THE ANALYTICAL ASPECTS OF THORIUM CHEMISTRY

THERALD MOELLER, GEORGE K. SCHWEITZER, AND DONALD D. STARR
The William Albert Noyes Laboratory, University of Illinois, Urbana, Illinois

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I. INTRODUCTION

Interest in the analytical chemistry of thorium has been extremely sporadic. The extensive use of thorium compounds in the incandescent mantle lamp industry prompted much exploratory work in thorium chemistry and in the development of analytical methods for the element during the latter part of the nineteenth century and the early part of the twentieth. However, decline in the use of such mantles in recent years has been paralleled by a general decline in interest in the characteristics of thorium as such. Recent observations upon the importance of the thorium nucleus in fission studies have again focussed attention upon the element, and it is apparent that much is still to be learned about the behavior of the element and its compounds. Because of the importance of the analytical properties of thorium in any studies relating to its chemistry, a detailed summary and critical review of available information seem apropos. Although a number of phases of the analytical chemistry of thorium have been treated previously (10a, 24, 38, 54, 89, 90, 91, 120, 134, 183, 231), no concise account embracing the entire subject is available.

The paucity of really characteristic reactions of thorium and its compounds and the marked similarities between the chemistry of thorium and that of almost every other element associated with it in nature complicate its analytical chemistry. Since but a single oxidation state (+4) is recognized, no reactions dependent upon change in oxidation state are possible. Furthermore, since the thorium ion is colorless and yields but few colored derivatives, distinctive reactions are rare.

Interferences produced by zirconium[1] and hafnium compounds[1] are in general less complex and less important than those produced by scandium, yttrium, and rare earth metal compounds. Separation of thorium from these materials is complicated by extreme similarities in compound solubilities and stabilities.

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[1] Because of the extreme similarities between zirconium and hafnium compounds and because most of the zirconium materials used in the investigations described herein undoubtedly contained hafnium compounds as well, the term zirconium, whenever used, may be taken to mean either the pure material or its admixture with hafnium.

Such similarities result from similarities in ionic charge–ionic size effects (189) and are very pronounced. Perhaps the greatest differences between these trivalent elements on the one hand and tetravalent thorium on the other are in basicity. The markedly reduced basicity of thorium is, however, but little different from that of cerium(IV). General trends in properties rather than sharp differences are the rule among these materials, and separational procedures involving them are commonly very involved and often only fractional in character.

Quantitative methods for the estimation of thorium are complicated by the same factors. Thorium may be determined readily and with extreme accuracy when present alone, but when other elements, particularly scandium, yttrium, and the rare earth elements, are present, its estimation is difficult and tedious. Even though a number of quantitative procedures have been proposed, really simple and at the same time accurate methods have yet to be developed.

II. Qualitative Detection of Thorium

A. SPECTROSCOPIC DETECTION

Thorium salt solutions show no absorption in the spectral range 2000–10,000 Å. and cannot be identified by direct absorption spectra measurements (92). However, Formánek (85) has shown that addition of the dye alkanet gives violet solutions which show maximum absorption in the range 6055–6081 Å. with thorium chloride and in the range 6066–6084 Å. with thorium nitrate, with bands of lesser intensities in the ranges 5599–5625 Å. and 5195–5222 Å. Unfortunately, salts of lanthanum, cerium, praseodymium, neodymium, erbium, yttrium, and zirconium give solutions with nearly identical absorption spectra, and detection of thorium in their presence would be exceedingly difficult.

The arc and spark spectra of thorium are rich in lines (104, 236). The most intense of these lines have been listed as 4019.137 Å., 3601.040 Å., 3538.75 Å., and 3290.59 Å. (104). These lines may be used for the identification of the element. The characteristic x-ray spectrum is also useful (88, 89).

B. RADIOMETRIC DETECTION

Thorium is a weak alpha emitter of half-life 1.34×10^{10} years. The short range of the emitted alpha particles (2.59 cm. in air at 760 mm. of mercury and 15°C.) and the slowness of the decay process combine to render detection of the element by means of its primary radiation a difficult task. Fortunately, a a number of its decay products, notably mesothorium II, have higher specific activities and may be detected more readily. If radioactive equilibrium has been attained, detection of thorium in this fashion is feasible. However, since uranium materials are often encountered in combination with those of thorium, this method is not necessarily accurate.

C. DETECTION THROUGH REACTIONS OF THE THORIUM ION

Thorium compounds are ordinarily white in the solid state and yield colorless solutions. The nitrate, perchlorate, acetate, sulfate, chloride, bromide, and iodide are the common water-soluble salts. From solutions of such materials, thorium may be precipitated as a white, gelatinous hydrous oxide (214) by aqueous ammonia, soluble metal hydroxides, or ammonium sulfide. The hydrous oxide is not amphoteric, but its precipitation may be inhibited by such complex-forming anions as acetate, tartrate, and citrate. The hydrous oxide may also be precipitated by hydrolytic reactions from hot solutions containing alkali metal thiosulfates, azides, or nitrites.

Soluble carbonates precipitate white basic thorium carbonate, soluble in excess ammonium carbonate solution. Thorium is completely precipitated as carbonate by barium carbonate. Oxalic acid precipitates crystalline normal thorium oxalate from dilute mineral acid solutions. Ammonium oxalate also precipitates thorium, but the precipitate dissolves in an excess of the reagent. In these behaviors thorium ion resembles the ions of the yttrium earths very closely.

Thorium ion is also precipitated as fluoride by either hydrofluoric acid or soluble metal fluorides, as double sulfates by alkali metal sulfates, as hydrated peroxide by hydrogen peroxide, as iodate by soluble iodates even in nitric acid solution, as ferrocyanide by soluble ferrocyanides, and as acid orthophosphate, pyrophosphate, or hypophosphate by the corresponding alkali metal salts. The majority of the thorium salts of organic acids are also water insoluble.

In systematic qualitative analysis, thorium ion is ordinarily concentrated and separated with scandium, yttrium, and the rare earth ions. After removal of scandium, thorium may be detected in the presence of the other materials by selective precipitation (26) from strongly acidic solutions with potassium iodate (186), alkali metal hypophosphates (151, 152, 209, 252), or alkali metal pyrophosphates (52) or from weakly acidic solutions with hydrogen peroxide (16, 28, 258, 259, 260, 262), alkali metal azides (70, 71, 72, 73), sebacic acid (222), *m*-nitrobenzoic acid (193, 194, 195), or sodium thiosulfate after boiling (16, 77, 87, 121, 122). Perhaps the most useful of these qualitative procedures is that employing iodate (120, 186), although zirconium and cerium(IV) materials also precipitate.

In the usual qualitative procedure, thorium ion is separated with the members of the ammonium sulfide group and is concentrated with iron and the other members of the so-called iron subgroup. A number of procedures have been recommended for its further separation. Thus, Browning (45) suggests precipitation of the fluorides of thorium and the rare earth elements from hydrochloric acid solution, followed by decomposition of these materials with concentrated sulfuric acid and precipitation of thorium with thiosulfate. Confirmation by dissolution of the oxalate in ammonium oxalate and reprecipitation with acid is further recommended (45). Noyes and Bray (198, 199, 200) also recommended separation by fluoride precipitation. This is followed by extraction of scandium as a soluble fluo complex ion with ammonium fluoride, decomposition of residual fluorides with perchloric acid, and detection of thorium by a method such as those outlined above. Still another procedure (38) involves precipitation with oxalic acid from a dilute hydrochloric acid solution, followed by extraction with ammonium oxalate solution. Dilution of the extract precipitates any zirconium and yttrium earth elements, and thorium oxalate is then precipitated by adding hydrochloric acid. Confirmation by either the iodate or the pyrophosphate procedure is recommended (38). All these general methods appear to be about equally effective. Microchemically, thorium may be identified as either the oxalate or the sulfate (90).

Thorium gives no characteristic dry reactions (213), and bead tests are equally ineffective. Vortmann (243) has outlined a general qualitative scheme involving dry reactions, although no ultimate provision for the detection of thorium is made. Successive fusions with sodium carbonate and sulfur and with potassium peroxydisulfate convert thorium, zirconium, and the rare earth elements to water-insoluble double sulfates. Separation from all materials except silica, barium sulfate, lead and bismuth compounds, and platinum is said to be effected in this fashion (243).

A number of colorimetric methods for the detection of thorium have been outlined (174, 241, 247, 263), but these procedures are not specific. Thus, the alkanet procedure of Formánek (85) referred to above is useful, but only in the absence of interfering elements. Kaserer (135) reported that as little as 0.1 mg. of thorium nitrate in 100 ml. of solution yielded a recognizable yellow color with pyrogallol aldehyde (2,3,4-trihydroxybenzaldehyde) and a flocculent yellow precipitate upon boiling. Zirconium compounds gave the same behavior, but cerium(III) compounds differed in failing to precipitate upon boiling. Aurintricarboxylic acid (aluminon) was found by Middleton (187a) to yield a bright red lake with thorium materials, but this reaction is sensitive to only one part in 10,000 (241) and is complicated by the similar behavior of rare earth metal and many more common ions (187a). Pavelka (202) obtained a violet coloration with as little as one part of thorium in 125,000 by impregnating paper with alizarin, treating with a slightly acidic thorium salt solution, and exposing to ammonia fumes. Both titanium and zirconium compounds gave reddish colors under similar conditions, but rare earth materials were apparently not investigated. Sodium alizarinsulfonate has been reported by Germuth and Mitchell (94a) to yield a red color with thorium ion, but the reaction is sensitive to only one part of thorium in 200 (241) and is far from specific (94a). Quinalizarin in the presence of sodium hydroxide has been found to give a blue color or precipitate with as little as one part of thorium in 150,000 (148). Both zirconium and the rare earth elements gave similar results, the latter when present to the extent of only one part in 1,000,000. Detection of thorium by means of the orange red color produced by addition of 1 per cent gallic acid solution to an ammoniacal salt solution has also been reported (217), although interference from a number of the rare earth elements occurs. Using tincture of cochineal in a nearly neutral solution, Beck (15) reported the detection of thorium through the production of a blue color. Under comparable conditions, the rare earth elements gave reddish colorations. Kuznetsov (160) obtained brownish yellow, crimson-pink, pink, and blue-violet colorations when thorium salt solutions were treated with 2-(*o*-arsonophenylazo)-*p*-cresol, 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, 1-(*o*-arsonophenylazo)-2-naphthol-6,8-disulfonic acid, and 3-(*o*-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, respectively. Such tests could not be applied in the presence of rare earth metal or zirconium ions since these materials, under comparable conditions, yielded colors differing only in shade. The conversion of the yellow 8-hydroxyquinoline derivative of thorium into a red material by excess 8-hydroxyquinoline at temperatures above 70°C. (115) may perhaps be of use in the detection of thorium in the presence of the rare earth elements, since the corresponding compounds of the latter materials are uniformly yellow regardless of conditions (92). Useful summaries of the applicabilities and limitations of these colorimetric tests are given by van Nieuwenburg *et al.* (241) and by Wenger and Duckert (247).

III. SEPARATION OF THORIUM FROM OTHER ELEMENTS

The most abundant natural sources of thorium are monazite and the monazite sands, its occurrence as orthosilicate (thorite) and oxide (thorianite) being of but little importance. The common natural associates of thorium are, therefore, scandium, yttrium, the rare earth elements, titanium, zirconium (plus hafnium), uranium, iron, aluminum, calcium, silica, and phosphorus as phosphate. Removal of the common elements from thorium presents no great problem, and separation from the periodic group IV analogs is not particularly difficult. However, the similarities existing between thorium compounds and those of scandium, yttrium, and the rare earth elements as mentioned in a previous section render the removal of these elements from thorium extremely difficult. The general methods of treating thorium minerals have been summarized in a number of publications (26, 38, 54, 120, 124, 176, 183, 215, 224) and need not be discussed here.

A. SEPARATION FROM THE COMMON ELEMENTS

General separations from the common elements have been indicated in the section on qualitative detection. These procedures are usually sufficiently quantitative in character to permit their application without essential modification. Perhaps the best general separational method involves precipitation of thorium with oxalic acid from slightly acidic solutions (37, 109, 224). Oxalate precipitation is effective not only in separating thorium from all the common metals but in removing phosphate as well. Of the various other procedures suggested for the removal of phosphate (224), precipitation of thorium as iodate from nitric acid solutions (180, 186) or as hydrous oxide with sodium hydroxide after digestion with sodium carbonate (124) or fusion with caustic alkali (46) appear to be the most effective. Baskerville's procedure (12, 13) of volatilizing phosphorus by high-temperature reduction of monazite with coke in the presence of lime and fluospar appears to offer no advantages because of the specialized equipment involved. The same may be said of the rather similar processes of Troost (235) and Weiss (245). Silica is usually removed as such after dehydration in the presence of acids. Iron, which is often a persistent impurity, may be removed through oxalate precipitation, by extraction as ferric chloride with ether (170), by precipitation as sulfide from tartrate medium (229, 230), or by electrolysis (134, 219). An electrolytic procedure depending upon amalgam formation has been suggested for the removal of barium ion (173).

B. SEPARATION FROM LESS COMMON ELEMENTS OTHER THAN YTTRIUM AND THE RARE EARTH ELEMENTS

Precipitation with oxalic acid from acidic solution frees thorium from essentially all of the less familiar elements except scandium, yttrium, and the rare earth metals. This procedure is particularly effective in removing titanium, zirconium, hafnium, and uranium compounds (38, 111, 120, 215). In a modified version, ammonium oxalate may be added in excess and thorium precipitated as oxalate by addition of acid. Removal of zirconium by this means is very effective (38, 127, 128). Precipitation with iodate does not free thorium from zirconium compounds, but treatment of the iodate precipitate with oxalic acid dissolves out zirconium materials effectively (38, 180, 183). Fusion with potassium acid fluoride to produce water-soluble fluo complexes, K_2MF_6, of titanium and zirconium and water-insoluble thorium fluoride has also proved useful for separation from these materials (69). Patents covering the removal of thorium and rare earth materials from titanium, zirconium, and iron compounds by precipitation of the former as fluorides have been issued (164). A partial separation of thorium from zirconium is effected by evaporation of sulfate solutions containing thallous sulfate (83), a double thorium salt, $2Th(SO_4)_2 \cdot 7Tl_2SO_4$, crystallizing first and being followed by a mixture containing $Zr(SO_4)_2 \cdot 2Tl_2SO_4 \cdot 4H_2O$. This separation is not efficient. Ammonium salicylate is reported to precipitate thorium but not titanium from a mixed salt solution (76). The bulk of the titanium and zirconium materials present in monazite remain as insoluble residues after the mineral is digested with sulfuric acid and then treated with cold water (124, 224). Many procedures, such as precipitation with pyrophosphate (49, 52), with hypophosphate (107, 252), with amines (105, 207), with bases such as lead carbonate (95), and with *m*-nitrobenzoic acid (193, 194, 195), are not effective in removing zirconium and its homologs. Removal of tungsten by extraction as water-soluble tungstate after fusion with sodium carbonate has been reported (257).

Similarities in basicities and complex-forming tendencies complicate the removal of scandium compounds from those of thorium. An excellent critical review of available methods has been given by Fischer and Bock (84). Precipitation with ammonia, with oxalic acid, with hydrofluoric or fluosilicic acid, with sodium alizarinsulfonate, or with phenylarsonic acid is not effective (84). Of the effective procedures (84), those involving excess ammonium fluoride (181) or excess potassium iodate in nitric acid solution (180) preferentially precipitate thorium, while those involving ammonia in ammonium tartrate solution (182) or boiling sodium carbonate solution (129, 187, 225) preferentially precipitate scandium. The ammonium fluoride and sodium carbonate procedures are the most commonly used. Separation by extraction of scandium thiocyanate with ether from aqueous solution (84), by fractional sublimation of the chlorides

(84), and by selective sublimation of scandium as acetylacetonate (84) have also been recommended for the complete removal of scandium from thorium.

C. SEPARATION FROM YTTRIUM AND THE RARE EARTH ELEMENTS

Separation of thorium from yttrium and the rare earth elements, while not as difficult as separations among the latter elements, is, nevertheless, far from simple. The abundant literature which has accumulated on methods for such separations (24, 25, 26, 52, 120, 124, 163, 167, 175, 178, 183, 224) may be cited as evidence for the complexity of the problem. In spite of the numerous investigations which have been carried out and of the variety of procedures which have been suggested, methods which combine rapidity with high efficiency have yet to be developed.

Proposed and recommended procedures may be classified conveniently as:

1. Those dependent upon differences in ease of accepting coördinating groups.
2. Those dependent upon differences in basicity.
3. Those dependent upon differences in solubilities of particular compound types.
4. Those dependent upon other differences in properties.

In all instances, separation from cerium(IV) compounds must be given special consideration, for in this state of oxidation cerium differs but little from thorium in the characteristics of its compounds.

1. Methods dependent upon differences in coördinating tendencies

Considerations based upon ionic charge–ionic size relationships (189) suggest sizable differences between thorium and these trivalent elements in ease of coördinate-bond formation. Thus, thorium would be expected to form coördination compounds much more readily than the cerium earth elements and, but to a lesser extent, more readily than yttrium and the yttrium earth elements. Only slight differences, however, would be expected between thorium and cerium(IV). Experimental observations are in accord with these predictions, and several useful methods of separation which take advantage of observed differences have been proposed.

(a) The oxalate procedure

Based upon an early observation by Bahr (9) that the oxalate of "wasium" (i.e., thorium) dissolved in ammonium oxalate solution, the method was first used for the purification of thorium compounds by Bunsen (47, 48), who found treatment of mixed rare earth and thorium oxalates with hot ammonium oxalate solution to dissolve the thorium material completely and the rare earth materials to only a slight extent. Dilution with water precipitated dissolved rare earth oxalates but was without effect upon the thorium compound. While several repetitions of the procedure were required, Bunsen found it to work to advantage upon thorium compounds which had been precipitated previously with sodium thiosulfate (48).

The basis for the method is apparent in the relative solubility data for thorium and rare earth oxalates in excess ammonium oxalate solution as given by Brauner (36, 37). Expressed in terms of the relative quantities of oxides dissolved, these solubilities were determined to be: Th, 2663; Yb, 105; Y, 11.0; Ce(III), 1.8; Nd, 1.5; Pr, 1.2; and La, 1.0. It is obvious that while thorium oxalate is by far the most soluble, appreciable quantities of rare earth oxalates, particularly those of the yttrium earths, may be expected to dissolve. The solubility of thorium oxalate as a function of ammonium oxalate concentration has been determined by Hauser and Wirth (106). Expressed as grams of ThO_2 per 100 ml. of solution at various normalities of ammonium oxalate, their values are: 0.01 *N*, 0.004 g.; 0.1 *N*, 0.22 g.; 0.5 *N*, 1.76 g.; saturated, 14.83 g. Thus, extraction can be effective only at high oxalate concentrations.

The composition of the complex oxalate derivative existing in solution has not been determined with accuracy. Brauner (36, 37) reported that 3.59 moles of oxalate ion were required to keep each mole of thorium in solution and suggested the formula $(NH_4)_2C_2O_4 \cdot 2Th(C_2O_4)_2 \cdot 7H_2O$ for the product crystallized from such solutions. Both this compound and a dihydrate were obtained by James, Whittemore, and Holden (130), and Hauser and Wirth (106) postulated the existence of the complex $[Th_2(C_2O_4)_5]^{--}$.

That the oxalate procedure effected only an incomplete separation of thorium from the rare earth elements and yttrium was recognized early (131), although Hintz and Weber (121, 122) found the method to be superior to that involving thiosulfate on a comparative basis. However, Drossbach (77) found thorium material extracted in this fashion to be contaminated with comparatively large amounts of the yttrium earths, and Benz (16), as a result of an extremely critical survey, reported the loss of as much as half the original thorium as well as an appreciable contamination of the product by cerium. Although the method has been a popular one (27, 32, 33, 69, 93, 97, 98, 99, 127, 128, 166, 178, 190, 214, 250, 256), the consensus of opinion at present is that it is inefficient (26, 120, 167, 224), particularly when relatively small quantities of thorium are to be removed from comparatively large amounts of rare earth materials (183).

From its solution in ammonium oxalate, thorium may be recovered by precipitation with acids (36, 37, 121), by precipitation with ammonia (99, 121), or by evaporation and ignition to oxide (47, 48). Zirconium oxalate is extracted with thorium oxalate but does not precipitate on acidification (55, 127, 128), while the major portion of dissolved yttrium earth oxalates is precipitated by dilution (47, 48, 224). Important modifications of the procedure involve dissolution of precipitated thorium oxalate in either ammonium acetate (97, 98, 99), ammonium carbonate (131), or sodium carbonate (147) solution. No advantages over the original oxalate procedure are apparent in such modifications. All these procedures entail repeated precipitations and extractions, and in every case prior reduction of cerium is desirable to prevent excessive contamination by that element.

(b) The carbonate procedure

Based upon an early observation by Damour (65) that thorium carbonate is more soluble in solutions containing excess carbonate than are the rare earth carbonates, this method is essentially the same as the oxalate procedure just discussed. In fact the dissolution of thorium oxalate in ammonium (131) or sodium (147) carbonate solution may be regarded as a variation of the general method. Separation by means of ammonium carbonate is incomplete (224), and no more than a concentration of the thorium is achieved. On the other hand, several procedures involving separation of thorium by dissolution in sodium carbonate or bicarbonate solution have been patented (61, 164, 165, 211). The procedure was recommended by Witt (255) for the elimination of cerium from thorium, but it has found little favor in recent years and appears to be about as inefficient as the oxalate procedures (224). Repeated extraction and reprecipitation is necessary, and the solubilities of the carbonates of the yttrium group of elements are sufficient to cause interferences. Thorium may be recovered from solutions containing the carbonate complex by evaporation or by precipitation with sodium hydroxide (165). The composition of the carbonate complex is not known.

(c) Miscellaneous procedures

Treatment of saturated sodium sulfite solution with a neutral solution of thorium and rare earth salts has been found (14, 56, 57) to precipitate the cerium earths completely but to leave most of the thorium in solution. However, Grossman (103) reported the separation to be inefficient in the presence of sizable quantities of the cerium earths, and but little attention has been paid to the method.

Few, if any, other procedures involving the formation of complex thorium compounds in solution have been proposed. The field of inner complexes has also been explored only rather superficially. The precipitation of thorium by a good many organic acids doubtless involves the pronounced tendency of thorium ion to act as an electron-pair acceptor, and in many instances chelate structures probably result. However, insufficient information is available to permit treatment of these cases as such, and they are, as a result, lumped together in the section on solubility differences. Formation of a chloroform-soluble acetylacetone derivative of thorium, $Th(CH_3COCH{=}COCH_3)_4$ (237, 238), by direct precipitation from aqueous solution may be cited as a possible means of separation, since the rare earth elements do not behave similarly. Correspondingly, the greater ease of formation and greater solubility in solvents such as chloroform and trichloroethylene of the 8-hydroxyquinoline derivative of thorium (92) may possibly be used to advantage in effecting separations. Much profitable investigative work remains to be done in this field.

2. Methods dependent upon differences in basicity

Comparisons of properties which measure the attraction of metal ions for electrons or anions indicate the basicity of the thorium ion to be much less than that of scandium, yttrium, or any trivalent rare earth ion (189). Such sizable differences render basicity methods far more feasible for the separation of thorium from these elements than for separations within the rare earth group (189). Numerous methods depending upon basicity differences have been proposed and used. Although some differences exist between thorium and cerium(IV) materials, these differences are so small as to render separation of these two elements impractical without prior reduction of cerium(IV) to cerium(III).

(a) Separation by alkaline precipitants

While the hydrous oxides and hydroxides of yttrium and the rare earth elements precipitate (at 25°C.) over the general pH range of 6.2 to 8.4 (41, 43, 189), hydrous thorium oxide forms at a much lower pH. Thus, by electrometric titration of thorium chloride solution at room temperature, Hildebrand (119) found precipitation to occur at a pH value of *ca.* 3. Similar measurements by Britton (40, 42) at 17–18°C. on solutions approximately 0.01 N in thorium ion indicated precipitation to begin at pH values of 3.51 for the chloride, 3.53 for the sulfate, and 3.57 for the nitrate. Bowles and Partridge (35) reported incidence of precipitation at pH 3.91 for thorium sulfate solutions and at 2.65 and 2.75 for cerium(IV) sulfate and cerium(IV) ammonium sulfate solutions, respectively, all measurements having been made with approximately 0.01 M solutions at 25°C. Thus, sufficient differences exist between precipitation pH values to permit separations of thorium from yttrium and the trivalent rare earth elements even if only moderately accurate pH control is maintained. Direct separation of thorium from cerium(IV) by this means appears impractical if not impossible.

Separation by alkaline precipitation was used extensively long before quantitative evaluation of pH differences was effected. The caustic alkalies and ammonia received some attention (24, 25, 220, 221), but, as is true with the rare earth elements alone (189), pH control with these highly alkaline reagents is too difficult to make their use practical. More success has attended the use of less basic metal oxides, hydroxides, and carbonates and of organic derivatives of ammonia.

Early work by de Boisbaudran (66, 67) showed that if solutions were first boiled with copper to reduce tetravalent cerium materials, thorium could be separated from the trivalent rare earth elements by precipitation with copper(I) oxide from hot solution. Removal of copper materials by hydrogen sulfide then yielded a purified thorium preparation free from rare earths. This procedure has never been widely used. Giles (95) separated thorium from the trivalent rare earth elements by treating a neutral or slightly acidic mixed nitrate solution with lead carbonate, lead ion being removed as sulfide after dissolution of the precipitated hydrous thorium oxide in acid. In addition to thorium, zirconium, cerium(IV), and iron(III) materials were found to precipitate completely, and partial precipitation of uranium, chromium(III), and aluminum was noted. Inasmuch as special precautions are necessary in the preparation of the lead carbonate, the method has assumed no large-scale importance. However, if zirconium materials have been removed and cerium(IV) materials reduced with sulfur dioxide, quantitative removal of thorium from rare earth materials may be effected in this fashion (188, 224). The use of mixed rare earth hydrous oxides and hydroxides for the precipitation of thorium and its concomitant separation from the rare earth elements has been patented (204). It has the advantage of avoiding addition of alkali and is said to be very effective (156), although zirconium, titanium, and cerium(IV) materials are precipitated as well. Barium carbonate is said to precipitate thorium and the cerium earths but not the yttrium earths from cold solution (26).

In an attempt to find specific metal oxides or carbonates for the precipitation of certain of the rare earth elements and thorium, Neish and Burns (196) compared the hydrogen-ion concentrations in 0.01 N nitrate solutions of lanthanum, cerium(III), cerium(IV), praseodymium, neodymium, and thorium with the hydroxyl-ion concentrations in creams of various water-insoluble oxides and carbonates at 25°C. On the basis of the relative quantities of hydrogen ion in the salt solution and of hydroxyl ion in contact with the oxide or carbonate, they predicted that:

1. Certain oxides, such as FeO and CoO, furnishing only small amounts of hydroxyl ion, would not be expected to precipitate thorium completely.
2. Other oxides, such as CdO and HgO, furnishing greater concentrations of hydroxyl ion, would precipitate thorium essentially completely.
3. Oxides and carbonates such as ZnO, CuO, PbO, $ZnCO_3$, and $PbCO_3$, furnishing still greater quantities of hydroxyl ion, would precipitate thorium and cerium(IV) completely but would not precipitate the trivalent rare earth elements.

Experimentally, complete precipitation of thorium was effected by treating thorium nitrate solution (followed by boiling or allowing to stand for several hours in the cold) with zinc oxide, cadmium oxide, lead oxide (Pb_3O_4), cuprous oxide, lead carbonate, zinc carbonate, cupric carbonate, and manganous carbonate, while only incomplete precipitation was effected with ferrous oxide, nickelous oxide, cobaltous oxide, cupric oxide, ferric oxide, and chromic oxide. The carbonates of manganese, copper, and lead gave precipitates which were easiest to handle. Cerium(IV) was precipitated in the same manner as thorium.

For the separation of thorium from the rare earth elements, Neish and Burns (196) recommended the following precipitants: lead carbonate, 60°C. for 2 hr.; cupric carbonate, cold; zinc carbonate, heated just to boiling; lead oxide (Pb_3O_4), cold; cuprous oxide, 100°C. for 1 hr.; manganous carbonate, 64°C.; and zinc oxide, cold. Precipitation of the trivalent rare earths was insignificant in all cases except with zinc oxide. For the systematic removal of thorium from the rare earth elements, prior reduction of cerium(IV) materials with hydrogen sulfide or sulfur dioxide followed by treatment in an atmosphere of carbon dioxide with either lead carbonate, zinc carbonate, cupric carbonate, lead oxide (Pb_3O_4), or zinc oxide in slight excess was recommended. The precipitated hydrous thorium oxide was then dissolved in acid, and thorium was reprecipitated as hydrous oxide free from the rare earth elements.

Separations based upon the concept of controlled pH which is implicit in the work of Neish and Burns (196) have also been effected by the use of organic derivatives of ammonia. Extensive investigations of the behavior of thorium, zirconium, lanthanum, cerium(IV), praseodymium, and neodymium salt solutions toward a variety of substituted ammonias have been reported by both Jefferson (132) and Hartwell (105). Jefferson found thorium to be precipitated quantitatively by aniline, dimethylaniline, diethylaniline, piperidine, quinoline, and pyridine and nearly quantitatively by *o*-toluidine and xylidine. Zirconium was precipitated quantitatively by all these reagents and cerium(IV) by most of them. For quantitative separation of thorium from the trivalent rare earth elements studied, Jefferson recommended the use of aniline or quinoline. Hartwell extended these observations to many other amines, both aromatic and aliphatic, and suggested the use of *p*-chloroaniline, hexamethylenetetramine, and *p*-toluidine for the removal of thorium. Other amines, such as benzidine, *m*- and *p*-bromoanilines, *p*-bromophenylhydrazine, *m*-tolylenediamine, isoquinoline, α-picoline, and tribenzylamine, were found to precipitate thorium (and zirconium) but not the rare earth elements. More alkaline amines, particularly the aliphatic derivatives, precipitated the rare earth elements as well as thorium.

The use of aniline for selective precipitation of thorium has also been recommended by Kolb (145) and Allen (2). Allen found titanium, zirconium, and cerium(IV) materials to be precipitated as well and reported hydrazine to behave in the same fashion as aniline (2). Pyridine has been used by Atanasiu (4) for the quantitative precipitation of thorium in the presence of the cerium earths, and quinoline has been suggested for the same purpose (214).

A much better reagent for the removal of thorium from the rare earth elements is hexamethylenetetramine (or hexamine). Since this material undergoes hydrolysis to ammonia in solutions containing even a small concentration of hydrogen ion, it may be used to give solutions of controlled pH. Although Ray (207) showed that both thorium and zirconium could be precipitated quantitatively by heating their aqueous salt solutions with hexamine, it remained for Ismail and Harwood (126) to apply the method to thorium–rare earth mixtures. Ismail and Harwood found the hydroxyl-ion concentration in an aqueous solution of hexamine to be sufficient, even in the presence of buffering ammonium salts, to precipitate thorium completely and leave the rare earth elements unprecipitated even at the boiling temperature. Their quantitative method for thorium estimation based upon this behavior will be discussed in detail in a later section. In the presence of much cerium, a second precipitation was required for the production of pure thorium material.

Neither acetamide (178), semicarbazide (178), succinimide (178), nor urea (50, 178) is sufficiently basic itself to precipitate thorium. However, slow decomposition of hot solutions of urea into ammonia and carbon dioxide might provide media of controlled pH suitable for separation of thorium from the rare earth elements. Although materials used by Fogg and Hess (84a) in their studies upon the separation of the yttrium earths by this means contained thorium, no record of the behavior of the thorium was reported. Extension of this and other methods involving rigid pH control should be fruitful for the selective precipitation of thorium.

(b) Separation by hydrolytic precipitation

Because of the reduced basicity of the thorium ion, salts containing rather strongly basic anions should, if soluble, be more susceptible to conversion into water-insoluble products by hydrolysis than the corresponding salts of the trivalent rare earth elements. Of the salts admitted by the basicity and solubility restrictions, the thiosulfates, azides, and nitrites have been investigated most extensively.

Separation of thorium by precipitation through hydrolysis of solutions containing thiosulfate ion is a classical procedure (22, 26, 38, 54, 89, 90, 120, 124, 162, 167, 183, 215, 224), which was apparently used first by Chydenius (59). Although Chydenius reported that treatment of a neutral or slightly acidic mixed salt solution with sodium thiosulfate precipitated thorium along with some sulfur, whereas the rare earth elements remained largely unprecipitated, he did not regard the method as completely separative. Lack of precipitation of lanthanum and didymium was verified shortly thereafter by Hermann (117, 118), and the procedure was adapted to thorium–rare earth separations by Bunsen (48) and to thorium recovery from monazite by Fresenius and Hintz (87). Witt (256) recommended several successive precipitations with warm thiosulfate followed by an oxalate extraction for the complete purification of thorium. The oxalate and thiosulfate procedures were found to be about equally efficient by Hintz and Weber (122), Drossbach (77), and Benz (16). Various other workers have also employed the method to advantage (94, 133, 178). In its present form, the procedure involves boiling after addition of thiosulfate (120, 183, 224), but since complete separation is not effected in a single step, the procedure must be repeated several times. It is, therefore, of but limited value for the rapid, large-scale separation of thorium from yttrium and the rare earth elements, although, if carefully controlled, it can effect quantitative separation (120). Although early investigators considered the precipitate to be thorium thiosulfate (59, 117, 118), more recent work has shown it to be the hydrous oxide admixed with sulfur (224). Both scandium and zirconium are precipitated with thorium in this procedure (224).

Dennis and Kortright (72, 73) reported that addition of 0.3 per cent sodium or potassium azide solution to a cold solution containing thorium and rare earth metal nitrates, followed by boiling, precipitated thorium quantitatively and effected its separation from lanthanum, cerium, and didymium. Further work by Dennis (70, 71) showed separation from lanthanum to be quantitative. In this procedure, thorium is precipitated as hydrous oxide because of extensive hydrolysis of the azide ion (119). In spite of the excellence of the results obtained by Dennis (and Kortright), Wyrouboff and Verneuil (261) found the procedure to be ineffective in the presence of cerium. Because of the cost of the reagent and the hazards attending its use, the method has never been favorably received.

Precipitation of thorium by hydrolysis of nitrite solutions has been reported (11), and an extension of the classical nitrite procedure (189) would be expected to concentrate thorium in the least basic fractions. Efficient separation of thorium in this fashion would be highly improbable because of difficulty in sufficiently accurately controlling the pH.

Precipitation of thorium as basic acetate by boiling thorium salt solutions with excess sodium acetate was found by Haber (103a) to yield thorium free from didymium. Although recommended as very effective by Mingaye (188), this method is too expensive to be of general use.

(c) Separation by miscellaneous procedures

The steady increase in pH in the vicinity of the cathode during electrolysis of aqueous nitrate solutions was used by Dennis and Ray (73a) for the rapid concentration of thorium from synthetic mixtures with the rare earth elements and from monazite extracts. The weakly basic thorium precipitated in the first fractions, and in a single step increases in thorium content from 14.76 per cent to 78.63 per cent and from 5 per cent to 52 per cent were effected. Although complete separation from the rare earth elements was not reported, the success which has attended fractional separation of the latter elements by this means (189) suggests its even greater effectiveness in the removal of thorium.

Use of chlorine and caustic alkali has been proposed (220, 221), the more basic hydrous oxides and hydroxides of yttrium and the trivalent rare earth elements being more soluble than hydrous thorium oxide. However, the procedure offers no advantages and is, of course, incapable of separating thorium from cerium. Some separation may be effected by treatment of the mixed oxides with acids, since thorium oxide is much less soluble than the others (140), but such separation is only fractional in character. Concentration of thorium in the least basic fractions in the nitrate fusion process (189) has been used to advantage for the removal of thorium from rare earth mixtures (158a, 197, 239), although separation from the least basic members of the rare earth series by this means is incomplete (23).

3. Methods dependent upon differences in solubilities of particular compound types

Separation of thorium from the rare earth elements by solubility differences may be effected by preferential precipitation, by preferential dissolution of precipitated materials, or by crystallization. Of proposed procedures based upon these principles, those involving crystallization are most apt to be fractional in character. Because of the difficulties imposed by the removal of phosphate, much of the investigative work which has been carried out has been directed toward removal of thorium by precipitation from solutions which are sufficiently acidic to prevent precipitation of phosphates of yttrium and the trivalent rare earth elements. In all methods embracing these general principles, complication by cerium(IV) compounds is to be expected.

(a) Precipitation from strongly acidic solutions

Most common of such procedures are those involving phosphates of various types. These procedures are all dependent upon precipitation of the thorium compounds from solutions which are too strongly acidic to permit precipitation of the corresponding derivatives of the trivalent rare earth elements. Britton (44) has reported precipitation from thorium chloride solutions containing phosphate at pH 2.72, but in the experience of the authors, precipitation occurs at even lower pH values. The true nature of the phosphate-containing precipitate is doubtless dependent upon the total acidity and previous treatment of the solution from which it is formed, but it appears not unlikely that the pyrophosphate is the common product (203). Removal of thorium by reduction of acidity through dilution or addition of ammonia or magnesium oxide from extracts obtained by sulfuric acid treatment of phosphate minerals such as monazite or xenotime is a classical procedure (25, 54, 124, 147, 163, 205, 224), variations of which have been covered by numerous patents (e.g., 19, 20, 100). Separation in this fashion is not complete, for complete removal of the thorium always results in its contamination by small amounts of the rare earth elements. The convenience of the procedure for direct recovery of relatively pure thorium from its most important sources, however, renders the method of extreme technical importance.

Direct precipitation of thorium with alkali pyrophosphate from solutions approximately 0.3 *N* in hydrochloric acid has been recommended by Carney and Campbell (49, 52) as a particularly efficient method of separation. While cerium (IV) and zirconium pyrophosphates are also precipitated under these conditions, those of the trivalent rare earth elements are not. The method is based upon early observations on the insolubility of the thorium derivative, $ThP_2O_7 \cdot 2H_2O$, by Cleve (62), and is sufficiently accurate to be adaptable to the quantitative estimation of thorium in mixtures (52).

Precipitation of thorium hypophosphate, $ThP_2O_6 \cdot 11H_2O$, from solutions containing sizable quantities of free acid was first recommended by Wirth (252) as a means of separation, since under such conditions yttrium and the rare earth elements are not precipitated. At almost the same time, the same procedure was reported by Koss (151), who recommended precipitation from 6 per cent hydrochloric acid solution, and by Rosenheim (209), who suggested generation of hypophosphoric acid within the salt solution by anodic oxidation of a copper(II) phosphide electrode. The basic features of the method have been patented (74, 152), and while either hypophosphoric acid or its alkali metal salts may be used, the former has been recommended for use in a sulfate medium (254) because of the possible precipitation of double sulfates of the cerium earths by the latter. In a more recent publication (107), the use of a 10 per cent hydrochloric acid medium has been suggested. Hypophosphates of titanium, zirconium, and cerium(IV) also precipitate from acidic solutions (107, 252), but interference from these materials may be eliminated by methods already discussed. Recovery of thorium may be effected by ultimate precipitation as oxalate after decomposition of the precipitate with sodium hydroxide (252) or mixed sulfuric and fuming nitric acids (224). Use of the hypophosphate method offers no apparent advantages over use of the pyrophosphate and has the disadvantage of requiring a less common and more expensive reagent.

Ryan has recommended both sodium metaphosphate (211) and disodium ammonium phosphate (212) as efficient precipitants for the removal of thorium from acidic solutions containing rare earth materials, but neither material has been widely used. It is not improbable that an adaptation of Willard and Freund's hydrolytic phosphate method (249) might be useful for at least the small-scale separation of these elements.

A procedure depending upon the precipitation of thorium as fluosilicate from boiling solutions containing large excesses of mineral acids and the lack of precipitation of the rare earth elements under the same conditions was patented by Rosenheim, Meyer, and Koppel (210). While this method has not been used extensively, it appears to yield excellent results and should be applicable to fairly large-scale separations. Recovery of thorium from the precipitate is effected by conversion to sulfate with sulfuric acid (210).

A convenient and precise method of effecting this separation on a laboratory scale is the iodate procedure of Meyer and Speter (186). Precipitation of thorium as iodate is reported to be complete even if the solution contains 40 per cent by volume of concentrated nitric acid, providing a large excess of potassium iodate is used as precipitant. Under these conditions the trivalent rare earth elements are not precipitated, but scandium, zirconium, and cerium(IV) are (39, 180). Prior reduction with sulfur dioxide renders separation from cerium complete (180), and scandium and zirconium may be removed as previously outlined. Recovery of thorium is effected by reduction of the iodate with sulfur dioxide and subsequent precipitation with oxalic acid. While the method has proved very effective (137, 139, 180, 186, 191) and has been recommended very highly (26, 38, 55, 120, 124, 162, 167, 184, 215, 224), precipitation of thorium is complete only in the presence of a comparatively large excess of iodate because of the measurable water solubility of the compound (92). Because of the quantities and high costs of the reagents involved, the method shows no promise for large-scale separations, but it does have the advantages of working in the presence or absence of phosphate and of being quantitative in nature (26, 38, 58, 92, 120, 156, 234). Detailed instructions for its application are to be found in the listed references.

(b) Precipitation from weakly acidic or neutral solutions

In 1885, both Cleve (64) and de Boisbaudran (68) reported precipitation of thorium by means of hydrogen peroxide. Although Kossman (153) employed this reaction for the separation of thorium, the first comprehensive studies were made by Wyrouboff and Verneuil (258, 259, 260, 262). As recommended by these authors, the method amounts usually to treatment of warm (60–80°C.), neutral or slightly acidic, nitrate solutions containing ammonium nitrate with 3–10 per cent hydrogen peroxide, although preliminary separations may be effected by use of the more basic barium peroxide (262). While solutions containing as little as 0.001 per cent of thorium will yield precipitates under these conditions (22, 167), removal of thorium from rare earth mixtures is complete only if the quantity of thorium is comparatively small (167). Cerium(IV), titanium, and zirconium materials are also precipitated by hydrogen peroxide, but a second precipitation is usually sufficient to remove cerium. While the method is satisfactory for the removal of the bulk of the rare earth elements from thorium, quantitative separation can be effected only if the operation is repeated numerous times. Under such conditions, the method becomes tedious and costly. Benz (16) regarded the hydrogen peroxide procedure as the equal of the thiosulfate method, and in modified form it has been patented for large-scale operation (60, 61). Early workers formulated the precipitated peroxy compounds variously as $Th_4O_7 \cdot SO_3$ (64) and $Th_4O_7 \cdot N_2O_5$ (258), but in the light of more modern evidence it is probable that $Th_2O_7 \cdot 4H_2O$ is formed (216).

A number of other precipitants have been suggested for use under these conditions, because thorium compounds are commonly less soluble than the corresponding compounds of yttrium and the rare earth elements. The majority of these materials give only fractional separations and cannot be used for the quantitative removal of thorium in a single operation. As a consequence, they are of no technical importance and are useful only for the laboratory concentration of the element. Among these precipitants are sodium acetate from acetic acid solutions (25, 163), guanidine carbonate (51), hydrofluoric acid or soluble fluoride (75), ammonium vanadate (194, 195), ammonium molybdate (179), sodium tungstate (194, 195), and potassium chromate (172, 192, 223) or dichromate (223). Original reports (179) of the completeness of the molybdate separation have been questioned recently (10a), but it is probably the most effective of those listed.

Purification of thorium compounds by precipitation as double sodium sulfate (21) or double potassium sulfate (33, 161) is a well-known procedure. That the thorium compounds are less soluble than the corresponding compounds of the cerium earth elements is the basis for separational methods depending upon fractional precipitation of these materials (63, 127, 128, 228). James (127, 128) has suggested removal of thorium from the yttrium earths by this means, with subsequent removal of coprecipitated cerium earths by the ammonium carbonate or hydrogen peroxide procedures.

The thorium salts of many organic acids are also markedly less soluble than corresponding salts of yttrium and the rare earth elements. The relative utilities of a number of such acids in effecting thorium–rare earth separations are summarized in table 1. Only fumaric (178), *m*-nitrobenzoic (194, 195), sebacic (222), phenoxyacetic (205), phenylarsonic (208), quinaldic (80), and alizarin-3-sulfonic (15) acids and 8-hydroxyquinoline (115) may be regarded as sufficiently effective to merit use. However, all of these reagents are costly and are therefore limited in their use to laboratory operations. Zirconium is also precipitated by the majority of these materials. Use of oxalic acid cannot be regarded as an effective means of separation, for although thorium oxalate is less soluble in acidic solutions than the oxalates of the other materials (253), solubility differences are insufficient to give anything but fractional separations.

The fumaric acid procedure of Metzger (178) entails use of a saturated solution of the reagent in 40 per cent ethanol and addition of 40 per cent ethanol by volume to the thorium–rare earth salt solution. It has been applied successfully to the removal of thorium from monazite (157). The isomeric nitrobenzoic acids are all effective in precipitating thorium, but the meta acid is preferred (194,

TABLE 1

Organic acids for removal of thorium from rare earth elements

REAGENT	REMARKS	REFERENCES
Alizarin-3-sulfonic acid	Precipitates thorium and scandium but not trivalent rare earth elements	(15)
Anisic acid	Only fair separation	(205)
Aspartic acid	Only fair separation	(205)
Benzoic acid	Incomplete separation	(146, 194, 195)
Cinnamic acid	Incomplete separation	(146, 178)
Citric acid	Ineffective	(194, 195)
8-Hydroxyquinoline	Effective at controlled pH	(115, 169)
Fumaric acid	Precipitates thorium and zirconium but not trivalent rare earth elements	(178)
Gallic acid	Ineffective	(194, 195)
Linoleic acid	Ineffective	(194, 195)
Maleic acid	Ineffective	(178)
Mucic acid	Only fair separation	(205)
m-Nitrobenzoic acid	Precipitates thorium but not trivalent rare earth elements	(194, 195)
Oleic acid	Ineffective	(194, 195)
Oxalic acid	Ineffective	(253)
Oxyisophthalic acid	Ineffective	(194, 195)
Phenoxyacetic acid	Precipitates thorium but not trivalent rare earth elements	(205)
Phenylarsonic acid	Precipitates thorium and zirconium but not trivalent rare earth elements	(208)
Phthalic acid	Ineffective	(178)
Picric acid	Ineffective	(178)
Picrolonic acid	Precipitates thorium and trivalent rare earth elements	(112)
Pyrotartaric acid	Only fair separation	(205)
Quinaldic acid	Precipitates thorium, zirconium, and uranium but not trivalent rare earth elements	(80)
Salicylic acid	Incomplete separation	(146, 194, 195)
Sebacic acid	Precipitates thorium, but not trivalent rare earth elements	(222)
p-Toluic acid	Ineffective	(194, 195)

195). Its effectiveness is said to equal that of fumaric acid, although two precipitations from neutral solution are required for complete separation (194, 195). Many investigators have employed this method to advantage (3, 96, 146, 172). Use of sebacic acid appears to be equally effective in nearly neutral boiling solutions (222), although it is complicated by precipitation of rare earth sebacates at high sebacate-ion concentrations, e.g., with ammonium sebacate (248), and by precipitation of cerium when present in high concentrations (136). In the presence of cerium, use of ethanol solutions of sebacic acid has been recommended (136). The sebacic acid procedure has given favorable results in the hands of several investigators (136, 229, 230), and its use has been patented (144). The phenylarsonic acid procedure (208) depends upon the relative insolubility of the thorium compound in acetic acid–ammonium acetate mixtures. The difficulty of removing cerium and the necessity for double precipitation complicate this procedure (138). Phenoxyacetic (205), alizarin-3-sulfonic (15), and quinaldic (80) acids all appear promising, especially the latter since separation from zirconium may also be effected from cold solutions. Use of 8-hydroxyquinoline as a precipitant has been confined largely to the estimation of thorium (17, 113, 115), but since Mannelli (169) has established pH differences for the precipitation of thorium and the rare earth elements with this reagent, separations at controlled pH values might be expected. Precipitation of the thorium compound is said to be complete at pH 4.4 (102), while 8-hydroxyquinoline derivatives of the trivalent rare earth elements are completely precipitated at pH values above 6 (92). Berg and Becker (18) effected complete separation of thorium from cerium(III) by first precipitating the thorium derivative from a solution containing 2.5 per cent of free acetic acid by volume and then precipitating the cerium(III) derivative from the filtrate by adding ammonia. Further work with this reagent is indicated.

(c) Fractional crystallization

Because of the existence of shorter and more precise methods, fractional crystallization procedures are of little or no importance for these separations. Of the several which have been suggested, the sulfate procedure is most important since it may be employed for the removal of small amounts of yttrium and cerium earth materials from thorium compounds (163). Based upon the fact that the solubility of hydrated thorium sulfate in water decreases more rapidly as the temperature is increased than do the solubilities of the rare earth metal sulfates (158, 158a, 197, 256), the method usually amounts to dissolving the impure sulfate in ice water and crystallizing the octahydrate by warming to 20°C. (163). Koppel and Holtkamp (147) have recommended crystallization from hydrochloric acid medium as requiring less careful temperature control. Two or three repetitions are needed to yield a pure product, and the method is particularly useful where the cerium content is low (251). Greater solubility differences are said to exist with the ethyl sulfates than with the sulfates alone (155).

Fractional crystallization of the double ammonium nitrates as suggested by

Witt (255) offers no advantages. A method of potential small-scale utility involves precipitation of practically all of the cerium earth elements as double thallous sulfates, followed by crystallization of a double thorium–thallous sulfate upon evaporation of the filtrate by one-third (83). Thorium material so obtained is said to be free from rare earths and zirconium, a double zirconium–thallous sulfate crystallizing only upon further evaporation. Crystallization of the mixed acetates, followed by selective leaching of rare earth metal acetates away from the less soluble thorium acetate, has been reported to be effective (25).

4. Methods dependent upon other differences in properties

Procedures dependent upon the greater covalent characteristics of thorium compounds should be effective for removal of this element from yttrium and the rare earth elements. But little is known about such procedures at the present time, although removal of thorium from cerium by volatilization of its chloride at 700–800°C. has been reported (34). On this basis, preferential extraction of thorium compounds from aqueous solution into organic solvents might be expected. Such a method should be of technical importance because of its applicability as a continuous process.

Another procedure which is showing some promise involves differences in rates of reaction of thorium and rare earth metal ions with cation exchangers (169a).

5. Summary

But few of the outlined procedures are adaptable to the large-scale separation of thorium from yttrium and the rare earth elements. Technically, the major part of the available thorium is recovered from monazite, in which mineral the ratio of thorium to rare earth elements is quite small. The simplest, most efficient, and most widely used procedure entails precipitation of a phosphate of thorium by careful reduction of acidity of the sulfuric acid extract of the mineral. Subsequent treatment by other procedures is essential for the preparation of thorium compounds completely free from the rare earth elements and yttrium. Thus, after removal of phosphate by oxalate precipitation or fusion with alkalies, final purification may be effected through the thiosulfate, peroxide, oxalate, sebacic acid, or sulfate crystallization procedures, all of which are tedious and somewhat costly. For laboratory-scale separations, use of more precise but more expensive methods, such as those involving iodate, *n*-nitrobenzoic acid, etc., is desirable. Ultimate separations from zirconium, cerium(IV), and the least basic members of the yttrium earth series are usually necessary for final purification. Methods which are at the same time rapid, quantitative, and inexpensive have yet to be developed.

IV. QUANTITATIVE ESTIMATION OF THORIUM

Exact methods for the quantitative estimation of thorium are of interest because of the growing importance of the element in the production of catalysts and alloys and in the investigation of nuclear phenomena. While accurate estimation of the element in its pure compounds or in the absence of materials such as uranium, zirconium, scandium, yttrium, and the rare earth elements is simple, procedures for use in the presence of these elements are often involved and complicated by interferences. Such procedures may take either of two forms; namely, prior removal of the interfering elements or determination of thorium in their presence. Because of difficulties attending removal of interfering elements (see Section III), reliable procedures of the second type are highly desirable. Unfortunately, adequate methods of this type are limited in number. Proposed procedures of all types may be classified conveniently as gravimetric, titrimetric, radiometric, and miscellaneous. Detailed summaries of quantitative procedures appear in many references (10a, 26, 38, 54, 89, 109, 110, 120, 134, 163, 174, 176, 183, 215, 224, 232, 233, 234, 241).

A. GRAVIMETRIC ESTIMATION

Almost without exception, gravimetric procedures involve ultimate weighing of thorium as the ignited oxide. Commonly, this is preceded by a separational procedure of the type already discussed (see Section III) to remove interfering materials. In most of the methods to be outlined below, the principles already discussed under separations in Section III are apparent, for separational procedures and those for quantitative estimation are often essentially the same. An excellent, albeit brief, review of existing gravimetric procedures has been published recently by Jüstel (134).

1. Estimation as oxide

Estimation as oxide ordinarily entails precipitation as hydrous oxide or oxalate, since these precipitates may be ignited directly. Because of the volatility or instability of ammonium salts at elevated temperatures, aqueous ammonia is preferable to the more difficultly removable fixed alkalies as a precipitant for hydrous thorium oxide. Precipitation from 5–10 per cent ammonium nitrate solution, followed by digestion on the steam bath and washing with warm 5–10 per cent ammonium nitrate solution containing 2 per cent ammonia, has been recommended as yielding quantitative results (109).

As substitutes for ammonia, many organic amines have been suggested (105, 132). Although many such compounds offer no advantages over ammonia, certain of them (see Section III) precipitate thorium without affecting yttrium and the rare earth elements. Thus, aniline (2, 145), pyridine (4), quinoline (214), and phenylhydrazine (2) have all been used for the estimation of thorium in the presence of rare earth elements. However, these precipitants appear too uncertain in their behavior to have merited widespread use, and interference from zirconium, titanium, and cerium(IV) materials is to be expected. Perhaps the best results have been obtained with hexamethylenetetramine. According to Ismail and Harwood (126) thorium is completely precipitated and quantitatively removed from the rare earth elements when a 10 per cent solution of the amine is added to a mixed salt solution containing about 5 per cent of ammonium chloride and the whole is warmed to 30°C. A second precipitation with the amine prior to ignition is recommended for complete removal of cerium, but under these conditions results comparable with those obtained with the classical thiosulfate procedure were reported. The method may be applied to the direct determination of thorium in monazite if preceded by two oxalate precipitations to remove zirconium (126), but its application to mixtures rich in the yttrium earth elements should be investigated further (134).

The principle of separation through controlled pH by use of metal oxides or carbonates as precipitants may also be applied to the estimation of thorium in the presence of yttrium and the rare earth elements. The copper(I) oxide procedure of de Boisbaudran (66, 67) is effective for the estimation of thorium under these conditions if preceded by boiling with copper to reduce interfering cerium(IV) compounds. Equally effective is the lead carbonate procedure of Giles (95), also if preceded by reduction of cerium(IV) materials. Reagents recommended by Neish and Burns (196), such as the carbonates of copper, zinc, and manganese and the oxides of zinc and lead (i.e., Pb_3O_4), may be expected to behave in the same fashion. Use of any of these precipitants must presuppose prior removal of zirconium as well as reduction of cerium(IV) and must be supplemented by removal of the introduced metallic ion. Ultimate precipitation of thorium as hydrous oxide or oxalate ordinarily completes the determination.

The principle of controlled pH is also implicit in the hydrolytic selective precipitation of hydrous thorium oxide with alkali metal azides (72, 73). Although quantitative separation of thorium from lanthanum, cerium, and didymium by this means has been claimed (70, 71, 72, 73), Wyrouboff and Verneuil (261) reported inaccuracies in the presence of cerium, and the method is of no present importance (134).

Precipitation as oxalate is most commonly effected by treatment of a nearly boiling thorium salt solution, containing not more than 4–5 per cent by volume of mineral acid (usually hydrochloric or nitric) (109, 114, 120), with saturated oxalic acid solution (26, 38, 109, 114, 120, 215). Filtration after a period of standing of at least 6 hr. (38) may then be followed by washing with warm, dilute oxalic acid solution and ultimate ignition at 950–1100°C. (109, 114, 120). In this form, the method is applicable to micro determinations as well as macro (114). No separation from the rare earth elements or yttrium is effected, but the method may be applied to the estimation of thorium in the presence of zirconium because of the non-precipitation of the latter element. Because of the marked solubility of thorium oxalate in strongly acidic solutions (106), reasonably rigid acidity control is essential for quantitative recovery. Owing to its solvent effect upon thorium oxalate, ammonium oxalate is not a suitable precipitant. Quantitative methods for thorium based upon extraction of its oxalate from a mixed oxalate precipitate in this fashion (77, 97, 98, 99, 121, 122, 178) are ineffective because of incompleteness of the separation (16, 26).

Estimation of thorium as oxide in tungsten–thorium mixtures by volatilizing the tungsten away by heating in a current of air and chloroform vapor and weighing the residue has been recommended (218).

2. Estimation in strongly acidic solutions

The direct estimation of thorium in solutions containing comparatively large quantities of free mineral acids is of considerable importance, because under such conditions prior removal of phosphates is unnecessary. Furthermore, such media are advantageous because of the rather sizable solubility differences noted between compounds of thorium and compounds of rare earth elements. As a consequence, these methods are often directly applicable to analyses of monazite and other phosphate minerals. Because they require fewer manipulations than do many other methods, such procedures are said to be rapid. The term is to be used advisedly.

(a) The iodate procedure

Perhaps the most highly recommended procedure for use under these conditions is the iodate procedure of Meyer and Speter (186). Indeed, Kaufmann (139) recommended it as being the simplest and most accurate of seven commonly used methods, including the gravimetric sebacic acid and volumetric molybdate procedures. Depending as it does upon the insolubility of thorium iodate in solutions containing excess iodate and up to 40 per cent of nitric acid by volume as contrasted with the solubilities of iodates of the trivalent rare earth metals under similar conditions, the method is directly applicable to mixtures containing these elements. Since cerium(IV) iodate is also precipitated (39, 180), prior reduction with sulfur dioxide (180) or hydrogen peroxide (58) is necessary. In its usual form, the method then consists of precipitation of the iodate from a cold solution, washing with a solution containing potassium iodate and nitric acid, dissolution in excess nitric acid, reprecipitation as iodate, dissolution in hydrochloric acid by reduction of iodate with sulfur dioxide, precipitation of the hydrous oxide with ammonia, dissolution in hydrochloric acid, and ultimate precipitation of ignitable thorium oxalate (26, 120, 186, 224). Final treatment with oxalic acid removes any titanium or zirconium, but scandium must be removed by previous precipitation (180). In this form the method has yielded excellent results, particularly in the analyses of monazite (92, 137, 138, 156, 186) and cyrotolite (191). It is said to be a standard procedure in the monazite industry (134, 156). It has the advantage of comparative rapidity (186) and is also adaptable to micro determinations (139). However, a number of difficulties are encountered in the handling of the precipitated iodate (92). Some of these may perhaps be obviated by using centrifugal separation (156). Because of the marked solubility of thorium iodate in the absence of iodate ion (92), large quantities of this ion are necessary for both precipitation and washing.

In a recent publication, Chernikhov and Uspenskaya (58) have reported precipitation of thorium as $4Th(IO_3)_4 \cdot KIO_3 \cdot 18H_2O$ and of cerium(IV) as $2Ce(IO_3)_4 \cdot KIO_3 \cdot 8H_2O$ from solutions containing excess nitric acid and about 5 per cent excess potassium iodate by weight. Although precipitation was carried out in the usual fashion, ultimate removal of nitric acid and excess iodate was effected by washing the precipitates with ethanol. Prior reduction of cerium with peroxide permitted quantitative precipitation of thorium free from cerium, the cerium then being recovered as iodate after bromate oxidation. While this modification is adaptable to the gravimetric estimation of cerium and thorium, it is chiefly useful as extended to a volumetric procedure.

(b) The hypophosphate procedure

Selective precipitation of thorium as hypophosphate from boiling, strongly acidic solutions (151, 209, 252) is useful for the quantitative estimation of the element in the presence of the rare earth elements and yttrium. For rough determinations, Rosenheim (209) recommended ignition of the hypophosphate to weighable pyrophosphate, but lack of constancy in composition of the ignition product (107, 209) requires decomposition of the precipitated compound with either caustic alkali (252) or mixed sulfuric and fuming nitric acids (224) followed by precipitation as oxalate for accurate results. Final precipitation with oxalic acid serves also to remove any precipitated titanium and zirconium, and interference from cerium(IV) may be obviated by reduction with hydrogen peroxide. Since precipitation from sulfate media may be complicated by separation of double alkali metal sulfates with the rare earth elements (254), use of chloride or nitrate media is preferred. Detailed studies by Hecht (107) have indicated best results from the method when precipitation is effected from 10 per cent hydrochloric acid solution after hydrogen peroxide reduction and is followed by successive fusions with alkali carbonates and pyrosulfates and ultimate oxalate precipitation. In the opinion of Jüstel (134), the hypophosphate procedure is more suited to the qualitative detection of thorium and requires verification in the presence of cerium and the other rare earth elements before it can be considered as quantitative.

(c) The pyrophosphate procedure

The pyrophosphate procedure of Carney and Campbell (52) is said to give excellent results (26, 120), although it is rather tedious of operation. As commonly employed (26, 52, 120), the method consists in precipitating thorium with sodium pyrophosphate from boiling solutions 0.3 *N* in hydrochloric acid. Under these conditions, the trivalent rare earth elements remain unprecipitated, but zirconium, titanium, and cerium(IV) compounds contaminate the thorium material. Either digestion of the precipitate plus filter paper with sulfuric acid and ammonium perchlorate or treatment with fuming nitric acid (53) is recommended, thorium being recovered by precipitation with sodium hydroxide. Dissolution of the precipitated hydrous oxide, reduction of cerium(IV) with sulfur dioxide, a second pyrophosphate precipitation and Kjeldahl digestion, and ultimate precipitation with oxalic acid yield pure thorium materials. Insufficient acid is said to prevent complete precipitation through formation of soluble $Na_4Th(P_2O_7)_2 \cdot 2H_2O$ (26) and may permit precipitation of compounds of the rare earth elements. The method is reported to be successful for routine analysis of monazite (26).

3. *Estimation in weakly acidic or neutral solutions*

Procedures suited to these media are commonly less clean-cut than those applicable to strongly acidic solutions, because solubility differences between compounds of thorium and compounds of rare earth metals are less well defined. Prior removal of phosphate is of course necessary and is usually effected by precipitation with oxalic acid. Ultimately, the mixed oxalates are converted to nitrates either directly by action of fuming nitric acid or indirectly by ignition to oxides and dissolution in the acid, excess acid being removed by evaporation. The majority of the methods listed by van Nieuwenburg *et al.* (241) and by Wenger and Duckert (247) are applicable to such solutions.

(a) The thiosulfate procedure

A favorite classical procedure (26, 38, 120, 167, 215, 224), the thiosulfate procedure is still fairly widely used (134), in spite of its tedious nature, for gravimetric estimation of thorium in the presence of yttrium and the rare earth elements. The method was but little used for analytical purposes until after the researches of Fresenius and Hintz (87) in 1896. Further work by Witt (256), Hintz and Weber (121, 122), Drossbach (77), Metzger (178), Benz (16), and Johnstone (133) developed the method into its present form (26, 120, 167, 224). The recommended procedure entails slow addition of sodium thiosulfate solution to the boiling mixed salt solution, followed by dissolution of the precipitated hydrous thorium oxide in hydrochloric acid to separate it from sulfur and ultimate precipitation as oxalate. Complete removal of the rare earth elements, especially if appreciable quantities of the yttrium group are present or if the ratio of rare earth elements to thorium is large, is difficult (77), and in practice three or four precipitations with thiosulfate are required (16, 178). Simultaneous precipitation of aluminum, titanium, zirconium, and scandium occurs. The first three elements are removed in the final oxalate precipitation, but removal of scandium must be effected by some procedure such as Meyer and Goldenberg's tartrate (182) method. In spite of the difficulties inherent in this determination, it has been used widely for routine analysis (26, 134), for it yields accurate final results.

(b) The peroxide procedure

The peroxide procedure of Cleve (64) and de Boisbaudran (68), as modified by Wyrouboff and Verneuil (258, 259, 260, 262), was shown by Benz (16) to be suited to the quantitative estimation of thorium in the presence of the rare earth elements. Benz's procedure, which is essentially that given in later summaries (26, 120, 163, 167, 185, 224), amounts to precipitation of a neutral nitrate solution, containing ammonium nitrate and heated to 60–80°C., with 3 per cent hydrogen peroxide, followed by washing with ammonium nitrate solution, reprecipitation to remove traces of cerium, and ultimate ignition to oxide. Although early workers noted decrepitation in direct ignition of the peroxy compound and preferred destruction of the peroxide with iodide in acid and ultimate precipitation of hydrous thorium oxide prior to ignition (258), both Benz (26) and Borelli (27) obtained precipitates which settled rapidly and could be ignited without difficulty when ammonium chloride or nitrate was present. Complete separation of thorium from the rare earth elements is difficult by the peroxide procedure, and several repetitions are usually necessary. Cerium appears to coprecipitate more extensively from chloride media than from nitrate (224). Some improvement may be effected by a preliminary precipitation of all the thorium and 20–30 per cent of the rare earth elements with barium peroxide and a subsequent ammonium oxalate extraction before final precipitation with hydrogen peroxide (262). Best results are obtained when the ratio of thorium to the rare earth elements is reasonably large and when the total amount of thorium present is not more than 0.5 g.

Although not a method now in common use, largely because it is tedious, the peroxide procedure has been employed to advantage in the analysis of many thorium-containing minerals such as monazite (82, 246, 250); euxenite, polycrase, and samarskite (82); bastnasite (1); and uranite (108), the last microchemically.

(c) Procedures involving organic acids

While many organic acids yield insoluble thorium salts, only comparatively few are adaptable to use in the estimation of the element. The utility of a number of these acids in selectively precipitating thorium from its mixtures with rare earth elements has been indicated in table 1. In the discussion which follows, only those materials which have been shown to be definitely useful are considered. Although predominantly basic in character, 8-hydroxyquinoline is also included because in its thorium derivative an essentially acidic hydrogen is replaced.

(*1*) *Fumaric acid:* Precipitation of thorium from hot solutions containing 40 per cent ethanol by volume with a saturated solution of fumaric acid in 40 per cent ethanol was recommended by Metzger (177, 178) for the quantitative estimation of thorium. Although zirconium, silver, mercury, and erbium were found to interfere, a second precipitation removed any coprecipitated rare earth elements. Ignition of the precipitate in oxygen gave a weighable oxide. Comparative studies by Metzger (178) indicated the method to be as reliable as either the thiosulfate or the ammonium oxalate procedure in the presence of rare earth elements and to be much more rapid. Although used successfully by Kress and Metzger (157) for the determination of thorium in monazite, the fumaric acid procedure has not been widely applied, largely because it is still too time consuming.

(*2*) *m-Nitrobenzoic acid:* Estimation of thorium through precipitation at 60–80°C. with *m*-nitrobenzoic acid and ultimate ignition to the weighable oxide was recommended by Neish (193, 194, 195) as being the equal of the fumaric acid procedure. As with fumaric acid, a second precipitation is necessary to free the product completely from rare earth elements. In the hands of Kolb and Ahrle (146) and McCoy and Ross (172) the method has yielded excellent results, and both Ashman (3) and Girotto (96) have applied it successfully to the estimation of thorium in minerals. Use of *m*-nitrobenzoic acid or fumaric acid seems to be a matter of choice.

(*3*) *Sebacic acid:* Smith and James (222) recommended treatment of a boiling salt solution with an excess of a hot, nearly saturated solution of sebacic acid as a means of quantitatively precipitating thorium free from the rare earth elements. The voluminous precipitate settled rapidly and could be ignited directly to oxide. No interference by the rare earth elements was found, but since ammonium sebacate will precipitate these elements as well as thorium (248), it is obvious that the total acidity must not be too low. Kaufmann (136) reported coprecipitation of cerium when that element was present in comparatively large quantities and suggested an alcoholic solution of sebacic acid as precipitant, with precipitation being repeated until a white product is obtained. Comparative studies by Kaufmann (139) on a number of procedures indicated sebacic acid to give reliable results, provided preliminary isolation of thorium and the rare earth elements had been effected. The sebacic acid procedure must be ranked with those employing fumaric and *m*-nitrobenzoic acids. Approximately 0.2 g. of thorium may be determined in this fashion (174).

(*4*) *Phenylarsonic acid:* Precipitation with 10 per cent phenylarsonic acid from boiling solutions containing definite quantities of acetic acid and ammonium acetate was recommended by Rice, Fogg, and James (208) for the estimation of either thorium or zirconium. Since the precipitate could not be ignited directly, dissolution in hydrochloric acid and ultimate precipitation as oxalate were found necessary. No separation of thorium from zirconium could be effected except by repeated precipitations, but two precipitations were found to remove cerium and the other rare earth elements, the phenylarsonates of these materials being soluble in the acetic acid–ammonium acetate buffer. Results comparable with those obtained with the pyrophosphate procedure were reported for the analysis of monazite. Kaufmann (138), however, found the procedure to offer no advantages in time or precision and noted considerable interference from cerium(IV). A single precipitation carried down some 90 per cent of the cerium (138), and its removal depended upon differential solubility in hydrochloric acid rather than in the buffer. Since the precipitation of thorium was found to be incomplete in the presence of hydrochloric acid, it is apparent that rigid pH control is necessary in the method. Although cited as suitable by Prodinger (206), use of phenylarsonic acid is of doubtful importance.

(*5*) *Picrolonic acid:* Quantitative precipitation of thorium as picrolonate, $Th(C_{10}H_7N_4O_5)_4 \cdot H_2O$, has been recommended by Hecht and Ehrmann (112) for the direct quantitative estimation of thorium in either macro or micro quantities. Direct weighing of the yellow precipitate after air drying gave excellent results, the low thorium content (17.82 per cent) being highly advantageous. Precipitation was effected by treating boiling nitrate solutions containing 3 per cent acetic acid by volume (final volume) with picrolonic acid solution, but the method could not be applied to the determination of thorium in the presence of the rare earth elements, lead, or calcium. Precipitation in the presence of ammonium salts or excess acid was incomplete. According to Tanii, Hosimuja, and Ikeda (226), precipitation of thorium picrolonate is best effected in the pH range 2–3.2. The method is apparently an excellent one in the absence of the rare earth elements (109, 142, 143, 206) and is adaptable to volumetric determinations. On a macro scale, determinations are accurate to 0.1 g. (174).

(6) *8-Hydroxyquinoline:* Quantitative determination of thorium by precipitation with 8-hydroxyquinoline (oxine) from a hot solution containing about 2.4 per cent acetic acid by volume was first reported by Hecht and Reich-Rohrwig (115). These authors found precipitation at 50°C. to yield a yellow product which changed to a more crystalline red material at 70°C. and reported excellent analytical results when the final precipitate was dried at 170°C. before being weighed. In an important paper, Frere (86) pointed out that the yellow material corresponded to $Th(C_9H_6ON)_4$, while the red compound amounted to $Th(C_9H_6ON)_4 \cdot C_9H_7ON$. The latter material was found to be stable at 110°C., but at 170°C. the added mole of 8-hydroxyquinoline was lost completely. These observations have been substantially confirmed in the University of Illinois Laboratories (92). Ishimaru (125) also studied the procedure, and Berg recommended Hecht and Reich-Rohrwig's general method in his monograph (17).

Hecht and Ehrmann (113) recommended precipitation of thorium from acetic acid solution buffered with ammonium acetate for both micro and macro determinations and preferred the procedure to that employing picrolonic acid on the bases of rapidity and simplicity. An important application to the separation and determination of both cerium and thorium was made by Berg and Becker (18). Based upon the fact that the cerium(III) derivative could not be precipitated from solutions containing acetic acid, their method consisted in reducing cerium(IV) with hydroxylamine hydrochloride, adding sufficient acetic acid to give 2.5 per cent by volume in the final solution, and precipitating thorium from the boiling solution with excess oxine acetate solution, ammonium acetate being added as buffer if necessary. Precipitation of cerium was then effected from the filtrate by adding sodium tartrate and ammonia to raise the pH and treating at 60°C. with alcoholic oxine solution. The final determination was carried out in each instance by igniting the precipitate with oxalic acid and weighing the resultant oxide. Results accurate to less than 0.5 per cent were obtained for a variety of mixtures (18).

The best conditions for gravimetric estimation of thorium by this means involve final precipitation at 70°C. or above. As in all determinations involving 8-hydroxyquinoline, pH control is essential. According to Gotô (102), complete precipitation of thorium occurs in the pH range 4.4–12.5, with no precipitation taking place below pH 3.7. To insure complete precipitation, therefore, provision is often made for neutralization with ammonia or caustic soda (115) prior to filtration. In this form, estimation of thorium in the presence of the rare earth elements would be inaccurate because of precipitation of the latter at higher pH values (92, 169). Sufficient differences do exist between the pH values required for precipitation of thorium and the trivalent rare earth elements to permit determination of the former in mixtures (92, 169), but extremely accurate control of hydrogen-ion concentration is necessary. The method is generally suitable but should be investigated further.

(7) *Miscellaneous acids:* A number of other organic precipitants have been

recommended for thorium, but little attention has been given them. Both salicylic acid (94) and ammonium salicylate (76) have been suggested, but results with the former have not been encouraging (146, 194, 195). The ammonium salt is said to be useful for both thorium and zirconium determinations (174). Pratt and James (205) reported quantitative separation of thorium from the rare earth elements by precipitation with phenoxyacetic acid, but this has not been confirmed. Use of cupferron as a precipitant was suggested by Thornton (229, 230), who reported complete precipitation in solutions containing ammonium acetate and acetic acid but incomplete precipitation in the presence of even traces of sulfuric acid. Matveev (171) used cupferron for thorium determinations in buffered acetic acid solutions after removing iron as sulfide. Information on the effects of rare earth materials is not available, but Lundell and Knowles (168) believed the method to be of no quantitative importance. Precipitation as alizarin-3-sulfonate (15) appears to offer promise for microchemical determination of thorium in the presence of the rare earth elements, but it does not effect separation from scandium. Quinaldic acid is also a potential reagent for thorium, since it has been found to precipitate neither the rare earth elements nor zirconium from cold solutions (80). From hot solutions zirconium precipitates were obtained, but they differed from those obtained with thorium in being soluble in acetic acid.

Hecht and Donau (109) discuss a series of microquantitative methods using benzenesulfinic acid and its *p*-bromo and *p*-iodo derivatives as worked out by Feigl, Hecht, and Korkisch (81). The thorium salts, $Th(C_6H_5SO_2)_4$ or $Th(C_6H_4XSO_2)_4$ (X = Br, I), are precipitated from hot solutions by addition of up to fourfold excesses of the acids or their sodium salts. The precipitates are removed by filtration, washed, dried at 110–120°C., and weighed. Benzenesulfinic acid and *p*-bromobenzenesulfinic acid are recommended for 1–4 mg. of thorium and the iodo acid for less than 1 mg. These methods appear to be convenient, but they are limited in scope, and no information about interferences is available. The comparatively low thorium content of each precipitate may be cited as an advantage of the method.

4. *Miscellaneous gravimetric procedures*

Few other gravimetric procedures have shown any promise. This is typical of precipitation with selenic acid (154), hydrofluoric acid (224), or tannin (233), and of the various older procedures employing double carbonates, double sulfates, or double oxalates. Such methods are better suited to the rough separation of thorium from other materials and must be followed by more refined methods for its ultimate determination (134).

B. TITRIMETRIC ESTIMATION

Comparatively few titrimetric methods have been reported for the determination of thorium. Of those which have been investigated, all are either involved, highly indirect, or inaccurate. As a consequence, the more accurate, although more tedious, gravimetric methods are preferred. A recent comparative study by Banks and Diehl (10a) may be cited as a reëmphasis of the need for accurate and simple titrimetric procedures, especially procedures adaptable to the estimation of thorium in the presence of other elements.

1. Direct acidimetric estimation

In a recent publication, Tanteri (227) has reported the estimation of thorium by addition of excess sodium hydroxide solution and back titration of the excess with standard acid after removal of the precipitated hydrous oxide. Chief among objections to such a procedure is the complication introduced by the presence of any element which forms an insoluble hydrous oxide or hydroxide. It can be regarded as an unimportant procedure except perhaps for the routine assay of pure thorium compounds.

2. Estimation as iodate

Volumetric estimation of both cerium and thorium by dissolution of the precipitated iodates in acidified iodide solution and titration of the liberated iodine with standard thiosulfate solution was reported by Chernikhov and Uspenskaya (58), results obtained volumetrically agreeing with those obtained gravimetrically. Estimation of thorium in the presence of cerium was effected by reduction of the latter with peroxide prior to precipitation of the iodate. Reoxidation of the filtrate with bromate then permitted precipitation of cerium(IV).

While other information on the iodate procedure suggests its adaptation to volumetric estimation to be feasible, both Jüstel (134) and Banks and Diehl (10a) have indicated need for further work in checking the method. These opinions are in accord with results obtained in the University of Illinois Laboratories (92), where repeated applications of the volumetric method to both pure thorium salt solutions and monazite samples have yielded a thorium recovery of not more than 98 per cent on the average. The major difficulty lies in the apparent impossibility of freeing the precipitate from adsorbed oxidizing anions (IO_3^- and NO_3^-) without effecting partial decomposition or dissolution of the precipitate. Use of alcohol by Chernikhov and Uspenskaya is to be questioned, as is their report of the formation of $4Th(IO_3)_4 \cdot KIO_3 \cdot 18H_2O$ as the precipitate. It appears (92) that the precipitate is, instead, the normal iodate. Further work is necessary before the merits of the method can be evaluated critically, particularly work in the presence of other elements. The advantage of initial precipitation from strongly acidic solutions is of such importance as to warrant an exhaustive study of the method.

3. Estimation as ferrocyanide

Attempts to determine thorium by potentiometric titration with ferrocyanide have given discouraging results, and the method is of no importance. Early work by Atanasiu (5) indicated the composition of the precipitate to vary with amount of added alkali ferrocyanide, and the titration curves obtained were such that electrotitration of mixtures containing thorium, lanthanum, and cerium compounds was virtually impossible. The investigations of Shemyakin and

Volkova (217a) confirm such observations. These investigators reported an inflection corresponding to precipitation of the normal ferrocyanide from pure thorium salt solutions. However, when cerium or cerium and lanthanum were present, two inflections, one corresponding to precipitation of cerium and the other to precipitation of thorium and cerium or cerium and lanthanum, resulted. Quantitative estimation was impossible.

4. Estimation as oxalate

Use of permanganate titration in conjunction with oxalate precipitation was offered by Gooch and Kobayashi (101) as a volumetric means of determining thorium. Either titration of excess oxalic acid after removal of precipitated thorium oxalate, or titration after dissolution of the precipitate in acid was found to be effective, but accurate results could be obtained only if the initial precipitation were effected by slow addition of the thorium salt solution to excess oxalic acid solution. The reverse procedure yielded basic salts of indeterminate compositions. Eichelberger and Bibler (79) used the method to advantage in estimating the thorium content of blood and muscle tissue, but, although the method is inherently accurate, it is applicable only in the absence of elements which are precipitated by oxalic acid.

Atanasiu (6, 7, 8) has reported the determination of thorium and the rare earth elements by potentiometric titration, using sodium or ammonium oxalate solution. The results obtained were generally unsatisfactory, since only a single inflection was obtained with a mixture of thorium with lanthanum and cerium. Estimation in alcoholic solutions was also impossible.

5. Estimation as molybdate

Direct titration of thorium with ammonium molybdate solution with diphenylcarbazide as external indicator was suggested by Metzger and Zons (179). Quantitative results were obtained without interference from the rare earth elements when titration was carried out at room temperature in acetic acid solutions buffered with sodium acetate, but the authors found the rose color produced at the end point to persist for not more than 15 sec. and to be difficult of identification without experience. Standardization of the reagent against a pure thorium salt solution and use of indicator solution at least 2 weeks old were essential. Kaufmann (139) recommended the method on a comparative basis for its rapidity but questioned its accuracy. The latter opinion is shared by Banks and Diehl (10a).

Banks and Diehl (10a) proposed two modifications of the molybdate procedure. The first of these amounts to precipitation of thorium as the normal molybdate from 7 per cent acetic acid solution, diphenylcarbazide being used to indicate completion of the precipitation process, followed by dissolution of the washed precipitate in hydrochloric acid, reduction of the molybdate with amalgamated zinc, and titration with standard cerium(IV) sulfate with ferroin as indicator. In this form, the method gave fairly reliable results when applied to pure thorium salts (errors up to 0.23 per cent) and to thorium–uranium combinations (errors up to 0.63 per cent), but was less accurate for thorium–calcium mixtures (errors up to 5.06 per cent) and was inapplicable to thorium–rare earth combinations. A second modification amounts to potentiometric titration in 7 per cent acetic acid medium with standard ammonium molybdate solution at 50–55°C. with a 0.1 *N* calomel reference electrode and a molybdenum wire indicator electrode. In this form, the method yielded better results with thorium–calcium combinations (errors up to 0.26 per cent). Extension to other systems appears highly desirable.

6. *Estimation as 8-hydroxyquinolate*

The gravimetric 8-hydroxyquinoline procedure for thorium, like most procedures involving this reagent, may be rendered volumetric by titration of the well-washed precipitate, preferably $Th(C_9H_6ON)_4 \cdot C_9H_7ON$, with potassium bromide–potassium bromate solution after dissolution in hydrochloric acid (18, 115, 169). Since bromination requires four atoms of bromine to each quinolate residue, a rather favorable factor characterizes the titration. Indigo-carmine may be used as an indicator, the color change being from blue through green to yellow. As a more standard practice, however, potassium iodide is added and iodine equivalent to excess bromate is determined with standard thiosulfate. Bromate titration is apparently accurate, but all of the previously discussed difficulties inherent in the use of 8-hydroxyquinoline as a precipitant also characterize this method.

7. *Estimation as picrolonate*

Kiba (141) has described a potentiometric procedure for thorium based upon titration of thorium picrolonate with standard titanium(III) chloride solution at 90–95°C. in 4 *N* acid and in an atmosphere of carbon dioxide. Under such conditions, reduction of nitro groups in the picrolonate residues occurs. According to Kiba (141), the method is limited to not more than 10 mg. of thorium expressed as metal. This procedure is not regarded as accurate (10a) and is of no importance for estimation of the element.

C. RADIOMETRIC ESTIMATION

Methods dependent upon radioactivity measurements must of necessity assume that radioactive equilibrium has been established between thorium and its decay products. Furthermore, such methods are complicated by the presence of radioactive materials from other disintegration series, and even reasonably accurate results cannot be obtained unless ample correction for other activities is made. In a measure, this may be done through preliminary standardization of the counter or electroscope used.

Direct measurements of radiations have been used for estimation of the thorium contents of minerals. Joly (133a) applied the method in this form to the determination of as little as 10^{-5} g. of thorium per gram of rock. Borgström (29) applied the method to the evaluation of thorium to uranium ratios by powdering the mineral, coating a surface of known area with a known amount of the mineral suspended in chloroform, and comparing rates of electroscope discharge for various samples. Sasahara (213) has also determined thorium contents of ores by radiation comparison. High accuracy does not characterize such procedures.

Much more work has been done with the so-called emanation method (10, 53, 116, 123, 240). This method depends upon sweeping gaseous decay products (i.e., thoron) out of the solutions to be analyzed and determining their activities by passing the mixed gases through an ionization chamber. Cartledge (53) checked the method against the pyrophosphate procedure of Carney and Campbell (52) and reported a maximum error of only 1.5 per cent. Helmick (116) refined the experimental technique but listed as disadvantages of the procedure the costly apparatus required, the necessity for freedom from vibration in the electroscope arrangement, and the necessity for complete absence of all other radioactive materials in the vicinity of the apparatus. To this might be added the absolute necessity for existence of radioactive equilibrium. Further improvements in the method have been made by Holmes and Paneth (123) and by Urry (240).

Because of the generally unsatisfactory character of the emanation method, Evans and coworkers (80a) proposed the following alternative procedures: (*1*) using a vacuum-tube electrometer to count all alpha particles emitted from smooth polished sample surfaces, (*2*) counting all alpha particles emitted from powdered specimens, (*3*) counting only the ThC′ alpha particles after excluding shorter-range alphas by use of suitable absorbers, and (*4*) detecting gamma rays emitted from larger sources with a sensitive screen-cathode counter. Of these alternatives, Evans considered methods 2 and 4 to be the most suitable. Method 3 gives the thorium content directly, while with the other methods correction for uranium content is necessary. With methods 2, 3, and 4, internal standardization may be employed. Use of alpha-particle measurements was employed by Finney and Evans (83a) for analyses of uranium–thorium mixtures, and gamma-ray counting was employed by Evans and Mugele (80b) for the estimation of thorium in rocks.

Radiometric titration using a standard disodium phosphate solution containing radiophosphorus has been suggested by Langer (160a) for the estimation of a number of elements, among them thorium. Although successful application of the method to thorium was hampered by the colloidal character of the thorium precipitate, the procedure appears entirely feasible. In principle it is dependent upon establishment of the equivalence point through a steady decrease in activity of the solution until precipitation is complete, followed by an increase as excess of the reagent is added.

D. ESTIMATION BY MISCELLANEOUS PROCEDURES

The successful polarographic estimation of thorium has been reported by Kryukova (159). Except for spectrographic or spectrometric methods, no other specialized procedures have been employed (134).

Spectral methods for thorium analysis have been employed for many years

(78, 85, 89, 224), but the quantitative aspects of these methods have received attention only in recent years. Thus, Parson (201) determined the thorium contents of thoriated tungsten filaments with mean deviation of ±3.54 per cent and maximum deviation of ±5.3 per cent by use of the 2899.3 Å. line as excited in a 2200-volt A.C. arc and of chemically analyzed comparison standards.

X-ray spectrographic methods have been explored more thoroughly (88, 89). Borovskiĭ and his coworkers (30, 31) reported determinations of thorium in error by some 5–20 per cent by this means, although by a refined technique errors were reduced to 5–7 per cent for synthetic thorium–rare earth mixtures. Improvements in analytical technique have been described by Komoviskiĭ and Golovchiner (149, 150), and Voronova (242) has obtained excellent results in the x-ray analysis of minerals with both high (35–50 per cent) and low (0.1 per cent) thorium and uranium contents, using strontium as a comparison element.

E. SUMMARY

Consideration of the quantitative methods listed indicates that most accurate results are still obtained by gravimetric means. If separation of interfering elements is complete, precipitation of thorium with ammonia or oxalic acid and ignition to the weighable oxide is a standard procedure which will invariably give reliable results. Oxalate precipitation has the further advantage of being directly applicable to thorium materials containing uranium, zirconium, hafnium, and titanium. In the presence of the rare earth elements, separation as iodate appears to be the most feasible preliminary to oxalate precipitation from the points of view of accuracy, cleanliness of separation, and time requirement. Other proposed means of separation appear to offer no major advantages, although further investigations upon certain of the organic precipitants such as hexamethylenetetramine, 8-hydroxyquinoline, *m*-nitrobenzoic acid, and sebacic acid are indicated.

No titrimetric procedure yet developed can compare in accuracy with the gravimetric methods. However, for routine assay where extreme accuracy is not essential titrimetric methods offer advantages in convenience and in rapidity of use. Of the methods proposed, those involving iodate and molybdate appear most promising and merit further considerations. Radiometric and other miscellaneous procedures are adaptable, at least in their present forms, only to analyses under specialized conditions, and their extension to routine and highly accurate work is extremely unlikely.

V. ANALYSIS OF THORIUM-CONTAINING MATERIALS

Applications of methods already outlined to the analysis of thorium-containing materials are considered in detail in the standard reference works (24, 26, 38, 89, 120, 163, 185, 215, 224, 234). Among such materials, those usually encountered are thorium compounds, minerals, alloys, catalysts, and incandescent-mantle residues (90). In all instances, analysis may be effected by procedures previously recommended, but ultimate analysis must, except when applied to relatively pure thorium compounds, be prefaced by sample preparation and removal of interfering elements. Methods suited to such separations have already been treated in detail.

Thorium-bearing minerals may be divided roughly into those rich in thorium (*ca.* 50–60 per cent ThO_2) and those poor in the element (*ca.* 4–10 per cent ThO_2). Representative of the first group are the silicate thorite and the oxide thorianite, and representative of the second class are the phosphate minerals monazite and xenotime and certain rare titano- and tantalo-columbates such as euxenite, fergusonite, and samarskite. Minerals rich in thorium are usually decomposed with hydrochloric or sulfuric acid, silica being removed by dehydration and the heavy metals by saturation with hydrogen sulfide (215, 224). Thorium (and any rare earth elements or yttrium present) is then precipitated with oxalic acid and analysis continued in the usual fashion.

Of the minerals which are poor in thorium, only monazite or monazite sand can be regarded as an important source of the element. Most of the thorium which is recovered technically does, however, come from this source, and the problems associated with its removal from the comparatively large quantities of rare earth elements which accompany it are still considerable. For analysis, a weighed quantity of the sand is usually decomposed by heating with excess concentrated sulfuric acid for several hours, after which the thick mass is added slowly to ice water and stirred until the sulfates have dissolved (120, 124, 215). After filtration, the thorium may be roughly separated from the rare earth elements by careful reduction of acidity through dilution or addition of magnesium oxide (224) and subsequently estimated after phosphate removal, or the solution may be diluted to a given volume and an aliquot analyzed by some method applicable to strongly acidic media (120). If the thorium content is exceptionally low, fusion with sodium fluoride and potassium pyrosulfate followed by leaching with hydrochloric acid and precipitation with oxalic acid is sometimes preferred as an alternative procedure (120).

Thorium-containing alloys are usually decomposed with either hydrochloric acid or sulfuric acid (134), although thoriated tungsten wires are better treated by direct chlorination or by dissolution in mixtures of hydrofluoric and concentrated nitric acids (134). Acid treatment is also applicable to catalysts, since cobalt, nickel, iron, magnesium, and silica are the materials most commonly present (134). Subsequent analysis of these acid extracts is effected in all instances by the usual methods.

Residues from the mantle-lamp industry consist primarily of thorium materials, together with comparatively small quantities of cerium compounds. Since these residues usually amount to oxides prepared by high-temperature reactions, they are perhaps best solubilized by acid fusion, say with alkali bi- or pyro-sulfate. Removal of cerium is desirable before estimation of thorium is attempted.

VI. Conclusion

In analytical characteristics, thorium bears an exceedingly close resemblance to scandium, yttrium, and the rare earth elements, particularly to cerium(IV) and to the least basic members of the yttrium subgroup. The analytical chemistry of the element is, therefore, complicated by the necessity for removing these interfering elements. Thus far, most of the reported processes for effecting such separations are either fractional in character or tedious and costly of operation. As a consequence, the development of clean-cut analytical methods for thorium has been slow, and present-day procedures are largely inadequate. It is to be hoped that renewed interest in the chemistry of the element will result in the development of rapid and accurate methods for its detection and estimation and that the problems imposed by the presence of the rare earth elements will meet with ultimate solution. Certainly, the need for further investigation is apparent from the summary here presented.

VII. References

(1) Alimarin, I. P.: Trans. Inst. Econ. Mineral. (U.S.S.R.) **44,** 55 (1930).
(2) Allen, E. T.: J. Am. Chem. Soc. **25,** 421 (1903).
(3) Ashman, G. C.: Am. J. Sci. [iv] **27,** 65 (1909).
(4) Atanasiu, I. A.: Ber. **60B,** 2507 (1927).
(5) Atanasiu, I. A.: Bull. chim., soc. română stiinte **30,** 51 (1928).
(6) Atanasiu, I. A.: Z. anal. Chem. **112,** 15 (1938).
(7) Atanasiu, I. A.: Z. anal. Chem. **112,** 19 (1938).
(8) Atanasiu, I. A.: Z. anal. Chem. **113,** 276 (1938).
(9) Bahr, J.: Ann. **132,** 231 (1864).
(10) Baltrick, M., and Weissenberger, G.: Z. anorg. Chem. **88,** 88 (1914).
(10a) Banks, C. V., and Diehl, H.: Anal. Chem. **19,** 222 (1947).
(11) Baskerville, C.: J. Am. Chem. Soc. **23,** 762 (1901).
(12) Baskerville, C.: J. Ind. Eng. Chem. **4,** 821 (1912).
(13) Baskerville, C.: Chem. News **106,** 271 (1912).
(14) Batěk, A.: Z. anorg. Chem. **45,** 87 (1905).
(15) Beck, G.: Mikrochemie **27,** 47 (1939).
(16) Benz, E.: Z. angew. Chem. **15,** 297 (1902).
(17) Berg, R.: *Die chemische Analyse. Vol. XXXIV. Das o-Oxychinolin, 'Oxin'*, pp. 60–2. Ferdinand Enke, Stuttgart (1935).
(18) Berg, R., and Becker, E.: Z. anal. Chem. **119,** 1 (1940).
(19) Berndt, O. N.: U. S. patent 1,323,735 (1919).
(20) Berndt, O. N.: U. S. patent 1,329,747 (1920).
(21) Berzelius, J. J.: Pogg. Ann. [ii] **16,** 385 (1829).
(22) Böhm, C. R.: *Die Darstellung der seltenen Erden*, Vol. I, pp. 90, 150–2. Veit and Company, Leipzig (1905).
(23) Reference 22, pp. 165–462.
(24) Böhm, C. R.: *Die Darstellung der seltenen Erden*, Vol. II, pp. 163–75. Veit and Company, Leipzig (1905).
(25) Böhm, C. R.: Chem. Ind. **29,** 450 (1906).
(26) Bonardi, J. P.: U. S. Bur. Mines Bull. **212,** 19 (1923).
(27) Borelli, V.: Ann. soc. chim. Milan **1908,** 112.
(28) Borelli, V.: Gazz. chim. ital. **39, I,** 425 (1909).
(29) Borgström, L. H.: Fenska Kem. Meddel **1917,** 14 pp.
(30) Borovskiĭ, I. B.: Trudy Vsesoyuz. Konferents. Anal. Khim. **1,** 135 (1939).
(31) Borovskiĭ, I. B., Blokhin, M. A., and Grzhibovskaya, L. A.: Bull. acad. sci. U.R.S.S., Sér. phys. **4,** 122 (1940).
(32) Böttinger, C.: Z. anorg. Chem. **6,** 1 (1894).
(33) Boudouard, O.: Bull. soc. chim. [iii] **19,** 10 (1898).

(34) Bourion, M. F.: Ann. chim. phys. [viii] **21,** 49 (1910).
(35) Bowles, J. A. C., and Partridge, H. M: Ind. Eng. Chem., Anal. Ed. **9,** 124 (1937).
(36) Brauner, B.: Jahresber. **1898,** 529.
(37) Brauner, B.: Trans. Chem. Soc. **73,** 951 (1898).
(38) Brinton, P. H. M.-P.: *Scott's Standard Methods of Chemical Analysis,* edited by N. H. Furman, 5th edition, Vol. I, pp. 946–53. D. Van Nostrand Company, Inc., New York (1939).
(39) Brinton, P. H. M.-P., and James, C.: J. Am. Chem. Soc. **41,** 1080 (1919).
(40) Britton, H. T. S.: J. Chem. Soc. **127,** 2110 (1925).
(41) Britton, H. T. S.: J. Chem. Soc. **127,** 2142 (1925).
(42) Britton, H. T. S.: *Hydrogen Ions,* 3rd edition, Vol. II, pp. 36–9. Chapman and Hall, Ltd., London (1942).
(43) Reference 42, pp. 79–84.
(44) Reference 42, pp. 122–30.
(45) Browning, P. E.: *Introduction to the Rarer Elements,* 4th edition, p. 215. John Wiley and Sons, Inc., New York (1917).
(46) Buddëus, W., and Preussner, L.: Z. angew. Chem. **1897,** 738.
(47) Bunsen, R.: Ann. phys. chem. **155,** 375 (1875).
(48) Bunsen, R.: Pogg. Ann. [ii] **155,** 380 (1875).
(49) Campbell, E. D., and Carney, R. J.: U. S. patent 1,182,880 (1916).
(50) Canneri, G.: Gazz. chim. ital. **55,** 33 (1925).
(51) Canneri, G.: Gazz. chim. ital. **55,** 39 (1925).
(52) Carney, R. J., and Campbell, E. D.: J. Am. Chem. Soc. **36,** 1134 (1914).
(53) Cartledge, G. H.: J. Am. Chem. Soc. **41,** 42 (1919).
(54) Caven, R. M.: *A Textbook of Inorganic Chemistry,* edited by J. N. Friend, Vol. V, pp. 278–81. Charles Griffin and Company, Ltd., London (1917).
(55) Reference 54, pp. 299–300.
(56) Chavastelon, R.: Chem. Ztg. **1,** 876 (1900).
(57) Chavastelon, R.: Compt. rend. **130,** 781 (1900).
(58) Chernikhov, Yu. A., and Uspenskaya, T. A.: Zavodskaya Lab. **9,** 276 (1940).
(59) Chydenius, J. J.: Pogg. Ann. [ii] **119,** 46 (1863).
(60) Clarke, J. V.: U. S. patent 1,335,482 (1920).
(61) Clarke, J. V., and Clarke, W. A.: British patent 120,748 (1917).
(62) Cleve, P. T.: Bull. soc. chim [ii] **21,** 116 (1874).
(63) Cleve, P. T.: Kgl. Svenska Vetenskapsakad. Handl. **2,** 187 (1874).
(64) Cleve, P. T.: Bull. soc. chim. [ii] **43,** 53 (1885).
(65) Damour, A.: Compt. rend. **34,** 685 (1852).
(66) de Boisbaudran, L.: Chem. News **50,** 201 (1884).
(67) de Boisbaudran, L.: Compt. rend. **99,** 525 (1884).
(68) de Boisbaudran, L.: Compt. rend. **100,** 605 (1885).
(69) Delafontaine, M.: Chem. News **75,** 230 (1897).
(70) Dennis, L. M.: J. Am. Chem. Soc. **18,** 947 (1896).
(71) Dennis, L. M.: Z. anorg. Chem. **13,** 412 (1897).
(72) Dennis, L. M., and Kortright, F. L.: Am. Chem. J. **16,** 79 (1894).
(73) Dennis, L. M., and Kortright, F. L.: Z. anorg. Chem. **6,** 35 (1894).
(73a) Dennis, L. M., and Ray, A. B.: J. Am. Chem. Soc. **40,** 174 (1918).
(74) Deutsche Gasglühlicht Akt.-Ges.: British patent 15,919 (1912); German patent 268,866 (1914).
(75) Dietsche, O.: U. S. patent 1,335,157 (1920).
(76) Dittrich, M., and Freund, S.: Z. anorg. Chem. **56,** 346 (1908).
(77) Drossbach, G. P.: Z. angew. Chem. **1901,** 655.
(78) Eberhard, G.: Ber. **38,** 828 (1905).
(79) Eichelberger, L., and Bibler, W. G.: J. Biol. Chem. **122,** 323 (1938).

(80) Erämetsä, O.: Suomen Kemistilehti **17B**, 30 (1940).
(80a) Evans, R. D., Finney, G. D., Kip, A. F., and Mugele, R. A.: Phys. Rev. **47**, 791 (1935).
(80b) Evans, R. D., and Mugele, R. A.: Phys. Rev. **47**, 427 (1935).
(81) Feigl, F., Hecht, F., and Korkisch, F.: Unpublished results; see reference 109.
(82) Fenner, C. N.: Am. J. Sci. [v] **16**, 369 (1928).
(83) Fernandes, L.: Gazz. chim. ital. **55**, 3 (1925).
(83a) Finney, G. D., and Evans, R. D.: Phys. Rev. **48**, 503 (1935).
(84) Fischer, W., and Bock, R.: Z. anorg. allgem. Chem. **249**, 146 (1942).
(84a) Fogg, H. C., and Hess, L.: J. Am. Chem. Soc. **58**, 1751 (1936).
(85) Formánek, J.: Z. anal. Chem. **39**, 673 (1900).
(86) Frere, F. J.: J. Am. Chem. Soc. **55**, 4362 (1933).
(87) Fresenius, R., and Hintz, E.: Z. anal. Chem. **35**, 525 (1896).
(88) Fresenius, R., and Jander, G.: *Handbuch der analytischen Chemie*, Part 3, Vol. III, pp. 717–24. J. Springer, Berlin (1942).
(89) Fresenius, R., and Jander, G.: *Handbuch der analytischen Chemie*, Part 3, Vol. IVb. J. Springer, Berlin (1944).
(90) Friedheim, C., and Peters, G.: *Gmelin-Kraut's Handbuch der anorganischen Chemie*, Vol. VI, Erster Abteilung, pp. 104–6. Carl Winter's Universitätsbuchhandlung, Heidelberg (1928).
(91) Reference 90, pp. 827–8.
(92) Fritz, N. D.: Private communication.
(93) Fronstein, M., and Mai, J.: Jahresber. **1897**, 686.
(94) Garelli, F., and Barbieri, N. A.: Chem. Ztg. **30**, 433 (1906).
(94a) Germuth, F. G., and Mitchell, C.: Am. J. Pharm. **101**, 46, (1929).
(95) Giles, W. B.: Chem. News **92**, 1, 30 (1905).
(96) Girotto, A.: Rev. chim. ind. **9**, No. 104, 10 (1940).
(97) Glaser, C.: J. Am. Chem. Soc. **18**, 782 (1896).
(98) Glaser, C.: Chem. Ztg. **20**, 612 (1896).
(99) Glaser, C.: Z. anal. Chem. **36**, 213 (1897).
(100) Goltz, M. A.: U. S. patent 1,322,185 (1919); Canadian patent 214,117 (1921).
(101) Gooch, F. A., and Kobayashi, M.: Am. J. Sci. [iv] **45**, 227 (1918).
(102) Gotô, H.: Science Repts., Tôhoku Imp. Univ., First Ser. **26**, 391 (1937).
(103) Grossman, H.: Z. anorg. Chem. **44**, 229 (1905).
(103a) Haber, L.: Monatsh. **18**, 687 (1897).
(104) Harrison, G. R.: *Massachusetts Institute of Technology Wavelength Tables*, p. xx. John Wiley and Sons, Inc., New York (1939).
(105) Hartwell, B. L.: J. Am. Chem. Soc. **25**, 1128 (1903).
(106) Hauser, O., and Wirth, F.: Z. angew. Chem. **22**, 484 (1909).
(107) Hecht, F.: Z. anal. Chem. **75**, 28 (1928).
(108) Hecht, F.: Am. J. Sci. [v] **27**, 321 (1934).
(109) Hecht, F., and Donau, J.: *Anorganische Mikrogewichtsanalyse*, pp. 210–15. J. Springer, Wien (1940).
(110) Reference 109, p. 289.
(111) Reference 109, pp. 319–23.
(112) Hecht, F., and Ehrmann, W.: Z. anal. Chem. **100**, 87 (1935).
(113) Hecht, F., and Ehrmann, W.: Z. anal. Chem. **100**, 98 (1935).
(114) Hecht, F., and Krafft-Ebing, H.: Mikrochemie **15**, 39 (1934).
(115) Hecht, F., and Reich-Rohrwig, W.: Monatsh., Wegscheider Festschrift, **53-54**, 596 (1929).
(116) Helmick, H. H.: J. Am. Chem. Soc. **43**, 2003 (1921).
(117) Hermann, R.: J. prakt. Chem. [i] **93**, 108 (1864).
(118) Hermann, R.: Bull. soc. chim. [ii] **3**, 187 (1864).

(119) Hildebrand, J. H.: J. Am. Chem. Soc. **35,** 847 (1913).

(120) Hillebrand, W. F., and Lundell, G. E. F.: *Applied Inorganic Analysis*, pp. 416–25. John Wiley and Sons, Inc., New York (1929).

(121) Hintz, E., and Weber, H.: Z. anal. Chem. **36,** 27 (1897).

(122) Hintz, E., and Weber, H.: Z. anal. Chem. **36,** 676 (1897).

(123) Holmes, A., and Paneth, F. A.: Proc. Roy. Soc. (London) **A154,** 385 (1936).

(124) Hopkins, B. S.: *Chapters in the Chemistry of the Less Familiar Elements*, Chap. 7. Stipes Publishing Company, Champaign, Illinois (1938).

(125) Ishimaru, S.: J. Chem. Soc. Japan **53,** 566 (1932).

(126) Ismail, A. M., and Harwood, H. F.: Analyst **62,** 185 (1937).

(127) James, C.: J. Am. Chem. Soc. **30,** 979 (1908).

(128) James, C.: Chem. News **97,** 205 (1908).

(129) James, C.: J. Am. Chem. Soc. **34,** 757 (1912).

(130) James, C., Whittemore, C. F., and Holden, H. C.: J. Am. Chem. Soc. **36,** 1853 (1914).

(131) Jannsch, P., Locke, J., and Lesinsky, J.: Z. anorg. Chem. **5,** 283 (1894).

(132) Jefferson, A. M.: J. Am. Chem. Soc. **24,** 540 (1902).

(133) Johnstone, S. J.: J. Soc. Chem. Ind. **33,** 55 (1914).

(133a) Joly, J.: Phil. Mag. **17,** 760 (1909).

(134) Jüstel, B.: Die Chemie **56,** 157 (1943).

(135) Kaserer, H.: Chem. Ztg. **42,** 170 (1918).

(136) Kaufmann, L. E.: J. Applied Chem. (U.S.S.R.) **8,** 1520 (1935).

(137) Kaufmann, L. E.: J. Applied Chem. (U.S.S.R.) **9,** 918 (1936).

(138) Kaufmann, L. E.: J. Applied Chem. (U.S.S.R.) **10,** 1648 (1937).

(139) Kaufmann, L. E.: Trav. inst. état radium (U.R.S.S.) **4,** 313 (1938).

(140) Kersten, C.: Pogg. Ann. [ii] **47,** 385 (1839).

(141) Kiba, T.: J. Chem. Soc. Japan **58,** 1283 (1937).

(142) Kiba, T.: J. Chem. Soc. Japan **60,** 911 (1939).

(143) Kiba, T.: J. Chem. Soc. Japan **60,** 1115 (1939).

(144) Knöfler, O., and Co.: German patent 266,459 (1912).

(145) Kolb, A.: J. prakt. Chem. [ii] **66,** 59 (1902).

(146) Kolb, A., and Ahrle, H.: Z. angew. Chem. **18,** 92 (1905).

(147) Koppel, I., and Holtkamp, H.: Z. anorg. Chem. **67,** 266 (1910).

(148) Komarovsky, A. S., and Korenman, I. M.: Z. anal. Chem. **94,** 247 (1933).

(149) Komovskiĭ, G. F., and Golovchiner, Ya.: Bull. acad. sci. U.R.S.S., Sér. phys. **5,** 201 (1941).

(150) Komovskiĭ, G. F., and Golovchiner, Ya.: J. Tech. Phys. (U.S.S.R.) **12,** 579 (1942).

(151) Koss, M.: Chem. Ztg. **36,** 686 (1912).

(152) Koss, M.: U. S. patent 1,069,959 (1913).

(153) Kossmann, B.: Z. angew. Chem. **1897,** 161.

(154) Kotá, J.: Chem. Listy **27,** 79, 100, 150, 194 (1933).

(155) Kreidl & Heller: German patent 233,023 (1911).

(156) Kremers, H. E.: Private communication.

(157) Kress, O., and Metzger, F. J.: J. Am. Chem. Soc. **31,** 640 (1909).

(158) Krüss, G., and Nilson, L. F.: Ber. **20,** 1665 (1887).

(158a) Krüss, G., and Nilson, L. F.: Ber. **20,** 1676, 2134 (1887).

(159) Kryukova, T. A.: Zavodskaya Lab. **9,** 699 (1940).

(160) Kuznetsov, V. I.: Compt. rend. acad. sci. U.R.S.S. **31,** 898 (1931).

(160a) Langer, A.: J. Phys. Chem. **45,** 639 (1941).

(161) Lesinsky, J.: Dissertation, Born, 1898.

(162) Levy, S. I.: *The Rare Earths*, pp. 250–64. Edward Arnold, London (1915).

(163) Reference 162, pp. 275–90.

(164) Lindsay Light Company: British patents 127,555 and 129,624 (1919).

(165) Lindsay Light Company: British patent 179,309 (1921).

(166) LING, J. W.: Chem. Ztg. **19**, 1468 (1895).
(167) LITTLE, H. F. V.: *A Textbook of Inorganic Chemistry*, edited by J. N. Friend, Vol. IV, pp. 319–22. Charles Griffin and Company, Ltd., London (1921).
(168) LUNDELL, G. E. F., AND KNOWLES, H. B.: Ind. Eng. Chem. **12**, 349 (1920).
(169) MANNELLI, G.: Atti X° congr. intern. chim. **2**, 718 (1938).
(169a) MATHESON, A. R.: Private communication.
(170) MATHEWS, J. M.: J. Am. Chem. Soc. **20**, 846 (1898).
(171) MATVEEV, N. I.: Zhur. Priklad. Khim. **4**, 275 (1931).
(172) McCOY, H. N., AND ROSS, W. H.: J. Am. Chem. Soc. **29**, 1709 (1907).
(173) McCUTCHEON, T. P.: J. Am. Chem. Soc. **29**, 1445 (1907).
(174) MELLAN, I.: *Organic Reagents in Inorganic Analysis*, pp. 572–6. The Blakiston Company, Philadelphia (1941).
(175) MELLOR, J. W.: *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. V, pp. 546–8. Longmans, Green and Company, London (1924).
(176) MELLOR, J. W.: *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VII, pp. 178–4. Longmans, Green and Company, London (1927).
(177) METZGER, F. J.: J. Am. Chem. Soc. **24**, 275 (1902).
(178) METZGER, F. J.: J. Am. Chem. Soc. **24**, 901 (1902).
(179) METZGER, F. J., AND ZONS, F. W.: J. Ind. Eng. Chem. **4**, 493 (1912).
(180) MEYER, R. J.: Z. anorg. Chem. **71**, 65 (1911).
(181) MEYER, R. J.: Z. anorg. Chem. **86**, 257 (1914).
(182) MEYER, R. J., AND GOLDENBERG, H.: Chem. News **106**, 13 (1912).
(183) MEYER, R. J., AND HAUSER, O.: *Die Analyse der seltenen Erden und der Erdsäueren*, Vol. XIV/XV of *Die chemischen Analyse*, pp. 171–7. Ferdinand Enke, Stuttgart (1912).
(184) Reference 183, pp. 248–52.
(185) Reference 183, pp. 258–66.
(186) MEYER, R. J., AND SPETER, M.: Chem. Ztg. **34**, 306 (1910).
(187) MEYER, R. J., AND WINTER, H.: Z. anorg. Chem. **67**, 398 (1910).
(187a) MIDDLETON, A. R.: J. Am. Chem. Soc. **48**, 2125 (1926).
(188) MINGAYE, J. C. H.: Records Geol. Survey N. S. Wales **8**, Pt. 4, 276 (1915).
(189) MOELLER, T., AND KREMERS, H. E.: Chem. Rev. **37**, 97 (1945).
(190) MOISSAN, H., AND ETARD: Compt. rend. **122**, 573 (1896).
(191) MUENCH, O. B.: Am. J. Sci. [v] **25**, 487 (1933).
(192) MUTHMANN, W., AND BAUR, E.: Ber. **33**, 2028 (1900).
(193) NEISH, A. C.: J. Am. Chem. Soc. **26**, 780 (1904).
(194) NEISH, A. C.: Chem. News **90**, 196 (1904).
(195) NEISH, A. C.: Chem. News **90**, 201 (1904).
(196) NEISH, A. C., AND BURNS, J. W.: Can. Chem. Met. **5**, 69 (1921).
(197) NILSON, L. F.: Ber. **15**, 2519 (1882).
(198) NOYES, A. A., AND BRAY, W. C.: Chem. Rev. **1**, 277 (1924).
(199) NOYES, A. A., AND BRAY, W. C.: *A System of Qualitative Analysis for the Rare Elements*, p. 148. The Macmillan Company, New York (1927).
(200) Reference 199, pp. 190, 210.
(210) PARSON, S. L.: J. Optical Soc. Am. **33**, 659 (1943).
(202) PAVELKA, F.: Mikrochemie **4**, 199 (1926).
(203) PEARCE, D. W., HANSON, R. A., AND BUTLER, J. C.: *Inorganic Syntheses*, Vol. II (edited by W. C. Fernelius), pp. 39–41. McGraw-Hill Book Company, Inc., New York (1946).
(204) POWELL, A. R., AND JOHNSON, MATTHEY AND Co.: British patent 510,198 (1938).
(205) PRATT, L. A., AND JAMES, C.: J. Am. Chem. Soc. **33**, 1330 (1911).
(206) PRODINGER, W.: *Organic Reagents Used in Quantitative Inorganic Analysis*, pp. 45–52. Elsevier Publishing Company, Inc., New York (1940).

(207) Ray, P.: Z. anal. Chem. **86,** 13 (1931).

(208) Rice, A. C., Fogg, H. C., and James, C.: J. Am. Chem. Soc. **48,** 895 (1926).

(209) Rosenheim, A.: Chem. Ztg. **36,** 821 (1912).

(210) Rosenheim, A., Meyer, R. J., and Koppel, I.: German patent 214,886 (1908).

(211) Ryan, L. W.: U. S. patents 1,307,152 (1919) and 1,351,489 (1920).

(212) Ryan, L. W.: U. S. patent 1,407,441 (1922).

(213) Sasahara, T.: Proc. World Eng. Congr., Tokyo, 1929 **35,** 359 (1931).

(214) Schiøtz, A. B.: Tids. Kemi. Farm. Terapi **14,** 270 (1917).

(215) Schoeller, W. R., and Powell, A. R.: *The Analysis of Minerals and Ores of the Rarer Elements*, pp. 104–11. Charles Griffin and Company, Ltd., London (1919).

(216) Schwarz, R., and Giese, H.: Z. anorg. allgem. Chem. **176,** 209 (1928).

(217) Shemyakin, F. M.: Compt. rend. acad. sci. (U.R.S.S.) **15,** 347 (1937).

(217a) Shemyakin, F. M., and Volkova, V. A.: J. Gen. Chem. (U.S.S.R.) **7,** 1328 (1937).

(218) Singleton, W.: Ind. Chemist **2,** 454 (1926).

(219) Smith, E. F.: J. Am. Chem. Soc. **25,** 883 (1903).

(220) Smith, J. L.: Am. Chem. J. **5,** 73 (1883).

(221) Smith, J. L.: Chem. News **48,** 29 (1883).

(222) Smith, T. O., and James, C.: J. Am. Chem. Soc. **34,** 281 (1912).

(223) Soc. Anon. des Éstablissements Poulenc Frères: French patent 374,540 (1906).

(224) Spencer, J. F.: *The Metals of the Rare Earths*, pp. 159–93. Longmans, Green and Company, London (1919).

(225) Sterba-Böhm, J.: Z. Elektrochem. **20,** 289 (1914).

(226) Tanii, K., Hosimuja, H., and Ikeda, T.: J. Chem. Soc. Japan **61,** 269 (1940).

(227) Tanteri, B.: Ann. chim. applicata **33,** 204 (1943).

(228) Thesen, G.: Chem. Ztg. **19,** 2254 (1895).

(229) Thornton, W. M.: Am. J. Sci. [iv] **42,** 151 (1916).

(230) Thornton, W. M.: Chem. News **114,** 13 (1916).

(231) Treadwell, F. P.: *Analytical Chemistry*, translated by W. T. Hall, Vol. I, 8th English edition, pp. 511–13. John Wiley and Sons, Inc., New York (1932).

(232) Treadwell, F. P.: *Analytical Chemistry*, translated by W. T. Hall. Vol. **II**, 8th English edition, p. 127. John Wiley and Sons, Inc., New York (1935).

(233) Reference 232, pp. 175–177.

(234) Reference 232, pp. 452–3.

(235) Troost, L.: Compt. rend. **116,** 1428 (1893).

(236) Twyman, F., and Smith, D. M.: *Wave Length Tables for Spectrum Analysis*, 2nd edition, p. 148. Adam Hilger, Ltd., London (1931).

(237) Urbain, G.: Bull. soc. chim. [iii] **15,** 339, 347 (1896).

(238) Urbain, G.: Ann. chim. phys. [vii] **19,** 184 (1900).

(239) Urbain, G., and Urbain, E.: Compt. rend. **132,** 136 (1901).

(240) Urry, W. D.: J. Chem. Phys. **4,** 34 (1936).

(241) van Nieuwenburg, C. J., Böttger, W., Feigl, F., Komarovsky, A. S., and Strafford, N.: *Tables of Reagents for Inorganic Analysis*, pp. 159–62. Akademische Verlagsgesellschaft m. b. H., Leipzig (1938).

(242) Voronova, L. A.: Zavodskaya Lab. **11,** 1075 (1945).

(243) Vortmann, G.: Z. anal. Chem. **87,** 190 (1932).

(244) Weiser, H. B.: *Inorganic Colloid Chemistry. Vol. II. The Hydrous Oxides and Hydroxides*, p. 272. John Wiley and Sons, Inc., New York (1935).

(245) Weiss, L.: J. Gasbeleucht. **45,** 809 (1902).

(246) Wells, R. C.: J. Soc. Chem. Ind. **29,** 1304 (1910).

(247) Wenger, P., and Duckert, R.: Helv. Chim. Acta **25,** 1110 (1942).

(248) Whittemore, C. F., and James, C.: J. Am. Chem. Soc. **35,** 127 (1913).

(249) Willard, H. M., and Freund, H.: Ind. Eng. Chem., Anal. Ed. **18,** 195 (1946).

(250) Williams, A. E.: Chem. Eng. Mining Rev. **33,** 112 (1941).

(251) Winkler, C.: Ber. **24,** 885 (1881).

(252) WIRTH, F.: Z. angew. Chem. **25,** 1678 (1912).
(253) WIRTH, F.: Z. anorg. Chem. **76,** 174 (1912).
(254) WIRTH, F.: Chem. Ztg. **37,** 773 (1913).
(255) WITT, O. N.: Chem. Ind. **17,** 161 (1894).
(256) WITT, O. N.: *Über den Cergehalt der Thorsalze,* 2nd edition, pp. 9, 13, 18. Berlin (1897).
(257) WUNDER, M., AND SCHAPIRA, A.: Ann. chim. anal. **18,** 257 (1913).
(258) WYROUBOFF, G., AND VERNEUIL, A.: Compt. rend. **126,** 340 (1898).
(259) WYROUBOFF, G., AND VERNEUIL, A.: Chem. News **77,** 245 (1898).
(260) WYROUBOFF, G., AND VERNEUIL, A.: Compt. rend. **127,** 412 (1898).
(261) WYROUBOFF, G., AND VERNEUIL, A.: Bull. soc. chim. [iii] **19,** 219 (1898).
(262) WYROUBOFF, G., AND VERNEUIL, A.: Ann. chim. phys. [viii] **6,** 487 (1905).
(263) YOE, J. H., AND SARVER, L. A.: *Organic Analytical Reagents,* p. 205. John Wiley and Sons, Inc., New York (1941).