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Determination of Uranium and Thorium
in Carbon and Silicon Carbide-Coated
Uranium-Thorium Carbide Fuel Beads

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

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DETERMINATION OF URANIUM AND THORIUM IN CARBON AND SILICON CARBIDE-COATED URANIUM-THORIUM CARBIDE FUEL BEADS

by

A. D. Hues, A. L. Henicksman, and W. H. Ashley

ABSTRACT

A method has been developed for titrimetric determination of uranium and thorium in uranium-thorium carbide fuel particles that have been coated with pyrocarbon, silicon carbide, and again with pyrocarbon. The particle coatings are stripped by heating alternately in oxygen and chlorine gases. The residue is dissolved, and the uranium and thorium are separated by ion exchange. The thorium is determined by titrating with Versene, using xylenol orange indicator. The uranium, after the impurities are removed by electrolysis with a mercury cathode, is reduced in a Jones reductor and determined by titration with ceric sulfate, using ferroin indicator. Because of the lack of suitable standards, the reliability of the method was estimated from measurements of known quantities of uranium and thorium in prepared solutions, and also from repeated analyses of the solutions of fuel bead samples. The average recovery of thorium from nine prepared solutions was 100.14%, with a standard deviation of 0.20%. The average recovery of uranium from 12 prepared solutions was 99.94%, with a standard deviation of 0.09%. In repeated analyses of nine samples of beaded fuel particles, the relative standard deviations were 0.13% for uranium and 0.15% for thorium.

1. INTRODUCTION

Reactor fuels, consisting of uranium-thorium carbide particles coated with pyrocarbon, silicon carbide, and again with pyrocarbon, are difficult to analyze because the coatings are extremely resistant to chemical attack. Smith¹ crushed the beads mechanically, then dissolved the core material by leaching with acid. He determined uranium in a phosphoric acid solution by reducing with ferrous ion and titrating the uranium(IV) potentiometrically with potassium dichromate. The thorium was determined by titration with Versene. Smith assumed that the leaching dissolved all the uranium and thorium, and that the volume errors caused by insoluble silicon carbide were negligible.

Palta² mentioned several mechanical, thermal, and chemical methods for removing the bead coatings,

including grinding followed by high-temperature chlorination to volatilize the uranium and thorium tetrachlorides. Uranium and thorium were separated either by ion exchange or by liquid-liquid extraction. The uranium(VI) was reduced by chromium(II) to uranium(IV), which was titrated with either ceric or dichromate solutions using an amperometric end point detection. The thorium was assayed by a chelatometric titration.

In our previous analyses, we fused the coated fuel particles with a mixture of sodium carbonate and lithium tetraborate. This method introduced large quantities of salts, and insoluble silica and residual carbon were troublesome. Uranium was determined titrimetrically with ceric sulfate after an ion-exchange separation from the thorium and salts. Thorium was not determined in this set of analyses.

In work reported subsequently by Robertson,³ uranium was determined in the coated fuel beads by a mass spectrometric technique after the coatings had been removed by successive ignitions in oxygen and chlorine. The outer pyrocarbon coating was removed by heating in oxygen gas at 800°C, the SiC layer was volatilized as SiCl₄ in a stream of chlorine gas at 1100 to 1200°C, and the inner pyrocarbon coating was oxidized in oxygen.

We modified Robertson's procedure for removing the coatings for the present work to permit analysis of samples weighing up to 15 g, and to provide for recovery of small amounts of uranium and thorium which otherwise might be lost. After removal of the coatings, the residue was dissolved and the uranium and thorium were separated by ion exchange. The uranium was reduced in a Jones reductor to uranium(IV) which was titrated with ceric sulfate. The thorium was determined by titrating with Versene.

II. EXPERIMENTAL

A. Improvements in Gas Reaction Apparatus

Previous work² had shown that uranium and thorium from the cores of the fractured beads were quantitatively volatilized as the tetrachlorides, and we observed and measured some thorium and uranium migration during our initial tests of Robertson's method. We observed only a very few fractured beads in one experimental lot before treatment, but removal of the outer pyrocarbon coat and the silicon carbide shell apparently fractured many more beads.

We modified Robertson's apparatus³ to prevent loss of uranium or thorium. We placed a glass frit in the exit end of the combustion tube to stop any particles and added a series of bubbler traps, through which the exit gases pass, to recover volatile compounds. The trap system consisted of one dry trap of about 100-ml capacity, followed by four 125-ml Erlenmeyer flasks in series, equipped with bubble tubes and containing water. The inlet tubes of the first two wet traps had to be cut off about 12 mm above the water surface to prevent their being plugged with hydrolyzed silica. The inlet tubes of the last two traps extended beneath the surface so that the gases were bubbled through the water. We placed a loose glass wool plug in the bulb in front of the exit tube in each trap to reduce the carry-over of silica. The modified apparatus (Fig. 1) was arranged so that the entire stripping process could be carried out in the reaction tube, avoiding possible losses in transferring the partially stripped material.

We used semiball joints or standard-taper glass joints to facilitate disassembling the apparatus to recover the core material after stripping. Copper and glass tubing were

Fig. 1.
Coating removal apparatus.

used throughout, in conformance with Braker's⁴ recommendations for construction materials. We calibrated the Variac by using a thermocouple to check the furnace temperatures attained at various settings. The times required for the temperature to reach equilibrium after various changes in the Variac setting were also observed and recorded.

We observed Braker's recommended safety precautions diligently and added others, because we recognized the hazardous nature of chlorine gas. The apparatus was assembled in a fume hood with enough exhaust capacity to prevent chlorine gas from escaping into the room. A Welsh Manufacturing Company full-face mask with filter canisters suitable for use with moderate amounts of acid gases was located near the working area for emergency use. A safety shower also was readily accessible.

B. Coating Removal

We studied the stripping process in some detail using a batch of experimental beads and an initial sample size of 100 mg which was gradually increased to 15 g as we refined the apparatus. We tried oxidation times of 15 to 60 min and furnace temperatures of 800 to 950°C for removing the pyrocarbon shells. We tried chlorination times from 0.5 to 2.5 h for removing the silicon carbide. We followed the progress of the stripping process by visual inspection of dip samples under low-power magnification. Inspection of the residue remaining after dissolution of the core material proved the efficiency of the overall process. At 950°C, the pyrocarbon coatings were consistently removed in 30 min in oxygen, and 1.5 h in chlorine completely removed the silicon carbide shells on the 15-g samples. Normally, only a very few shell fragments remained, along with some elemental carbon

formed during chlorination of the silicon carbide and carried by the gas flow to cooler parts of the combustion tube.

Minor modifications to the procedure, such as the order of oxidation and chlorination, would permit analysis of beads whose pyrocarbon and silicon carbide layers are in a different sequence, or omission of the part of the procedure dealing with coating removal would permit analysis of mixtures of uranium and thorium oxides.

C. Uranium and Thorium Migration

We tried to minimize loss of uranium and thorium from the reaction tube during stripping, but with only limited success. Because of the relatively high gas velocity through the system, dust particles are readily carried out of the combustion tube. Attempts to filter out these particles with a glass wool plug in the combustion tube cap were fairly successful, but recovery of the trapped material was difficult. A coarse glass frit sealed into the tube cap (see Fig. 1) was more efficient and easier to clean. Using the experimental batch of fuel beads and, later, uranium oxide, we followed the uranium and thorium migration by checking various parts of the trap system beyond the filter. The trap system described previously prevented appreciable loss of uranium and thorium from the system. Although as much as 600 μg of uranium was found in the combined contents of the first three traps, only 6 μg , or <0.01% of the uranium present, was found in the last trap after 100 mg of uranium oxide (U_3O_8) had been stripped. This 100-mg sample represents a fuel material in which all of the beads are fractured and all of the uranium in the cores is exposed during the chlorination. This amount of uranium oxide is equivalent to that in 2 g of fuel beads containing 4% uranium. We also determined the uranium in the contents of the last trap separately in each case after removing the coatings from nine actual bead samples that contained 3.3% uranium. The amount ranged from 0 to 8 μg , less than 50 ppm of the uranium present. We also found that no uranium was carried by backflow into the gas inlet tube preceeding the combustion tube.

We also measured the thorium in the trap solutions. In a series of tests using experimental beads, the total thorium in the traps varied from 60 to 420 μg , whereas the uranium found was 440 to 580 μg . As the thorium content of the samples was about five times that of the uranium, the thorium seems somewhat less mobile than the uranium under the chlorination conditions. Thorium losses from the system, therefore, would be even less significant than uranium losses.

We had difficulty with the copious quantities of SiCl_4 formed during chlorination of the larger samples. Silicon tetrachloride hydrolyzes readily to form deposits in the tips of the tubes in the wet traps and on the glass wool plugs in the trap bulbs. These deposits often partially or completely blocked the system. We cut off the tips of the tubes in the first two traps to get the maximum cross section and leave about 12 mm above the surface of the liquid. The SiCl_4 contact with the water was still adequate. After removal of the coatings from a 15-g sample, the contents of the first trap was a rigid gel, and a considerable amount of SiCl_4 also was hydrolyzed in the second and third traps. During work with large samples, a liquid, possibly Si_2Cl_6 that formed as a result of a chlorine deficiency during the peak of the silicon carbide and chlorine reaction, condensed in the dry trap, but it completely volatilized by the end of the chlorination. We placed glass wool plugs in the exit bulbs of the first three wet traps to retard uranium and thorium migration. These plugs, especially that in the first trap, were loosely packed to prevent the silica deposit from restricting the gas flow.

We tried various means to improve the trap efficiency and thus simplify the apparatus somewhat. We used 8M HNO_3 -0.05M HF, which is used for dissolving the core materials, and also dilute nitric acid in the traps, but found no improvement in the efficiency. We packed ice around a dry trap to condense the UCl_4 and ThCl_4 at that point, but the uranium detected in the final flask was not significantly decreased below the 8- μg level. We tried to prevent accumulation of hydrolyzed silica by using 1M HF in the first two wet traps, but a hard crust of silica still formed on the surface of the liquid.

D. Dissolution of Residues

We dissolved the uranium and thorium oxides remaining after the stripping process in the 8M HNO_3 -0.05M HF that Robertson³ recommended. Cleaning the dust particles and carbon from the frit in the tube cap was relatively simple. Several small portions of the acid mixture were introduced into the upper part of the cap and forced through the frit by air pressure from a rubber bulb. Particles adhering to the walls and frit of the combustion tube were effectively removed by refluxing the acid mixture as described in *Dissolution of Residues* in the Recommended Procedure. The presence of some elemental carbon and considerable silica in the upper part of the combustion tube necessitated filtering the solution obtained. We then ignited the residue to remove carbon and added 48% HF to remove the silica. The final treated residue dissolved readily in the 8M HNO_3 -0.05M HF mixture.

The contents of the traps were washed into a Teflon beaker with 5% HF, and the resulting solution was evaporated to dryness to remove the silica. When necessary, additional 48% HF was added dropwise to remove the hydrolyzed silica from the first wet trap. The remaining residue was dissolved by boiling with 8M HNO₃-0.05M HF, and the resulting solution was added to the original sample solution. Occasionally some insoluble material, mainly SiO₂, survived this treatment and was filtered off, ignited, and again evaporated with hydrofluoric acid.

E. Sample Analysis

We determined the uranium and thorium in the solutions by well-established methods.^{5,6} The 8M HNO₃-0.05M HF solutions were evaporated, and the residues were dissolved in 6M HCl for the anion-exchange separation of uranium and thorium. Thorium was determined by titration with Versene at pH 2.0 using xylenol orange indicator. In general, the only interfering elements were those that would either form stable complexes with the Versene at a pH of 2.0 or interfere with the indicator's color change. Uranium was removed from the ion exchange column by eluting with 0.1M HCl, and the eluate solution was electrolyzed with a mercury cathode to remove impurities. The uranium was reduced in a Jones reductor, oxidized to uranium(IV) by aerating the solution, and then titrated with a ceric sulfate solution. Of the elements that followed uranium through the ion-exchange separation, the only ones that interfered were those, like molybdenum, that were not removed by electrolysis with the mercury cathode. It was essential to remove all traces of nitrates and organic matter that form interfering products when reduced by the zinc amalgam.

The zinc reduction of the uranyl ion,

proceeds with the formation of some uranium(III) which is readily oxidized by air to uranium(IV). The quadravalent state of uranium is stable in a cool solution and in the absence of catalysts. Above 30°C, or in the presence of molybdenum or copper, the uranium(IV) is air-oxidized to uranium (VI). Conditions that permit oxidation of uranium(IV) are avoided in the recommended method.

III. APPARATUS AND REAGENTS

A. Apparatus

Adapter, 24/40 to 34/45 T.

Beakers, Pyrex, 150- and 250-ml Griffin.

Beaker, Teflon, 250-ml.

Buret, 50-ml, NBS certified, or calibrated.

Coating-removal apparatus (Figs. 1 and 2), consisting of combustion tube with provisions for heating, a supply of oxygen, chlorine, and argon gases, and a series of traps.

Crucible, platinum, 20-ml.

Flasks, Erlenmeyer, 125-ml, with 24/40 T joint.

Flasks, volumetric, 50- and 100-ml, calibrated.

Funnel, 60°, 75-mm-i.d.

Ion exchange columns, 13-mm-i.d. by 250-mm-long, having a coarse glass frit near the tip to support the resin. Jones reductor, prepared according to Furman.⁷

Mercury cathode apparatus, Dyna-Cath, made by Eberbach and Sons, or equivalent.

Paper, filter, Whatman No. 42, 125-mm.

pH meter, Beckman Expandomatic or equivalent, with glass and calomel electrodes.

Pipets, transfer, various sizes, calibrated.

Stirrer, magnetic, with Teflon-coated stirring bar.

Tube, gas-dispersion, sintered glass of medium porosity.

B. Reagents

Anion-exchange resin, Bio-Rad Laboratories AG1-2X, 100-200 mesh.

Argon, 99.995%, cylinder gas.

Ceric sulfate, 0.01M in 0.5M sulfuric acid. Prepare by diluting 0.05M ceric sulfate solution (G. F. Smith Chemical Co.) with 0.5M sulfuric acid, and standardize against NBS uranium oxide sample No. 950a. Use the titration procedure described under *Separation and Determination of Uranium and Thorium*.

Chlorine, 99.5% pure, cylinder gas.

Ferric ammonium sulfate, approximately 0.1M.

Ferriin indicator, 0.025M solution, prepared by dissolving 1.5 g of 1,10-phenanthroline and 1.2 g of ferric ammonium sulfate hexahydrate in 100 ml of water.

Hydrochloric acid, 12, 6, and 0.1M.

Hydrofluoric acid, 48 and 5%.

Nitric-hydrofluoric acid mixture, 8M in nitric acid, 0.05M in hydrofluoric acid.

Fig. 2.
Combustion tube.

Oxygen, 99.6% pure, cylinder gas.

Perchloric acid, 70%, reagent grade.

Sodium hydroxide, 5M.

Sulfuric acid, 18M and 5%.

Versene, 0.01M solution of disodium versenate. Standardize by titrating a solution of thorium metal containing no more than 500 ppm of impurities, by the method described under *Separation and Determination of Uranium and Thorium*. Calculate the titer of the solution in grams of thorium equivalent to 1 ml of solution.

Xylenol orange indicator, 0.1% solution in 20% ethanol.

IV. RECOMMENDED PROCEDURE

A. Coating Removal

1. Adjust the furnace temperature to 950°C; place loose glass wool plugs in the bulbs of traps 1 and 2, and in the exit arm of trap 3; and add 50 ml of water each to traps 1 and 2, and 75 ml each to traps 3 and 4.

2. Transfer the weighed sample to the combustion tube, assemble the system, admit oxygen at 500 cm³/min, and allow 30 min for complete removal of the outer pyrocarbon coating. Turn off the oxygen.

3. Readjust the furnace temperature to 1100 to 1200°C, admit argon at 200 cm³/min, and allow at least 15 min for the furnace to come to temperature.

4. Turn off the argon, turn the stopcock at the inlet of the rotameter, and admit chlorine at 500 cm³/min. The silicon carbide coating is converted to the chloride and volatilized in 1-1/2 h.

5. Turn off the chlorine at the cylinder, turn the stopcock to admit argon at about 200 cm³/min, and adjust the furnace temperature to 950°C. Allow about 10 min to cool to this temperature.

6. Turn off the argon, start a flow of oxygen at 500 cm³/min, and allow 30 min for removal of the inner pyrocarbon coating. Turn off the oxygen.

7. Disconnect the traps and delivery tubes, remove the combustion tube from the furnace, and allow the tube to cool.

B. Dissolution of Residues

1. Rinse the combustion tube cap with about 15 ml of 8M HNO₃-0.05M HF, and transfer the rinsings to a 125-ml Erlenmeyer flask having a 24/40 T joint.

2. Connect the combustion tube, containing the sample residue, to the Erlenmeyer flask as shown in Fig. 3. Reflux until the combustion tube is clean and the sample, except for free carbon, appears to have dissolved. (Wrap

Fig. 3.
Apparatus for dissolving oxide residues.

asbestos tape around the combustion tube, if necessary, to get good reflux action through the frit.)

3. Rinse the combustion tube, filter the sample solution through No. 42 paper, wash the paper thoroughly with water, and ignite the paper and residue in a platinum crucible to remove the carbon.

4. Treat the residue with a few drops of 48% HF and evaporate to dryness.

5. Add a few milliliters of 8M HNO₃-0.05M HF to the crucible, boil the solution until any remaining residue has dissolved, and add this solution to the filtrate.

6. Rinse the upper delivery tube and all traps except the last one into a 250-ml Teflon beaker, using water, then 5% HF. (Dropwise addition of 48% HF will be needed to remove the hydrolyzed silica from the first wet trap.)

7. Add 48% HF to the Teflon beaker until the solution is clear, then evaporate to dryness on the hot plate.

8. Add 10 ml of 8M HNO₃-0.05M HF and boil to dissolve the residue in the beaker. Filter the cool solution through No. 42 paper.

9. Wash the filter paper with water and add the filtrate to the sample solution.

10. Ignite the paper and residue in a platinum crucible, add 5 to 10 drops of 48% HF, and evaporate to dryness.

11. Add 3 to 5 ml of 8M HNO₃-0.05M HF to the crucible, boil until any remaining residue has dissolved, and add this solution to the original sample solution.

12. Evaporate the combined sample solution to dryness, add 5 ml of 12M HCl, and again evaporate to dryness.

13. Dissolve the residue in 6M HCl and dilute to volume, in an appropriate size volumetric flask, with 6M

HCl in preparation for the uranium and thorium separation.

14. Evaporate the contents of the final trap to dryness, dissolve the residue in 1 drop of 12M HCl and a few drops of water, and determine the uranium in this solution using a spectrophotometric measurement.⁸

C. Separation and Determination of Uranium and Thorium

1. Prepare two ion exchange columns by adding a water slurry of AG1-2X to give a resin height of about 125 mm. Wash the columns with 50 ml of 0.1M HCl and then with 50 ml of 6M HCl, and clamp the columns one above the other on a ring stand.

2. Add an aliquot of the sample solution, from Step 13 of *Dissolution of Residues*, which contains about 100 mg of uranium, to the upper column, and collect the eluant in a 100-ml volumetric flask.

3. Wash the columns with enough 6M HCl to nearly fill the collecting flask. Make the solution to volume and mix well. This fraction contains the thorium.

4. Place a 150-ml beaker under the lower column, and strip the uranium from the resin with 50 ml of 0.1M HCl. This fraction contains the uranium.

5. Transfer an aliquot of the thorium solution (from Step 3) that contains about 50 mg of thorium to a 150-ml beaker, dilute to 30 to 40 ml with water, and adjust the pH to 2.0 using 5M NaOH.

6. Add 4 to 5 drops of xylenol orange indicator and titrate with 0.01M Versene solution. The end point color change is from red to yellow.

7. Calculate the percentage of thorium in the sample as follows:

$$\text{Th (\%)} = \frac{(\text{titer})(\text{ml Versene})(\text{sample volume, ml})(10)}{(\text{ml from Step 5})(\text{ml from Step 2})(\text{g sample})}$$

8. To the uranium solution from Step 4, add 5 ml of 18M H₂SO₄, and fume to dryness. Add another 5 ml of H₂SO₄ and a few drops of HClO₄ and again fume to dryness.

9. Dissolve the residue with 2 to 3 ml of water and 5 ml of H₂SO₄, transfer the solution to the Dyna-Cath cell, and electrolyze with a 15-A current for 30 min.

10. Drain the cell into a 250-ml beaker and carefully wash down the cell walls, keeping the total solution volume to 100 ml or less. Tip the cell during washing, to wash the glass surface that is usually covered with mercury.

11. Add 100 ml of 5% H₂SO₄ to a Jones reductor, discarding the eluant. Pass the uranium solution through,

and collect the solution in a 250-ml beaker. Wash the reductor with about 100 ml of 5% H₂SO₄, added in several portions. The total volume collected should be 200 ml or less.

12. Cover the 150-ml beaker with a watch glass, aerate the cool reduced solution for 5 min with a stream of air through a gas-dispersion tube, and then rinse and remove the aerating tube and cover glass.

13. Stir the solution with a magnetic stirrer, add 2 drops of ferroin indicator, and titrate with ceric sulfate until the orange color begins to fade. At this point interrupt the titration and add 3 ml of ferric ammonium sulfate solution, which should restore the orange color of the solution. Continue the titration until the color changes sharply from orange to green. Record the titration volume and the temperature.

14. Repeat Steps 11 through 13, but omit adding the uranium solution in Step 11 to measure the titration blank.

15. Convert the titration volume to standard temperature according to Table I and subtract the blank.

16. Calculate the percentage of uranium in the sample as follows:

$$\text{U (\%)} = \frac{(\text{ml ceric})(N)(\text{sample volume, ml})(\text{factor})(100)}{(\text{ml aliquot})(\text{g sample})}$$

The factor in this calculation is the milliequivalent weight of uranium with suitable corrections for the isotopic composition.

For depleted uranium use	0.11903
For normal uranium use	0.11902
For 93% U-235 use	0.11760*

*Based on a typical isotopic composition of 93% U-235, 1% U-234, 0.5% U-236, and the remainder U-238.

TABLE I
TEMPERATURE CORRECTION FOR CERIC SULFATE

ml	18°C	20°C	22°C	24°C	26°C	28°C	30°C	32°C
5	+0.02	+0.02	+0.01	+0.01	+0.01	0	0	0
10	+0.03	+0.03	+0.03	+0.02	+0.01	+0.01	0	-0.01
15	+0.05	+0.05	+0.04	+0.03	+0.02	+0.01	0	-0.01
20	+0.07	+0.06	+0.05	+0.04	+0.03	+0.01	0	-0.01
25	+0.09	+0.08	+0.06	+0.05	+0.03	+0.02	0	-0.02
30	+0.11	+0.10	+0.08	+0.06	+0.04	+0.02	0	-0.02
35	+0.13	+0.11	+0.09	+0.07	+0.05	+0.02	0	-0.02
40	+0.15	+0.13	+0.10	+0.08	+0.05	+0.03	0	-0.03
45	+0.17	+0.14	+0.12	+0.09	+0.06	+0.03	0	-0.03
50	+0.19	+0.16	+0.13	+0.10	+0.07	+0.03	0	-0.03

V. RELIABILITY

No representative standard reference material was available for use in measuring the accuracy of the complete procedure. Although the special care taken and the design and arrangement of the traps should ensure that neither uranium nor thorium is lost from the system during removal of the pyrocarbon and silicon carbide coatings, we could not measure the method bias accurately. Although we found as much as 600 μg of uranium in the combined contents of the traps during analysis of bead samples weighing up to 15 g, we never found more than 8 μg of uranium in the final trap. This amounted to less than 50 ppm of the uranium present. The amount of uranium going beyond this last trap, and thus escaping from the system, was considered negligible. We found less thorium than uranium in the traps and considered it also insignificant. Repeated analyses of nine samples of beaded fuel particles provided data for estimating the precision. Triplicate aliquots of the uranium and thorium solutions were analyzed for three of the samples, which weighed approximately 15 g; the uranium and thorium were determined in duplicate for the other six samples, which weighed from 7 to 8 g. From the differences of the 21 individual results from the average values, we calculated relative standard deviations of 0.13% for the uranium and 0.15% for the thorium.

Prepared solutions containing known amounts of uranium and thorium were titrated along with the uranium and thorium from actual bead samples. The average thorium recovery in nine solutions was 100.14%, with a standard deviation of 0.20%. Analysis of 12 known uranium solutions gave an average recovery of 99.94%, with a standard deviation of 0.09%.

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