ANALYTICAL CHEMISTRY OF URANIUM AND THORIUM

THE ANALYTICAL CHEMISTRY OF URANIUM AND THORIUM

By FRANK S. GRIMALDI, U. S. Geological Survey

CONTENTS

ABSTRACT

Under the impetus of the Atomic Energy program intensive investigations of the analytical chemistry of uranium have been made both in the United States and abroad and a considerable literature has accumulated. There has been less research on thorium chemistry.

In discussing current analytical methods and recent advances in the analytical chemistry of uranium and thorium the emphasis is on wet chemical methods, but for a proper perspective other approaches and techniques are considered.

Uranium is usually separated by organic solvent extraction of uranyl nitrate from solution salted with nitrates, by chromatographic methods, or by precipitation and extraction methods involving the use of cupferron. Uranium is determined by fluorimetric, colorimetric, volumetric, polarographic, coulometric, radioactivation, X-ray spectrometric, and nuclear photographic-plate techniques.

Separations of thorium are based on the precipitation of thorium with phosphate, ammonia at controlled acidity, potassium iodate, potassium iodate-oxalic acid, organic acids, hexamine, oxalic acid, and hydrofluoric acid. Thorium may also be separated by chromatographic techniques and by solvent extraction such as with mesityl oxide. It may be determined spectrophotometrically with thoron as well as by polarographic, titrimetric, mass spectrometric, and fluorescent X-ray spectrometric methods.

INTRODUCTION

With the impetus of the Atomic Energy program, intensive investigations of the analytical chemistry of uranium have been made both in the United States and abroad and considerable literature has accumulated. There has been less research on thorium chemistry.

The present report does not attempt a critical review of the voluminous literature on methods for the determination of uranium and thorium but deals primarily with current techniques of analysis. The emphasis is on wet chemical methods, but for a proper perspective other approaches and techniques are discussed briefly, stressing principles rather than details. A selected bibliography is included to serve both novice and advanced workers. Some items listed are not readily available, but are included to give credit to the early workers in this field.

METHODS OF ANALYSIS FOR URANIUM

Many methods are used for the determination of uranium. These include fluorimetric, colorimetric, volumetric, coulometric, radiometric, polarographic,

X-ray spectrometric, mass spectrometric, radioactivation, and nuclear-emulsion methods. The choice of method is determined by many factors such as the concentration of uranium in the sample, its chemical complexity, the accuracy sought, the speed required, and the availability of the instrumentation. The ranges of all methods overlap to a considerable degree, and the more sensitive methods can readily be applied even to samples of high uranium content provided the limits of accuracy of such methods are acceptable. Classified loosely on the basis of the smallest amount of uranium that can be detected, the fluorimetric, radiometric, radioactiviation, mass spectrometric, and photographic emulsion methods are highly sensitive; the coulometric, polarographic, and colorimetric methods are sensitive; and the X-ray fluorescence and volumetric methods least sensitive. Excluding the photographic method, in which at present the results are less accurate, the relative error in all methods of determination is usually less than ± 5 percent. The relative error in the coulometric, colorimetric (with differential methods), and volumetric methods can be as low as ± 0.1 percent.

FLUORIMETRY

Melts obtained by fusing uranium salts with sodium fluoride fluoresce a brilliant yellow green when exposed to ultraviolet light (Nichols and Slattery, 1926). The intensity of the fluorescence is proportional, within wide limits, to the amount of uranium present, and this relationship is the basis for the quantitative fluorimetric determination of uranium. As little as 10^{-10} g of uranium can be detected.

The fluorescence test for uranium is specific when the excitation is with long-wavelength (3650 A) ultraviolet light. Niobium fluoresces only weakly when exposed to short wavelength light (2536 A). In spite of this specificity, many elements may interfere by quenching the uranium fluorescence. For example, a few micrograms of Co, Cr, Ni, or Mn will reduce the fluorescence of uranium by more than 10 percent. The magnitude of quenching produced by various elements is described in several publications (Grimaldi and others, 1952, 1954; Rodden and Warf, 1950; Zebroski and Newton, 1946).

Two techniques are commonly used to reduce or eliminate interference due to quenching. One called the "dilution" method, originated with Price, Ferretti, and Schwartz (1953) who found it possible to reduce quenching to a negligible factor by using sufficiently small samples for analysis. The degree of quenching depends only on the concentration of the quencher in the flux and not on the ratio of concentration of quencher to concentration of uranium.

In the second technique the uranium is separated from quenching elements before the fluoride phosphor is prepared. Uranium may be free from quenching ele ments by precipitating them with alkali carbonate so lution (Grimaldi and others, 1952, 1954); the uraniun remains in solution as a complex carbonate. Alterna tively, the separation may be accomplished by extrac tion of uranyl nitrate by organic solvents.

The "dilution" fluorimetric method (Price, Ferrett and Schwartz, 1953) consists of taking a small aliquc of an acid solution of the sample, evaporating it in standard platinum container, adding the fluoride flu and preparing the phosphor by fusing it at controlle temperature. The relative fluorescence intensity of tl melt can be compared visually or, preferably, in fluorimeter.

The size of the aliquot in the "dilution" metho should contain negligible amounts of quenching el ments and would thus depend on the composition of t material to be analyzed, the uranium content of t sample, and the sensitivity of the fluorimeter in us This size may range from a few micrograms of samp (for materials containing very strong quenchers such manganese) to a few milligrams of sample (for materi with low concentration of quenchers and (or) containi relatively mild quenchers). In general, a 0.1-mg samp results in negligible quenching for most rock sampl The measurement of very low fluorescence intensi levels requires the use of sensitive fluorimeters.

The extraction-fluorimetric method involves the e traction by means of organic solvents of uranyl nitr from nitric acid solution after the addition of a salt agent. A portion of the solvent is then transferred the standard container and the phosphor is prepa after the evaporation of the solvent. The fraction uranyl nitrate extracted depends both on the solv and on the salting agent used, and thus a particu procedure may lend itself either to batch or to c tinuous extraction. For example, with ammoni nitrate as the salting agent and ether as the solv continuous extraction is recommended. The Geolog Survey procedures (Grimaldi and others, 1952, 19 use batch extraction with aluminum nitrate as the s ing agent and ethyl acetate as the solvent. Alumir nitrate serves also to complex F^-, $PO_4^{\equiv}$, and $SO_4^{=}$ which otherwise seriously hinder the extraction uranium. Use of aluminum nitrate is also advantag in that any aluminum extracted does not quench uranium fluorescence. Vanadium, cerium (IV), tl um, and zirconium are partly extracted. Vanad does not quench the uranium fluorescence significa Although zirconium is not a quencher, the small amc that does extract may cause low results.

Refractory ZrO_2 may be formed during the prep tion of the phosphor, and the uranium it may occlu not available to the flux. A small amount of phosp

can be added to the solution before the extraction to prevent the extraction of zirconium. Quenching from ...am and thorium may interfere seriously, and special techniques are used when these elements are major constituents of the sample.

In the carbonate-fluorimetric method an aliquot of a sulfuric acid solution of the sample, representing 15 mg or less of the sample, is treated with alkali carbonate solution in excess to precipitate quenching elements. An aliquot of the filtered solution is transferred, and after evaporation the standard melt is prepared as before. Cerium, cobalt, copper, and thorium may interfere in this procedure. With suitable modification the procedure may be used even for the determination of uranium in monazite. Cobalt is quantitatively removed when another element in addition to cobalt is precipitated with alkali carbonate. A small amount of hydroxylamine is added during the precipitation with alkali carbonate to precipitate Cu_2O if copper is a major constituent of the sample.

The flux employed at the Geological Survey is a mixture of 9 parts by weight NaF, 45.5 parts by weight Na_2CO_3, and 45.5 parts by weight K_2CO_3. This flux melts at about 605° C, does not stick to the platinum fusion vessels, produces mechanically strong melts, and gives about the same sensitivity as pure NaF. For the measurement of fluorescence obtained from less ...n 10^{-8} g of uranium, a flux that yields reproducible ...anks at high instrumental sensitivity is necessary. This flux is prepared by fusing together in platinum the three components in large batches and grinding the melts, preferably in an agate mortar. For amounts of uranium greater than 10^{-8} g, the instruments are used at a lower sensitivity; a sufficiently uniform flux is obtained by simple mixing or grinding of the components in a ball mill.

The fluorimeters, and details on the fluorimetric methods in use, are described by Grimaldi and others (1952, 1954), Center (1948), Galvanek and Morrison (1954), Kaufman and others (1950), Kelley and others (1954), Kennedy (1950), Kinser (1954), Koskela and Kaufman (1949), Price (1948), Zimmerman (1951), and Zimmerman and others (1951). Until very recently no instrument was commercially available and many laboratories have had to design and build their own. The GM fluorimeter (Galvanek and Morrison, 1954), now commercially available, is very sensitive, detecting as little as 4×10^{-10} g of uranium.

COLORIMETRY

Many reagents have been used for the colorimetric determination of uranium. The most popular at ...resent are hydrogen peroxide in sodium hydroxide ...ution and ammonium thiocyanate in acid solution.

In the alkaline-peroxide procedure provision must be made not only to remove elements that precipitate in sodium hydroxide solution but also to remove vanadium and chromium that give yellow solutions similar to that given by uranium. Iron, manganese, and cerium disturb the system because of their catalytic destruction of H_2O_2, and in the case of Fe and Mn extinction may be caused by hydroxides that precipitate in a highly dispersed state. Iron and manganese may also interfere by adsorption of uranium when these elements are separated by filtration. Phosphate, sulfate, nitrate, chloride, silicate, and fluoride ions do not interfere.

Several separation procedures may be used. One procedure used at the Geological Survey is based on the extraction of uranyl nitrate by ethyl acetate from solutions salted with aluminum nitrate as described previously. As a small amount of vanadium accompanies uranium in the extraction, it can be removed by cupferron before the colorimetric estimation of uranium, or the vanadium can be stripped from the organic solvent by several washings with a solution 2.5 M in aluminum nitrate and 0.6 N in HNO_3. Alternately, the vanadium color may be destroyed by heating the alkaline peroxide solution (Goldbeck and others, 1945). A separation procedure especially useful for rocks utilizes cupferron (Grimaldi and others, 1954). The uranium is first reduced by means of a Jones reductor and the reduced uranium precipitated with cupferron using titanium as a carrier. The cupferron precipitate is ignited and dissolved, and uranium is oxidized to the sexivalent state and separated from elements that accompanied uranium by extracting the cupferrates of these elements with ethyl acetate. Uranium remains in the water layer and is then determined colorimetrically with hydrogen peroxide in sodium hydroxide solution after the destruction of organic matter. Transmittancy measurements are made with the Beckman spectrophotometer at 400 mμ. With a 0.1-mm slit width, 1-cm light path, and water as the reference solution, an absorbance of about 0.9 is obtained for solutions of concentration 0.2 mg of uranium per milliliter of solution. With the spectrophotometer a precision of ±1 percent of the uranium content can be obtained. For details and modifications of the peroxide-colorimetric method for uranium see Rodden and Warf (1950), Assayer's Guide (1949), Begg and others (1948), Kaufman and Galvanek (1950), and Guest and Zimmerman (1955).

The thiocyanate method, described by Crouthamel and Hubbard (1952), Crouthamel and Johnson (1952), Currah and Beamish (1947), and Nelson and Hume (1945), for the spectrophotometric determination of uranium is probably the most useful of the present day colorimetric procedures for uranium. In water-acetone

medium (Crouthamel and Hubbard, 1952; Crouthamel and Johnson, 1952) and in ethyl acetate-acetone-water medium (DeSesa and Nietzel, 1954) the method is relatively free from both anionic and cationic interferences. Relatively large amounts of copper, zirconium, tin, mercury, manganese, sulfate, fluoride, acetate, chloride, and nitrate do not interfere. More than unit molar ratios of foreign ion to uranyl ion may be present for fluosilicate, phosphate, citrate, nickel, chromium, and iron. Ordinarily iron would be a serious interference, but the addition of stannous chloride to the system prevents the interference of milligram amounts of iron.

Molybdenum and hydrogen peroxide interfere seriously. Small amounts of cobalt interfere if absorbance of the uranium thiocyanate is measured at 375 mμ. At higher wavelengths the interference is considerably decreased. Vanadium and lead interfere moderately. Copper may give a thiocyanate precipitate. Thiocyanate ion polymerizes if the acidity is not controlled and yields a colored solution whose color becomes intensified with time.

The extraction of uranyl nitrate overcomes all interferences except vanadium. In the Geological Survey's modification of the thiocyanate method, the vanadium accompanying uranium in the ethyl acetate extract is stripped from the solvent layer by several washings with aluminum nitrate solution as described previously. The uranium is then stripped with water. The procedure has been applied even to carnotite ores. Absorbance measurements are made with a spectrophotometer at 375 mμ. With a slit width of 0.13 mm, a 1-cm light path, and water as reference solution, an absorbance of about 0.62 is given by a concentration of 1 mg of uranium per 25 milliliters of solution. Uranyl thiocyanate is soluble in organic solvents and may be extracted and concentrated in this manner. Details are given in the papers by Silverman and Moudy (1953) and Gerhold and Hecht (1951).

Ammonium thioglycolate has been proposed by Davenport and Thomason (1949) as a colorimetric reagent for uranium. The method is not affected by relatively large amounts of chloride, nitrate, sulfate, perchlorate, oxalate, tartrate, citrate, acetate, and fluoride. The concentration range is 0.1 mg to 1.6 mg uranium per 25 ml of solution. The pH may range from 7.6 to 10.7. In addition to elements that precipitate from alkaline solution, Fe, Cu, Ni, Pb, and Co interfere. Uranium can be determined in the presence of iron if the absorbances are measured at two wavelengths (380 mμ and 600 mμ).

Yoe, Fritz, and Black (1953) have proposed dibenzoylmethane for the spectrophotometric determination of uranium. The reagent has a sensitivity that is several times that of the thiocyanate, 250 micrograms of uranium per 50 ml of solution giving an absorbance of about 0.39 at 395 mμ with a 1-cm light path. The reaction proceeds best at a pH of 7 where unfortunately many elements interfere. Separation of uranium is made by ether extraction of uranyl nitrate from solutions heavily salted with ammonium nitrate. Adams and Maeck (1954) have applied the method to the determination of as little as 1 ppm of uranium in rocks.

A very rapid direct spectrophotometric method for the determination of uranium is based on the reduction of uranium (VI) to uranium (IV) by ferrous sulfate in 40 volume-percent phosphoric acid solution (Cannin and Dixon, 1955). With liquid samples estimation may be completed in an hour with a standard deviation of about 1.5 percent over the range 0.5 to 5.0 grams per liter of U_3O_8. A two-wavelength method using wavelengths of 660 and 700 mμ is applied in the presence of vanadium. A satisfactory reference solution is obtained in the same concentration of phosphoric acid by treating half of the solution with hydrogen peroxide to oxidize all components fully, boiling to destroy peroxides of vanadium and titanium, and then treating with sodium sulfite to destroy any remaining peroxide. The other half of the solution is treated similarly and then ferrous sulfate is added to form the reduced solution. The uranium concentration is determined from calculations based on absorbance "difference" curves of uranium and vanadium. The method is applicable in estimating uranium in sulfate solutions containing vanadium, chromium, and rare earths in concentrations of 1 to 5 grams per liter of the respective oxides, titanium up to 10 grams per liter of titanium oxide, and ferrous and ferric iron up to a total of 40 grams per liter of ferric oxide. Molybdenum and copper (in the presence of chloride) interfere. Nitrate should be removed.

TITRIMETRY

The volumetric method is the standard procedure for the determination of macro amounts of uranium. It has been used also for the determination of as little as a few tenths of a milligram of uranium. The most common procedure depends on the reduction of uranium to the quadrivalent state and titration with a standard oxidizing solution. The reduction of uranium is generally accomplished by means of amalgamated zinc or lead in the Jones reductor (Carson, 1953; Cooke and other, 1950; Sill and Peterson, 1952). The cadmium amalgam (Furman and others, 1950) has also been used. Some trivalent uranium is formed during reduction with amalgamated zinc. U(III) is oxidized readily to U(IV) by passing air through the solution before titration. U(IV) is stable to air in acid solutions but auto-oxidation may occur in the presence of traces of cupric

The most common oxidizing agents for titrating U(IV) to U(VI) are potassium permanganate, ceric ate, and potassium dichromate. Standard uranium solutions should be used in the standardization of all three oxidizing agents. For example, it has been observed that potassium permanganate gives a slightly different titer when standardized against sodium oxalate. The oxidizing agent should be standardized against various amounts of uranium solution and a working curve prepared. As much as 4 percent difference has been observed at the Geological Survey when the titer of the oxidants against 10 mg and 150 mg of uranium are compared.

No indicator is needed with potassium permanganate but ferroin may be used. The titration is sharp with potassium permanganate but sluggish with ceric sulfate and especially with potassium dichromate. Sharp end points are obtained with ceric sulfate if excess ferric iron is added before titration. Phosphoric acid also has been recommended to speed the uranium reaction. Ferroin is used as indicator. In titrations with potassium dichromate, ferric chloride followed by a mixture of phosphoric-sulfuric acid are added to catalyze the reaction. Sodium diphenylamine sulfonate is used as an indicator. Heavy metals are removed by a hydrogen sulfide precipitation although thioacetamide is preferred by some (Sill and Peterson, 1952). The remaining interfering elements are removed by extraction of their perferrates from (1+9) mineral acid solution using such solvents as chloroform or ethyl acetate. Uranium in the sample must be in the sexivalent state, and as such it is not extracted. After organic matter is destroyed, the uranium is reduced and titrated with a standard oxidizing agent. Details of the procedures are given by Rodden and Warf (1950), Assayer's Guide (1949), Sill and Peterson (1952), Furman and others (1953), Kennedy and Kaufman (1949), Pepkowitz (1945), and Rodden and Tregoning (1955). Nickel is not removed in the separations discussed and may interfere with zinc reductors amalgamated with 2 to 3 percent mercury. The plating out of nickel on such reductors is accompanied by excessive evolution of hydrogen and incomplete reduction of uranium. Grimaldi (1954) has found that a zinc reductor amalgamated with 10 percent mercury is not poisoned by nickel-bearing solutions.

Tillu (1954) isolates UF_4 after the reduction of uranium with stannous chloride from minerals such as samarskite, columbite-tantalite, and titano-niobates. The UF_4 is dissolved, fluoride expelled with acid, and the uranium determined volumetrically. Reports by Carson (1953) and Furman and coworkers (1953) deal with the coulometric determination of uranium. As little as 5 micrograms can be determined.

In another interesting titrimetric method, Main (1953, 1954) reduces U (VI) to U (IV) with stannous chloride in nearly boiling 6 to 12 N HCl. The reaction is catalyzed by ferric iron and driven to completion by orthophosphate. The excess stannous chloride is oxidized in the cold with mercuric chloride, and the uranium and iron catalyst are titrated with standard dichromate. Molybdenum, copper (II), vanadium, and titanium interfere.

Workers in the British Commonwealth countries have made extensive investigations on the separation of uranium (and also of thorium) by inorganic chromatography on cellulose columns or compound columns of alumina and cellulose in combination with solvent (ether-nitric acid) extraction of uranium (Arden and others, 1949; Burstall and Wells, 1951; Kember, 1952; Overton and Williams, 1950; Rabbitts, 1952; Ryan and Williams, 1949, 1952; Smith and Williams, 1950; and Williams, 1952). Uranium as uranyl nitrate is dissolved and moves with the solvent front. Most other metals remain stationary or move only slowly in comparison with uranium. The uranium in the eluent is determined by fluorimetric, colorimetric, polarographic, volumetric, and other techniques.

POLAROGRAPHY

Harris and Kolthoff (1945, 1947) have studied systematically the polarographic properties of uranium in acid, neutral, and alkaline solutions. In 0.01–0.2 N HCl the diffusion current at −0.3 volt saturated calomel electrode (S. C. E.) of the first polarographic wave [U(VI)−U(V)] is proportional to the uranium concentration between 5×10^{-4} and 4×10^{-3} moles per liter. A precision of 2 percent is obtained. As 5 ml of solution is often polarographed, about 0.5 mg can be determined within ±2 percent. In the concentration range down to 2.4×10^{-5} molar where the diffusion current diverges from proportionality by about 10 percent, approximately 30 micrograms can be determined. Using a supporting medium of 0.1 N HCl, Tishkoff (1948) has applied the method to the determination of U(VI) in UO_2 and in U(IV) salts.

The two-electron uranyl reduction wave in 1 N to 2 N sulfuric acid, measured at about −0.3 volt (S. C. E.), has also been used (Ballinger, 1948). The sensitivity is twice as great compared to hydrochloric acid supporting medium. The most serious interferences in sulfuric acid as well as hydrochloric acid media are Fe (III), Cu, Mo, Ti, and V. Lead interferes in hydrochloric acid media but can be precipitated as sulfate and determined in hydrochloric acid media (Holmes and Smales, 1948). Hydroxylamine hydrochloride prevents iron interference (Strubl, 1938). Kilner (1948) determined uranium in ferric hydroxide using a

385115—56——40

supporting electrolyte of 2 N hydroxylamine hydrochloride and 0.1 N hydrochloric acid. Other media such as citrate and tartrate have been used; only lead or phosphate is stated to interfere in citrate media (Rodden and Warf, 1950). Legge (1954) separates uranium by eluting with a nitric acid-ether solution through a short column of cellulose pulp. The uranium is determined polarographically in an electrolyte containing oxalic and sulfuric acids. The diffusion current is observed at −0.5 volt. The minimum concentration of uranium that can be determined is about 10^{-5} molar (2.4 γ per ml).

Šušic, Bal, and Cuker (1954) determine uranium polarographically at pH 3.6 to 4.0 with ascorbic acid as a supporting electrolyte. The diffusion current is observed at −0.36 (S. C. E.). Ascorbic acid reduces Fe (III), V (V), Mo (VI), and Cr (VI), and the reduced forms of these ions does not interfere with the uranium wave. Titanium is complexed with ascorbic acid, and the titanium wave is more negative than that of uranium. Tellurium, thallium, lead, and moderate amounts of copper and antimony interfere. The method is suitable for ore samples with more than 0.01 percent uranium. The relative error, in the range 0.01 to 0.05 percent uranium, is 5 to 9 percent.

MISCELLANEOUS METHODS

NUCLEAR PHOTOGRAPHIC EMULSIONS

In the nuclear emulsion photographic plate technique, as described by Bremner (1951), Delaney and others (1953), Isaac and Picciotto (1953), Poole and Matthews (1951, 1952), and Senftle, Farley, and Stieff (1954), the material to be analyzed is placed in contact with the nuclear emulsion or the nuclear emulsion is loaded with a solution of the sample and then dried. After suitable exposure and development γ-ray tracks or stars from atoms that had undergone disintegration can be observed. The length of the γ-ray tracks or the number of 3-, 4-, and 5-branched stars per unit area can be correlated to the uranium and thorium contents of the sample. Less than microgram amounts of uranium and thorium may be determined.

RADIOACTIVATION

The method of radio activation analysis is based on the measurement of nuclear radiation from radioactive isotopes produced by interaction of nuclear particles with a stable isotope (or isotopes) of an element. The method is specific, each induced radionuclide having its own decay scheme and decay constant. For most elements the sensitivity is extremely high.

In one method (Singer, 1952; Smales, 1952) microgram amounts of uranium in rocks and minerals can be determined by neutron irradiation followed by radiochemical separation and measurement of the activity of the fission product, barium formed according to the scheme: $^{234}_{92}U$ (n, γ) fission products. The ultimate sensitivity is estimated to be 10^{-8} grams of uranium.

In another method, of Mahlman and Leddicotte (1955), the activity of neptunium, produced according to the scheme

$$^{238}_{92}U\ (n, \gamma)\ ^{239}_{92}U \xrightarrow[\beta^-]{} ^{239}_{93}Np$$

is detected by means of a gamma scintillation counter. About 0.1 microgram of uranium per gram of sample can be determined with a relative error of about 10 percent. Mahlman and Leddicotte believe that it is possible to extend the method to as small a concentration of uranium as 0.0001 microgram per gram of sample.

MASS SPECTROMETRY

In the isotope-dilution mass-spectrometric technique the general requirements, according to Tilton (1954), are as follows:

1. A standardized solution (usually called the spike) of an isotopically altered carrier of the element to be determined.
2. A procedure for equilibrating a known weight of the carrier (spike) with the sample to be analyzed and for extracting enough of the element to be determined to permit isotope analysis.
3. A mass spectrometer to perform isotopic analyses of the carrier, of the carrier plus sample, and (for elements of variable isotopic composition) of the sample alone. In addition a blank is usually necessary.

Chemical processing need be quantitative only during the dissolution of the sample and its equilibration with the spike. Beyond this point the result will depend only upon the new ratio(s) produced in the carrier by the sample rather than upon the degree of recovery of the element under analysis.

Hess and coworkers (1953) have used the isotope-dilution technique for the determination of traces of uranium in minerals and meteorites. The spike used is uranium enriched in U^{235}. The principal uranium separation was accomplished by extraction of uranyl nitrate into methyl isobutyl ketone (hexone) from a solution salted with nitrate ion. A few micrograms of uranium were analyzed with the mass spectrometer. According to Tilton, the sensitivity of the mass spectrometric method for uranium can be made to surpass that of the fluorimetric method. The relative error is generally of the order of ±2 percent.

FLUORESCENT X-RAY SPECTROMETRY

A few methods using X-ray spectroscopy have been published by Rodden and Warf (1950). Birks and Brooks (1951, 1953) determine uranium in aqueous solution in concentrations as low as 0.05 g per liter. The

procedure is fast, requiring less than 10 minutes for ·h analysis. Heavy elements, such as lead, interfere ,present in concentration exceeding 10 percent of the uranium concentration. Kerr and Pill (1951) have determined uranium in uraninite by X-ray spectroscopy.

METHODS OF ANALYSIS FOR THORIUM

Chemical methods for the determination of thorium are complex, involve difficult and tedious manipulation, and require the services of thoroughly experienced analysts. The analytical chemistry of thorium is complicated by the colorless nature of the ion, by its single valence state, by the lack of selective and sensitive reagents, by the refractory nature of its ores, and by its association with elements that present difficult analytical problems.

In most thorium analyses, provisions must be made for the separation of thorium not only from elements commonly determined in rock and mineral analyses, but also from the rare earths, from the quadrivalent elements such as Sn, Ti, and Zr, from quinquevalent elements such as Nb and Ta, and from sexivalent elements such as W. There are many procedures for the separation of thorium from the rare earths; few procedures are available for the separation of thorium from Sn, Ti, Zr, Nb, Ta, and W.

PRECIPITATION REACTIONS

THORIUM ORTHOPHOSPHATE

With zirconium as a carrier, thorium is precipitated quantitatively as the phsophate from solutions 2.5 percent by volume in hydrochloric acid (that is, 0.3 N) and containing 2 g diammonium phosphate per 100 ml of solution (Grimaldi and others, 1954). The precipitation reaction separates thorium from most of the major constituents of rock samples and is a useful concentration procedure in the analysis of rocks. In addition to titanium and zirconium, some rare-earth phosphates and members of the acid-insoluble group are also precipitated. This same procedure has been used also by Tillu and Athavale (1954a).

SEPARATION OF THORIUM FROM RARE EARTHS

Ammonium hydroxide.—Thorium is separated from calcium, magnesium, manganese, and most of the rare earths by ammonium hydroxide precipitations at controlled acidity (Grimaldi and others, 1954). At a pH corresponding to the neutral color of methyl red, thorium is precipitated quantitatively, whereas most of the trivalent cerium and the other rare earths remain in solution. Either nitrate or chloride solutions of thorium may be used, but the sulfate ion must be absent. If much sulfate is present, considerable loss of thorium ·esults at the methyl red end-point, although pre-·pitation of thorium is complete when excess ammonia is used. Sulfate can be removed by preliminary precipitations of thorium with sodium hydroxide.

Complete separation of thorium from the rare earths is not obtained in this separation, as the last few milligrams of rare earths are retained persistently by the thorium precipitate. The separation, however, is simple and exceedingly useful for removing most of the rare earths. Zirconium and titanium are not separated.

Potassium iodate.—The separation of thorium from the rare earths by precipitation as iodate (Rodden and Warf, 1950; Meyer, 1911) is one of the best procedures. For macro amounts the reaction is carried out in 6N nitric acid solution. For quantities less than a few milligrams the final acidity of the solution (after all reagents are added) should not exceed 1N nitric acid because loss of thorium results at higher acid concentrations. Two precipitations of thorium iodate from 6N nitric acid solutions are usually sufficient for separating the rare earths; four or five precipitations may be necessary at low acidities. Lead, mercury, tin, niobium, tantalum, cerium (IV), uranium (IV), zirconium, titanium, and to a lesser extent, iron, bismuth and silver also are precipitated by iodate. Cerium (IV) can be reduced by hydrogen peroxide to cerium (III). More elements tend to coprecipitate with thorium iodate at low acidity than at high. At high acidities the precipitation of thorium iodate is made by adding 50 ml of nitric acid and 100 ml of 15 percent solution of potassium iodate in (1+1) nitric acid to 100 ml of slightly acid solution of the sample. For low acidities 3 ml of nitric acid and 8 ml of 7.5 percent water solution of potassium iodate are added to the slightly acid solution of the sample, and the total volume of the solution is made to 50 ml by the addition of water (Grimaldi and others, 1954). Thorium iodate can be dissolved by reducing acids, such as hydrochloric acid, and also by concentrated nitric acid.

Tillu and Athavale (1954b) precipitated thorium iodate from 40 percent nitric acid solution containing oxalic acid. Up to 20 mg Ti, 40 mg Zr, and 20 mg Bi did not precipitate and the authors outlined a rapid method for the determination of thorium where the iodate-oxalic acid separation is the only one used. No information is given on the behavior of Pb, Hg, Sn, Nb, Ta, and larger amounts of Ti, which would be expected to interfere. The procedure has great promise but unfortunately cannot be applied to low-grade thorium ores except at low acidity where it loses its effectiveness as a major separation. Stine and Gordon (1953) precipitate thorium iodate from homogeneous solution in a dense and granular form with iodate produced by the reduction of periodate with ethylene glycol, which is slowly produced by the hydrolysis of β-hydroxyethyl acetate.

Hydrogen peroxide.—Thorium is precipitated by hydrogen peroxide as the peroxynitrate from solutions 0.03N or less in nitric acid. The concentration of hydrogen peroxide used is 5 ml of 30 percent hydrogen peroxide per 100 ml of solution. The method adopted by the Geological Survey (Grimaldi and others, 1954) uses 0.03N nitric acid because few elements are precipitated at this higher acidity. The precipitation of thorium with hydrogen peroxide is somewhat sensitive to changes in conditions of precipitation. Zirconium causes low recovery of thorium and must be removed completely before applying the peroxynitrate precipitation. Very slight losses of thorium (about 1 mg or less of thorium oxide) occur in the presence of the sulfate ion.

Organic acids.—A large number of organic acids such as m-nitrobenzoic acid, sebacic acid, and m-cresoxyacetic acid (Venkataramaniah and others, 1952) have been proposed for the separation of thorium, especially from uranium and rare earths. Venkataramaniah and Rao have done a considerable amount of work in this field. An article by Banks and Byrd (1953) includes most of the references on this subject.

Hexamethylenetetramine (hexamine) was originally proposed by Ismail and Harwood (1937) and has received much attention. Details concerning its use are given by Rodden and Warf (1950), Assayer's Guide (1949), and Rodden and Tregoning (1955). Phosphate, Zr, and Ti must be absent.

SEPARATION OF THORIUM FROM Ti, Zr, Nb, Ta, Sn, W, AND MEMBERS OF R_2O_3 GROUP

Oxalic acid.—The separation of thorium by precipitation as the oxalate is a standard method for the separation of thorium and rare earths and is widely used. Kall and Gordon (1953) have shown that losses of from a few tenths of a milligram to more than 1 mg of ThO_2 may result when conditions are not controlled. These authors studied the effects of ammonium salts and acidity on the solubility of thorium oxalate precipitated either heterogeneously with oxalic acid or from homogeneous solution with dimethyl oxalate. It seems desirable to precipitate thorium oxalate in the absence of ammonium salts. In the absence of rare earths, a pH of 0.7 is most suitable whereas in the presence of rare earths a pH of 1 to 2 is recommended. Prolonged digestion periods are also desirable. For heterogeneous precipitation Kall and Gordon found that the procedure of Ewing and Banks (1948) gave the smallest losses of thorium. These workers precipitate thorium from solutions containing 5 ml of $HClO_4$ and 5 g of oxalic in a total volume of 300 ml.

Willard and Gordon (1948) recommend precipitation of thorium oxalate from homogeneous solution through the hydrolysis of dimethyl oxalate. In this manner dense, easily filterable precipitates are obtained. The solubility of thorium oxalate is such that for small amounts of thorium (less than a few milligrams) precipitation as the oxalate is not always applicable.

Hydrofluoric acid.—Hydrofluoric acid provides approximately the same separations as oxalic acid. It is especially useful in the concentration of traces of thorium. Lanthanum is frequently used as a carrier. Hydrofluoric acid separations have been used at the Geological Survey for both small and large amounts of thorium (Grimaldi and others, 1954). In the presence of alkalies and alkaline earths the precipitates from hydrofluoric and oxalic acid tend to occlude zirconium and titanium.

ORGANIC SOLVENTS

Mesityl oxide.—This procedure originated at the Geological Survey (Grimaldi and others, 1954) and has received wide attention. Thorium nitrate is quantitatively extracted by mesityl oxide from solutions 2.5 M in aluminum nitrate and 1.2 M in nitric acid. The concentration of nitric acid is not critical. We have used the procedure for amounts of thorium ranging from a few tenths of a milligram to several hundred milligrams of thorium dioxide. Marechal-Cornil and Picciotto (1953) have shown that thorium in concentrations as small as 10^{-12} g of thorium per ml of solution may be extracted quantitatively. The extraction is a batch extraction. All of the uranium and about 75 percent of the zirconium is extracted with thorium. Small amounts of vanadium, rare earths, and iron are extracted, but these elements may be stripped from the mesityl oxide by several washings with a solution 2.5 M in aluminum nitrate and 1.2 M in nitric acid. Tin, Ti, Pb, and most other elements are not extracted. Marechal-Cornil and Picciotto (1953) report that bismuth and polonium are quantitatively extracted and found the procedure especially useful in radiochemical work where it is desired to separate members of radioactive series. Thorium is stripped from the mesityl oxide with water.

The mesityl oxide separation is a useful means of concentrating trace quantities of thorium and may be applied in the presence of phosphate and arsenate. The separation is especially important for the separation of large amounts of thorium from small amounts of rare earths where precipitation reactions may not be effective. Banks and Edwards (1955) have shown that lithium nitrate can also be used as a salting agent in the mesityl oxide extraction method.

Warf (1949) has indicated that tributyl phosphate may be a useful solvent for the extraction of thorium nitrate.

α-Thenoyltrifluoroacetone (TTA).—Solutions of TTA in benzene have been used for the "chelating extrac-

tion" of tracer to gram amounts of thorium by Hageman (1950), Meinke and Anderson (1952), and Tilton and 'drich (1954). A pH of 2 to 2.5 is generally used. This .eagent has been especially useful for the separation of macro amounts of thorium from highly radioactive spallation and fission products.

CHROMATOGRAPHY

British investigators have developed two important chromatographic separation procedures. In one, developed by Kember (1948, 1952), thorium nitrate is adsorbed on activated cellulose and eluted with ether containing 12.5 percent (v/v) of nitric acid. Cerium (IV), Zr, and Sc in part, and to a lesser extent Fe, accompany thorium. Phosphate interferes. Zirconium and Sc can be held on the column if tartaric acid is added to the nitric acid solution of thorium before extraction. Phosphate is removed by preliminary treatment of the sample with HF. The determination of thorium is completed gravimetrically after precipitation of thorium oxalate and ignition to oxide. The procedure has been applied to the determination of thorium in monazite and uranothorianite.

In another procedure (Williams, 1952; Guest and Proulx, 1952) activated alumina is used with activated cellulose, alumina being the principal absorbent. The thorium nitrate is eluted with the same solvent as before. The great advantage of this procedure is that ores conining phosphate can be handled directly. The movement of zirconium is suppressed by adding phosphate ion, which is in turn complexed by ferric nitrate. The procedure has been applied to the determination of thorium in monazite, samarskite, fergusonite, euxenite, and pyrochlore. Macro amounts of thorium are determined by the conventional oxalate precipitation; small amounts are determined spectrographically.

COLORIMETRY

Few colorimetric procedures have been developed for the determination of thorium. p-Dimethylaminoazophenylarsonic acid has been used at the Geological Survey (Grimaldi and others, 1954). Thoron, the sodium salt of 2-(2-hydroxy-3,6,-disulfo-1-naphthylazo)-benzene arsonic acid, is the most widely used reagent for the spectrophotometric determination of thorium (Thomason and others, 1949). In acid solution (pH 0.5 to 1.5) a red-colored complex is formed with thorium which absorbs strongly at 545 mμ. As thoron also absorbs at this wavelength the absorbance of the thorium-thoron solution is measured against a reagent blank. The sensitivity is high; a net absorbance of 0.25 is given by solutions containing 100 micrograms of ThO_2 in 25 ml volume for a 1-cm light path. Zr, Ti, Bi, Fe (III), Sn, Ta, Nb, Sc, Ce (IV), and U (IV) are erious interferences. The interference of Fe (III) is somewhat lessened by the addition of hydroxylamine hydrochloride. Many other elements such as the cerium earths cannot be tolerated in amounts greater than several tenths of a milligram.

Thoron has been used successfully for the determination of thorium in monazite and black sands by Banks and Byrd (1953) and by Banks and others (1953), and in waters by Taylor and Dillon (1952). A report based on a Ph. D. thesis by Byrd (Byrd and Banks, 1953) is comprehensive. Ingles (1951) examined a number of procedures for the separation and determination of thorium and discusses the determination of thorium with thoron.

Frank Cuttitta of the Geological Survey (written communication) adds a small amount of phosphate to prevent the extraction of zirconium in the mesityl oxide separation. The colorimetric determination of thorium in zircon with thoron is thus facilitated.

Morin has been studied at the Geological Ssrvey both as a colorimetric and fluorimetric reagent for thorium (Fletcher and Milkey, 1954). At a pH of 2 the sensitivity of the color reaction is about 2½ times that given by thoron. The thorium-morin complex has a maximum absorbance of 410 mμ. Zirconium and aluminum seriously interfere. The method has not been applied to the analysis of rocks and ores.

MISCELLANEOUS METHODS

TITRIMETRIC "VERSENE" METHODS

In the method of Fritz and Ford (1953) thorium is titrated directly with the disodium salt of ethylenediaminetetraacetic acid (versene), a soluble complex being formed. Stoichiometric results are obtained in the pH range 2.3 to 3.4. With Alizarin Red S indicator the following ions interfere, either by forming stable versene complexes or by reacting with the indicator: Ti, Zr, Ce, V, Fe, Ni, Cu, Sn, Pb, and Bi. Sulfate, phosphate, fluoride, and oxalate also interfere. Extraction of thorium with mesityl oxide separates thorium from all metals except Zr, U, and V. Six to 50 mg of thorium in 25 ml of solution and 0.12 to 0.24 g of thorium in 100 ml of solution can be determined rapidly with less than 1 percent relative error.

In the indirect titration of thorium (Malmstadt and Gohrbrandt, 1954) a known excess of versenate solution is added to the thorium solution, the solution is diluted to about 100 to 150 ml and buffered with acetate, a suitable wavelength is selected (290 or 320 mμ), and the excess versenate is titrated with standard copper solution. The strong ultraviolet absorption band of copper versenate is used to determine the end point. A precision of about 1 part per thousand in the range of 1 mg to 50 mg of thorium per 125 ml of solution is obtained.

POLAROGRAPHY

Amperometric titration of thorium with molybdate has been reported by Smales and Airey (1952) and by Gordon and Stine (1953). In the pH region 2.3 to 2.7, quantities as small as 1 mg may be titrated with a relative error of 10 percent. Gordon and Stine (1953) titrate at an applied potential of −0.95 volt versus S. C. E. A sodium chloride medium at pH of 1.8 is used. Nitrate, perchlorate, and sulfate ions interfere seriously. The procedure permits the determination of 10 to 30 mg of thorium oxide in the presence of up to 800 mg of rare earth oxides.

Thorium has also been determined, by Komarek (1950), indirectly by precipitation of thorium iodate and determination of the iodate ion polarographically. The method yields good results for as little as 20 micrograms of thorium.

MASS SPECTROMETRY

The isotope dilution-mass spectrometric technique has been used by Tilton, Aldrich, and Inghram (1954) for the determination of thorium in minerals of igneous rocks.

The preparation of the isotopic carrier Th^{230} is described. The sample is completely dissolved and an aliquot of the Th^{230} carrier is equilibrated with the solution of the sample. From this point three methods were found useful for the separation and purification of thorium: extraction at a pH of 2 into a 0.1–M solution of thenoyltrifluoroacetone in benzene, extraction from a nearly saturated solution of aluminum nitrate into hexone, and precipitation of thorium oxalate using lanthanum as carrier. One microgram of thorium is more than sufficient for a satisfactory analysis using multiplier and surface ionization techniques. The accuracy of a single determination is about ±1.5 percent.

FLUORESCENT X-RAY SPECTROMETRY

A fluorescent X-ray spectrographic method for the determination of thorium in rocks and in a variety of thorium ores is described by Adler and Axelrod (1955). Measurements are made with a two-channel spectrometer equipped with quartz analyzing crystals. Thallium is used as internal standard. Because the relatively weak L spectra must be used, sensitivities are limited, 0.2 percent ThO_2 being considered the lower limit of detection. Uranium, niobium, barium, strontium, and iodine in large concentrations interfere.

SELECTED PROCEDURES FOR DETERMINATION OF THORIUM

DETERMINATION OF SMALL AMOUNTS

The procedure of Tillu and Athavale (1954a) outlined below is similar in many respects to the Geological Survey method (Grimaldi and others, 1954). The features of the method include:

1. Decomposition of the sample with Na_2O_2.
2. Precipitation of thorium as phosphate with Zr as carrier.
3. Separation and concentration of ThF_4 using lanthanum as carrier.
4. Precipitation of thorium as iodate in potassium iodate-oxalic acid mixture.
5. Estimation of thorium by titrating against thiosulfate, the iodine having been liberated in acid solution with KI.

SPECTROPHOTOMETRY

The procedure of Banks and coworkers (1953a) is applicable to both high- and low-grade ores. The features of the method include:

1. Decomposition of the sample by fusion with KHF_2.
2. Digestion of the melt with HF.
3. Centrifugation of the insoluble fluorides.
4. Solution of the insoluble fluorides by heating with aluminum nitrate solution.
5. Extraction of thorium with mesityl oxide.
6. Stripping the thorium from mesityl oxide with water.
7. Spectrophotometric determination with thoron.

REFERENCES CITED

Adams, J. A. S., and Maeck, W. J., 1954, Fluorometric and colorimetric microdetermination of uranium in rocks and minerals: Anal. Chemistry, v. 26, p. 1635–1639.

Adler, Isidore, and Axelrod, J. M., 1955, Determination of thorium by fluorescent X-ray spectrometry: Anal. Chemistry, v. 27, p. 1002–1003.

Arden, T. V., Burstall, F. H., and Linstead, R. P., 1949, A new method for the detection and determination of uranium Chem. Soc. (London) Jour., Supplementary Issue no. 2 p. S311–S313.

Assayer's Guide, [New Brunswick Laboratory], 1949, U. S Atomic Energy Comm., AECD-2640, 82 p., declassifie 1949.

Ballenger, H. F., 1948, Polarographic method for the quant tative determination of uranium in atmospheric dust: U. S Atomic Energy Comm. AECD-2065, 11 p., 1944, (decla sified) 1948, issued by U. S. Atomic Energy Comm. Tec Inf. Service, Oak Ridge, Tenn.

Banks, C. V., and Byrd, C. H., 1953, Spectrophotometric d termination of thorium in monazite sands: Anal. Chemistr v. 25, p. 416–419.

Banks, C. V., and Edwards, R. E., 1955, Separation and d termination of thorium and aluminum: Anal. Chemist v. 27, p. 947–949.

Banks, C. V., Klingman, D. W., and Byrd, C. H., 1953, Sp trophotometric determination of thorium in black san Anal. Chemistry, v. 25, p. 992–993.

Begg, M. R., Williams, A. F., and Wood, G. A., 1948, Ch Research Lab., Teddington [England], unpub. inf.

Birks, L. S., and Brooks, E. J., 1951, Analysis of uranium s tions by X-ray fluorescence: Anal. Chemistry, v. 23, 707–709.

Birks, L. S., Brooks, E. J., and Friedman, H., 1953, Fluores X-ray spectroscopy: Anal. Chemistry, v. 25, p. 692–697

Bremner, J. W., 1951, A method for determining uranium thorium in rocks by the nuclear photographic plate: P ical Soc. (London) Proc., v. 64A, p. 25–31.

Burstall, F. H., and Wells, R. A., 1951, Inorganic chromatography on cellulose—part V. The use of columns of cellulose in combination with organic solvent extraction for the separation of uranium from other metals: Analyst, v. 76, p. 396–410.

Byrd, C. H., and Banks, C. V., 1953, Spectrophotometric determination of thorium with the trisodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid and some properties of complexes involved: U. S. Atomic Energy Comm. ISC–456, 96 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service, Oak Ridge, Tenn.

Canning, R. G., and Dixon, P., 1955, Direct spectrophotometric determination of uranium in aqueous solutions: Anal. Chemistry, v. 27, p. 877–880.

Carson, W. N., Jr., 1953, coulometric determination of uranium: Anal. Chemistry, v. 25, p. 466–470.

Center, E. J., 1948, Topical report on the direct micro-determination of uranium using a modified fluorophotometer: U. S. Atomic Energy Comm. AECD–3006, 22 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service, Oak Ridge, Tenn.

Cooke, W. D., Hazel, Fred, and McNabb, W. M., 1950, Application of the lead reductor to the determination of uranium. Anal. Chemistry, v. 22, p. 654–655.

Crouthamel, C. E., and Hubbard, H. M., 1952, The application of differential colorimetry to the thiocyanate-acetone analysis for uranium. U. S. Atomic Energy Comm. ANL–4940, 11 p.

Crouthamel, C. E., and Johnson, C. E., 1952, Spectrophotometric determination of uranium by thiocyanate method in acetone medium. Anal. Chemistry, v. 24, p. 1780–1783.

Currah, J. E., and Beamish, F. E., 1947, Colorimetric determination of uranium with thiocyanate. Anal. Chemistry, v. 19 p. 609–612.

Davenport, W. H., Jr., and Thomason, P. F., 1949, Determination of uranium (VI) in presence of anions—Ammonium thioglycolate as a colorimetric analytical reagent. Anal. Chemistry, v. 21, p. 1093–1095.

Delaney, C. F. G., Matthews, C. M. E., and Poole, J. H. J., 1953, The uranium content of some specimens of phosphate rock. Royal Dublin Soc. Sci. Proc., v. 26, no. 10, p.165–172.

DeSesa, M. A., and Nietzel, O. A., 1954, Spectrophotometric determination of uranium with thiocyanate: U. S. Atomic Energy Comm. ACCO–54, 19 p. (Microcard copy on file in U. S. Atomic Energy Comm. depository libraries.)

Ewing, R. E., and Banks, C. V., 1948, Analysis of thorium-chromium mixtures: Anal. Chemistry, v. 20, p. 233–235.

Fletcher, M. H., and Milkey, R. G., 1954, U. S. Geol. Survey unpub. inf.

Fritz, J. S., and Ford, J. J., 1953, Titrimetric determination of thorium: Anal. Chemistry, v. 25, p. 1640–1642.

Furman, N. H., Bricker, C. E., and Dilts, R. V., 1953, Titration of uranium (IV) by electrolytically generated ceric ion: Anal. Chemistry, v. 25, p. 482–486.

Galvanek, Paul, Jr., and Morrison, T. J., Jr., 1954, A new fluorimeter for the determination of uranium: U. S. Atomic Enery Comm. ACCO–47, 38 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service, Oak Ridge, Tenn.

Gerhold, Max, and Hecht, Friedrich, 1951, Die photometrische Bestimmung kleiner Uranmengen mit Kaliumrhodanid: Mikrochemie ver. Mikrochim. Acta, Band 37, p. 1100–1105.

Grimaldi, F. S., May, Irving, and Fletcher, M. H., 1952, U. S. Geological Survey fluorimetric methods of uranium analysis: U. S. Geol. Survey Circ. 199, 20 p.

Grimaldi, F. S., May, Irving, Fletcher, M. H., and Titcomb, Jane, 1954, Collected papers on methods of analysis for uranium and thorium: U. S. Geol. Survey Bull. 1006, 184 p.

Goldbeck, C. G., Petretic, G. J., Minthorn, M. L., and Rodden, C. J., 1945, Colorimetric determination of uranium by means of peroxide: Natl. Bur. Standards (Washington, D. C.), Rept. A–1074, 14 p.

Gordon, Louis, and Stine, C. R., 1953, Amperometric titration method for thorium in the presence of the rare earths of monazite sand: Anal. Chemistry, v. 25, p. 192–194.

Guest, R. J., and Proulx, E. I., 1952, The determination of thorium in ores by the column method: Canada Dept. Mines Tech. Surveys, Mines Branch, Radioactivity Div., Topical Rept., TR–94/52, 8 p.

Guest, R. J., and Zimmerman, J. B., 1955, Determination of uranium in uranium concentrates. Use of ethyl acetate: Anal. Chemistry, v. 27, p. 931–936.

Hageman, French, 1950, The isolation of actinium: Am. Chem. Soc. Jour., v. 72, p. 768–771.

Harris, W. E., and Kolthoff, I. M., 1945, The polarography of uranium—1, Reduction in moderately acid solutions. Polarographic determination of uranium: Am. Chem. Soc. Jour., v. 67, p. 1484–1490.

——— 1947, The polarography of uranium—3, Polarography in very weak acid, neutral or basic solutions: Am. Chem. Soc. Jour., v. 69, p. 446–451.

Hess, D. C., Brown, Harrison, Ingraham, M. G., Patterson, Claire and Tilton, George, 1953, Measurement of trace quantities of uranium and lead in minerals and meteorites: Natl. Bur. Standards [Washington, D. C.], Circ. 522, p. 183–187.

Holmes, Arthur, and Smales, A. A., 1948, Monazite from Bodmin Moor, Cornwall—A study in geochronology, Part 2. Analysis of Bodmin Moor monazite for lead, thorium, and uranium, by A. A. Smales: Royal Soc. Edinburgh Proc., v. 63B, p. 125–129.

Ingles, J. C., 1951, The chemical determination of thorium in its ores: Canada Dept. Mines Tech. Surveys, Mines Branch, Memo. Ser., No. 110, 26 p.

Isaac, N., and Picciotto, E. E., 1953, Ionium determination in deep-sea sediments: Nature, (London) v. 171, p. 742–743.

Ismail, A. M., and Harwood, H. F., 1937, The use of hexamine (hexamethylenetetramine) for the separation of thorium from the rare earths and its application to the determination of thorium in monazite sand: Analyst, v. 62, p. 185–191.

Kall, H. L., and Gordon, L., 1953, Quantitative insolubility of thorium oxalate: Anal. Chemistry, v. 25, p. 1256–1258.

Kaufman, David, Castillo, Mario, Koskela, Urpo, 1950, New fluorimeters for the determination of uranium, MIT Models I, II, III and IV: U. S. Atomic Energy Comm. MITG–A70, 32 p. (Microcard copy on file in U. S. Atomic Energy Comm. depository libraries.)

Kaufman, David, and Galvanek, Paul, Jr., 1950, Modifications in the peroxide-colorimetric method for uranium developed at the MIT Mineral Engineering Laboratory: U. S. Atomic Energy Comm. MITG–A67 (AECD–3137), 19 p., declassified 1951. (Microcard copy on file in U. S. Atomic Energy Comm. depository libraries.)

Kelley, M. T., Hemphill, H. L., and Collier, D. M., 1954, An improved fluorophotometer for determination of uranium in fused sodium fluoride pellets: U. S. Atomic Energy Comm. ORNL 1445, 15 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service, Oak Ridge, Tenn.

Kember, N. F., 1948, Chem. Research Lab., Teddington [England], unpub. inf.

——— 1952, Inorganic chromatography on cellulose. Part VII. The determination of thorium in monazite and of thorium and uranium in uranothorianite: Analyst, v. 77, p. 78–85.

Kennedy, R. H., 1950, The use of the paper column separation in the estimation of microgram quantities of uranium: U. S. Atomic Energy Comm., MITG–A84 (AECD–3187), 21 p., declassified 1951.

Kennedy, R. H., and Kaufman, D., 1949, MITG–A60, U. S. Atomic Energy Comm. unpub. inf.

Kerr, P. F., and Pill, R. J., 1951, X-ray fluorescent data on Marysvale uraninite, *in* Annual report for July 1, 1950 to June 30, 1951: U. S. Atomic Energy Comm. RMO–797, p. 8–23, issued by U. S. Atomic Energy Comm., Oak Ridge, Tenn.

Kilner, S. B., 1948, Determination of small amounts of uranium by the polarographic method: U. S. Atomic Energy Comm., AECD–2059, 1 p., 1942, declassified 1948, issued by U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

Kinser, C. A., 1954, The Model VI transmission fluorimeter for the determination of uranium: U. S. Geol. Survey Circ. 330, 9 p.

Komarek, K., 1950, Polarographic determination of thorium: Chemicke Listy, v. 44, p. 255–259.

Koskela, U., and Kaufman, D., 1949, U. S. Atomic Energy Comm. unpub. inf.

Legge, D. I., 1954, Polarographic determination of uranium: Anal. Chemistry, v. 26, p. 1617–1621.

Mahlman, H. A., and Leddicotte, G. W., 1955, Determination of microgram and submicrogram quantities of uranium by neutron activation analysis: Anal. Chemistry, v. 27, p. 823–825.

Main, A. R., 1953, The determination of uranium by reduction with stannous chloride: Canada Dept. Mines Tech. Surveys, Mines Branch, Radioactivity Div., Topical Rept. TR–111 53, 16 p.; also, Anal. Chemistry, v. 26, p. 1507–1509, 1954.

Malmstadt, H. V., and Gohrbandt, E. C., 1954, Determination of milligram quantities of thorium by automatic spectrophotometric titration: Anal. Chemistry, v. 26, p. 442–445.

Marechal-Cornil, J., and Picciotto, E. E., 1953, Separation des radioelements naturels par l'oxyde de mesityle: Soc chim. Belge Bull., v. 62, p. 372–382.

Meinke, W. W., and Anderson, R. E., 1952, Method for continuous extraction with a chelating agent: Anal. Chemistry, v. 24, p. 708–710.

Meyer, R. J., 1911, Der Nachweis und die Bestimmung des Thoriums mit Jodsaure: Zeitsch. anorg. Chemie, v. 71, p. 65–69.

Nelson, C. M., and Hume, D. W., 1945, The spectrophotometric determination of microgram amounts of uranium by means of ammonium thiocyanate: U. S. Atomic Energy Commission. Mon–C–28, 18 p.

Nichols, E. L., and Slattery, M. K., 1926, Uranium as an activator: Optical Soc. America Jour., v. 12, p. 449–466.

Overton, K. C., and Williams, A. F., 1950, Chem. Research Lab. Teddington [England], unpub. inf.

Pepkowitz, L. P., 1945, Microvolumetric assay of uranium: U. S. Atomic Energy Comm. MDDC–727, 9 p., declassified 1947.

Poole, J. H. J., and Matthews, C. M. E., 1951, The theory of the use of alpha ray ranges in nuclear emulsions for the determination of the radioactive contents of materials: Royal Dublin Soc. Sci. Proc., v. 25, no. 23, p. 305–316.

——— 1952, Use of nuclear plates for the determination of the uranium and thorium contents of radioactive ores: Nature (London), v. 169, p. 408–409.

Price, G. R., 1948, The design and construction of sensitive fluorophotometers Part 1, Principles: U. S. Atomic Energy Comm. AEC–2677, 51 p., declassified 1949 (Microcard copy on file in U. S. Atomic Energy Comm. depository libraries).

Price, G. R., Ferretti, R. J., and Schwartz, Samuel, 1953, Fluorophotometric determination of uranium: Anal. Chemistry, v. 25, p. 322–331; also, 1945, The microfluorometric determination of uranium: U. S. Atomic Energy Comm. AECD–2282, 52 p., declassified 1948.

Rabbitts, F. T., 1952, Determination of uranium in ores. Review of chemical methods; cellulose column method: Canadian Min. Met. Bull., v. 45, no. 477, p. 27–29.

Rodden, C. J., and Tregoning, J. J., 1955, Manual of analytical methods for the determination of uranium and thorium in their ores: 51 p., Washington, U. S. Government Printing Office.

Rodden, C. J., and Warf, J. C., 1950, Uranium, Thorium, Chap. 1 and 2, *in* Rodden, C. J., ed., Analytical chemistry of the Manhattan Project: National Nuclear Energy Series, Div. VIII, v. 1, 748 p., New York, McGraw-Hill Book Company, Inc.

Ryan, W., and Williams, A. F., 1949, Chem. Research Lab., Teddington [England], unpub. inf.

——— 1952, Inorganic chromatography of cellulose Part 8, The use of a "compound" column of alumina and cellulose for the determination of uranium in minerals and ores containing arsenic and molybdenum: Analyst, v. 77, p. 293–296.

Schreyer, J. M., and Baes, C. F., Jr., 1953, Volumetric determination of uranium (VI) in phosphate solutions: Anal. Chemistry, v. 25, p. 644–645.

Senftle, F. E., Farley, T. A., and Stieff, L. R., 1954, A theoretical study of alpha star populations in loaded nuclear emulsions: Geochim. Cosmochim. Acta, v. 6, p. 197–207.

Sill, C. W., and Peterson, H. E., 1952, Volumetric determination of milligram quantities of uranium: Anal. Chemistry, v. 24, p. 1175–1182.

Silverman, L., and Moudy, L., 1953, Photometric determination of uranium as thiocyanate; Penta-ether extraction method: U. S. Atomic Energy Comm. NAA–SR–244, 25 p.

Singer, S. F., 1952, Radioactivation method for the determination of micro-quantities of uranium: Office Naval Research, London, England, ONRL–76–52, 3 p.

Smales, A. A., 1952, The determination of small quantities of uranium in rocks and minerals by radioactivation: Analyst, v. 77, no. 920, p. 778–789.

Smales, A. A., and Airey, L., 1952, A method for the amperometric titration of thorium: Atomic Energy Research Establishment, Harwell, (England) 6 p.

Smith, G. H., and Williams, A. F., 1950, Chemical Research Laboratory, Teddington [England], 10 p., unpub. inf.

Stine, C. R., and Gordon, Louis, 1953, Precipitation of iodates from homogeneous solution. Separation of thorium iodate Anal. Chemistry, v. 25, p. 1519–1522.

Strubl, R., 1938, Polarographic studies with the dropping mercury cathode. Part 75, The estimation of uranium and other heavy metals in the excess of iron: Collection des Travaux Chimiques de Tchecoslovaquie, v. 10, p. 466–474.

Šušic, M., Gal, Ivan, and Cuker, E., 1954, Polarographic determination of uranium in ores in ascorbic acid supporting electrolyte: Anal. Chim. Acta, v 11, p. 586–589.

Taylor, A. E., and Dillon, R. T., 1952, Determination of microgram quantities of thorium in water: Anal. Chemistry, v. 24, p. 1624–1625.

Thomason, P. F., Perry, M. A., and Byerly, W. M., 1949, Determination of microgram amounts of thorium: Anal. chemistry, v. 21, p. 1239–1241.

Tillu, M. M., 1954, Rapid determination of uranium in complex minerals like samarskite, columbite-tantalite, and titanoniobates—1. Volumetric determination: Indian Acad. Sci. Proc., sect. A, v. 40, No. 3, p. 110–113.

Tillu, M. M., and Athavale, V. T., 1954a, Rapid determination of thorium in ores—2. Estimation of trace amounts of thorium in complex minerals and ores: Anal. Chim. Acta, v. 11, p. 324–328.

——— 1954b, Rapid determination of thorium in ores—1, Separation as iodate in presence of oxalic acid: Anal. Chim. Acta, v. 11, p. 62–67.

Tilton, G., 1954, Isotope dilution techniques, *in* Faul, Henry, ed. 1954, Nuclear Geology; New York, John Wiley and Sons, Inc., p. 70–73.

Tilton, G. R., Aldrich, L. T., and Inghram, M. G., 1954, Mass spectrometric determination of thorium: Anal. Chemistry, v. 26, p. 894–898.

Tishkoff, G. H., 1948, Polarographic analysis of uranium: U. S. Atomic Energy Comm. AECD–2005, 4 p., 1944, declassified 1948, issued by U. S. Atomic Energy Comm. Tech. Inf. Service, Oak Ridge, Tenn. (Superseded by: Flagg, J. F., 1949, Analytical methods, *in* Voegtlin, C., and Hodge, H. C., eds., Pharmacology and toxicology of uranium compounds: p. 125–143, National Nuclear Energy Series, Div. VI, 1, pt. 1, New York, McGraw-Hill Book Co., Inc.)

Venkataramaniah, M., Raghava Rao, B. S. V., and Lakshmana Rao, C., 1952, m-Cresoxyacetic acid as a reagent for thorium—Separation of thorium from the rare earth of monazite and from uranium: Anal. Chemistry, v. 24, p. 747–749.

Warf, J. C., 1949, Extraction of cerium (IV) nitrate by butyl phosphate: Am. Chem. Soc. Jour., v. 71, p. 3257–3258.

Willard, H. H., and Gordon, Louis, 1948, Thorium in monazite sand. Separation and determination by precipitation from homogeneous solution: Anal. Chemistry, v. 20, p. 165–169.

Williams, A. F., 1952, Inorganic chromatography on cellulose—Part 9, The use of alumina and cellulose adsorbents for the determination of thorium and the simultaneous determination of thorium and uranium in minerals and ores: Analyst, v. 77, p. 297–306.

Yoe, J. H., Fritz, W., 3d, and Black, R. A., 1953, Colorimetric determination of uranium with dibenzoylmethane: Anal. Chemistry, v. 25, p. 1200–1204.

Zebroski, E., and Newton, T. W., 1946, Fluorescence analysis for uranium: U. S. Atomic Energy Comm. MDDC–443, 16 p., declassified 1946 (Microcard copy on file in U. S. Atomic Energy Comm. depository libraries.)

Zimmerman, J. B., 1951, The determination of uranium in ores; fluorophotometric method: Canada Dept. Mines Tech. Surveys, Mines Branch, Memo. Ser. 114, 29 p.

Zimmerman, J. B., Rabbitts, F. T., and Kornelsen, E. D., 1953, The determination of uranium in concentrates by the fluorophotometric method: Canada Dept. Mines Tech. Surveys, Mines Branch, Radioactivity Div., Topical Rept. TR–112/53, 8 p.