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THE DETERMINATION OF THORIUM IN THE PRESENCE OF URANIUM, TITANIUM AND TUNGSTEN

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Work done under the auspices of the Atomic Energy Commission

ABSTRACT

Thorium is separated from uranium, titanium and tungsten by precipitation as fluoride. The precipitate is ignited to oxide, dissolved in nitric acid, evaporated with perchloric acid, neutralized to a pH between 2.0 and 2.5 and titrated with the disodium salt of ethylenediamine tetraacetic acid, using Eriochrome Cyanine as indicator. If less than 30 milligrams of thorium is present, lanthanum is added as a carrier.

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Most of the older accepted methods for the determination of thorium are gravimetric.(3,5) A large number of insoluble compounds have been used in separations but the element is usually weighed as oxide after ignition. The oxalate method which has been used in this laboratory for the determination of thorium in uranium alloys has not been satisfactory for alloys containing less than 0.5% of thorium because the loss due to solubility becomes significant.(4) Increasing the size of the sample is impractical because of the limited solubility of uranyl oxalate. A spectrophotometric procedure(6) is available for very small amounts of thorium in uranium but it lacks the precision required for the range of 0.1 to 1.0%.

The precipitation of small amounts of thorium fluoride in the presence of other metals has been described by Grimaldi and Fairchild.(2) They showed that it was a good separation from uranium and certain other metals such as tantalum, niobium, titanium, zirconium and iron. By using a carrier they obtained quantitative recoveries of less than milligram amounts. Fritz and Ford(1) have described the titration of thorium with disodium ethylenediamine tetraacetate (EDTA) using alizarin as indicator. A combination of these two processes described in this paper has afforded a rapid and accurate procedure for the determination of thorium in the presence of large amounts of uranium and many other metals. The thorium fluoride with a carrier of lanthanum fluoride is ignited to the oxide, dissolved in nitric acid, and evaporated with perchloric acid. The solution is adjusted to a pH of 2 and titrated with EDTA using eriochromcyanine as indicator.

EXPERIMENTAL

Apparatus. Polyethylene beakers, funnels and stirring rods.

Reagents. Ammonium fluoride solution, 10 grams of reagent grade in 100 ml. of water in a plastic bottle.

Ammonia, hydrochloric acid, nitric acid, concentrated.

Hydrofluoric acid, 48%.

Perchloric acid, 70%. All acids were analytical reagent grade.

Hydrogen peroxide, 30% analytical reagent.

Indicator solution, 100 milligrams of Eriochrome Cyanine R. C. (from Hach Chemical Co., Ames, Iowa) dissolved in 100 ml. of water.

EDTA, standard solution, 0.025 M. Dissolve 9.3088 grams of dry, reagent quality, disodium ethylenediamine tetraacetate in water and dilute to 1 liter. The dry reagent may be considered a primary standard or it may be standardized against pure thorium oxide.

Thorium nitrate, standard solution, 2 mg. per ml. of thorium. Dissolve 4.7580 grams of pure thorium nitrate tetrahydrate in water and dilute to 1 liter. Standardize by titrating against the standard EDTA solution and also by determining the thorium gravimetrically by the oxalate method.

Uranium solution. Dissolve the metal in hydrochloric acid, oxidize it with hydrogen peroxide, destroy the excess by heat and dilute it to a suitable concentration, such as 0.3 gram per ml.

Wash solution. Add 25 ml. of 48% hydrofluoric acid to 475 ml. of water, and store in a plastic bottle.

PROCEDURE

Dissolve the sample in concentrated hydrochloric acid and add an excess of hydrogen peroxide to oxidize the uranium. Heat the solution to boiling to complete the dissolution of the sample and continue heating to remove the excess of peroxide. If titanium is present, leave a little hydrogen peroxide in solution. If tungsten is present leave as much peroxide as necessary to keep the tungsten in solution but not so much as to precipitate uranium peroxide. If there is so much tungsten that it cannot be kept in solution with hydrogen peroxide, add the 5 ml. of hydrofluoric acid and 20 ml. of 10% ammonium fluoride from a subsequent step and immediately transfer the solution to a plastic beaker. The quantity of ammonia to be added in the later step must then be estimated to be equivalent to the excess hydrochloric acid used to dissolve the sample. Dilute the solution to 25 ml. and add 5 ml. of the lanthanum solution. Adjust the pH to between 2.0 and 3.0 with ammonia using a glass electrode and stirring constantly with a magnetic stirrer. The solution at this point should contain no precipitate. Transfer the solution to a plastic 250 ml. beaker and add a little ashless filter paper pulp. Add from a plastic graduate 5 ml. of hydrofluoric acid and 20 ml. of 10% ammonium fluoride solution, stirring with a plastic rod.

Allow the precipitate to digest for at least 2 hours (preferably over night) at room temperature. Filter the solution through a 9 cm. Whatman #42 or similar dense, ashless paper. Use a plastic funnel, with no suction and place a little paper pulp in the filter before starting the filtration. Wash the precipitate with hydrofluoric acid wash solution until all the uranium is removed and use a piece of dry filter paper to wipe out the beaker to insure complete removal of the precipitate. Ignite it in a platinum crucible at 800° C. Wash it into the 100 ml. beaker in which the sample was dissolved. Heat some nitric acid in the crucible to dissolve any thorium oxide that may have adhered to it and rinse it into the beaker. Add 15 to 20 ml. of nitric acid and heat until the oxide has dissolved. If this requires more than 20 to 30 minutes, add 1 drop of 5% hydrofluoric acid and continue heating.

To the clear solution add 1 ml. of perchloric acid and evaporate until a moist residue remains. Dissolve this in 20 to 25 ml. of water, adjust the pH to between 2.0 and 2.5 with hydrochloric acid or sodium hydroxide using a pH meter and magnetic stirrer. Add 2 drops of indicator solution and titrate with standard EDTA solution until the color changes sharply from purplish red to salmon pink.

Multiply the number of milliliters of EDTA solution by 0.005803 (or whatever the titer of the solution was determined to be), to find the weight of thorium. Multiply this by 100 and divide by the weight of the sample to obtain the percent of thorium.

DISCUSSION

In the analyses of actual samples it was sometimes found that an undetermined impurity masked the end point in the titration. In these cases it was necessary to reprecipitate the thorium from the solution of the ignited oxide.

Evaporation of the solution of the oxide with perchloric acid served to remove traces of fluoride which interfered seriously with the titration, but since the oxide was not dissolved by perchloric acid, it was necessary to dissolve it first in nitric acid. Large amounts of perchloric acid made the end point indistinct.

The color change of the indicator was sharpest at a pH of 2. Other indicators tried were: alizarin, carminic acid, chromazurol, ammonium purpurate and purpurin sulfonate. None of these could be used in the presence of lanthanum although Fritz and Ford(1) claimed that lanthanum did not interfere when alizarin was used.

Attempts were made to destroy the filter paper with nitric and perchloric acids instead of igniting the fluoride to oxide. Although this was rapid and convenient the resulting solution showed no end point when titrated with EDTA. This was apparently not due to any material removed from pyrex glass because small amounts of boron and arsenic showed no effect. When quartz beakers were used no trouble was experienced at first, but in later experiments a turbidity was produced when the pH was adjusted to between 2 and 2.3, and no titration was possible. No explanation has been found for these phenomena.

The volume of solution from which thorium fluoride was precipitated varied from 50 to 100 ml., but with 3 grams of uranium in 50 ml. of solution a greenish yellow, crystalline precipitate of uranyl ammonium fluoride was formed. Under these conditions a volume of at least 100 ml. is recommended.

Effects of Titanium and Tungsten. When titanium was present, hydrogen peroxide prevented its precipitation. It was usually not present in the thorium fluoride but even large amounts of it did not interfere with the EDTA titration because the titanium complex with the reagent is unstable. When titanium was present the thorium fluoride had a bluish tint and turned brown on ignition, due to the presence of a trace of uranium which is not carried down in the absence of titanium.

Tungsten tended to precipitate as tungstic acid shortly after the sample was dissolved. An excess of hydrogen peroxide kept a limited amount of tungsten in solution but was inadequate for 20 mg. or more. If the precipitate of tungstic acid was allowed to stand for a time it did not dissolve when hydrofluoric acid was added, but remained with the thorium fluoride, where it interfered with the titration. When such amounts of tungsten were present best results were obtained by adding the hydrofluoric acid as soon as the alloy was in solution and neutralizing part of the acid later by adding a calculated amount of ammonia. This prevented any tungsten from contaminating the thorium precipitate.

EXPERIMENTAL RESULTS

A number of determinations were carried out on solutions made up to simulate alloys of uranium and thorium varying from 0.1 to 1.0% thorium. The results are shown in Table I.

Table I

DETERMINATION OF THORIUM IN KNOWN SOLUTIONS

No. of Determinations	Thorium Taken, mg.	Uranium Present, grams	Average Error Thorium, mg.	Average Thorium Found %	Standard Deviation, %
9	3.0	3.0	+0.01	100.4	1.03
8	6.0	3.0	-0.02	99.6	0.40
9	9.0	3.0	-0.03	99.7	0.30
10	12.0	3.0	-0.05	99.6	0.27
24	10.0	2.0	-0.06	99.4	0.36
7	30.0	3.0	-0.12	99.6	0.32
5	40.0	2.7	0	100.0	0.22
10	50.0	1.7	0.40	99.2	0.33

Several series of determinations were made according to the procedure given, on samples containing titanium and tungsten as well as uranium.

The simulated titanium alloy was made from solutions containing uranium, thorium and titanium. However, in the case of tungsten, since the main problem was to keep it in solution while the thorium fluoride was precipitated, an alloy of tungsten and uranium was prepared and samples from it were dissolved in the presence of known amounts of thorium. The determination was then made according to the special directions in the procedure. The results are shown in Table II.

Table II

EFFECT OF TITANIUM AND TUNGSTEN IN THE DETERMINATION OF THORIUM

No. of Determinations	Thorium Taken, mg.	Titanium Present, mg.	Tungsten Present, mg.	Uranium Present, grams	Average Error Thorium mg.	Average Thorium Found %	Standard Deviation, %
13	19.78	10.		2	-0.02	99.1	0.46
27	9.89	10		2	-0.07	99.3	0.34
15	10.00		10	2	-0.04	99.6	0.62
9	9.82		20	2	-0.05	99.5	0.45
15	5.89		10	2	-0.06	99.0	0.58

The amount of thorium that can be determined by this method is limited only by the precision of the titration. Three milligrams was the smallest amount titrated in these experiments, but by using a more dilute EDTA solution and, if necessary, a photometric end point much smaller amounts could doubtless be determined. As little as 0.05 mg. of thorium was recovered from complex synthetic mixtures by Grimaldi and Fairchild.(2)

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