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DETERMINATION OF THORIUM, URANIUM AND TRANSURANIUM ISOTOPES IN SILICEOUS AND REFRACTORY MATERIALS BY HIGH-RESOLUTION ALPHA SPECTROMETRY

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BRIEF. After separation on barium sulfate, thorium and the transuranium elements were precipitated as hydroxides and uranium as fluoride for alpha spectrometry. Precision and accuracy were about 1% relative standard deviation.

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ABSTRACT. Samples of siliceous solids up to 1 gram were dissolved completely by fusion with potassium fluoride in platinum dishes in the presence of appropriate isotopic tracers. The fluoride cake was then transposed with concentrated sulfuric acid to a pyrosulfate fusion with simultaneous volatilization of all silica and fluoride. Samples which contaminate or react deleteriously with platinum were treated extensively with hydrofluoric and perchloric acids before fusion with pyrosulfate in glass. The pyrosulfate cake was dissolved in dilute hydrochloric acid and thorium and the transuranium elements were precipitated isomorphously with barium sulfate. The barium sulfate was dissolved in alkaline ethylenediaminetetraacetic acid (EDTA), and the thorium and transuranium elements were precipitated as the hydroxides, filtered on a membrane filter and analyzed in an alpha spectrometer. When much natural thorium-232 was present, the hydroxides were converted to fluorides before analysis by alpha spectrometry. The original filtrate containing the uranium was reduced, and the quadrivalent uranium was precipitated isomorphously with barium sulfate. The barium sulfate was dissolved in alkaline EDTA, and the uranium was precipitated consecutively as the hydroxide and fluoride for

mounting and analysis by alpha spectrometry. The procedure was much simpler and faster than others available. Resolution of the subsequent alpha spectra was comparable to that obtained by electrodeposition. When sufficient activity was present, the results could be reproduced with a relative standard deviation of about 1% for the entire determination. The accuracy of the determination on standards was always as good as the statistical uncertainty of the measurement would permit.

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Replicate determinations of thorium-230, uranium-238 and -234 were required in some large homogenized samples of soil, uranium ores and uranium mill tailings, and also of thorium-232 in some mixtures of thorium and uranium ores. These samples were prepared for use by analytical laboratories involved in the remedial action program on uranium mill tailings as standards to evaluate their initial performances and for continuing quality control. Consequently, it was necessary that the results be as precise, accurate and reliable as possible to verify the homogeneity of the 200-pound batches prepared and to gain their acceptance as analyzed standards by all concerned. Determination of uranium and the transuranium (TRU) isotopes present in samples of ash and condensates from incineration of various radioactively-contaminated wastes was also required. The incinerator ash frequently contained ruthenium-106 which contaminates platinum dishes irretrievably. The baghouse dusts and other condensed material generally contained high concentrations of inorganic carbon and oxides of easily reducible metals which can be very deleterious to platinum and should be dissolved by methods not requiring use of platinum containers.

Recently, general procedures were published for precipitation of actinides isomorphously in cerium or neodymium fluorides or hydroxides in a form suitable for high-resolution alpha spectrometry (1). Yields were generally larger than 98% and the resolution of the resultant alpha spectra with most of the actinides was generally 50 to 60 keV full-width-half-maximum (FWHM) with a 450-mm^2 surface-barrier detector at 27% counting efficiency. This resolution was virtually as good as could be obtained from sources prepared by electrodeposition on polished steel plates for the same nuclides and counting conditions. Because time-consuming steps involving liquid-liquid extraction, ion exchange, and electrodeposition were not required, the precipitation procedures were much faster and more reliable than others available. The present procedure describes the application of the precipitation techniques specifically to the high-precision determination of thorium and uranium isotopes in small samples of refractory and siliceous soil, ores and mill tailings, and to the determination of uranium, thorium, and the TRU isotopes in incinerator ash and baghouse dusts.

EXPERIMENTAL SECTION

INSTRUMENTATION. The alpha spectrometer using a 450-mm^2 surface-barrier detector, the Cartesian manostat, absolute pressure gauge and battery installations necessary to minimize recoil contamination of the detector, and the sodium iodide well counter used in the determination of chemical yields with gamma-emitting tracers have been described (2).

APPARATUS. The 50-mL conical polysulfone filtering funnel with a stainless steel support screen for 25-mm filters and the tall-form bell jar used in mounting precipitates for alpha spectrometry so that filtrates could be collected directly in centrifuge tubes, jars and counting bottles have also been described (2). The Teflon PFA jars and centrifuge tubes used to prepare solutions in small volumes for precipitation and mounting are described in (1).

REAGENTS. Alkaline EDTA, Potassium Salt, 0.05 M. Five grams of solid potassium hydroxide was added to a suspension of 7.31 g of EDTA as the free acid in 450 mL of water. After both solids had dissolved, the solution was filtered through a 0.45-um membrane filter. The pH was then raised to 10.6 by dropwise addition of filtered 10 M potassium hydroxide and the solution was diluted to 500 mL. If required, higher concentrations were prepared similarly by scaling up the potassium hydroxide and EDTA proportionately.

Most of the other reagents are described in (1) except the tellurous acid and barium sulfate seeding suspension in (3).

SAMPLE SIZE. Proper sample size is of paramount importance in the success of this method to obtain adequate resolution without undue loss of sensitivity and precision. Because some prior knowledge of sample composition is therefore necessary, only general guidance can be given. Uranium 238 and thorium 232 both have halflives of the order of 10^{10} years so that even small activities are accompanied by significant mass which causes objectionable degradation of the alpha spectra. In addition, an "average" soil contains about 180 ug/g of yttrium and the lanthanides from lanthanum through samarium, all of which are carried quantitatively in barium sulfate and part of which precipitate as both hydroxides and fluorides, thus ending up in the thorium fraction. There is also about 13 ug/g of natural thorium and 2.5 ug/g of natural uranium in soil. The best compromise between resolution and sensitivity is obtained with about 50 ug of uranium or 150 ug of thorium on the mounted source, although probably twice as much can be used before the overlap in the peaks becomes undesirably large. The counting time must then be increased substantially to make up for the lack of activity. Much more thorium than uranium can be tolerated before overlapping becomes objectionable because the thorium peaks are more widely separated and the fluoride is much less crystalline. However, the half life of thorium-232 is also three times as long as that of uranium-238 so that the activity present is actually less for the same mass. If both natural thorium and uranium were to be determined on the same sample, the sample size was chosen to contain the limiting mass of the one present in smaller quantity and the other reduced to its limiting mass by aliquoting the final fraction before mounting for alpha spectrometry. Conversely, the specific activity of thorium 230 is so large that the mass of either thorium or lanthanides will rarely be a problem with the small samples generally required for its determination in uranium ores and mill tailings.

Uranium does not precipitate by itself as fluoride until relatively large quantities are present (1), and the precipitate of $UF_4 \cdot 2.5H_2O$ is very coarsely crystalline, producing severe degradation of the alpha particles as they escape the lattice. The quadrivalent hydroxide does not precipitate readily with quantities smaller than about 40 ug. Thorium precipitates by itself at even very small concentrations but flocculates easily as the hydroxide. The resolution is not as good when either element is precipitated by itself as when carried isomorphously in cerous hydroxide or fluoride (1), even with the additional mass. However, the cerium carrier added to the thorium fraction should be reduced to compensate for that expected to be in the sample. Assuming about 50% recovery of the more soluble lanthanides, no extra cerium was added with 1-gram samples, only 50 ug. with 0.5-gram samples and 100 ug with samples smaller than 0.25-gram or with pure solutions (1).

SAMPLE DISSOLUTION. The appropriately sized sample up to 1 gram was weighed into a 50-mL platinum dish, moistened with water and then treated carefully with nitric acid to eliminate carbonates before the appropriate tracers (4) were added. The sample was then fused with 3 grams of anhydrous potassium fluoride, the fluoride cake was transposed with 4 mL of concentrated sulfuric acid and 2 grams of sodium sulfate, and the pyrosulfate cake was dissolved in 35 mL of water and 5 mL of concentrated hydrochloric acid in a 100-mL beaker as described under "Sample dissolution." (2) with two exceptions. The barium-133 tracer was omitted and the quantity of hydrochloric acid was increased from that permitted for separation of radium on lead sulfate. The dilute hydrochloric acid must be preheated to boiling before addition of the cake to ensure maximum dissolution of calcium sulfate.

Tracers were not added until after evolution of carbon dioxide had ceased to avoid disproportionate loss of the small volume of tracer used. The desired tracers were then added and the solution was evaporated very gently to near dryness with the platinum dish supported on a clay triangle near the edge of the hotplate to avoid any loss of solution before complete exchange with tracer could be ensured. If the samples were allowed inadvertantly to evaporate to dryness, 3 or 4 drops of 48% hydrofluoric acid were added to ensure sufficient acidity in the potassium fluoride fusion to obtain complete sample dissolution before hydrolysis begins and sample dissolution ceases (2). The thorium-234 tracer was freshly-ingrown into a column of depleted uranium (4) and about 80,000 cpm was used to minimize the activity of thorium-230 added with the thorium-234 tracer while giving sufficient activity to achieve the counting precision desired. The activity of uranium-232 tracer added was about equal to that of the uranium-238 expected so that the statistical uncertainty would be distributed equally between the nuclide being determined and the tracer. Similarly, if the TRU nuclides were to be determined, plutonium-236 or -242 and americium-243 tracers were added in activities appropriate to those being determined.

PRECIPITATION OF BARIUM SULFATE. Five hundred microliters of 25% potassium metabisulfite was diluted with 5 mL of water and added to the boiling solution of the pyrosulfate cake in the 100-mL beaker (2). The ferrous iron produced provides a holding reductant to ensure reduction of neptunium and plutonium and precipitation in the thorium fraction to avoid their interference in the subsequent uranium fraction if present, whether or not they are to be determined. One milliliter of the barium sulfate seeding suspension was added, and then four successive 1-mL portions of 0.45% barium chloride dihydrate at a rate of about 1 drop every 2 sec with 1-minute of boiling after each 1-mL portion to precipitate all large ter- and quadrivalent elements exponentially in the barium sulfate (5). The suspension was transferred to a 40-mL conical Pyrex centrifuge tube, centrifuged hot to avoid precipitation of calcium sulfate, and the supernate was decanted back into the same 100-mL beaker for the determination of uranium. The barium sulfate was thoroughly suspended in 15 to 20 mL of water directed at the precipitate in a forceful jet from a polyethylene squeeze bottle. The solution was recentrifuged and the wash was discarded. Before returning the tube to its upright position, the walls were washed thoroughly with water to remove as much as possible metal ions from the sample such as iron which will precipitate subsequently as hydroxide and decrease the resolution of the alpha spectra.

DETERMINATION OF THORIUM OR TRU RADIONUCLIDES. Soil, Uranium Ores and Mill Tailings. Three drops of 25% hydrazine base was added to the centrifuge tube and the barium sulfate was dispersed thoroughly in the few drops of liquid by shaking the tube repeatedly in a sharp downward flipping motion. Six milliliters of 0.05 M potassium EDTA solution at pH 10.6 and enough cerium carrier to give a total of 100 ug of total lanthanides with that already present from the sample were then added. The tube was placed in a beaker of boiling water for 5 minutes to dissolve the barium sulfate completely and form the EDTA complexes of thorium and the other actinides and lanthanides. Heating for much longer times will cause spontaneous precipitation and flocculation of the quadrivalent nuclides, particularly if much natural thorium is present. It was particularly helpful to examine the tubes with a flashlight in a darkened room to detect incomplete dispersion of any tiny lumps of barium sulfate in the tip of the tube to avoid subsequent degradation of the alpha spectra if not dissolved completely. If much calcium sulfate coprecipitated with the barium sulfate, additional 100-uL aliquots of 0.5 M potassium EDTA were added to dissolve the additional precipitate.

The solution was cooled to room temperature, 2 mL of filtered 10 M potassium hydroxide was added, and the solution was swirled as rapidly as possible but for only 5 seconds to avoid increasing flocculation and losses to the wall, and decreasing resolution of the subsequent alpha spectra. The tube was placed in a bath of boiling water for 5 minutes to obtain complete precipitation of the hydroxides without allowing any further motion of the solution. The solution should have a distinct opalescence when viewed with a flashlight in a darkened room, with no detectable sign of flocculation or scum floating on the meniscus or the subsequent alpha spectrum will be degraded. Flocculation is more rapid with mixed lanthanides from the sample than with straight tervalent cerium. If the flocculation is slight, the resolution can be improved somewhat by placing the tube in an ultrasonic bath for a few minutes immediately prior to filtration. If the precipitate flocculates coarsely due to the presence of significant quantities of zirconium or natural thorium from the sample, the hydroxides were converted to the fluorides for alpha spectrometry as described below for thorium ores. The tube was then placed in a beaker of cold water for about 5 minutes, and the precipitate was mounted on a membrane filter having 0.1-um straight-through capillary pores such as the Gelman Metricel Polypropylene as described previously (1). The centrifuge tube was washed consecutively with 5 mL each of 0.25 M potassium hydroxide and 80% ethanol, pouring each wash in turn around the walls of the chimney. The filtering chimney was then washed three times with 80% ethanol dropwise around the perimeter of the chimney. The filter was dried under a 250-watt infrared lamp at a distance of about 4 inches for at least 10 minutes, and stored in a labeled petri dish for identification and preservation. The precipitate will have a pale yellow color due to partial air oxidation of the cerous hydroxide to ceric hydroxide.

The mounted precipitate was then counted in a plastic jig in a gamma well counter (2) for about 2 x 10^5 counts before alpha counting to minimize decay of the thorium-234 tracer during the subsequent long alpha counting times. The chemical yield was determined by comparison of the net sample counting rate with that of a standard prepared in the same way and corrected for its own chemical yield by counting all the minor fractions, including the filtrate, washes, and an acid cleanup of both the centrifuge tube and filtering chimney as described previously (1). The standard should be counted near the middle of the group of samples being counted to minimize differences caused by differences in the decay. The sample was then counted in the alpha spectrometer for whatever length of time was necessary to give the statistical significance desired. In the present work, the samples were counted to approximately 5 x 10^4 total counts in the thorium-230 peak with uranium ores and mill tailings, and for 24 to 60 hours with TRU's and low-grade samples such as soils. The thorium-230 spectra were corrected for (1) thorium-230 added with the thorium-234 tracer, (2) thorium-232 when high thorium-230 activities overlap the thorium-232 region, (3) 0.127 of the protactinium-231 activity exposed that was under the thorium-230 peak, and (4) the instrument background for the same length of counting time. The results were calculated using a counting efficiency determined for the particular conditions being used as described previously (1). All statistical uncertainties incurred anywhere in the entire measurement process of any of the radionuclides were propagated and reported with the final result as one standard deviation.

If the uranium activity of the sample was sufficiently high compared to that of the thorium-234 tracer added, a correction was made for the thorium-234 daughter of the uranium-238 in the sample, corrected if necessary for decay between the time of separation and counting. The counting efficiency for thorium-234 in the gamma well counter can be determined easily by precipitating the thorium-234 from a known quantity of uranium with barium sulfate, dissolving the barium sulfate in alkaline EDTA and precipitating and mounting the hydroxides under the conditions being used with samples. The correction can then be determined from the known activity of uranium present in the sample.

In the determination of the TRU's, both chemical yield and counting efficiency are corrected for automatically because of the alpha-emitting tracers being used. When maximum sensitivity is desired,it might be necessary to separate the TRU nuclides from the thorium isotopes invariably present, or to eliminate other spectral interferences, such as that between americium-241 and plutonium-238. In this case, the hydroxide precipitate was wetashed and the fluoride separations in the presence of permanganate or peroxydisulfate described previously (1) were used to separate the interfering radionuclides.

Natural Thorium Ores and Tailings. When thorium isotopes were determined in samples containing significant quantities of thorium-232, as in the mixed uranium-thorium standards, the maximum quantity of 150 ug permitted for acceptable resolution with well-dispersed precipitates was used to obtain as high sensitivity and precision as possible for a given counting time. However, even in the presence of 100 ug of cerium to carry most of the thorium isomorphously, it was virtually impossible to prevent the thorium hydroxide from flocculating in the hot solution required to obtain complete precipitation. The resulting alpha spectra were completely unresolvable because of the thickness of the individual flocs. Consequently, it was necessary to convert the hydroxide precipitate to the fluoride for alpha spectrometry in which form flocculation at room temperature was easily controlled.

The determination was carried out as described above for thorium-230 in uranium ores and mill tailings up to the point of filtration of the hydroxides for alpha spectrometry, omitting the cerium carrier. The solution was heated for a couple extra minutes until the precipitate was well flocculated, and the suspension was cooled and centrifuged for 5 minutes at the maximum speed permitted for Pyrex tubes so that the small fragile precipitate of thorium and lanthanide hydroxides was stuck tightly to the wall. The supernate was decanted carefully and discarded. Before returning the tube to its upright position, the walls of the tube were washed with water to ensure as complete elimination of barium sulfate and EDTA as possible, being careful that the precipitate was not disturbed. About 0.5 mL of 0.25 M potassium hydroxide were added to the tube and the precipitate was dispersed thoroughly with a small polypropylene stirring rod to ensure complete removal of barium-EDTA. The stirring rod was rinsed down with 5 mL more of the 0.25 M potassium hydroxide and the solution was swirled gently to suspend the precipitate uniformly in the wash. The walls were rinsed with a small quantity of water to wash down the precipitate on the walls above the liquid level, and the solution was recentrifuged for 5 minutes at maximum speed. The wash was decanted carefully and discarded, and the walls were again washed carefully with water before returning the tube to its upright position. Plastic tubes should not be used because the precipitate does not stick well to the walls and large losses occur during decantation.

A half milliliter of concentrated hydrochloric acid was added dropwise around the lower walls of the centrifuge tube to dissolve the hydroxides. The solution was diluted with 2 mL of water and recentrifuged at maximum speed for 5 minutes. An aliquot of the supernate was then transferred to a 50-mL conical polycarbonate (PC) centrifuge tube using a suction-type pipet with a polypropylene tip. Because of the tracer present, the aliquoting does not have to be very accurate. At least 95% can be transferred easily when maximum sensitivity and precision are desired, but with the distinct advantage that the last traces of insoluble material remaining from the sample dissolution or from the reagents can be eliminated, thus improving the resolution further. This is the only place in the procedure at which a small quantity of insoluble material can be safely removed. Slightly lower yields will also result in significantly better resolution. Enough more of the 0.5 mg/mL cerium carrier solution to give 100 ug of total lanthanide with that already present in the aliquot from the sample, 3 drops of 20% ferrous perchlorate to reduce both ceric ion and the TRU's, and enough more concentrated hydrochloric acid and water to give totals of 0.5 mL and 5 mL, respectively, were added to the aliquot in the PC tube. The fluorides were precipitated with 1 mL of 48% hydrofluoric acid, mounted on a Metricel Polypropylene filter and counted in the alpha spectrometer as described for thorium-230. Without aliquoting, the overall yields were about 94%. Without the recoil protection described previously (1), the detector will become seriously contaminated with 4-day radium-224 recoils from the thorium-228 with subsequent rapid ingrowth of the radon-220, polonium-216 and lead-bismuth-212 daughters.

DETERMINATION OF URANIUM. If uranium was to be determined, the washed barium sulfate precipitate in the centrifuge tube containing the thorium or TRU isotopes was reserved for their later determination so that the uranium could be determined before precipitation of calcium sulfate occurred. The procedures used for reduction of iron, separation of polonium-210, and precipitation of uranium with barium sulfate are as published previously under "Determination of Uranium" (3) with a few small changes. In the second paragraph of the cited section, only 0.5 gram of solid potassium metabisulfite per gram of sample was added initially to avoid adding too large excess of sulfite which must be removed subsequently. The beaker was covered with a cover glass and the solution was heated to near boiling. When the first bubbles broke the surface of the solution, the beaker was removed from the hot plate and allowed to stand without further heating for 5 or 10 minutes until a permanent black suspension of elemental tellurium formed in an otherwise colorless solution, indicating that reduction of ferric iron was complete. If the solution remained clear and colored, indicating a higher iron content, more metabisulfite was added in small increments and the solution was reheated until the black suspension was obtained. The beaker was placed back on the hotplate and the solution was boiled for 10 minutes to boil out all sulfur dioxide and reduce the volume to 35 mL. Precipitation and filtration of elemental tellurium and polonium-210 were carried out as described in the third paragraph of the cited section. Uranium was precipitated isomorphously in barium sulfate as described in the fourth paragraph, except that four 1-mL portions of the barium chloride were added instead of the two portions indicated erroneously, and the barium sulfate precipitate was centrifuged in a conical Pyrex centrifuge tube and washed with 15 mL of water as described above for the thorium fraction, again rinsing the walls of the tube before returning it to its upright position.

The mass limitation on natural uranium and the method for its preparation for alpha spectrometry are similar to that described for natural thorium. Because of a small quantity of titanium that is carried from the tervalent state in barium sulfate in the uranium separation, the difficulty of preventing flocculation of the hydroxides, and the fact that there will generally be too much uranium present to give adequate resolution on the same sample size desired for thorium-230 and the TRU's, the hydroxide precipitate was converted to the fluoride for alpha spectrometry as described for natural thorium. Titanous hydroxide was used as an excellent carrier and holding reductant to ensure complete reduction of uranium to the quadrivalent state without producing any insoluble compounds in the subsequent fluoride precipitation from either oxidation state. It is also superior to dithionite as a holding reductant for uranium, being more stable and reducing the uranium probably just to the quadrivalent state. The quadrivalent hydroxide is more insoluble and less susceptible to air oxidation than the tervalent hydroxide produced with dithionite. The overall chemical yields without aliquoting are consistently about 98% in the presence of titanous hydroxide and drop abruptly to about 50% in its absence, probably due to uncontrollable air oxidation of the uranous hydroxide to the more soluble amphoteric uranyl hydroxide. Use of carrier in the thorium hydroxide precipitation is unnecessary and counter-productive because it increases the recovery of the more soluble lanthanides from the sample and decreases the resolution.

The washed barium sulfate containing the uranium was dissolved completely in 6 mL of 0.05 M potassium EDTA at pH 10.6 in a hot water bath, 1 drop of 10 M potassium hydroxide, 1 drop of 20% titanium trichloride, and 2 mL of 10 M potassium hydroxide were added in order with rapid swirling, and the hydroxides were flocculated, centrifuged, washed, dissolved in acid and aliquoted as described above for natural thorium. There is no advantage to centrifuging the uranium fraction after dissolving the hydroxides in acid as there is with the thorium fraction containing the residual insol. The aliquot containing 50 to 100 ug of natural uranium was diluted with enough hydrochloric acid and water to give totals of 0.5 mL and 5 mL, respectively. The uranium was reduced with 4 drops of 20% titanium trichloride instead of ferrous perchlorate for 3 minutes in a boiling water bath and cooled in a cold water bath. Two hundred microliters of the 0.5 mg/mL solutions of cerium carrier was added and the fluorides were precipitated with 1 mL of 48% hydrofluoric acid and mounted as described. Counting times of as much as 60 hours were used on 1-gram soil samples.

ACID DISSOLUTION WITHOUT USE OF PLATINUM. Although fusion with potassium fluoride as described above is the most rapid and efficient method for complete dissolution of siliceous sample, there are some cases in which it cannot be used. Samples that contain moderate quantities of organic matter, inorganic carbon or compounds of easily reducible elements should not be dissolved in platinum containers or severe corrosion or other deterioration of the platinum can occur. Ruthenium-106 and lead-210 have been found to contaminate platinum dishes extensively and irretrievably. However, sample dissolution must still be essentially complete to make the analysis as accurate as possible, to ensure complete exchange with tracers, and to eliminate residual insol to avoid degradation of subsequent alpha energy spectra.

For baghouse dusts containing much elemental carbon from incinerators, 1 gram of sample was weighed directly into a 250-mL Erlenmeyer flask, 2 mL of concentrated nitric acid was added and the solution was heated to boiling. If a reaction occurred, more nitric acid was added as necessary. When the reaction had abated, 5 mL of 72% perchloric acid was added and the solution was boiled gently until the black elemental carbon had been oxidized completely. Frequently, as much as an hour of continuous boiling was required so that addition of more perchloric acid was necessary. Addition of a few drops of nitric acid periodically to the boiling perchloric acid was helpful in speeding up the oxidation synergistically. If the typical scarlet color of chromic acid was present, the chromium could be volatilized as chromyl chloride by addition of successive 0.5-gram portions of solid sodium chloride. About 5 mL of concentrated sulfuric acid and 9 grams of anhydrous potassium sulfate were added and the solution was evaporated to a pyrosulfate fusion. After most of the excess sulfuric acid had volatilized, 5 grams of anhydrous sodium sulfate was added and the fusion was continued at as high a temperature as possible over the full heat of the blast burner until the melt was as clear as possible.

With ash from incineration of radioactively-contaminated materials, or other samples containing strongly-ignited oxides, phosphates or silicates that might contain ruthenium-106, 1 gram of sample was weighed into a 60-mL Teflon PFA jar, 5 to 10 mL of 48% hydrofluoric acid was added and the solution was evaporated to dryness. Another 5 mL of hydrofluoric acid and 5 mL of 72% perchloric acid were added and the solution was reevaporated to fumes of perchloric acid to remove most of the hydrofluoric acid and to oxidize residual organic matter. About 5 mL of concentrated sulfuric acid was added, the solution was heated and swirled until the residual solids were well suspended, and the acid was transfered to a 250-mL Erlenmeyer flask containing 9 grams of potassium sulfate. The solution was heated over a blast burner as quickly as possible to remove the last traces of hydrofluoric acid, and evaporated to a potassium pyrosulfate fusion. About 5 grams of anhydrous sodium sulfate was added and the fusion was continued for another minute or so at as high a temperature as possible to render refractory silicates as susceptible to further subsequent treatment with hydrofluoric acid as possible.

With either method of initial sample dissolution, a mixture of 70 mL of water and 10 mL of concentrated hydrochloric acid was heated to boiling and added to the Erlenmeyer flask containing the pyrosulfate cake. The dilute acid was heated to boiling before addition to the cake to facilitate dissolution of calcium sulfate. A couple of boiling stones was added and the solution was heated back to boiling as rapidly as possible. If TRU isotopes are being determined, 500 uL of 25% potassium metabisulfite diluted with 5 mL of water was added after the cake had been completely dissolved to reduce some of the iron present to provide a holding reductant for neptunium and plutonium. Boiling was continued for at least 10 minutes to dissolve any anhydrous sulfates that might be present, to hydrolyze condensed phosphates and to reduce the volume to about 75 mL. The boiling solution and residual insol were transferred into a 100-mL round-bottomed centrifuge tube and centrifuged for 5 minutes. The empty flask was rinsed thoroughly, discarding the rinses, and the supernate was decanted back into the same flask for the determination of uranium.

About 2 mL of concentrated sulfuric acid and 6 drops of 48% hydrofluoric acid were added directly to the residual solid remaining in the centrifuge tube with as little contact with the sides as possible and the solution was allowed to stand for 1 or 2 minutes. The solution was boiled over the blast burner while swirling the solution rapidly and continuously so that any silicon tetrafluoride was expelled rather than being allowed to hydrolyze and condense on the sides. The solution was heated strongly so that the condensing sulfuric acid refluxed down the sides of the tube. About 1 gram of anhydrous potassium sulfate was added and the solution was evaporated to a pyrosulfate fusion. About 0.5 gram of anhydrous sodium sulfate was added and the mixture was heated over the blast burner as strongly as possible. The cake was cooled, 10 mL of the dilute hydrochloric acid was added and the solution was heated to boiling until the solution cleared as much as possible. Whether or not the solution appeared to be clear, the solution was centrifuged for 5 minutes and decanted carefully into the Erlenmeyer flask containing the main solution. The slightest insoluble residue allowed to remain will carry through to the final alpha mount and cause undesirable degradation of the resultant alpha spectra. If necessary, treatment of the insoluble residue with hydrofluoric acid and pyrosulfate fusion was repeated until dissolution was acceptably complete.

The determination of both uranium and the TRU's was completed as described above with the following changes: Because of the increased volume required, the barium sulfate precipitation was made by addition of four 2-mL portions of the barium chloride solution. The suspension of barium sulfate in the wash solution was transferred from the 90-mL round-bottomed centrifuge tube to a conical 40-mL one before centrifuging to facilitate subsequent steps.

RESULTS AND DISCUSSION

There is no place in the present procedure at which significant quantities of residual insoluble material can be filtered off and discarded without risking possibly serious loss of the nuclide being measured. Because heterogeneous exchange does not occur significantly between the water-soluble tracer and the insoluble material, the activity lost in the residue is not corrected for in the chemical yield. Of equal importance, the insoluble material carries through to the final precipitate being measured by alpha spectrometry and as little as 100 ug produces an undesirable loss of resolution. Fusion with anhydrous potassium fluoride in a platinum dish followed by transposition with sulfuric acid to a pyrosulfate fusion is virtually the only procedure that can guarantee such complete dissolution and elimination of all absorbing material in a single operation (2). The fusion procedure is much faster and sample dissolution is more complete and unequivocal than other procedures available. Both silica and fluorides are eliminated completely by volatilization during the process. Complete exchange between tracer and the radionuclides being determined is guaranteed at the same time.

The resulting solution containing high concentrations of both sulfate and potassium ions is ideally suited for complete and efficient separation of all large ter- and quadrivalent lanthanides and actinides from almost all other ions by isomorphous precipitation with barium sulfate (5). The quantity of any small di- and tervalent ions, such as iron and aluminun, and quadrivalent titanium that is carried in barium sulfate under the conditions used is virtually undetectable. A very small fraction of any titanium present in the tervalent state is carried. Zirconium is about the only element other than the actinides that is carried efficiently enough to interfere seriously but is encountered infrequently. The small quantity of lanthanides present in small samples of soils, uranium ores and tailings less than about 1 g can be used as all or part of the carrier for the subsequent precipitation so that lanthanides do not need to be removed. Consequently, the barium sulfate can be dissolved in alkaline EDTA and the actinides precipitated directly as hydroxides without significant precipitation of other insoluble hydroxides. Any lead, calcium, strontium or radium coprecipitated in the barium sulfate will remain in the strongly alkaline EDTA filtrate. Thorium-230 is the only alpha-emitting radionuclide normally expected to be encountered in quantity in the barium sulfate from uranium ores and mill tailings. As mentioned above,mixtures with natural thorium ores will have to be limited in sample size because of the mass of thorium present. Transuranium elements are not likely to be present in significant quantities in thorium or uranium ores or tailings, and their determination in such materials is not likely to be necessary. Even if they were present and could not be resolved by energy discrimination, the hydroxides could be dissolved and the radionuclides separated by the fluoride precipitation procedures in the presence of various oxidizing agents previously described (1). Conversely, high activities of thorium-230 or -232 are not encountered frequently in the types of samples in which determination of TRU nuclides is desired.

Uranium is not carried in barium sulfate from the hexavalent state so that it can be made to precipitate in a separate fraction after removal of the ter- and quadrivalent elements. This is a very fortunate and desirable situation. Although uranium can be precipitated with the other elements by reduction before the initial precipitation with barium sulfate, the additional isotopes increase the interferences and difficulty of interpreting the alpha spectra, and the extra mass degrades the spectra of all radionuclides present. Uranium is determined sequentially by reduction to the quadrivalent state and repeating the barium sulfate separation after all lanthanides and other actinides have been removed.

Although the barium sulfate from 10 mg of barium can be dissolved easily and completely in 6 mL of 0.05 M EDTA at pH 10.6 as the sodium salt as described previously (1,6), larger quantities of barium sulfate require scaling up the total volume of solution used as well as the EDTA because of solubility limitations. Much larger quantities of barium sulfate can be dissolved more rapidly and completely in smaller volumes of solution if the potassium salt of EDTA is used rather than the sodium salt. Because smaller volumes of solution give lower solubility losses and better resolution of the subsequent alpha spectra, the potassium salt of EDTA and potassium hydroxide are now recommended for all quantities of barium sulfate except when presence of potassium ion is contraindicated, e.g., in the presence of sulfate or perchlorate ions due to precipitation of sparingly soluble potassium salts.

After each standard had been thoroughly blended, ten small samples were removed periodically as the material was being removed from the blender for packaging to give a systematic sampling of the 200-pound batches prepared. A single aliquot of each of the ten individual samples was then analyzed to evaluate the homogeneity of the standard and the precision with which the measurements were being reproduced. A summary of the large number of results obtained is given in Table I. The uncertainty given with each result is the experimental standard deviation of the ten individual results about their own mean. The same uncertainty is also given in the first parenthesis as the relative experimental standard deviation in percent to facilitate comparison. The absolute uncertainty given in the second parenthesis with each result is the average standard deviation with which each individual measurement was made, and includes all random uncertainties incurred anywhere in the entire measurement process.

The average relative experimental standard deviation obtained for the 21 sets of 10 individual measurements of two isotopes of uranium and thorium was 1.2%. The remarkably close agreement of the uncertainty of each set of ten results obtained experimentally with the random uncertainty with which each individual measurement was made indicates that there was little or no systematic uncertainty present, either from the analytical procedure or from real differences among aliquots of a given sample due to a slight residual inhomogeneity. In many cases, particularly with the uranium determination, the uncertainties of the means of each set of ten measurements are significantly less than the random uncertainties with which the individual measurements were made, probably due to chance. It may be noted that the uranium-238 and -234 are statistically almost in secular equilibrium, within 1 or 2% at most. However, the samples are mixtures of ores, tailings, and other types of materials from milling operations and no equilibrium among the other nuclides is present or expected. The experimental standard deviations obtained above are virtually identical to those obtained previously with more radioactive uranium ores and tailings (1).

Because of the complete dissolution of the sample and exchange with tracer guaranteed by the fusions employed, the excellent resolution of the alpha spectra obtained, and that standardization of counters and tracer solutions are traceable to the U.S. National Bureau of Standards, the accuracy of the procedure must be as good as the statistical uncertainty of the measurements will permit, i.e., about 2-3% at the 95% confidence level.

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Table I. Thorium and Uranium Isotopes in Analyzed Standards

Sample Type	Th-232, pCi/g	Th-230, pCi/g	U-238, pCi/g	U-234, pCi/g
Uranium Standard (15 pCi/g)			15.10±0.12 (0.8%) (±0.2)	14.95±0.14 (0.9%) (±0.2)
Uranium Standard (45 pCi/g)			43.9 ±0.5 (1.1%) (±0.5)	43.4 ±0.6 (1.4%) (±0.5)
Uranium Standard (90 pCi/g)			85.6 ±0.6 (0.6%) (±1.0)	84.8 ±0.7 (0.8%) (±1.0)
Thorium Standard (25 pCi/g)		24.8 ±0.4 (1.4%) (±0.3)		
Thorium Standard (45 pCi/g)		44.7 ±0.4 (0.9%) (±0.4)		
Thorium Standard (60 pCi/g)		59.1 ±0.8 (1.4%) (±0.5)		
U-Th Mixed Std. (10 pCi/g)	9.36±0.26(2.8%) (0.09)	13.25±0.15(1.1%) (±0.12)	11.60±0.14(1.2%) (±0.16)	11.42±0.14(1.2%) (±0.16)
U-Th Mixed Std. (20 pCi/g)	17.92±0.36(2.0%) (0.2)	25.41±0.49(1.9%) (0.3)	21.93±0.20(0.9%) (0.3)	21.54±0.20(0.9%) (0.3)
U-Th Mixed Std. (40 pCi/g)	34.39±0.38(1.1%) (±0.4)	49.75±0.66(1.3%) (±0.5)	42.46±0.35(0.8%) (±0.5)	41.70±0.38(0.9%) (±0.5)