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Determination of Oxygen
in Irradiated Reactor Fuels
and Cladding Materials

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by

Carolyn S. MacDougall
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Work supported by the Division of Reactor Development and Technology.

Fig

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ABSTRACT

A method for determining oxygen was adapted and remotized for analysis of irradiated fuels and claddings in a hot cell. The sample is reacted with carbon at 2000 °C to liberate oxygen as carbon monoxide and dioxide which are measured gravimetrically or manometrically, depending on their quantities. Oxide fuels are mixed with graphite and pressed into pellets before the reaction. The evolved carbon dioxide is absorbed on Ascarite and weighed, and the carbon monoxide is oxidized over copper oxide to carbon dioxide before being trapped and weighed. The oxygen content is calculated from the weight increases of the two tubes. Analyses of 1-g samples of oxide fuels that had undergone 6.5 and 8.5 at. % burnup showed that the relative standard deviation of the method is 0.4%.

Carbide fuel and cladding samples, which have low oxygen contents, generate only carbon monoxide when heated to 2000 °C in a graphite crucible containing platinum. The carbon monoxide is oxidized by Schütze reagent to carbon dioxide which is collected in a capillary trap and measured manometrically. The relative standard deviation of this method is 10% in the analysis of 100-mg samples of carbide fuel or cladding.

INTRODUCTION

The dependence of the properties of refractory fuels and cladding materials upon their oxygen contents necessitated development of a method¹⁻³ for accurately determining this constituent or impurity. In addition, this method is needed in studies of oxygen migrations during burnup of the fuel. The method also is used in estimating the oxygen-to metal atom ratio of oxide fuels, provided the metal contents are also measured. Experience with the gravimetric method for determining oxygen in oxides has been so satisfactory that its modification for use in a remote facility did not present insurmountable difficulties. In the interest of economical use of equipment and of space in a hot cell, only the furnace originally designed for heating oxide samples was installed, with the option of using either a gravimetric or manometric finish. The combined method is sensitive enough for measurement of microgram quantities of oxygen in carbides and claddings, and yet gives satisfactory precision

in measuring oxygen in the oxide fuels. The method has been applied to date to the analysis of (uranium, plutonium) dioxides, uranium oxides, and stainless steel cladding samples.

The equipment used, therefore, is extremely versatile, being able to measure microgram or milligram quantities of oxygen. The method applies equally well to any material that reacts completely with carbon in an inert atmosphere but does not form volatile products other than carbon monoxide or carbon dioxide.

APPARATUS AND REAGENTS

Apparatus⁴

Absorption Tubes, 100-ml Schwartz (two required). Fill two-thirds of each tube with Ascarite, and the remaining third with anhydrous magnesium perchlorate. Pack the openings to both tubes with glass wool to prevent physical loss of dust from the tubes.

Balance, analytical, with nonbrowning glass, Ainsworth Right-a-Weigh or similar.

Balance, analytical, for weighing absorption tubes, Ainsworth BCT or similar, with set of S-grade weights.

Ball Bearings, 0.25-in.-diam, chrome steel.

Base Plate, brass, for sealing furnace tube, see Fig. 1.

Blender, yoke, see Fig. 2

Boat, sample, glass. Cut off the top half of a 30-ml beaker, so that the remaining cup is 1-1/8-in. high.

Brush, for cleaning die plunger, see Fig. 3.

Brushes, brass, 12-gauge shotgun and 0.27 calibre rifle, for cleaning die and grinding capsule.

Combustion Train, Arrange the equipment listed here as shown in Fig. 4.

Desiccant Tube, prepare by filling three-fourths of a 200-ml Schwartz tube with anhydrous magnesium

Fig. 2. Yoke blender.

Fig. 1. Furnace, brace, and base plate.

Fig. 3. Pellet die and brush.

perchlorate. Fill the remaining one-fourth of the tube with Schütze reagent. Pack the openings of the tubewith glass wool to prevent dust from passing into the analytical train.

Dewar, 2.93-in.-i.d., 6-in.-high, to fit under manometer.

Die, 0.25-in. pellet die, see Fig. 3.

Drying Tower, stainless steel, 30-in.-long, 3-in.-diam, having a screw cap fitted with an O-ring to make a gastight seal, filled with molecular sieve.

Engraving Tool, Vibrograver or similar.

Flow Gauge, Hoke Bantam or similar.

Funnel, for pouring sample into die, see Fig. 5.

Furnace Tube, fused-silica, see Fig. 1.

Furnace Tubes, nickel, 16-in.-long, 1.125-in.-

Fig. 4. Combustion train with insert of manometer.

diam, having a screw cap fitted with a lead gasket to make a gastight seal, to fit resistance furnaces, two required.

Furnaces, tube, 1.25-in. -bore, 12-in. Hevi-Duti or similar, two required, with 7.5-A variable transformers for temperature control.

Generator, induction, 25-kW, Lepel Type T-751-32 or similar.

Guide Tube, to guide sample into crucible, 0.825-in. -o.d., 8.5-in. -long, with bottom recessed to 0.625-in. o.d.

Lift, mechanical, see Fig. 1.

Manometer, with meter stick, see Fig. 4.

Mixer-Mill, Spex Type 8000 II or similar, with Spex 8004 tungsten carbide grinding vial (50-g quantities of oxide) and Crescent dental capsule 6114 (2- to 5-g quantities of oxide).

Moto Tool, Dremel Mfg. Co. Model 270 or similar, two required. Modify each to accept gun brushes previously described.

O-Ring, Viton, 2.125-in. -i.d. by 2.5-in. -o.d.

Pedestal, boron nitride, see Fig. 6.

Pellet-Grasping Tool, see Fig. 7.

Pellet Trough, see Fig. 8

Pyrometer, graduated from 0 to 1000 °C, Sim-Ply-Trol Assembly Products, Inc., or equivalent, with Chromel-Alumel thermocouples, two required.

Regulator, low-pressure, measuring 0 to 50 in. water, Moore Products or similar.

Remote Facility, similar to that described by Lilienthal⁵ and by Burwell, Schulte, and Wilson.⁶

Ring, Lavite, for binding furnace to base plate, see Fig. 1.

Thimble Assembly, with crucible, cap, and insulation, see Fig. 6.

Trap, straight length of 12-mm-i.d. tubing filled with 25-g polyethylene beads, for removal of fission products.

Tweezers, 12-in. -long, suitably modified for easy handling by manipulators.

U-Tube, filled with 50 g of Schütze reagent.

Vacuum Pump, Cenco, Hyvac, Model 91135, or similar.

Weighing Scoopula, suitably modified for manipulators.

Fig. 5. Funnel.

Reagents

Argon, tank.

Ascarite, 8- to 20-mesh.

Copper Oxide, wire-form.

Graphite, SP-1 grade, for making pellets.

Graphite, 200-mesh, for crucible insulation.

Magnesium Perchlorate, anhydrous, reagent grade.

Molecular Sieve, Linde 5-A.

Nitrogen, liquid.

Polyethylene Beads, 8-mesh.

Schütze Reagent, iodine pentoxide on silica gel, prepare by Smiley's original method.²

Uranium Turnings, unoxidized metal.

Vacuum Grease, Fluorlube GR-362.

SAMPLE PREPARATION

Oxides

Visually inspect fuel for any signs of contamination, and clean or discard contaminated samples.

Fig. 6. Pedestal and crucible assemblies.

Place the uncontaminated oxide pellets in the stainless steel mixer-mill capsule, along with a chrome-steel ball bearing or, for large numbers of pellets, use the tungsten carbide capsule. Grind and mix the pellets for 2 min in the mixer-mill, pour the powder into a sample boat, and remove the ball bearing with tweezers. The powder is then ready for pellet preparation.

Cladding

Visually inspect the sample for contamination. In particular, be certain that no fuel adheres to the cladding. Weigh approximately 100 mg within ± 0.1 mg and transfer it into a clean sample boat. Handle carbide fuels similarly, but in an inert atmosphere.

RECOMMENDED PROCEDURE

Caution: Health and safety rules for handling of radioactive materials must be rigidly followed, and adequate protection of operators must be ensured by use of a suitable shielded facility and protective clothing.

Fig. 7. Pellet-grasping tool.

OXIDE FUEL ANALYSIS

Pellet Preparation

1. Accurately weigh (± 0.1 mg) approximately 1 g of the oxide powder and approximately 0.2 g of SP-1 graphite into a weighed sample boat, and transfer the powders into a blender.
2. Blend the sample for 2 min and pour the mixed powder through a funnel into the pellet die, using a Vibrograver to vibrate the blending vessel and funnel to ensure nearly quantitative transfer.
3. Press the mixture into a pellet (8000-lb gauge pressure), replace the bottom half of the die with the pellet trough, and press the pellet into the original sample boat.
4. Weigh the pellet to ± 0.1 mg and calculate the

Fig. 8. Pellet trough.

weight of oxide, W , in the pellet using

$$W = \left(\frac{W_p}{W_c + W_o} \right) W_o, \quad (1)$$

where

- W_o = original weight of oxide,
- W_c = original weight of carbon,
- W_p = weight of finished pellet.

(A proportionate loss of both oxide and graphite during pelletizing is assumed. This assumption is less valid the greater the loss, and the precision of the method becomes poorer.)

5. After each pellet is prepared, use the circular brush (Fig. 3) to remove any oxide clinging to the die plunger, and clean the die bore with the 0.27 cal. rifle-brush Moto tool.
6. Clean the stainless steel mixer-mill capsule using the Moto-tool shotgun brush and vibrate the blender capsule with the Vibrograver to make certain that no oxide remains.

Sample Analysis

1. Check the apparatus to be sure that the induction generator is off and that valves V_4 , V_5 , V_6 , S_5 , S_6 , S_7 , and S_8 are closed (see Fig. 4). Insert weighed absorption tubes into the analysis assembly.

2. Close V_3 , open V_1 and V_2 , and adjust the regulator to provide 20-in. H_2O pressure to ensure a positive pressure in the fused-silica furnace tube.
3. Remove the cap from the furnace assembly, remove the crucible cover with long tweezers, and set the cover out of the way.
4. Insert the sample guide tube into the furnace, drop the pellet through the tube into the crucible, remove the guide tube, and replace the crucible cover.
5. Replace the cap on the furnace tube, allowing about 2 min for the argon from the furnace to purge air from the cap, and then fasten the cap securely in place.
6. Open valves V_3 , S_5 , S_6 , S_7 , and S_8 , and slowly open needle valve V_7 until the argon flow is 100 ml/min.
7. Turn on the induction generator, and slowly warm the sample from the preset value of 1000 °C to 2000 °C in about 25 min.
8. Maintain the 2000 °C pellet temperature for 1 h; then turn off the induction generator, and simultaneously close valves S_5 and S_8 , followed by valves S_6 , S_7 , and V_3 .
9. Remove the preweighed Ascarite tubes from the analysis line, wipe them with a damp chamois, allow to sit for 20 min, and then weigh within ± 0.1 mg.
10. From the weight increases of these two absorption tubes, calculate the amount of oxygen in the sample as follows.

$$\text{Oxygen (\%)} = \left[\left(\frac{32.00}{44.01} \right) W_1 + \left(\frac{16.00}{44.01} \right) W_2 \right] 100 / W, \quad (2)$$

where

W_1 = weight increase in Ascarite tube No. 1,

W_2 = weight increase in Ascarite tube No. 2

W = weight of oxide in pellet.

11. Remove the furnace cap, the crucible cover, and the spent pellet, using 12-in. tweezers. Replace the crucible cover and furnace cap, and repeat Steps 1 through 10 to analyze another pellet.

CLADDING AND CARBIDE ANALYSIS

1. Turn on the argon, adjust the regulator to 5-in. gauge pressure, open valves V_1 , V_2 , and V_4 , and close valve V_6 .
2. Turn on the vacuum pump, slowly open valves V_6 and V_5 , and set the argon flow to 100 ml/min by adjusting valve V_8 . Measure the gas flow by passing the pump exhaust through a wet-test meter.
3. Close valve V_4 and adjust the regulator to 20-in. pressure to create a positive pressure in the furnace tube.
4. Remove the cap from the furnace, insert the sample guide tube into the furnace, and drop the sample into the crucible.
5. Remove the guide tube, replace the cap on the furnace, allow 1 min for argon from the furnace tube to purge the air from the cap, and then seat the cap firmly with a slight twist.
6. Open valve V_4 and allow argon to flush the line for 1 min.
7. Immerse the capillary trap in a liquid-nitrogen bath, turn on the induction generator, and allow 15 min. for reaction at 2000 °C and flushing of the reaction products from the furnace tube.
8. Close valve V_5 , wait about 1 min for the pump to evacuate the capillary manometer, and then close valve V_6 .
9. Remove the liquid-nitrogen bath from the capillary trap, warm the trap to room temperature, and measure the manometer to ± 0.5 mm.
10. Calculate the micrograms of oxygen using

$$W = 0.00086 (V_o x + S x^2), \quad (3)$$

where

W = weight of oxygen in micrograms,
 V_o = volume of U-trap in cubic millimeters,

S = cross section of manometer in square millimeters,

x = sample pressure in millimeters.

11. Determine an apparatus blank by performing Steps 1 through 10, but omit addition of the sample in Step 4.
12. Subtract the micrograms of oxygen in the blank from the total micrograms found in the sample.

EXPERIMENTAL

A discussion of the chemical aspects of the method, including gas purification, sample preparation, and the manometric and gravimetric measurements is given in previous reports.¹⁻³ The major problem in modifying the methods for hot-cell use was the design of new hardware to facilitate remote maintenance and operation of the equipment. Because of the long leads from the power generator to the induction coil, an insulated crucible was used to maximize the usable power. To avoid use of powdered graphite insulation that might react slightly with the fused-silica thimble, we tried pyrolytic boron nitride (200-mesh) insulation. At 2000 °C, however, we obtained a high apparatus blank (80 µg O₂). We tried to bake the thimble assembly at 2200 °C and then lower the temperature to 2000 °C for analyzing samples. The boron nitride began to decompose at above 2000 °C, and the decomposition products attacked the carbon crucible. Therefore, we did not pursue use of boron nitride further, and selected powdered graphite insulation. With the graphite insulation, a preliminary baking of the assembly at 2500 °C before operation at 2000 °C reduced the apparatus blank to 5 µg of oxygen.

The thimble assembly facilitated handling and replacement of the crucibles in the hot cell. Thimble and crucible assemblies were fabricated in advance outside the cell, and whole units were replaced as needed without difficulties.

A new type of fused-silica furnace was designed for use in the hot cell. The modifications consisted primarily of a wide top opening that permitted removal of oxide pellets from the dry crucible, and a wide flanged bottom opening for easy replacement of the thimble assembly. A brass base plate mechanically raised the pedestal and crucible assembly into place, and at the same time, made a seal between the base and the furnace tube. Water lines were connected to the water jacket through ball joints, as opposed to nipples, to facilitate making the connection with manipulators.

The silicone high-vacuum grease, previously used to make leaktight seals outside the hot cell, deteriorated upon exposure to high-level radiation. Fluorlube GR-362, which remained pliable under irradiation and also maintained vacuum seals at the

operating temperature of the apparatus, was found to be satisfactory.

We designed numerous small tools for adapting the pellet-making process to the hot cell. These included funnels for powder transfer, tweezers for reaching into the furnace and removing the pellet, brushes for cleaning the equipment, and guides for positioning equipment to circumvent the loss of depth-perception inherent in remote operation. These are described more fully in the section on Apparatus.

RELIABILITY

The method and apparatus were evaluated for determining oxygen in oxides using a test sample of uranium oxide (U₃O₈) prepared from uranium metal containing less than 100 ppm of total detected impurities. The calculated oxygen content based on the weight increase was 15.24%. An average value of 15.25% oxygen was measured in the hot cell. The precision of the method was 0.1 to 0.2% which was comparable to that obtained using the method outside the hot cell. Irradiated samples were then analyzed with the results shown in Table I.

Table I
ANALYSES OF IRRADIATED OXIDE FUELS FOR OXYGEN

Sample	Burnup (%)	Oxygen (%)	No. Analyses	Relative Standard Deviation (%)
1	6.29	11.97	3	--
2	6.06	11.74	8	0.4
3	unknown	11.95	6	0.3
4	8.50	11.94	5	0.2
5	unknown	11.86	5	0.9

Unfortunately, an irradiated oxide fuel standard of known O₂ content was not available, but analysis of the U₃O₈ sample indicated adequate accuracy for the equipment. We found no difficulties that could be attributed to the high radiation level.

We have made analyses for micro quantities of oxygen on three unirradiated samples, and have compared the results with those obtained on an inert-gas-fusion apparatus in a "cold" area (see Table II).

Table II

OXYGEN ANALYSIS RESULTS OBTAINED INSIDE
AND OUTSIDE THE HOT CELL

Sample	Oxygen Content (ppm)	
	In Cell	Out of Cell
Nb	2300	2300
NbC	925	1000
W-Mo	2500	2200

As these data show, the results obtained in the hot cell and outside it are essentially equal.

Samples of irradiated stainless steel cladding have been analyzed, but again, no irradiated standards were available, and comparison with another apparatus was impossible owing to lack of another facility for analyzing the highly radioactive cladding for oxygen. However, unirradiated steel samples are analyzed routinely by this method outside the cell.

SUMMARY

Two methods for measuring oxygen have been successfully adapted for use in a hot cell to measure the oxygen in irradiated fuels and claddings. The apparatus is very versatile, being able to measure 5- μ g to 130-mg quantities of oxygen. Approximately 2 analyses of oxides or 10 analyses of cladding materials can be performed in 8 h.

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