1946

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Recommended Citation

Banks, Charles Vandiver, "New titrimetric methods for thorium " (1946). *Retrospective Theses and Dissertations*. 13197.
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NEW TITRIMETRIC METHODS FOR THORIUM

by

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A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

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1946

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INTRODUCTION

Discovery

The discovery and history of thorium is very interesting. In 1817 Jöns Jacob Berzelius (8) isolated from a Swedish mineral now known as "gadolinite", $Be_2Fe(YO)_2(SiO_4)_2$, what he believed to be a new earth for which he suggested the name "thorine" after Thor, son of Odin, Scandinavian God of War. Seven years later, however, Berzelius (9) concluded that his new earth was a basic phosphate of yttrium, a metal which had been discovered by Gadolin (22) in 1794. In 1828 the dark brown or black mineral "thorite", $ThSiO_4$, was discovered in the syenite on the island of Lövö in the fiord Langesund near Brevig, Norway by H. M. T. Esmark (12). A specimen of this mineral was sent to Berzelius by Jens Esmark (53) who believed it to be the earth of tantalum because of its high specific gravity. In the same year Berzelius, during the investigation of the mineral thorite, was successful in isolating a new earth which he called "thoria" because of its similarity to the former thorine.

Preparation

Metallic thorium was first prepared in an impure state in 1828. Berzelius (11) accomplished this by heating a mixture of potassium and potassium thorium fluoride in a glass tube. The thorium prepared in this manner, like that prepared by J. J. Chydenius (16), L. F. Nilson (45) and others, was contaminated with much thoria. Relatively pure thorium was prepared for the first time in 1914 by D. Lely and L. Hamburger (38). They prepared 99 per cent pure thorium metal by distilling sodium and thorium chloride into an exhausted steel cylinder. The metal thus obtained was compressed into a rod and sintered together by passing an alternating current through it in a vacuum furnace.

Occurrence

The more important minerals of thorium are thorite, orangite, thorianite, and monazite.

Thorite

Thorite, $ThSiO_4$, is mainly composed of thorium orthosilicate but contains small quantities of the cerium and yttrium earths along with silicates of uranium, iron, manganese, copper, magnesium, lead, tin, aluminum, sodium, and potassium. Thorite is usually dark brown or black and contains about 60 per cent thoria. The mineral occurs at Lovo, Brevig, Arendal, and Hitterö in Norway and in various places in the United States.

Orangite

In 1850 A. Krautz (36) discovered the clear orange-yellow mineral orangite which was so named because of its color. For some time thorite and orangite were considered to be different minerals but in 1859, T. Scheerer (48) claimed they were chemically similar and this view was later supported by other investigators.

Thorianite

The jet-black mineral thorianite, $ThO_2.U_3O_8$, was discovered about 1904 (18, 19) while a systematic survey of the economic minerals of Ceylon was being made by the Government of Ceylon with the cooperation of the Scientific and Technical department of the Imperial Institute. In the course of this survey W. D. Holland gave A. K. Coomaraswamy and J. Parsons a sample of a heavy black mineral that he found in gem washings near Balangoda, in the Sabaragamuwa Province. This mineral was sent to W. R. Dunstan at the Imperial Institute where it was analyzed by G. S. Blake. It was found to contain about 75 per cent thoria and W. R. Dunstan suggested that it be called "thorianite".

This rare mineral was the chief source of thorium until the discovery of monazite. Small amounts of thorianite are found in Betroka, Madagascar but the chief deposit is found in Balangoda, Ceylon. Thorite and thorianite were once considered as the only valuable sources of thorium, but they are not now found in large enough quantities to be important as compared with the large deposits of monazite sands.

Monazite

This red-brown colored mineral is essentially an orthophosphate of the cerium group of rare earth elements, but almost invariably contains some thorium, probably as the phosphate (37).

In addition to the mineral monazite, there is also its disintegration product the yellow-brown monazite sand. These sands have been produced by the weathering of rocks (pegmatites, granites and gneisses) which originally contained a very small percentage of monazite. Deposits of monazite sand consists of a fine gravel or sand and is found on river banks and on the seashore in Brazil, North and South Carolina, and Australia. It also occurs in large tracts in the Urals and in very rich and extensive beds in the state of Travancore, India. From 1902-1913 the deposits along the seashores of Brazil supplied most of the World's thoria. These deposits contain about 6 per cent thoria. About 1912 India became a real competitor for the world market for monazite sand and since 1918 India has almost completely controlled the world market. The deposits in India contain about 11 per cent thoria.

From 1893-1910 the Carolina river bed deposits were worked actively but the American supply has been kept from the World's market because of the difficulty of mining and the low (4.3 per cent) thoria content. Recently Brazil has shown some signs of revival and there has been some talk about renewed activity in the Carolinas.

Uses

No particular attention was paid to thorium until C. A. von Welsbach (54) devised the incandescent gas mantle in 1885. At that time the only sources of thorium known were the rare earth minerals and they were not available in quantities large enough to supply any considerable commercial demand. A geological survey was conducted and extensive deposits of monazite sand became available.

The first important commercial use of thorium was in the manufacture of incandescent gas mantles. The first of these were made of lanthana, lanthana and magnesia, zirconia and lanthana, and zirconia and yttria but these were not satisfactory. In 1892 "Welsbach's mixture" was adopted for the manufacture of mantles. Even after numerous attempts, no improvement has been made on this mixture which consists of 99 per cent thoria and 1 per cent ceria.

The use of thorium metal in photoelectric cells, glow tube electrodes and X-ray targets give promise of commercial importance. In addition thorium is used as an alloying material, in the production of tungsten-thorium filaments, and as a catalyst.

Present Analytical Methods

The analytical determination of thorium is important not only for the analysis of monazite sands, the important raw material for the production of different common commercial compounds, but also for the thorium manufacturing industry, for the gas mantle industry, for thorium employed as an alloying constituent, for the branches of industry which use thorium as a catalyst in their processes, and for the electrical engineering industry which produce conduits and condensers. The analysis of thorium is also important for mineralogical researches and for the work on geological time determinations.

A large number of methods have appeared in the literature for the determination of thorium. Practically all of them are based on precipitating out the thorium in some form from an acid or neutral solution, and finishing by a gravimetric method. The precipitate is either ignited to the dioxide directly or dissolved and the thorium precipitated as the oxalate after which it is converted to the dioxide by ignition.

A survey of the gravimetric methods for determining thorium by means of (a) sodium thiosulfate, (b) hydrogen peroxide, (c) potassium azide, (d) sebacic acid, (e) lead carbonate, (f) metanitrobenzoic acid, (g) fumaric acid in a 40 per cent alcohol solution, (h) ammonium oxalate, (i) potassium iodate and (j) sodium hypophosphate has been made by J. P. Bonardi (44).

In addition to these, other gravimetric methods making use of (a) sodium pyrophosphate, (b) 8-hydroxyquinoline, (c) benzenearsonic acid, (d) hexamethylenetetramine, (e) aniline, (f) quinoline, (g) sodium or magnesium sulfite, (h) picrolonic acid, (i) sodium alizarin-3-sulfonate and (j) benzenesulfinic acids have been reviewed by B. Justel (29) and found to leave much to be desired.

There have been relatively few titrimetric methods reported in the literature and these will be discussed in the next section.

Statement of the Problem

Since the large majority of methods that have been devised in the past have been gravimetric and because of the need for a rapid, accurate method for determining thorium in various alloys and mixtures resulting from the recent work on this metal, the titrimetric determination of thorium was investigated.

LITERATURE SURVEY

Precipitation Methods

Molybdate method

In this method thorium is precipitated at room temperature from a 7 per cent acetic acid solution as the normal molybdate.

$$Th(NO_3)_4 + 2(NH_4)_2MoO_4 \longrightarrow Th(MoO_4)_2 + 4NH_4NO_3$$

F. J. Metzger and F. W. Zons (42) claim that thorium is quantitatively separated from rare earths such as cerium, lanthanum, neodymium, praseodymium, erbium, yttrium, gadolinium, etc., by this method. Diphenylcarbazide is used as an external indicator. The equivalent weight of thorium is Th/4.

This method has also been studied by L. E. Kaufman (30) and compared (31) with six other methods for determining thorium. This study revealed that the method of F. J. Metzger and F. W. Zons is applicable when speed is desired but that it is not as accurate as the other methods. The author's experience with this method is in agreement with that of others (44) in that the end-point is very difficult to distinguish.

Oxidimetric Methods

Oxalate method

F. A. Gooch and M. Kobayashi (23) report that thorium can be determined titrimetrically by precipitating the thorium as the oxalate and titrating the precipitated oxalate or the excess oxalic acid with a 0.1 N potassium permanganate solution.

$$Th(NO_3)_4 + 2H_2C_2O_4 \longrightarrow Th(C_2O_4)_2 + 4HNO_3$$

$$5Th(C_2O_4)_2 + 4KMnO_4 + 16H_2SO_4 \longrightarrow 5Th(SO_4)_2 + 4MnSO_4 + 20CO_2 + 2K_2SO_4 + 16H_2O$$

Although excellent results were obtained it was necessary to add the thorium nitrate solution gradually to an excess of a hot oxalic acid solution in order to obtain a precipitate of constant composition. When a hot oxalic acid solution is added to a thorium nitrate solution the precipitate does not correspond to the normal oxalate and hence cannot be used in titrimetry. It is rather inconvenient to add the unknown solution to the precipitating agent. A modification of this method might be to dissolve the thorium oxalate in an excess ceric sulfate and the excess back titrated with ferrous sulfate using ferroin as the indicator. The equivalent weight of thorium is Th/4.

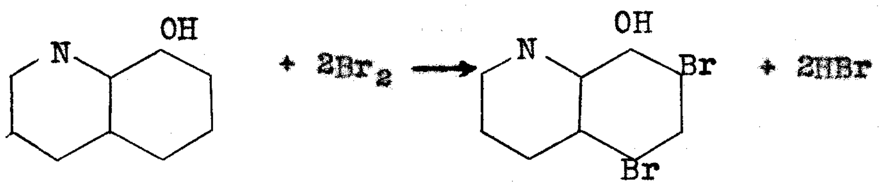
Oxine method

The use of 8-hydroxyquinoline as a reagent for thorium was proposed by I. M. Kolthoff (35) in 1927. Since then several studies have been made on the determination of thorium as the 8-hydroxyquinolate. H. Gotô (24, 25) found that precipitation begins at a pH of 3.7, is complete between the pH of 4.4 and 8.8, and that the precipitate redissolves at a pH of 12.5.

Other studies (6,21,27,28,39) have shown that when thorium is precipitated from an acetic acid solution buffered with ammonium acetate the precipitate corresponds to $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$. This 8-hydroxyquinolate can be weighed or titrated by the method of R. Berg (5) in which case the equivalent weight of thorium is Th/20.

$$Th(NO_3)_4 + 5C_9H_6NOH \longrightarrow Th(C_9H_6NO)_4 \cdot C_9H_6NOH + 4HNO_3$$

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 6KCl + 3H_2O$$



Thorium-8-hydroxyquinolate is suitable for both the macro and micro determinations of thorium but is not a separation of thorium from any metal precipitated by oxine from an acetate buffered solution.

Iodate method

The most recent oxidimetric method for determining thorium is that of Yu. A. Chernikhov and T. A. Uspenskaya (15). These workers precipitated the thorium by adding an equal volume of a solution containing 100 grams of potassium iodate and 333 ml. of 1.24 N nitric acid per liter. The precipitate, $4Th(IO_3)_4 \cdot KIO_3 \cdot 18H_2O$, was filtered onto a sintered glass filter, washed with a nitric acid solution of potassium iodate, then 95 per cent alcohol and finally with ether. After drying for 10-15 minutes at 40-45° the precipitate was dissolved in acidified potassium iodide and the liberated iodine titrated with 0.1 N sodium thiosulfate.

$$4Th(NO_3)_4 + 17KIO_3 + 18H_2O \longrightarrow 4Th(IO_3)_4 \cdot KIO_3 \cdot 18H_2O + 16KNO_3$$

$$KIO_3 + 5KI + 6HCl \longrightarrow 3I_2 + 6KCl + 3H_2O$$

$$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

The equivalent weight of thorium is 4Th/102. This method has been used as a separation from trivalent cerium which can later be oxidized and precipitated as $2Ce(IO_3)_4 \cdot KIO_3 \cdot 8H_2O$.

Electrometric Methods

Oxalate method

I. A. Atanasiu (2) first reported that attempts to titrate thorium chloride or nitrate with sodium oxalate failed but later reported (3) that salts of thorium can be titrated electrometrically with solutions containing ammonium or sodium oxalate.

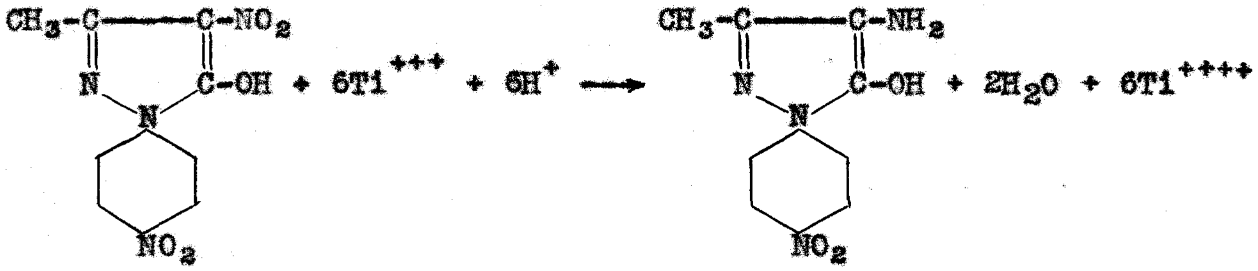
$$Th(NO_3)_4 + 2Na_2C_2O_4 \longrightarrow Th(C_2O_4)_2 + 4NaNO_3$$

Picrolonate method

Thorium in amounts up to 10 mg. can be determined by precipitating as the picrolonate, $Th(C_{10}H_7N_4O_5)_4 \cdot H_2O$, (26).

T. Kiba (32) has titrated thorium picrolonate with a titanous solution. The end-point was determined potentiometrically. The titration was made in a carbon dioxide atmosphere at 90-95° and in about 4 N acid. The equivalent weight of thorium is Th/24.

$$Th(NO_3)_4 + 4C_{10}H_8N_4O_5 + H_2O \longrightarrow Th(C_{10}H_7N_4O_5)_4 \cdot H_2O + 4HNO_3$$



The method has found very little use because the time required for a titration is more than two hours.

Ferrocyanide method

I. A. Atanasiu (1) found that when thorium nitrate was potentiometrically titrated with potassium ferrocyanide, thorium ferrocyanide, $Th[Fe(CN)_6]$, was formed at the equivalence point but that the compound varied with an excess of the alkali ferrocyanide.

$$Th(NO_3)_4 + K_4[Fe(CN)_6] \longrightarrow Th[Fe(CN)_6] + 4KNO_3$$

This method is unsatisfactory for a quantitative method of determining thorium.

F. M. Shemyakin and V. A. Volkova (49) found that an inflection is observed when $Th[Fe(CN)_6]$ is precipitated from a 30 per cent ethanol solution at 70° with a potassium ferrocyanide solution.

EXPERIMENTAL WORK

Materials Used

(1) Acetic Acid, CH_3COOH: Baker and Adamson reagent grade. Glacial, Sp. Gr.: 1.05; 99.9% CH_3COOH.

(2) Ammonium Acetate, Crystal, CH_3COONH_4: Baker and Adamson reagent grade.

(3) Ammonium Hydroxide, NH_4OH: Baker and Adamson reagent grade. Sp. Gr.: 0.90; 28% NH_3.

(4) Ammonium Nitrate, NH_4NO_3: Baker and Adamson reagent grade.

(5) Ammonium Paramolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (52): Baker and Adamson reagent grade. Solution: Dissolve 7.6 grams of ammonium paramolybdate in one liter of water.

(6) Ammonium Phosphate, Dibasic, $(NH_4)_2HPO_4$: Baker and Adamson reagent grade.

(7) Calcium Nitrate, $Ca(NO_3)_2 \cdot 4H_2O$: Baker and Adamson reagent grade.

(8) Ceric Sulfate, Anhydrous, $Ce(HSO_4)_4$: G. Fredrick Smith Chemical Company, Columbus, Ohio. GFS reagent. Solution: Dissolve ceric sulfate in dilute sulfuric acid, dilute to about 0.1 N and filter through glass wool.

(9) Cerous Oxide, Ce_2O_3: A measured volume of standard ceric sulfate was reduced with hydrogen peroxide and the solu-

tion boiled to destroy the excess peroxide. The cerous sulfate solution thus obtained was used as a source for cerium.

(10) Diphenylcarbazide, $C_6H_5NHNHCONHNHC_6H_5$: Eastman Kodak Company, Rochester 4, N. Y. Eastman (618) white label quality. Solution: Prepared according to the directions of F. J. Metzger and F. W. Zons (42). Dissolve 0.5 gram of diphenylcarbazide in 200 ml. of 95 per cent ethanol and allow to stand two weeks before using. The solution, when ready for use, should be yellowish in color, but show no pink tinge.

(11) Ethanol, C_2H_5OH: U. S. Industrial Chemicals, Inc., 642 South Michigan Ave., Chicago, Illinois. 95% C_2H_5OH.

(12) Ether, Absolute, $C_2H_5OC_2H_5$: Merck & Co., Inc., Rahway, N. J. Merck reagent grade. Sp. Gr.: 0.710.

(13) Ferric Ammonium Sulfate, $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$: Baker and Adamson reagent grade. Solution: Dissolve 10 grams of ferric ammonium sulfate in enough water to make one liter of solution.

(14) Ferrous Sulfate, $FeSO_4.7H_2O$: Baker and Adamson reagent grade.

(15) Filter Paper: 11-cm. Whatman #42, Ash: 0.0001 g.; 9-cm. Whatman #42, Ash: 0.00006 g.

(16) Filter Pulp: Whatman ashless tablets. Ash: 0.00025 g./tablet.

(17) Hydrazine Hydrate, $NH_2NH_2.H_2O$: Eastman Kodak Company,

Rochester 4, N. Y. Eastman (P902-X) yellow label quality. 85% in water.

(18) Hydrochloric Acid, HCl: Baker and Adamson reagent grade. Sp. Gr.: 1.178-1.188; 35-37% HCl.

(19) Hydrogen Peroxide, Superoxol, H_2O_2: Merck & Co., Inc., Rahway, N. J. Merck chemically pure grade. 30% H_2O_2.

(20) Indigo Carmine, Carmine Blue, 5,5'-Sodium Indigodisulfonate, (CI 1180), $(5\text{-}NaOSO_2)\underbrace{C_6H_3\text{-}1\text{-}COC(NH}_{2}):C(\underbrace{NH)CO\text{-}1'\text{-}C}_{2'}{}_6H_3(5'\text{-}SO_3Na)$: Hartman-Ledden Co., Philadelphia, Pa. Solution: 0.1%.

(21) Lanthanum Nitrate, $La(NO_3)_3 \cdot 6H_2O$: City Chemical Corporation, 132 West 22nd Street, New York, N. Y. Chemically pure grade.

(22) Lanthanum Oxide, La_2O_3: Prepared by igniting lanthanum nitrate at 600-700°. Dissolved in dilute nitric acid and added as the nitrate.

(23) Methyl <u>iso</u>-Butyl Ketone, "Hexone", $CH_3CH(CH_3)CH_2COCH_3$: Eastman Kodak Company, Rochester 4, N. Y. Eastman (416) white label quality.

(24) Methyl Violet, (CI 680), $[4\text{-}(CH_3)_2NC_6H_4]C[:C_6H_4\text{-}4\text{-}:N\text{-}(CH_3)_2Cl][C_6H_4\text{-}4\text{-}NHCH_3]$: Hartman-Ledden Col, Philadelphia, Pa. Solution: 0.25%.

(25) Molybdenum Wire, Mo: Fansteel Metallurgical Corporation, North Chicago, Illinois. Diameter: 40 mils. 99.9$^+$% Mo.

(26) Neodymium Oxalate, $Nd_2(C_2O_4)_3 \cdot 10H_2O$: Lindsay Light & Chemical Company, West Chicago, Illinois.

(27) Neodymium Oxide, Nd_2O_3: Prepared by igniting neodymium oxalate at 500-600°. Dissolved in concentrated hydrochloric acid, diluted and added as the chloride.

(28) Nitric Acid, HNO_3: Baker and Adamson reagent grade. Sp. Gr.: 1.42; 70% HNO_3.

(29) Oxalic Acid, $H_2C_2O_4 \cdot 2H_2O$: Baker and Adamson reagent grade.

(30) Perchloric Acid, $HClO_4$: G. Fredrick Smith Chemical Co., Columbus, Ohio. GFS reagent. Sp. Gr.: 1.54; 60% $HClO_4$.

(31) 1,10-Phenanthroline Ferrous Sulfate, Ferroin, $Fe(C_{12}H_8N_2)_3SO_4$: Solution: Prepared according to Smith and Richter (51). Dissolve 14.8662 grams of 1,10-phenanthroline monohydrate and 6.9505 grams of ferrous sulfate heptahydrate in enough distilled water to make one liter of solution. This solution is 0.025 M in ferroin.

(32) 1,10-Phenanthroline Monohydrate, $C_{12}H_8N_2 \cdot H_2O$: G. Fredrick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio. GFS reagent.

(33) Phenosafranine, (CI 840), $(4\text{-}NH_2)\underbrace{C_6H_3N{:}}_{6}C_6H_3(4'\text{-}NH_2)$ $[6'\text{-}{:}N(Cl)(C_6H_5)]$: Hartman-Ledden Co., Philadelphia, Pa. Solution: 0.5%.

(34) Phenylarsonic Acid, $C_6H_5AsO_3H_2$: Eastman Kodak Company, Rochester 4, N. Y. Eastman (2020) white label quality.

(35) Phenylhydrazine, $C_6H_5NHNH_2$: Eastman Kodak Company, Rochester 4, N. Y. Eastman (329) white label quality.

(36) Phosphoric Acid, H_3PO_4: Baker and Adamson reagent grade. Sp. Gr.: 1.69; 85% H_3PO_4.

(37) Potassium Ethyl Xanthate, C_2H_5OCSSK: Eastman Kodak Company, Rochester 4, N. Y. Eastman (1568) white label quality.

(38) Potassium Ferrocyanide, $K_4Fe(CN)_6$: Baker and Adamson reagent grade.

(39) Potassium Pyrophosphate, $K_4P_2O_7$: Baker and Adamson chemically pure grade.

(40) Potassium Thiocyanate, KCNS: Baker and Adamson reagent grade.

(41) Rhodamine 6G, (CI 752), $[3\text{-}(C_2H_5)(H)N]C_6H_3OC_6H_3[3\text{-}:N(H)(C_2H_5)(Cl)]\text{-}6\text{-}:C[C_6H_4\text{-}2\text{-}COOC_2H_5]$: Hartman-Ledden Co., Philadelphia, Pa. Solution: 0.1%.

(42) Samarium Oxalate, $Sm_2(C_2O_4)_3 \cdot 10H_2O$: Fairmount Chemical Co., Inc., 600 Ferry Street, Newark, N. J.

(43) Samarium Oxide, Sm_2O_3: Prepared by igniting samarium oxalate at 500-600°. Dissolved in concentrated hydrochloric acid, diluted and added as the chloride.

(44) Sodium Thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$: Merck & Co., Inc., Rahway, N. J. Merck reagent grade.

(45) Sulfuric Acid, H_2SO_4: Baker and Adamson reagent grade. Sp. Gr.: 1.84; 95-96% H_2SO_4.

(46) Tannin, Tannic Acid, m-Digallic Acid, 3,4,5-$(OH)_3$-$C_6H_2COOC_6H_2$-5-COOH-2,3-$(OH)_2$: Eastman Kodak Company, Rochester 4, N. Y. Eastman (422) white label quality.

(47) Tartrazine, (CI 640), (4-$NaOSO_2C_6H_4$)NN:C(COONa)C(N:NC_6H_4-4-SO_3Na):COH: Hartman-Ledden Co., Philadelphia, Pa. Solution: 0.5%.

(48) Thorium (95%)-Columbium Alloy: Prepared by A. I. Snow. Rolled into a sheet by A. H. Daane.

(49) Thorium Nitrate, $Th(NO_3)_4 \cdot 4H_2O$: Lindsay Light & Chemical Company, West Chicago, Illinois. Atomic weight grade. Purified as described on page (24).

(50) Thorium Perchlorate, $Th(ClO_4)_4$: Prepared by fuming purified thorium nitrate with perchloric acid to near dryness and diluting until 1 ml. is equivalent to about 5 mg. of Mo.

(51) Uranium-Molybdenum Alloys: Prepared by D. H. Ahmann and A. I. Snow.

(52) Uranium-Thorium Alloys: Prepared by O. N. Carlson.

(53) Uranous Uranate, $U(UO_4)_2$, U_3O_8: Prepared from uranyl nitrate hexahydrate as follows: Uranyl nitrate hexahydrate was extracted with diethyl ether. The ether was evaporated and the purified uranyl nitrate was recrystallized from water. These crystals were dried and ignited in a muffle at 1000°. The resulting product was ground, ignited, ground, ignited and ground

again. The U_3O_8 prepared in this manner was used as a primary standard.

(54) Uranyl Nitrate Hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$: Mallinckrodt Chemical Works. Reagent grade. Purified by extracting with diethyl ether and then recrystallizing from water.

(55) Yttrium Nitrate, $Y(NO_3)_3 \cdot 6H_2O$: City Chemical Corporation, 132 West 22nd Street, New York, N. Y. Chemically pure grade.

(56) Yttrium Oxide, Y_2O_3: Prepared by igniting yttrium nitrate at 600-700°. Dissolved in dilute nitric acid and added as the nitrate.

(57) Zinc, Amalgamated, 20 mesh: Baker and Adamson reagent grade.

Methods of Procedure

Precipitation methods

Adsorption indicator methods. The determination of a metal ion by adsorption indicators depends upon the formation of a difficultly soluble compound which adsorbs the anions of the precipitant, thus giving the precipitated particles a negative charge, when the equivalence point is passed. Positive ions of a dyestuff may then be adsorbed by the precipitated particles or actually exchanged for some of the cations of the precipitate. The deformation of the dyestuff ions, as a result of being adsorbed by the precipitate, is accompanied by a color change which is the basis of these titrations (34). Basic dyestuffs, such as rhodamine 6G, phenosafranine, and methyl violet should be applicable to the titration of thorium with anions such as phenyl-arsonate, molybdate, phosphate, and pyrophosphate. Tartrazine, although an acid dye, has been found (7) to work best when the cation is titrated with the anion.

A solution of thorium nitrate, to which a small amount of acetic acid and methyl violet had been added, was titrated with an ammonium paramolybdate solution. The thorium molybdate adsorbed the methyl violet giving the precipitate a slight lilac color but no end-point was observed. Phenylarsonic acid, ammonium phosphate, and potassium pyrophosphate were also tried as precipitants but no end-point could be detected.

Thorium nitrate solutions containing a small amount of acetic acid, were titrated with each of the above mentioned precipitants in the presence of phenosafranine. No end-point could be detected in any of the experiments.

When similar experiments were run using rhodamine 6G as indicator it was strongly adsorbed in the case of thorium molybdate giving a pink colored precipitate but no end-point was observed. Attempts to detect an end-point with the other precipitants also met with failure.

The only indicator that gave any evidence of an end-point was tartrazine. In the case of thorium molybdate there was some indication of a change from yellow to pale green around the equivalence point but the change was not sharp. The other precipitants gave no better results.

Oxidimetric methods

General. This method is based on the quantitative precipitation of thorium as the normal molybdate and the subsequent reduction and titration of the molybdenum that is combined with the thorium.

$$Th(NO_3)_4 + 2(NH_4)_2MoO_4 \longrightarrow Th(MoO_4)_2 + 4NH_4NO_3$$

$$Th(MoO_4)_2 + 4HCl \longrightarrow ThCl_4 + 2H_2MoO_4$$

$$2H_2MoO_4 + 3Zn + 12HCl \longrightarrow 2MoCl_3 + 3ZnCl_2 + 8H_2O$$

$$2MoCl_3 + 6Ce(HSO_4)_4 + 8H_2O \longrightarrow 2H_2MoO_4 + 3Ce_2(SO_4)_3 + 6HCl + 15H_2SO_4$$

According to H. T. S. Britton and W. L. German (13) thorium begins to precipitate at a pH of 3 when an alkali molybdate is added. They claim that the normal compound is precipitated and give as evidence for this that (a) precipitation takes place at a pH value lower than that at which the hydroxide separates, (b) a sharp inflection is produced when an equivalent amount of the titrant has been added, (c) the final pH of the solution is just above 7, (d) on analysis the precipitate, after being dried at 100°, was found to contain molybdic oxide and thoria in the ratio of 2.07:1. That the normal thorium molybdate is precipitated is also suggested by the findings of F. J. Metzger and F. W. Zons (42) who analyzed the precipitate they obtained and found it to contain molybdenum and thorium in the ratio 2.017:1 and 2.03:1.

H. T. S. Britton and W. L. German (13) also found that when an alkali paramolybdate or an alkali metamolybdate is used as the precipitant the thorium para- or metamolybdate is not precipitated. In these cases thorium is precipitated as the normal molybdate but the precipitate is contaminated with coprecipitated molybdic oxide. The rest of the molybdic oxide is liberated in the solution which accounts for the initial decrease in pH when thorium is precipitated with sodium paramolybdate.

Determination of thorium alone. The thorium nitrate used in the following experiments was carefully purified in the following manner.

Two hundred fifty grams (ca. 0.45 mole) of thorium nitrate tetrahydrate was mixed with 450 grams (ca. 2 moles) of calcium nitrate tetrahydrate. To this mixture was added 193 ml. of concentrated nitric acid (ca. 3 moles) and enough water to make one liter of solution. This solution was extracted with two one-liter portions of hexone that had been saturated with a nitric acid-water mixture by shaking equal volumes of hexone and 4 N nitric acid for 5-10 minutes. The two liters of hexone, containing the extracted thorium, were extracted with an equal volume of water to remove the thorium from the hexone.

To the two liters of water, containing the purified thorium, was added 100 grams (ca. 1.25 moles) of ammonium nitrate to prevent the precipitation of calcium and the thorium was precipitated with ammonia. The thorium hydroxide thus obtained was filtered, redissolved in nitric acid and the thorium precipitated again in the same way. The thorium hydroxide was again dissolved in nitric acid and the solution was filtered to remove any suspended material. The thorium was precipitated two more times with ammonia and washed 5-6 times with distilled water. The pure white thorium hydroxide thus obtained was dissolved in just enough nitric acid to effect solution. This solution was filtered into a bottle and diluted to about five liters. The above purification effectively separates thorium from the rare earths and most other ions.

This solution was standardized by precipitating the thorium as the hydroxide, filtering onto 9-cm. Whatman #42 filters, washing, and igniting to the dioxide. Weight burets were used throughout this investigation. The results of this standardization are summarized in Table 1.

Table 1

Standardization of Thorium Nitrate Solution

Trial	Wt.sol'n, g.	Wt.ThO_2+x'ble, g.	Wt. x'ble, g.	G.ThO_2/g.sol'n
1	11.5778	14.8308	14.7105	0.01039
2	8.7474	13.6012	13.5100	0.01042
3	10.6524	13.8252	13.7144	0.01040
4	10.2106	12.3472	12.2409	0.01041
5	8.7131	12.3002	12.2094	0.01042
			Average value:	0.01041

Several samples of the standardized thorium nitrate solution were weighed into 250 ml. beakers. These samples were diluted to 150 ml. with water and made 7 per cent in acetic acid. About 15 ml. of thick filter pulp was added to each sample and 40 ml. of the ammonium paramolybdate solution was slowly added from a buret with stirring. The samples were then heated to boiling and filtered, while hot, through 11-cm. Whatman #42 filters into 400 ml. beakers. The thorium molybdate precipitates were washed 5-6 times with hot 1:100 acetic acid. The precipitates and filters were transferred to the 250 ml. beakers in which the precipitations were carried out. To each of these beakers was added 25 ml. of concentrated hydrochloric acid and the contents stirred until the thorium molybdate had dissolved and the filters had disintegrated. Seventy-five ml. of water was added to each beaker and the solutions were brought to a boil. After 5 minutes of slow boiling the solutions were filtered through 11-cm. Whatman #42 filters into 400 ml. beakers. Longer boiling at this point is accompanied by partial reduction of the molybdate and a coloring of the solution and the filter pulp. This should be avoided. The filter pulp and filters were washed 5-6 times with hot 1:100 hydrochloric acid. The filtrates, after being cooled to room temperature, were passed through an amalgamated zinc

Jones reductor into an excess (50 ml. of 10 per cent) of ferric alum to which had been added 2-3 ml. of concentrated phosphoric acid to decolorize the ferric iron which would otherwise tend to obscure the end-point. The Jones reductor quantitatively reduces molybdenum from the hexavalent (colorless) state to the trivalent (green) state (47). The ferric alum, containing phosphoric acid, oxidizes the trivalent molybdenum mainly to the quinquivalent (red) state. Contrary to A. D. Mitchell and A. M. Ward (43) it is believed that trivalent molybdenum is largely oxidized to the hexavalent state by ferric alum in the absence of phosphoric acid. This belief is based on the fact that a nearly colorless solution is obtained when phosphoric acid is added to the ferric alum solution after the trivalent molybdenum has been introduced.

The solutions containing mainly quinquivalent molybdenum and ferrous iron were titrated with 0.1 N ceric sulfate using two drops of ferroin as indicator. The end-point is taken as that point when the pink color changes to colorless or light blue. The end-point in the absence of phosphoric acid is shown by a color change from pink to light green but the pink color returns several times before a permanent light green color is obtained. This sluggish end-point is eliminated by the addition of phosphoric acid which increases the rapidity of oxidation by the ceric sulfate (50). The results of this experiment are recorded in Table 2.

Table 2

Determination of Thorium in Thorium Nitrate

Trial	Wt. sol'n., g.	ThO_2 taken, g.	Ml. $Ce(HSO_4)_4$*	ThO_2 found, g.	% Error
1	15.1528	0.1577	36.20	0.1606	+1.84
2	15.0465	0.1566	33.85	0.1502	-4.08
3	14.9088	0.1552	35.25	0.1564	+0.77
4	15.5812	0.1622	36.70	0.1628	+0.37
5	15.6084	0.1625	36.80	0.1633	+0.49
6	15.7187	0.1636	38.00	0.1686	+3.03
7	15.8522	0.1650	37.80	0.1677	+1.51
8	18.5516	0.1931	43.68	0.1938	+0.36
9	17.0996	0.1780	40.80	0.1811	+1.74
10	14.9555	0.1557	36.52	0.1620	+4.05

*N = 0.1008

From these data it is seen that the smallest error was on the sample containing the largest amount of thorium and this suggested that the error might be associated with the amount of excess ammonium paramolybdate that was present. This is in agreement with the findings of H. T. S. Britton and W. L. German (13) that some molybdic oxide is coprecipitated with the normal thorium molybdate when an alkali paramolybdate is used as the precipitant.

The necessity for some way to approximate the equivalence point was apparent so that the addition of a large excess of ammonium paramolybdate could be avoided. The use of diphenylcarbazide as an inside indicator was tried. Several samples were weighed out and prepared for precipitation in exactly the same manner as described above. About 1 ml. of diphenylcarbazide solution was added to each sample and the ammonium paramolybdate solution added until a deep pink color appeared. This deep pink color appeared when 0.5-1 ml. excess of the precipitating agent had been added. These samples were prepared for titration in the same manner as before. The diphenylcarbazide is easily and completely removed from the precipitate during the washing. The results from these analyses are summarized in Table 3.

Table 3

Determination of Thorium in Thorium Nitrate

Trial	Wt. sol'n., g.	ThO_2 taken, g.	Ml. $Ce(HSO_4)_4$*	ThO_2 found, g.	% Error
1	16.2594	0.1693	38.15	0.1693	±0.00
2	14.7097	0.1531	34.44	0.1528	-0.20
3	14.5649	0.1516	34.12	0.1514	-0.13
4	16.4202	0.1709	38.42	0.1705	-0.23
5	13.9584	0.1453	32.70	0.1451	-0.14
6	15.4413	0.1607	36.20	0.1606	-0.06
7	16.4647	0.1714	38.64	0.1715	+0.06
8	15.0989	0.1572	35.40	0.1571	-0.06

*N = 0.1008

The data of Table 3 show conclusively that thorium can be determined quantitatively by precipitation with ammonium paramolybdate and the subsequent titration of the combined molybdenum. Chloride and perchlorate solutions may also be used. The recommended procedure for determining thorium in thorium solutions is given below.

Samples containing 0.15 to 0.2 gram of ThO_2 are weighed into 250 ml. beakers. After the samples have been dissolved any large excess of mineral acid is destroyed by evaporating the solutions nearly to dryness. The samples are then diluted to 150 ml. with water and made about 7 per cent in acetic acid by adding 11 ml. of glacial acetic acid. Fifteen ml. of thick filter pulp and 1 ml. of the diphenylcarbazide solution are added. The ammonium paramolybdate solution is added from a buret with stirring until the diphenylcarbazide imparts a deep pink color to the solution. After the precipitates have settled the supernatant liquids may be tested for complete precipitation. The contents of the beakers are heated to the boiling point and filtered, while hot, through 11-cm. Whatman #42 filters into 400 ml. beakers. The precipitates are washed 5-6 times with hot 1:100 acetic acid. The 250 ml. beakers need not be scrubbed out with a policeman but only carefully rinsed out 2-3 times with wash solution. The washed precipitates and filters are transferred to the 250 ml. beakers in which the precipitations were carried out and 25 ml. of concentrated hydrochloric acid added to each beaker. The contents are stirred until the filters have disintegrated. Seventy-five ml. of water is added, the mixtures heated to boiling and filtered, while hot, through 11-cm. Whatman #42 filters into 400 ml. beakers. The filter pulp and filters are washed 5-6 times with hot 1:100 hydrochloric acid. The filtrates, after being cooled to room temperature, are passed through a Jones reductor into an excess (50 ml. of 10 per cent) of ferric alum to which 2-3 ml. of concentrated phosphoric acid has been added and titrated with 0.1 N ceric sulfate using two drops of ferroin as indicator. The end-point is taken as that point when the pink color of the solution changes to colorless or light blue. The equivalent weight of thorium in this titration is Th/6.

Thoria can easily be dissolved in nitric acid and a trace of sodium fluosilicate and analyzed for thorium by the above procedure.

<u>Separation of thorium from calcium.</u> The possibility of separating thorium from calcium with ammonium paramolybdate might at first seem unlikely since calcium can be precipitated quantitatively as calcium molybdate from slightly acid solutions (55).

Calcium molybdate is not precipitated from 7 per cent acetic acid solutions containing as much as 1.5 moles of calcium nitrate per liter. This may be due to the incomplete dissociation of calcium acetate. F. H. MacDougall and W. D. Larson (41) claim that the following equilibria exist in aqueous solution and that the first stage of the ionization is complete but that the second stage is only partially complete.

$$Ca(OAc)_2 \rightleftharpoons CaOAc^+ + OAc^-$$
$$CaOAc^+ \rightleftharpoons Ca^{++} + OAc^-$$

They estimated the ionization constant for this second stage to be 0.15. In contradiction to this C. W. Davies (17) claims that calcium acetate is a stronger electrolyte than calcium nitrate and that in dilute solutions (0.02 M) it is nearly completely dissociated.

The suitability of determining thorium in the presence of calcium with molybdate was tested by adding different amounts of calcium nitrate to thorium nitrate solutions and separating the thorium as the molybdate. The results from this series of experiments are shown in Table 4.

From the data in Table 4 it is apparent that thorium can be quantitatively separated from as much as 0.4 gram of calcium in a 7 per cent acetic acid solution. The high results obtained when extremely large amounts of calcium are present may be due to coprecipitation. Large amounts of calcium nitrate give a pink coloration with diphenylcarbazide, thus it

Table 4

Separation of Thorium from Calcium

Trial	Ca present, g.	ThO_2 sol'n., g.	ThO_2 taken, g.	Ml. $Ce(HSO_4)_4$*	ThO_2 found, g.	% Error
1	0.1	16.4799	0.1716	38.72	0.1716	±0.00
2	0.1	14.2149	0.1480	33.42	0.1481	+0.07
3	0.2	15.1263	0.1575	35.60	0.1578	+0.19
4	0.2	15.6770	0.1632	36.90	0.1635	+0.18
5	0.4	15.9747	0.1663	37.56	0.1665	+0.12
6	0.4	16.7403	0.1743	39.38	0.1746	+0.17
7	3.0	15.3525	0.1598	36.58	0.1623	+1.56
8	3.0	16.8670	0.1756	39.90	0.1770	+0.80
9	6.0	15.0145	0.1563	35.95	0.1595	+2.04
10	6.0	16.3740	0.1705	39,15	0.1737	+1.88
11	9.0	13.4716	0.1402	33.20	0.1473	+5.06
12	9.0	16.2633	0.1693	38.35	0.1702	+0.53

* N = 0.1007

is impossible to use this indicator for approximating the equivalence-point when these conditions exist. Solutions 1.5 M in calcium would not ordinarily be encountered in a thorium analysis but in case they are they should be diluted prior to analysis.

The recommended procedure for determining thorium in the presence of calcium is the same as that outlined for determining thorium in thorium solutions on page (31).

<u>Separation of thorium from uranium</u>. Uranyl molybdate is insoluble in aqueous solutions and solutions containing acetic acid. Ammonium acetate prevents uranyl molybdate from precipitating for about three hours even if the solution is boiled but a precipitate appears after standing twelve hours.

A series of experiments were conducted in order to determine whether or not thorium could be separated from uranyl salts in an ammonium acetate solution with ammonium paramolybdate. Different amounts of uranyl nitrate were added to thorium nitrate and the thorium determined by separating it as thorium molybdate. All solutions were made 7 per cent in acetic acid and contained 5 grams of ammonium acetate. The results are tabulated in Table 5.

In this series of experiments the amount of uranium was varied while the amount of ammonium acetate was constant.

Table 5

Separation of Thorium from Uranium

Trial	U_3O_8, g.	ThO_2 sol'n., g.	ThO_2 taken, g.	Ml.$Ce(HSO_4)_4$*	ThO_2 found, g.	% Error
1	0.1	14.6614	0.1526	34.05	0.1509	-1.11
2	0.1	16.3293	0.1700	38.00	0.1683	-0.88
3	0.2	15.1806	0.1580	35.15	0.1558	-1.39
4	0.2	17.1680	0.1787	40.30	0.1786	-0.06
5	0.4	15.6443	0.1629	36.30	0.1609	-1.25
6	0.4	14.9347	0.1555	34.75	0.1540	-0.96

* N = 0.1007

In trial four an excess of four ml. of precipitant was added and in all other cases an excess of two ml. was added. Since the errors were consistently one per cent low they were probably due to the ammonium acetate since it was present in constant amount while the uranium was not. Since trial four gave quantitative results and contained four ml. excess of precipitant it seemed that a larger excess of precipitant was all that was necessary to overcome the effect of the ammonium acetate. A series of experiments were made to determine whether this was true. The results obtained are recorded in Table 6.

The data in Table 6 show clearly that the excess of precipitant must be controlled. From four to six ml. must be present in order to get quantitative separation of the thorium. Smaller or larger amounts give low or high results respectively. This need for regulating the amount of excess precipitant necessitates a knowledge of the amount of thorium present or a method to determine the approximate equivalence-point. Diphenylcarbazide is not satisfactory in this case. The only satisfactory method found was to test the supernatant liquid for complete precipitation or make a preliminary determination to find approximately the amount of thorium present.

The recommended procedure for determining thorium in

Table 6

Effect of Excess Precipitant*

Trial	ThO_2 sol'n., g.	ThO_2 taken, g.	Ml.excess	Ml.$Ce(HSO_4)_4$**	ThO_2 found, g.	% Excess
1	15.1806	0.1580	2	35.15	0.1558	-1.39
2	17.1680	0.1787	4	40.30	0.1786	-0.06
3	17.0598	0.1776	6	40.10	0.1778	+0.11
4	16.7195	0.1740	8	39.50	0.1751	+0.63
5	13.8577	0.1443	10	32.72	0.1450	+0.49
6	17.5897	0.1831	12	41.60	0.1844	+0.71
7	15.8660	0.1652	14	37.66	0.1669	+1.03
8	13.6257	0.1418	16	32.28	0.1431	+0.92

* = 0.2 gram of U_3O_8 was present in each trial

** N = 0.1007

the presence of uranium is given below.

Samples containing 0.15 to 0.2 gram of ThO_2 and not more than 0.5 gram of U_3O_8 are weighed into 250 ml. beakers. After the samples are dissolved any large excess of mineral acid is destroyed by evaporating the solutions nearly to dryness. Five grams of ammonium acetate and 11 ml. of glacial acetic acid are added to each sample and they are then diluted to 150 ml. with water. Twenty-five ml. of thick filter pulp is added and the thorium precipitated by adding ammonium paramolybdate solution from a buret with stirring. The amount of ammonium paramolybdate solution that is necessary is determined by testing the supernatant liquid for complete precipitation or by making a preliminary determination. Four ml. in excess of that required for complete precipitation is added. The contents of the beakers are heated to boiling and filtered through 11-cm. Whatman #42 filters into 400 ml. beakers. The precipitates are washed 5-6 times with hot 1:100 acetic acid. The 350 ml. beakers need not be scrubbed out with a policeman but only carefully rinsed out 2-3 times with the wash solution. The washed precipitates and filters are transferred to the 250 ml. beakers in which the precipitations were carried out and 25 ml. of concentrated hydrochloric acid added to each beaker. The contents are stirred until the filters have disintegrated. Seventy-five ml. of water is added, the mixtures heated to boiling and filtered, while hot, through 11-cm. Whatman #42 filters into 400 ml. beakers. The filter pulp and filters are washed 5-6 times with hot 1:100 hydrochloric acid. The filtrates, after being cooled to room temperature, are passed through a Jones reductor into an excess (50 ml. of 10 per cent) of ferric alum to which 2-3 ml. of concentrated phosphoric acid has been added and titrated with 0.1 N ceric sulfate using two drops of ferroin as indicator. The endpoint is observed as a change in the color of the solution from pink to colorless or light blue.

The above method has been used to advantage in analyzing thorium-uranium alloys for thorium. These alloys are easily decomposed with hydrochloric acid and then brought into solution by fuming with perchloric acid. Typical results obtained by this method are shown in Table 7. The uranium was determined on a separate sample by reducing in a Jones reductor, aerating, and titrating the uranous solution with 0.1 N ceric sulfate in the usual manner (50, p. 67).

Table 7

Analysis of Thorium-Uranium Alloys*

Sample	% Thorium	% Uranium	Total, %
1	1.67	97.60	99.27
2	16.10	82.60	98.70
3	23.60	76.90	100.50

* These analyses made by J. H. Patterson.

Separation of thorium from rare earths. According to F. J. Metzger and F. W. Zons (42) an excess of ammonium paramolybdate when added to a solution of a thorium salt under proper conditions of temperature and acidity will quantitatively precipitate the thorium as molybdate. It is also stated that rare earths such as cerium, lanthanum, neodymium, praseodymium, erbium, yttrium, gadolinium, etc., give no precipitation whatever under these conditions. The above workers recommend that thorium be precipitated as the molybdate at room temperature from a 7 per cent acetic acid solution. The determination of thorium in the presence of various rare earths was tried as follows:

Samples of the standard ThO_2 solution were weighed into 250 ml. beakers. One hundred mg. of a rare earth oxide was added, as a solution, to each of the samples. Fifteen ml.

of thick filter pulp was added to each beaker. These mixtures were diluted to 100 ml. and made 7 per cent in acetic acid. The thorium was precipitated at room temperature by adding 2 ml. excess of an ammonium paramolybdate solution.

The beakers containing the precipitated thorium molybdate were heated just to boiling and the precipitates filtered onto 11-cm. Whatman #42 filters. The beakers and precipitates were washed thoroughly with hot 1:100 acetic acid. The filters containing the thorium molybdate were returned to the 250 ml. beakers in which the precipitations were carried out. Twenty-five ml. of concentrated hydrochloric acid was added to each beaker and the contents stirred until the filters were disintegrated. Seventy-five ml. of water was then added to each beaker and they were placed on a hot plate. After boiling for a few minutes the thorium molybdate solutions were filtered through 11-cm. Whatman #42 filters. The filters were washed carefully with hot 1:100 hydrochloric acid. The filtrates, when cool, were passed through a Jones reductor into ferric alum to which phosphoric acid had been added and titrated with ceric sulfate using ferroin as indicator. The results obtained are shown in Table 8.

The data in Table 8 show that part of the rare earths were precipitated as the molybdate along with the thorium. It was thought that perhaps this precipitation of rare earth

Table 8

Separation of Thorium from Rare Earths

Trial	RE_2O_3, g.	ThO_2 sol'n., g.	ThO_2 taken, g.	Ml. $Ce(HSO_4)_4$*	ThO_2 found, g.	% Error
1	0.1 La_2O_3	15.7839	0.1643	39.00	0.1729	+5.2
2	0.1 La_2O_3	15.5380	0.1618	38.80	0.1720	+6.3
3	0.1 Y_2O_3	15.7030	0.1635	38.30	0.1698	+3.9
4	0.1 Y_2O_3	16.0973	0.1676	39.75	0.1762	+5.1
5	0.1 Sm_2O_3	16.2549	0.1692	39.72	0.1761	+4.1
6	0.1 Sm_2O_3	14.9834	0.1560	38.02	0.1686	+8.1
7	0.1 Nd_2O_3	15.6247	0.1627	38.95	0.1726	+6.1
8	0.1 Nd_2O_3	16.1526	0.1681	39.80	0.1764	+4.9
9	0.1 Ce_2O_3	16.2042	0.1687	39.85	0.1767	+4.7
10	0.1 Ce_2O_3	15.7928	0.1644	38.42	0.1703	+3.6

* N = 0.1007

molybdates could be prevented by the addition of more acetic acid since F. J. Metzger and F. W. Zons (42) found that a certain minimum amount of acetic acid was necessary to prevent the rare earths from being precipitated.

A study was made of the effect of varying the amount of acetic acid in the following manner. To several solutions of thoria was added 0.1 gram of lanthanum oxide, as a nitrate solution, and varying amounts of acetic acid. The analyses were carried out as before. The data obtained from this study are shown in Table 9.

The data of Table 9 show that the amount of acetic acid present definitely affects the coprecipitation of the lanthanum molybdate. This coprecipitation appears to be a minimum when the solution is about 20 per cent in acetic acid but even then it is not reduced sufficiently so that thorium can be determined quantitatively.

All the above analyses were made by heating the contents of the beakers to boiling before filtering the thorium molybdate. It was thought that temperature might have some effect on the coprecipitation of the rare earth molybdates so a series of determinations were made without heating to boiling before filtering off the thorium molybdate. The solutions were made 20 per cent in acetic acid. The data obtained from this series of determinations are recorded in Table 10.

The data of Table 10 show that temperature has little ef-

Table 9

Effect of Acetic Acid on Coprecipitation of Lanthanum Molybdate

Trial	% HOAc	La_2O_3, g.	ThO_2 taken, g.	Ml.$Ce(HSO_4)_4$*	ThO_2 found, g.	% Error
1	7	0.1	0.1618	38.80	0.1720	+6.3
2	15	0.1	0.1728	41.30	0.1831	+6.0
3	20	0.1	0.1794	41.15	0.1824	+1.7
4	25	0.1	0.1426	33.10	0.1467	+2.9
5	30	0.1	0.1811	42.75	0.1895	+4.6
6	40	0.1	0.1588	38.50	0.1707	+7.5
7	50	0.1	0.1492	36.05	0.1598	+7.1

* N = 0.1007

Table 10

Effect of Temperature on the Coprecipitation of Lanthanum Molybdate

Trial	La_2O_3, g.	ThO_2 sol'n., g.	ThO_2 taken, g.	Ml. $Ce(HSO_4)_4$*	ThO_2 found, g.	% Error
1	0.1	14.2026	0.1478	33.95	0.1505	+1.8
2	0.1	15.4268	0.1606	36.84	0.1633	+1.7
3	0.1	16.3252	0.1699	38.89	0.1724	+1.5
4	0.1	16.1112	0.1677	38.44	0.1704	+1.6
5	0.1	16.5212	0.1720	39.34	0.1744	+1.4
6	0.1	15.7628	0.1641	37.65	0.1669	+1.7

* N = 0.1007

fect on the coprecipitation of lanthanum molybdate because the per cent error observed in the determination of thorium under similar conditions, with the exception of temperature, was +1.7 as shown in Table 9. The perfectly clear filtrates obtained from the above analyses were heated to boiling and a slight turbidity appeared indicating that thorium molybdate is not immediately precipitated quantitatively in the cold. Lanthanum nitrate, in the absence of thorium, gives absolutely no precipitation under the above conditions.

From the above experiments it was concluded that thorium cannot be determined quantitatively by the molybdate method.

Determination of molybdenum by reversal. The determination of molybdenum by precipitating it as thorium molybdate is very useful in that it affords a means of separating molybdenum from certain other elements from which it cannot be conveniently separated otherwise. Such an example is the separation of molybdenum and uranium. Several methods have been studied (4) in connection with this separation but all leave much to be desired. The precipitation of ammonium diuranate by the urea hydrolysis method (56) does not give a complete separation except for very low uranium alloys. The a-benzoinoxime method (33) is only satisfactory for low molybdenum alloys. Chatard's (14) lead molybdate method, Mc Cay's silver molybdate method (40) and the Berzelius-Rose mercurous molybdate method were all found to have only limited use. Pèchard's method (46) of volatilizing molybdic oxide hydrochloride, $MoO_3 \cdot 2HCl$, was found to work well but was lengthy. Other methods involving MoS_3 and peruranic acid were not satisfactory.

The separation of molybdenum from uranium as the thorium molybdate was studied by adding known amounts of molybdate to uranyl solutions and recovering the molybdate as follows.

Measured amounts of a uranyl nitrate solution were placed in 400 ml. beakers and 16 ml. of glacial acetic acid was added to each beaker. To these solutions was added known amounts of ammonium paramolybdate and the solutions diluted to 200 ml. About 15 ml. of thick filter pulp was added to each beaker and the molybdate precipitated as thorium molybdate by adding a thorium perchlorate solution. The thorium perchlorate solution was added slowly from a buret with stirring until a 25 per cent excess was present. The contents of the beakers were digested just below the boiling point for a few minutes. The thorium molybdate was filtered, while hot, onto 11-cm. Whatman #42 filters and washed 5-6 times with hot 1:100 acetic acid. The precipitates and filters were placed in the beakers in which the precipitations were carried out and 25 ml. of concentrated hydrochloric acid was added to each. After stirring until the filters were disintegrated 75 ml. of water was added to each beaker and the contents heated to boiling and filtered through 11-cm. Whatman #42 filters into 400 ml. beakers. The filter pulp and filters were washed 5-6 times with hot 1:100 hydrochloric acid. The filtrates, after being cooled to room temperature, were passed through a Jones reductor into an excess (50 ml. of 10 per cent) of ferric alum to which had been added 2-3 ml. of concentrated phosphoric acid and titrated with 0.1 N ceric sulfate using two drops of ferroin as indicator. The data obtained from this study are recorded in Table 11.

These data show that molybdenum can be conveniently separated from uranium as thorium molybdate. The above procedure has been successfully applied to the analysis of uranium-molybdenum alloys. The recommended procedure for the analysis of uranium-molybdenum alloys is outlined below.

Samples containing 0.1 to 0.15 g. MoO_3 are weighed into 400 ml. beakers and dissolved in as small a volume of 1:1 hydrochloric acid as possible. The mixtures may be warmed to aid solution. Hydrogen peroxide is added to dissolve the black hydrated uranium dioxide, and to oxidize both elements to the hexavalent state. The solutions are boiled about 10 minutes to destroy the excess hydrogen peroxide and then diluted to 200 ml. Sixteen ml. of glacial acetic acid is added to each sample and enough ammonium acetate, usually 1 g., to react with the mineral acid present. About 15 ml. of thick

Table 11

Separation of Molybdenum from Uranium

Trial	U_3O_8, g.	MoO_3 taken, g.	Ml. $Ce(HSO_4)_4$*	MoO_3 found, g.	% Error
1	0.24	0.1381	36.55	0.1373	-0.58
2	0.24	0.1381	36.70	0.1379	-0.14
3	0.24	0.1381	36.65	0.1377	-0.29

* N = 0.0783

filter pulp is added to each beaker and the molybdenum analysis carried out as described above.

In case the 1:1 hydrochloric acid does not dissolve the sample a little concentrated nitric acid is added, and the solution boiled. It is best to avoid the use of nitric acid if possible, for it must be removed prior to reducing the uranium in the Jones reductor. The use of nitric acid is, however, necessary for the higher (20 per cent or more) molybdenum alloys. The nitric acid, when used, cannot be fumed off immediately after dissolving the sample because (a) the use of sulfuric acid precipitates thorium sulfate, and (b) fuming with perchloric acid causes molybdic oxide to precipitate.

The filtrates containing the uranium are concentrated to a convenient volume or fumed with perchloric acid, if nitric acid was used in dissolving the samples, and diluted to a convenient volume. These solutions are analyzed for uranium by passing through a Jones reductor, aerating for about five minutes, and titrating with 0.1 N ceric sulfate using two drops of ferroin as indicator.

Larger samples can be weighed out, dissolved, diluted to a known volume, and aliquots used for analysis if the sample form demands it or variation because of non-homogenious samples is to be avoided.

Typical analyses of uranium-molybdenum alloys obtained by the above procedure are recorded in Table 12.

Table 12

Analysis of Uranium-Molybdenum Alloys

Sample	% Mo	% U	Total %
1*	0.46	99.10	99.56
1*	0.48	99.50	99.98
2	4.00	99.06	100.06
2	4.00	99.06	100.06
3	7.26	91.91	99.17
3	7.22	91.91	99.13
4	15.93	83.19	99.12
4	15.91	83.30	99.21
5	20.66	78.59	99.25
5	20.65	77.73	98.38

* Analyzed by R. W. Holmberg

Thorium-molybdenum alloys could no doubt be analyzed for thorium by dissolving in hydrochloric and nitric acids, adjusting the acidity, adding enough ammonium paramolybdate to complete the precipitation and proceeding with the analysis in the usual manner. Molybdenum could be determined by reducing the molybdenum in a separate sample if nitric acid was not necessary in effecting solution or by adjusting the acidity, adding an excess thorium nitrate, and determining the molybdenum in the precipitated thorium molybdate if nitric acid was used in dissolving the sample.

Electrometric methods

General. Even though thorium can be determined very accurately by the oxidimetric method described above it has the disadvantage of being rather lengthy. It was apparent that much time could be saved if a direct titrimetric method could be devised. Such substances as potassium thiocyanate, potassium ferrocyanide, sodium thiosulfate, tannin, phenylhydrazine, hydrazine, and potassium ethylxanthate were found to be unsatisfactory for detecting an excess of molybdate when thorium was titrated with an ammonium paramolybdate solution. The possibility of detecting the end-point electrometrically was studied.

The Foulk-Bawden (20) technique of detecting the end-point was tried using two thorium electrodes but no break was observed.

Titrations were carried out using a 0.1 N calomel electrode and a thorium electrode under the following conditions: (a) 7 per cent acetic acid at 25°, (b) 7 per cent acetic acid at 25° with osmic acid as catalyst, (c) 7 per cent acetic acid at 25° with iodine monochloride as catalyst, (d) 7 per cent acetic acid at 55°, and (e) 7 per cent acetic acid at 70°. The results were very erratic in every case and this electrode system was not studied further.

The following conditions were tried for the titration using a 0.1 N calomel as the reference electrode and a molybdenum wire as the indicator electrode: (a) 7 per cent acetic acid at 25°, (b) 7 per cent acetic acid at 25° with osmic acid as catalyst, (c) 7 per cent acetic acid at 25° with iodine monochloride as catalyst, (d) 7 per cent acetic acid at 55°, (e) 7 per cent acetic acid at 70°, and (f) 7 per cent acetic acid and 30 per cent ethanol at 70°.

In experiment (a) equilibrium was very slowly attained while in experiments (b) and (c) normal potentiometric titration curves were not obtained. Experiments (d) and (e) gave normal titration curves with the exception of a slight perturbation just preceeding the end-point. Equilibrium was readily attained at both 55° and 70°. The presence of ethanol in experiment (f) was of no advantage since a titration curve very similar to those in experiments (d) and (e) was obtained. The conditions of experiment (d) seemed most promising and the possibility of using these conditions for the potentiometric estimation of thorium was further studied.

Determination of thorium potentiometrically. It was found that when thorium nitrate solutions were potentiometrically titrated with ammonium paramolybdate the thoria titer of the ammonium paramolybdate solution was about 0.6 per cent higher than that obtained by reducing the ammonium paramolybdate solution in a Jones reductor and titrating with ceric sulfate. For this reason it was necessary to standardize the ammonium paramolybdate solution potentiometrically against known amounts of thorium.

An ammonium paramolybdate solution was standardized as follows. Known amounts of a standard thorium nitrate solution were weighed into 250 ml. beakers and diluted to about 10^0 ml. After making these solutions 7 per cent in acetic acid they were heated to 50°-55° and potentiometrically titrated with ammonium paramolybdate using a 0.1 N calomel reference electrode and a molybdenum indicator electrode. In each case the data were plotted and the end-point determined from the graph. The results obtained by this procedure are shown in Table 13.

The data of Table 13 show that the method is reproducible and that thorium can be determined quantitatively by titration with ammonium paramolybdate when the end-point is detected potentiometrically. A typical titration curve is shown in Fig. 1.

Determination of thorium in the presence of calcium. This study was made by weighing out known amounts of a standard thorium nitrate solution, diluting to about 100 ml., adding known amounts of calcium nitrate, making the solutions 7 per cent in acetic acid, warming to 50°-55° and titrating as outlined above. Thorium can be quantitatively estimated in the presence of calcium as shown by the data of Table 14.

Table 13

Potentiometric Standardization of Ammonium Paramolybdate

Trial	ThO_2 sol'n., g.	ThO_2 taken, g.	Ml.Molybdate	Titer	% Error*
1	10.1913	0.1061	18.00	0.005894	+0.22
2	10.0647	0.1048	17.80	0.005888	+0.12
3	9.2445	0.09624	16.35	0.005886	+0.09
4	10.5175	0.1095	18.60	0.005887	+0.10
5	9.4638	0.09852	16.80	0.005864	-0.29
6	10.4490	0.1088	18.55	0.005865	-0.27
7	17.3922	0.1811	30.78	0.005883	+0.03

* Calculated as deviation from the average titer: 0.005881

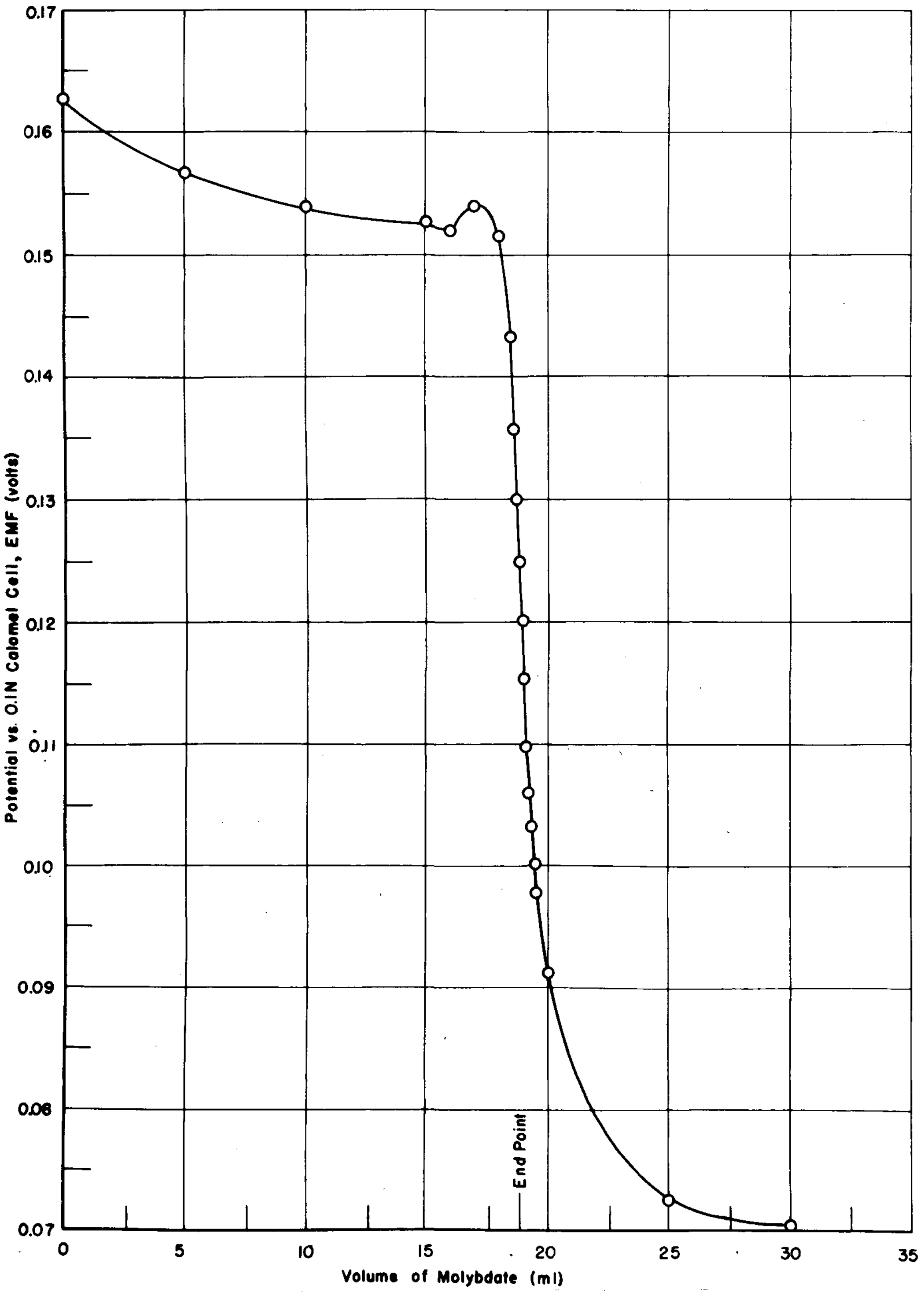


Fig. 1. Potentiometric Titration of Thorium

Table 14

Determination of Thorium in the Presence of Calcium

Trial	Ca, g.	ThO_2 sol'n., g.	ThO_2 taken, g.	Ml. Molybdate	ThO_2 found, g.	% Error
1	0.2	15.5495	0.1619	27.50	0.1617	-0.12
2	0.4	14.7772	0.1538	26.23	0.1542	+0.26

DISCUSSION

In an attempt to determine the general applicability of the molybdate method for thorium, a series of qualitative experiments were conducted. In these experiments an aqueous solution of the ion to be tested was made about 7 per cent in acetic acid and an equal volume of ammonium paramolybdate was added. In the cases of the anions another 7 per cent acetic acid solution was prepared and diluted with an equal volume of a thorium nitrate solution. Each solution was heated to boiling and allowed to stand for 12 hours. If no precipitate formed the ion in question was considered as not to interfere.

The following ions were found to be interferences according to the above experiments: silver, strontium, barium, zirconyl, stannous, stannic, lead, bismuth, tungstate, ferrous, and ferric.

According to the above experiments it was found that lithium, sodium, potassium, ammonium, cupric, calcium, beryllium, magnesium, zinc, cadmium, mercuric, lanthanum, borate, aluminum, gallium, indium, nitrate, vanadate, sulfate, chromic, dichromate, molybdate, selenate, uranyl, manganous, permanganate, chloride, perchlorate, bromide, iodide, cobalt, and nickel would probably not interfere in the determination of thorium.

Further quantitative work should be done on checking the thorium molybdate method for interferences.

CONCLUSIONS

1. A new oxidimetric method for determining thorium in the presence of calcium or uranyl salts has been developed.

2. Uranium-thorium alloys can be analyzed using the thorium molybdate method.

3. Molybdenum can be conveniently separated from certain other ions as thorium molybdate when other methods are not satisfactory.

4. Uranium-molybdenum alloys can be analyzed conveniently by separating the molybdenum as thorium molybdate.

5. Thorium cannot be separated from the rare earths as the molybdate from a 7 per cent acetic acid solution.

6. No satisfactory method of determining the end-point in the titration of thorium with ammonium paramolybdate using adsorption indicators has been devised.

7. A new potentiometric method of titrating thorium has been devised which is quantitative in the presence of calcium.

SUMMARY

A brief account of the history of thorium has been presented. The present analytical methods for determining thorium have been discussed and found to be largely gravimetric. Because of a definite need for a rapid, accurate method for determining thorium, a study of the titrimetric determination of thorium was made. This study has resulted in the development of a new oxidimetric method in which thorium is precipitated as the normal molybdate and the molybdenum equivalent to the thorium is reduced and titrated. This method was found to work very well in the presence of calcium and uranium but not so in the presence of the rare earths.

Molybdenum can be conveniently separated from certain ions as thorium molybdate and this method has been successfully applied to the analysis of uranium-molybdenum alloys.

A new potentiometric method for determining thorium has been devised in which the thorium is titrated with ammonium paramolybdate and the end-point detected by means of a molybdenum-calomel electrode system.

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to those who have so kindly aided him during the course of this study.

Dr. Harvey C. Diehl was in immediate charge of the author's research and his interest and cooperation are deeply appreciated.

Dr. F. H. Spedding, as project director, made it possible to carry this work to completion.

Mr. J. C. Warf made helpful suggestions from time to time during the course of this study.

Mr. R. W. Holmberg and Mr. J. H. Patterson made a few of the analyses reported in this thesis.

The research described in this thesis was sponsored by the Corps. of Engineers, Manhattan District, United States Army, and the funds for its support came from Contract No. W-7405-eng-82 between the Manhattan District and the Iowa State College.