 3 parts per thousand (average deviation on six results) and fair accuracy; the inaccuracy, of 7 parts per thousand, may be accounted for by the solubility and mechanical losses discussed earlier. These indirect determinations should be sensitive in two meanings of the word: the metal to reagent ratio (1:5) is very favourable, and the present work has shown that thorium can be determined by this method in concentrations at least as low as 2 x 10^{-3} M.

The stoichiometric nature of thorium 3-methyl-8-hydroxyquinolate and its precipitation properties, together with the feasibility of determining 3-methyl-8-hydroxyquinoline polarographically, lead to an indirect method of determining thorium.

From Fig. 5, it is seen that the diffusion current due to the reduction of 3-methyl-8-hydroxyquinoline in a sodium hydroxide-disodium hydrogen phosphate buffer (pH 11.3) is linearly proportional to the concentration of 3-methyl-8-hydroxyquinoline over at least the range

1.5×10^{-4} M to 1.5×10^{-3} M.

The polarographic wave is of good form over this range and easily measureable. The slight variation of the diffusion current with pH that was noticed (about 0.05 microamperes per pH unit) was of no significance in view of the buffer capacity of the solution. There is no problem with the stability of 3-methyl-8-hydroxyquinoline in the solutions used; it was polarographically stable for at least 36 hr.

Even though the precision obtained ($\pm$ 2 to $\pm$ 3%) is very acceptable for a polarographic technique, this method is not as precise as the bromometric procedure for the determination of thorium. The polarographic method, however, is sensitive, being capable of determining thorium concentrations at least as low as 1×10^{-4} M.

One hazard of this method is the possibility of coprecipitation of 3-methyl-8-hydroxyquinoline in the precipitation of the thorium compound, particularly when small amounts of thorium ($\leqslant 13$ mg.) are involved. Extensive washing appears to overcome the difficulty (as evidenced by the linearity of the calibration curve); very likely it could also be overcome by using a lesser excess of 3-methyl-8-hydroxyquinoline in precipitating such small amounts of thorium.

Composition of Thorium 8-Hydroxyquinolate

The technique of vacuum-drying, developed for thorium 3-methyl-8-hydroxyquinolate, was applied to thorium 8-hydroxyquinolate (prepared from an acetate buffer at pH 5.0-5.6, using nine moles of 8-hydroxyquinoline per mole of thorium). The results were gratifying: the average of 3 determinations of 8-hydroxyquinoline content (Table VI) was less than 1 part per thousand higher than the theoretical value for a compound of exact 1:5 stoichiometry, and the results were precise (an average deviation of less than 2 parts per thousand).

As was pointed out in the Introduction, there is a confused and confusing literature on thorium 8-hydroxyquinolate, with the existence of a compound such as $ThQ_4 \cdot HQ$ or $HThQ_5$ still in question. The present work supports the view that a compound of this exact stoichiometry does indeed exist, and also accounts for the fact that some investigators have claimed to have prepared it whereas others have doubted its existence. The truth of the matter is that the thorium-8-hydroxyquinolate system is complex: more than one compound can be precipitated, and what is obtained depends on the conditions of precipitation.

The realization of the complexity of this system came during precipitation studies with thorium 8-hydroxyquinolate which were initially undertaken to establish its pH-precipitation curve, relative to that of thorium 3-methyl-8-hydroxyquinolate and thorium 2-methyl-8-hydroxyquinolate. (Earlier work (8) bearing on the pH-precipitation curve for thorium 8-hydroxyquinolate is open to some question, as has been pointed out earlier.)

In brief, the following was found: a yellow compound or compounds can be precipitated; an orange compound or compounds, with an 8-hydroxyquinoline content quite different from the yellow compound, can be precipitated; moreover, under appropriate conditions of pH and digestion, the orange material will convert to the yellow material.*

The experiments that are summarized in Tables VII-X allow some

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*During the course of this work, it was learned that studies of this same system were underway in the laboratory of Dr. L. Gordon of the Case Institute of Technology, and that he, too, had concluded that the composition of the precipitate was dependent on the conditions of precipitation.

reasonably firm, and other tentative, conclusions to be drawn but, because of the way in which the phenomena came to notice and the limited time that has so far been given to the study of it, the experiments are of preliminary nature and not as systematic as they could be.

With these limitations in mind, the following may be said, based on the data of Tables VII-X. The yellow compound(s) is favoured by a low pH (< 4) and, at such a pH, by long digestion periods. The direct analysis of this yellow material, after it has been dried for 3 hr. at 60°C. (but not in vacuo) shows it to have an 8-hydroxyquinoline content of close to 58.1% and, after drying for 3 hr. at 50°C. at 40 mm. pressure*, a thorium content close to 31.9%. These experimental values correspond to a molar ratio, HQ/Th, of 2.9. Indirectly, from elemental analyses (Table X), an HQ/Th molar ratio of slightly less than 3.2 can be deduced. Thus two lines of evidence point to this ratio being 3. The analytical data show that about 10% of the substance is something other than thorium and 8-hydroxyquinoline and that, in fact, it is largely oxygen. More than one argument can be adduced that the oxygen is not in the form of either acetate (82) or nitrate (which are present in the solution, the former particularly in high concentration). In fact, all the data so far available on this substance is consistent with the formulation ThQ_3OH (or, equally well, the dimer, $Th_2Q_6(OH)_2$) together with a few per cent of water. The water could be sorbed, occluded, or water of hydration. (If the substance is a hydrate, the data accord best with the formulation $ThQ_3OH \cdot 3H_2O$.)

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*The gravimetric data indicated that this method of drying at a reduced pressure was not more efficient than the ordinary procedure of air-drying at 60°C.

As the pH of precipitation is raised, the formation of an orange compound, with an 8-hydroxyquinoline content of greater than 70%, is favoured. As might be expected, so also is a greater extent of precipitation favoured as the pH is raised. From pH 4.6 upwards, however (with the excess of reagent, digestion time, etc. used in these experiments) the effect is predominantly that of increased degree or extent of precipitation, rather than change in composition. Thus, between pH 4.6 and 5.2 (with otherwise identical conditions of precipitation) the weight of precipitate increased by 14%, but the percentage of 8-hydroxyquinoline in the precipitate by only 0.4%. With the most favourable conditions, the percentage of 8-hydroxyquinoline in the precipitate attained a value of 73.7 ± 0.1%, but this, it is to be stressed, is as determined in precipitates that had been "dried" under the relatively mild conditions of 3 hr. at 60°C. in air. These results are reproducible as shown, for example, in Table VIII. This value is well below that of the 8-hydroxyquinoline content of pure (anhydrous) thorium 8-hydroxyquinolate of 1:5 stoichiometry (76.10%), and well above that of thorium 8-hydroxyquinolate of 1:4 stoichiometry (71.80%).

When, however, a precipitate was prepared in precisely the same way* but dried <u>in vacuo</u> at 53°C., the percentage of 8-hydroxyquinoline rose from $73.7_6 \pm 0.0_8\%$ (Table VIII) to $76.1_5 \pm 0.1_4\%$ (Table VI). This latter value is in strict accord with the theoretical value for an anhydrous 1:5 chelate.

The data is consistent with the orange material, as analyzed after only air-drying at 60°C., being 1:5 thorium 8-hydroxyquinolate together

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*The methods were identical with regard to thorium concentration, excess of reagent, buffer system, time and temperature of digestion, etc.

with some water, which may be sorbed, occluded, or water of hydration. (If the orange compound were $ThQ_4 \cdot HQ \cdot 2H_2O$, its 8-hydroxyquinoline content would be 73.3%; the content found was 73.7 ± 0.1%.) This assumption of water in the air-dried material accounts for the fact that there is obtained a weight of precipitate that is significantly (and appropriately) higher than that expected (from the thorium titer of the solution) for the quantitative precipitation of an anhydrous 1:5 chelate while at the same time the absolute amount of 8-hydroxyquinoline contained in the precipitate corresponds closely (97.9-98.8%) to the amount expected for the quantitative precipitation of a 1:5 compound (groups E and F in Table VII, at pH values 4.8 and above).

It is apparent that a gravimetric procedure for thorium based on a weighing of the 1:5 chelate would involve either rigid and elaborate drying conditions or a standardized conventional drying procedure combined with an empirical correction factor for the moisture content: both of these alternatives are unattractive. On the other hand, a bromometric procedure appears very feasible, capable of determining thorium at a level at least as low as 2×10^{-3} M with an accuracy of at least 98-99%, with apparently high precision (± 2 parts per thousand).

This investigation, preliminary though it is, sheds light on the confusion and disagreement in the literature concerning thorium 8-hydroxyquinolate. In the past, there has been a lack of awareness of the fact that more than one substance containing thorium and 8-hydroxyquinoline can be precipitated, and that what is precipitated depends on the conditions of precipitation. Different investigators have used different conditions, and not always well-defined ones, either. Bearing this and the now known complexity of the system in mind, it is quite conceivable how, three decades after the first report (6) of a 1:5 thorium 8-hydroxyquinolate, Gordon et al. (12) report that this "compound" has uncertain composition, and Crouthamel and Johnson (13) also find it to be non-stoichiometric and to contain an appreciable amount of water. Even neglecting consideration of the variables that complicate thermogravimetric studies, it is little wonder that disagreement on the thermal behaviour of 1:5 thorium 8-hydroxyquinolate exists, since most of the investigators (6,7,9,13-19) have not used carefully controlled conditions of precipitation.

There are many unresolved questions about thorium 8-hydroxyquinolate. A thorough study of the system, with strict control of the variables, should be made.

Thermal Studies with Thorium 8-Hydroxyquinolate and Thorium 2-Methyl-8-hydroxyquinolate

The D.T.A. curve of thorium 8-hydroxyquinolate in air is shown in Fig. 3,b; the general features of this curve correspond closely to the curve reported for the same compound in an argon atmosphere (23). The authors of the latter paper assign the origin of the sharp endothermic peak at about 150°C. to "the desolvation of the complex from the 5:1 to the 4:1 chelate" and suggest that the presence of a small shoulder peak, with a maximum temperature at 140°C., could be explained by a two-step decomposition which had previously been proposed in a T.G.A. study (19). There is some doubt as to whether this comparison is a valid one: in the T.G.A. work, the proposed reactions occurred about 100°C. apart, while the endotherms in the D.T.A. are only about 10°C. from one another.

In the present work it was also concluded that the "activity" in this region (140°-155°C.) of the D.T.A. curve is associated with the removal of a molecule of 8-hydroxyquinoline. A colour change over the temperature range 120°-190°C. (occurring most rapidly at about 130°C.) from yellow-orange to yellow occurs while the major portion of the sample remained in the solid form. It has been established (83) that a 1:4 thorium chelate may be prepared thermally from the 1:5 complex in this temperature range provided conditions are controlled carefully. When observations from the melting-point determination were considered in conjunction with the D.T.A. curve, it was concluded the remaining two large endotherms (max. temp.: about 303° and 390°C.) were due to reactions involving structural rearrangement or volatilization of some constituent, and a melting of the solid to a black tar, respectively.

The D.T.A. curve of thorium 2-methyl-8-hydroxyquinolate (Fig. 3,c), is similar to the curve established in an inert atmosphere (23). T.G.A. curves of thorium 2-methyl-8-hydroxyquinolate, which are essentially in agreement with one another, have been reported (57,46,33). In what follows, attention is drawn to the correlation which exists among the T.G.A. curve, the D.T.A. curve, and the melting-point determination.

The bright yellow colour of the compound changed little until about 260°C. From this temperature to about 360°C., a gradual darkening of the colour occurred. The D.T.A. curve shows a curving exothermic trend from about 250°C., which becomes a rounded exotherm (max. temp.: about 368°C.) and in the range 360° to 400°C., the colour changed more quickly from brown-yellow to brown. The T.G.A. curve (57) remains nearly level to about 300°C., and then the single, rapid weight loss (which is its only prominent feature) begins. All of this data is consistent with the oxidative pyrolysis of the metal chelate.

There is a slowing or levelling of the T.G.A. rapid drop from about 360° to 435°C., where the plateau of the thorium dioxide is reached (57). The small D.T.A. endotherm (max. temp.: about 400°C.) may correlate to some event near the start of this break in T.G.A. curve. At about 404°C., in the melting-point determination two events occurred together: the compound shrank rapidly and the colour darkened further to brown-black. These events may be the origin of the shoulder (max. temp.: about 434°C.) on the D.T.A. endotherm (max. temp.: about 438°C.). This latter peak is probably due to the melting of the compound to a black tar, which was observed visually at about 416°C. The trend of the D.T.A. curve becomes exothermic again as the pyrolysis to thorium dioxide is completed.

The D.T.A. curves of thorium 3-methyl-8-hydroxyquinolate and thorium 8-hydroxyquinolate are similar to one another, featuring three prominent endotherms, and differ from the D.T.A. curve of the 2-methyl-8-hydroxyquinolate chelate, which has only one prominent endotherm.

Comparison of 3-Methyl-8-hydroxyquinoline, 8-Hydroxyquinoline, and 2-Methyl-8-hydroxyquinoline in their Reaction with Thorium

From the present study on thorium 3-methyl-8-hydroxyquinolate, it is evident that its properties resemble those of thorium 8-hydroxyquinolate, and both these compounds differ significantly from thorium 2-methyl-8-hydroxyquinolate.

This is apparent in the compositions of the chelates that may be prepared. Thorium compounds of both 3-methyl-8-hydroxyquinoline and 8-hydroxyquinoline with strict 1:5 stoichiometry can be prepared; as ordinarily prepared, however, these compounds contain significant amounts of water, which accounts for apparent deviations from this composition. On the other hand, thorium 2-methyl-8-hydroxyquinolate has only a 1:4 stoichiometry. The 1:4 thorium chelate of 8-hydroxyquinoline and, in all likelihood, that of 3-methyl-8-hydroxyquinoline can be prepared thermally; in these reactions, the colour changes (orange to bright yellow) are similar.

The similarities between 3-methyl-8-hydroxyquinoline and 8-hydroxyquinoline are also shown in the D.T.A. studies of their thorium chelates, whereas the chelate of 2-methyl-8-hydroxyquinoline behaves differently.

Moreover, the pH of precipitation (incipient and quantitative) of both thorium 3-methyl-8-hydroxyquinolate and thorium 8-hydroxyquinolate are significantly lower than the corresponding values for thorium 2-methyl-8-hydroxyquinolate.

The similarity of 3-methyl-8-hydroxyquinoline and 8-hydroxyquinoline extends beyond analoguous behaviour towards thorium. The present work and an earlier study (68,69) have shown that changes in the shape of the polarographic wave of 3-methyl-8-hydroxyquinoline in the pH range from 7.5 to 13.4 resemble closely the reported behaviour of 8-hydroxyquinoline (84). Paper chromatography (67) has also shown the resemblance; the compounds have very similar ionization constants (63,78); and 3-methyl-8-hydroxyquinoline, like 8-hydroxyquinoline but unlike 2-methyl-8-hydroxyquinoline, will precipitate aluminium-ion (63,69).

Accordingly, the position of the methyl group on the nitrogen-containing ring is very important. In the 2-position, the methyl group produces two effects: there is steric inhibition to bond formation, and the basicity of this atom (and of the phenolic oxygen, too), is considerably increased. These effects can account for most of the differences in the behaviour of 2-methyl-8-hydroxyquinoline and 8-hydroxyquinoline. In the 3-position, however, the methyl group is not capable of sterically hindering chelate formation and the inductive effect of the methyl group is not felt by the nitrogen and phenolic oxygen to any appreciable degree. It is not suprising, therefore, that the 3-methyl compound has properties similar to those of 8-hydroxyquinoline.

SUMMARY

1. Thorium 3-methyl-8-hydroxyquinolate has been shown to be a compound with 1:5 stoichiometry. Apparent deviations from this are due to the presence of water. A method of preparation of the pure anhydrous compound, involving a vacuum-drying technique, has been developed.
2. The pH-dependence of the precipitation of this thorium chelate has been studied. The position of this curve, in relation to those for thorium 2-methyl-8-hydroxyquinolate and thorium 8-hydroxyquinolate, has been accounted for theoretically.
3. The thermal behaviour of thorium 3-methyl-8-hydroxyquinolate has been investigated. The thermogravimetric curve strongly suggests the existence of a 1:4 species. This species can almost certainly be prepared thermally, but rigorous control of the conditions would be necessary.
4. A combination of thermal studies, including thermogravimetric analysis and differential thermal analysis, has thrown light on the complex series of reactions that thorium 3-methyl-8-hydroxyquinolate undergoes on heating.
5. A method of preparation, involving a vacuum-drying technique, of a pure thorium 8-hydroxyquinolate of 1:5 stoichiometry has been developed. Apparent deviations from this composition are due to the presence of water.
6. A preliminary investigation of precipitation conditions has shown

that more than one compound of thorium and 8-hydroxyquinoline can be precipitated from solution. There is evidence that one of these (a yellow compound) may be a hydroxo-complex, ThQ_3OH, which might be hydrated. Another (orange) is the 1:5 complex, which, too, may be hydrated on precipitation.

7. The determination of thorium by 3-methyl-8-hydroxyquinoline has been studied, and a bromometric method has been shown to be precise (± 3 parts per thousand) with at least 99.3% accuracy at thorium concentrations at least as low as 2×10^{-3} M. The gravimetric determination of thorium by this reagent cannot, however, be recommended. Also, the determination of thorium by 8-hydroxyquinoline by a bromometric procedure has been shown to be precise (± 2 parts per thousand) with an accuracy of at least 98-99% at thorium concentrations at least as low as 2×10^{-3} M. A gravimetric procedure for the determination of thorium by 8-hydroxyquinoline is not convenient.

8. A possible method for the polarographic determination of thorium by means of 3-methyl-8-hydroxyquinoline has been developed. The curve relating the diffusion current of 3-methyl-8-hydroxyquinoline to the thorium content of the original solution is linear over at least a tenfold range of concentration of thorium from 2×10^{-4} M to 2×10^{-3} M. The method is precise to ± 3% (or better) of the amount of thorium present, and sensitive to concentrations of thorium at least as low as 1×10^{-4} M.

   Evidence has been provided that the polarographic reduction of 3-methyl-8-hydroxyquinoline, at least in the pH range 10.0-11.3, is diffusion controlled and involves hydrogen ions. A close resemblance between 3-

methyl-8-hydroxyquinoline and 8-hydroxyquinoline in polarographic behaviour has been noted.

9. Studies of composition, pH-dependence of precipitation curves, and thermal properties, all join in illustrating the similarities between thorium 3-methyl-8-hydroxyquinolate and thorium 8-hydroxyquinolate and the differences of these compounds from thorium 2-methyl-8-hydroxyquinolate. Theoretical considerations can account for this.

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