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MEASUREMENT OF OXYGEN-TO-METAL ATOM RATIOS IN URANIUM AND PLUTONIUM OXIDES

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ABSTRACT

Optimum conditions to produce stoichiometric dioxides from high-purity uranium and plutonium metals were determined. The results of this investigation led to modifications to improve two thermogravimetric methods of analysis which are described. The problems in O/M measurement caused by the lack of a standard oxide reference material and inhomogeneity of the sample and the difficulties in interpretation of results obtained by various methods are discussed.

I. INTRODUCTION

The oxygen-to-metal, O/M, atom ratio of mixed-oxide fuels is an important chemical property because of its effect on fuel-performance characteristics, such as thermal conductivity, reaction with cladding materials, swelling, and tensile strength. Therefore, reactor-fuel engineers need accurate measurements of O/M ratios to assist in predicting reactor-fuel dependability.

The most obvious way to determine O/M ratios is to measure the oxygen and metal contents independently, and then calculate their ratio. This approach has been successful, but the methods are time-consuming.[1,2] Other proposed methods include special dissolution procedures followed by measurement of uranium(IV) either polarographically[3,4] or by coulometric[5] or potentiometric titration,[6-8] measurement of hydrogen evolved during dissolution to indicate uranium(III) content,[9] x-ray diffraction,[10,11] or emf measurements of solid electrolyte cells.[12-15] The possibilities of determining O/M ratios using optical and ir spectrometry or magnetic susceptibility have also been discussed.[16] In some thermal methods, the quantities of specific gases evolved under controlled temperatures and atmospheres are used to calculate the O/M ratio. The usual approach in this type of method is to reduce a hyperstoichiometric oxide at a controlled temperature with hydrogen, carbon monoxide, or carbon and then measure the evolved water or carbon dioxide. This technique has been applied to analysis of uranium oxides[17] and uranium-plutonium oxides.[18]

Thermogravimetric methods are the most popular for determining O/M ratios, judging by the number of papers written. In these methods, the oxide is heated at a controlled temperature in a special atmosphere until the stoichiometric dioxide product is obtained. The O/M ratio is calculated from the change in sample weight. For samples containing only uranium oxide, the usual procedure is to oxidize the sample in air to U_3O_8[7,19-24] or to reduce the U_3O_8 to UO_2 in a hydrogen atmosphere[10,22,24-28] at 300 to 1300°C. A limited study of the reduction of plutonium oxide in hydrogen showed that it was not reduced at 750°C and only slightly reduced at 950°C, but considerably reduced at 1150°C.[10,21,22] Determination of O/M ratios using only the weight change when the sample is air-oxidized is not so reliable for the mixed oxide as for uranium alone because of the uncertain composition of the oxides produced.[16] Perhaps the most popular method for determining O/M ratios in mixed oxides has been to reduce the hyperstoichiometric dioxide to the stoichiometric dioxide and to calculate the O/M ratio from the change in sample weight. Generally, a carbon monoxide-carbon dioxide[29] or a partial hydrogen atmosphere[10, 16, 21, 22, 30-33] at 700 to 1200°C is used to reduce the oxide.

The thermogravimetric technique seemed the best approach for routinely determining O/M ratios in uranium-plutonium oxide fuels because of its relative simplicity, inexpensive equipment requirements, and adaptability for analysis in gloveboxes and by remote control. We investigated two sets of conditions recommended for production of the stoichiometric dioxide: (a) reduction of hyperstoichiometric dioxide using He-6% H_2 at 700°C,[16] and (b) reaction at 800°C with Ar-8% H_2 containing 4-mm pressure of water.[33] On the basis of this investigation, we chose a set of conditions in which the weighed oxide is oxidized in air and then reduced at 1000°C in dry He-6% H_2.

II. APPARATUS AND REAGENTS

A. Apparatus

Balance, analytical, Ainsworth Model BCT or equivalent

Boats, fused-silica, 120-mm-long by 19-mm-wide by 12-mm-deep

Drying tower, glass, containing anhydrous magnesium perchlorate

Flask, dewar, 1-liter, wide-mouth

Furnace, tube-type, 12-in.-long, 1.25-in.-diam, 750-W, Hevi Duty or equivalent

Induction heating unit, 2.5-kW, with related equipment

Pyrometer, 0 to 1000°C, with a Chromel-Alumel thermocouple

Timer, interval, 0- to 12-h

Tube, furnace, fused-silica, 500-mm-long, 28-mm-o.d., with a 29/26 standard-taper end cap to permit entry of sample boats

Variac, voltage-control, 10-A

Water bubbler, consisting of a "U" tube containing water submerged in ice in a dewar flask

B. Reagents

Argon, high-purity. (< 100 ppm of total impurities)

Ar - 8% H_2, high-purity. (< 100 ppm of total impurities)

Helium, high-purity. (< 100 ppm of total impurities)

Hydrogen, high-purity. (< 100 ppm of total impurities)

Ice

Plutonium metal, high-purity. (The total concentration of detected impurities was < 200 ppm in the metal used.)

Plutonium oxide, prepared by slowly oxidizing an accurately weighed sample of the metal in air at 150 to 200°C until the weight is constant, then heating to 800°C for 16 h. The composition of the oxide was obtained from the initial and final weights. Chemical analysis showed that this oxide contained < 5 ppm of nitrogen.

Uranium metal, high-purity. (The total concentration of detected impurities was < 200 ppm in the metal used.)

Uranium oxide, prepared by slowly oxidizing an accurately weighed sample of the metal in air by heating to 900°C over a 6-h period, then maintaining that temperature for 16 h. The composition of the oxide was obtained from the initial and final weights. Chemical analysis showed that this oxide contained < 5 ppm of nitrogen.

Uranium-Plutonium oxide mixture, prepared by mechanically mixing accurately weighed portions of three parts of uranium oxide to one part of plutonium oxide. The percentages of uranium and plutonium in this mixture were calculated using the weights of the original metals and the prepared oxides. Accurately weighed 5-g portions of this mixture were then used as standard uranium-plutonium oxide material having precisely known uranium and plutonium contents.

III. RECOMMENDED PROCEDURE

CAUTION: Health-safety rules for handling plutonium must be rigidly followed, and adequate protection for the operator must be ensured by use of suitable gloveboxes and protective clothing.

1. Dry and equilibrate a clean fused-silica boat by heating to 1000°C in air, then cool it to room temperature in a stream of dried argon.
2. Weigh the dried, equilibrated boat (W_B), add the sample, and reweigh the boat. Dry the sample by heating to 110°C in dry argon, cool, and weigh again (W_1).

3. Place the boat and sample in the tube furnace, and heat the sample to 1000°C with the end cap removed from the furnace tube to allow air to diffuse back over the sample.

4. After the furnace has reached 1000°C, replace the furnace-tube end cap, start the flow of dried He- 6% H_2 at 1 liter/min, and maintain the temperature and gas-flow rate for 6 h.

5. Cool the sample to room temperature in the reducing-gas atmosphere, and weigh the boat plus sample to obtain W_2.

6. Calculate the O/M ratio using

$$O/M = 2.000 - \frac{M}{16}\left(\frac{W_2 - W_1}{W_2 - W_B}\right),$$

where M = average molecular weight of the stoichiometric mixed oxide,
W_1 = initial weight of sample plus boat,
W_2 = final weight of sample plus boat,
and W_B = weight of boat.

7. Calibrate the method by determining the O/M ratio of the oxide produced when the uranium-plutonium oxide mixture is treated as described in Steps 1 - 5. The O/M ratio of the product should be 2.000 ± 0.002. If the result is significantly different, check the entire system and repeat the method calibration.

IV. EXPERIMENTAL

We investigated the oxide composition produced under two sets of conditions: reduction of a hyperstoichiometric dioxide using He - 6% H_2 at 700°C, and reaction at 800°C with Ar - 8% H_2 containing 4-mm pressure of water.

A. Reduction Using He - 6% H_2 at 700°C

In this method,[16] the weighed sample in a clean dry boat is slowly heated to 750°C over a 30- to 45-min period, in dried argon flowing at 5 cfh. The argon flow is stopped, and the end cap is removed from the furnace for 30 min to allow air to enter to oxidize the sample. The end cap is replaced, and the 5-cfh argon flow is started while the furnace temperature is held at 750°C for 30 min. The furnace temperature is then reduced to 700°C, a 5-cfh flow of He - 6% H_2 gas mixture is started, and this temperature and atmosphere are maintained for 9 h. The sample is cooled in the reducing atmosphere and then weighed. The O/M ratio is calculated from the initial and final weights using the formula given under RECOMMENDED PROCEDURE.

B. Reaction with Moist Ar - 8% H_2 at 800°C

In this method,[33] the weighed sample is placed in a clean boat that has been equilibrated by heating to 800°C in an Ar - 8% H_2 atmosphere that has been passed at 1 cfh over water at 0°C. The boat and sample are then heated under the same conditions for 6 h. The sample is cooled to room temperature and weighed. The O/M ratio is calculated using the formula given under RECOMMENDED PROCEDURE.

C. Testing of Methods

To establish a reliable point of reference, we used high-purity uranium and plutonium metals as starting materials in testing these methods. These metals, which contained < 200 ppm of detected impurities, were oxidized as described under Reagents. The manner in which the oxide, particularly the plutonium oxide, is formed is very important. Rapid oxidation of plutonium metal produces a hypostoichiometric plutonium dioxide cinder that is not oxidized to stoichiometric or hyperstoichiometric plutonium dioxide even at 1000°C in oxygen. This plutonium dioxide will remain hypostoichiometric throughout redox cycles of the thermogravimetric methods, and the O/M ratio of the product will be low. Uranium metal generally can be oxidized at a faster rate than plutonium, but one must be careful to avoid loss from too-rapid oxidation.

Each oxide contained more oxygen than required to produce a stoichiometric dioxide. The prepared oxides, individually and in mixtures, were treated as described in each method. The weights of these metals and oxides were accurately known, permitting the O/M ratios of the final oxides to be calculated reliably. Deviations of the product's O/M ratio from 2.000 were a measure of the error to be expected under the given set of conditions.

We reacted four 5-g portions of the prepared uranium oxide with each reducing-gas atmosphere. The O/M ratio of the product was high in each case, averaging 2.019 (Table I). We made six measurements, using the prepared plutonium oxide under each set of conditions used for reduction of the uranium oxide. The average O/M ratio of the product heated in He-6% H_2 was 2.010, and that of the product heated in moist Ar-8% H_2 was 2.016 (Table II).

TABLE I

O/M RATIOS OF URANIUM OXIDE PRODUCT
(5-g sample)

Atmosphere	Temp (°C)	Reaction Time (h)	O/M Ratio
He-6% H_2	700	9	2.019
			2.020
			2.018
			2.019
			Av. 2.019
Ar-8% H_2 (4 mm H_2O)	800	6	2.017
			2.021
			2.023
			2.015
			Av. 2.019

TABLE II

O/M RATIOS OF PLUTONIUM OXIDE PRODUCT
(5-g sample)

Atmosphere	Temp (°C)	Reaction Time (h)	O/M Ratio
He-6% H_2	700	9	2.013, 2.011
			2.007, 2.012
			2.010, 2.009
			Av. 2.010
Ar-8% H_2 (4 mm H_2O)	800	6	2.015, 2.017
			2.016, 2.016
			2.014, 2.017
			Av. 2.016

We made a mechanical mixture containing 80% uranium oxide and 20% plutonium oxide from the prepared oxides. The average O/M ratio for the product was 2.016 for 10 samples heated at 700°C in He-6% H_2 and 2.017 for 10 samples heated at 800°C in moist Ar-8% H_2 (Table III).

D. Effect of Temperature

We made a limited investigation of the effect of reduction temperature on the composition of the product oxide heated in He-6% H_2. Other parameters were kept constant, as described previously, and the temperature during sample reduction was varied between 700 and 1000°C. We used samples of the mixed oxide, and the O/M ratio decreased with increasing temperature (Fig. 1). A slight extrapolation of the plot shows that the stoichiometric dioxide would be obtained at approximately 1015°C under these conditions. This "optimum" temperature may differ at other locations where the atmospheric pressure is not about 590 mm Hg.

At 1000°C, the maximum continuous temperature of the furnace in use, the average of 17 determinations of the O/M ratio was 2.001_5 for oxides reduced in He-6% H_2. We then used the same temperature with the moist Ar-8% H_2 atmosphere.

TABLE III

O/M RATIOS OF URANIUM-PLUTONIUM OXIDE PRODUCT
(5-g sample)

Atmosphere	Temp (°C)	Reaction Time (h)	O/M Ratio
He-6% H_2	700	9	2.017, 2.018
			2.019, 2.016
			2.016, 2.019
			2.013, 2.010
			2.016, 2.016
			Av. 2.016 ± 0.003
Ar-8% H_2 (4 mm H_2O)	800	6	2.017, 2.018
			2.020, 2.022
			2.016, 2.017
			2.020, 2.019
			2.013, 2.012
			Av. 2.017 ± 0.003

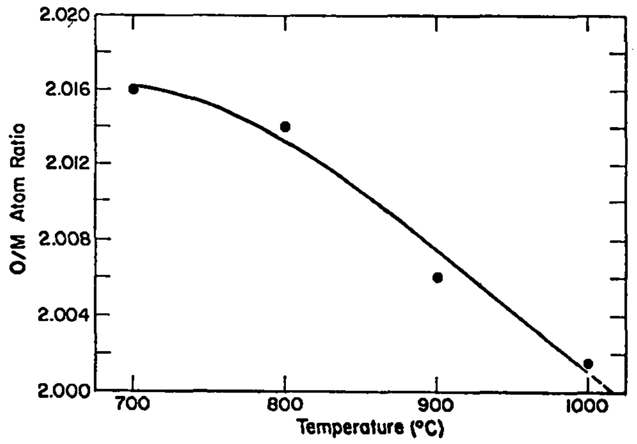

Fig. 1. Reduction of 80% uranium - 20% plutonium oxide by He - 6% H_2.

For 18 samples of the mixed oxide, the average O/M ratio was 2.007_9 (Table IV). These data indicate that the oxide formed in He-6% H_2 at 1000°C is very slightly hyperstoichiometric, but that the reduction in moist Ar-8% H_2 at 1000°C is significantly less effective.

In an effort to improve the results obtained using the moist Ar-8% H_2 atmosphere, we cooled the sample to room temperature in dry gas (< 1 ppm H_2O) after the 6-h reaction period. This lowered the O/M ratio of the product oxide to 2.006. Because of this improvement, we cooled all subsequent samples in dry gas. Next, we tried a higher temperature of 1250°C. The average of four determinations of O/M ratio on uranium oxide showed that values of 2.004, 2.002, and 2.000 were obtained using reaction times of 7, 15, and 20 h, respectively. When we used an approximately 3:1 uranium-to-plutonium ratio, the average O/M ratio obtained after 8 h at 1250°C was 2.003; after 16 h, 2.002; and after 24 h, 2.002, for 6, 5, and 3 determinations, respectively.

Because we got more accurate results sooner and at lower temperatures using the dry He-6% H_2 atmosphere at 1000°C, we did not continue investigation of the reduction in moist Ar - 8% H_2.

E. Effect of Oxidation Procedure and Reduction Time Using Dry He-6% H_2.

Previously, the sample was heated in argon to 750°C and then air was allowed to diffuse back over it to form a hyperstoichiometric dioxide.

TABLE IV

O/M RATIOS OF URANIUM-PLUTONIUM OXIDE PRODUCT
(5-g sample)

Atmosphere	Temp (°C)	Reaction Time (h)	O/M Ratio
He-6% H_2	1000	9	2.000, 2.000
			1.999, 2.003
			2.004, 2.001
			1.999, 2.002
			2.000, 2.001
			2.003, 2.001
			2.003, 2.001
			2.003, 2.001
			2.003, 2.003
			2.003
		Av.	$2.001_5 \pm 0.002$
Ar-8% H_2 (4 mm H_2O)	1000	6	2.012, 2.008
			2.011, 2.008
			2.009, 2.007
			2.010, 2.007
			2.006, 2.006
			2.006, 2.006
			2.008, 2.005
			2.007, 2.010
			2.008, 2.008
		Av.	$2.007_9 \pm 0.002$

Then the sample was cooled to 700°C in an argon atmosphere and reduced for 9 h in the He-6% H_2 atmosphere. Instead of heating the samples in an argon atmosphere, we left off the end cap of the furnace and heated them in air to 1000°C. Then the samples were reduced in He-6% H_2 for 2 to 6 h. Oxygen-to-metal atom ratios of 2.006, 2.002, 2.002, and 2.000 were obtained for 2-, 4-, 5-, and 6-h reducing periods, respectively.

To determine the relative rate of the reduction reaction as a function of time, we monitored the exhaust gas while a 4-g sample of uranium-plutonium oxide was reduced to the stoichiometric dioxide. Before the hydrogen was added, the gas contained < 1 ppm of water (Fig. 2). Less than 1 min after the hydrogen was added, the water content increased very rapidly to > 1000 ppm and remained there for over 11 min. After 12 min,

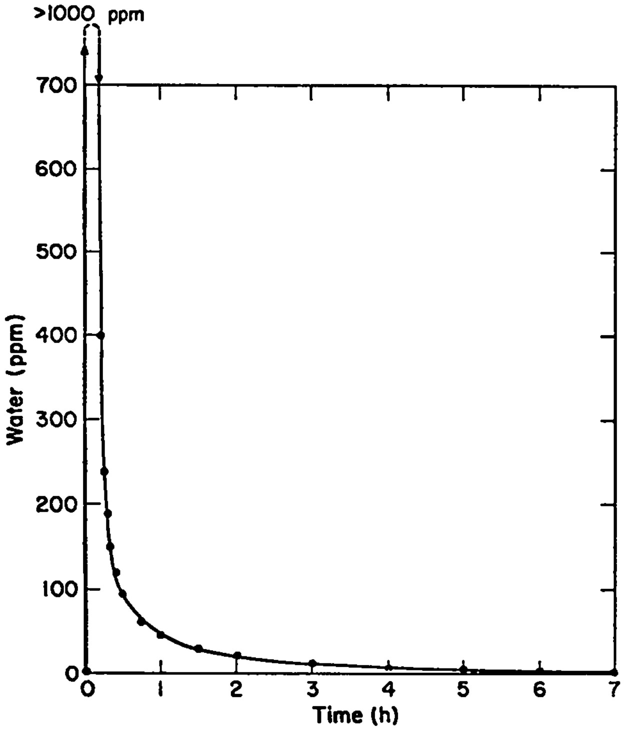

Fig. 2. Water content of the furnace exhaust gas during reduction of uranium-plutonium oxide by He-6% H_2.

the water content decreased swiftly to 400 ppm; after 13 min, to 240 ppm; and after 14 min, to 180 ppm. The water content of the gas then decreased at a slower rate so that after 1 h it was 46 ppm; after 3 h, 13 ppm; and after 7 h, 2 ppm. This shows that almost all of the reaction takes place during the first 15 min. The slowly decreasing rate thereafter may be due to small amounts of incompletely reacted sample that take longer to react quantitatively, or it could be due to slow recovery of the water-sensitive cell in the meter after exposure to large amounts of water.

F. Effect of Gas-Flow Rate and Gas Purification

When the He-6% H_2 gas-flow rate was reduced from 2 to 1 liter/min, we found no significant change in results. We also found no change in results when we passed the He-6% H_2 gas through uranium or copper metal turnings heated to 800°C in an attempt to remove any oxygen present. To determine further whether oxidants were present in the system, we heated uranium metal to 800°C for 2 h in the helium gas with no change in weight. We therefore concluded that no gas purification was needed.

We then checked this modified method by oxidizing 12 samples of the uranium-plutonium oxide standard material in air at 1000°C, then reducing for 6 h in a 1-liter/min reducing-gas flow. As shown in Table V, the average O/M ratio obtained was 2.001 ± 0.001.

G. Effects of Impurities

To determine the effects of impurities commonly found in reactor fuels, we prepared test samples from a mechanical mixture of unsintered, high-purity uranium and plutonium oxides, and also from finely ground, sintered uranium-plutonium oxide pellets. These materials were mechanically mixed with approximately 1000 ppm of various impurities. The mixtures were then treated as described under RECOMMENDED PROCEDURE. The effect of the impurity was determined by comparing the O/M ratio obtained when the impurity was present to that obtained when no impurity was added. We found that 375 to 2000 ppm of nickel, nickel oxide, iron, and aluminum oxide as the metal did not change the measured O/M ratio of either the sintered or unsintered oxides by more than 0.003 (Table VI), but calcium, calcium oxide, iron oxide, aluminum, and carbon, at metal or elemental concentrations of 400 to 1100 ppm, caused errors of 0.004 or more.

Combinations of aluminum, iron, chromium, nickel, silicon, and titanium and combinations of their oxides at a total metal concentration of 1000 ppm caused comparatively small changes, possibly because of some balancing of opposing effects of the individual elements.

TABLE V

O/M RATIOS OF URANIUM-PLUTONIUM OXIDE PRODUCT OBTAINED USING MODIFIED METHOD
(5-g sample)

Reaction Conditions		O/M Ratio
Oxidized at 1000°C, reduced in He-6% H_2 at 1000°C, for 6 h		2.001, 2.000
		2.001, 2.000
		2.003, 2.002
		2.002, 1.999
		2.000, 2.003
		2.001, 2.002
	Av.	2.001 ± 0.001

TABLE VI

EFFECTS OF SELECTED IMPURITIES ON THE THERMOGRAVIMETRIC DETERMINATION OF O/M RATIO

Element	Form	Concentration[a]		Effect on O/M Ratio[b]	
		Unsintered	Sintered	Unsintered	Sintered
Ca	metal	1027	1107	- 0.006	- 0.005
	CaO	420	572	+ 0.004	+ 0.006
Ni	metal	1048	2000	- 0.003	- 0.003
	Ni_2O_3	533	888	+ 0.003	- 0.002
Fe	metal	967	774	- 0.003	0.000
	Fe_2O_3	593	617	+ 0.004	+ 0.006
Al	metal	997	1036	- 0.026	- 0.025
	Al_2O_3	376	567	0.000	- 0.001
C	elemental	964	856	+ 0.013	+ 0.014
Na, S	Na_2SO_4	700	[c]	+ 0.094	- - -
Al, Cr, Fe	metal	300 to 600 ppm each		- 0.009 to - 0.032	- 0.006
Ni, Si, Ti	oxides	50 to 150 ppm each		+ 0.003 to - 0.001	+ 0.005 to + 0.008

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[a] Metal in compound or oxide, ppm.

[b] Average of duplicate determinations.

[c] Na_2SO_4 corroded fused-silica materials and was not reanalyzed using sintered oxide.

We added sodium sulfate as an impurity to try to determine the combined effects of sodium and sulfate on the O/M-ratio determination. The effect is large and due mainly to a reaction with the fused-silica sample boat. In general, these impurity effects agree with some calculated effects.[29]

The < 200 ppm of detected impurities contained in the original uranium and plutonium metals are such that some would cause the O/M ratio to be high and others would cause it to be low. A calculation of the collective effects of the individual detected impurities showed that their net effect would be negligible.

The problem of impurities becomes especially important as fission products grow into the irradiated fuels. If the net effect is increased oxygen potential, the fuel may become more reactive or corrosive. The reliabilities of methods for measuring O/M ratios in fuels following significant burnup are not known, but recent studies showing nonuniformity in fission-product distributions indicate that O/M ratios vary as a function of position.[34]

One further difficulty related to impurities is the incapability of analytical methods to differentiate reliably the oxygen combined with the uranium or plutonium from that combined with the impurities. Therefore, when many impurities are present, the O/M ratio obtained is not that of the fuel, but that of the fuel-impurity mixture. The actual O/M ratio of the fuel could be very different.

V. PREPARATION OF A REFERENCE MIXED OXIDE

Analysis of a well-characterized oxide reference material sintered and otherwise treated like a fuel sample would be an ideal way to determine the reliability of an analytical method for determining O/M ratios. However, no suitable reference material is known. One alternative, used in this work, is to make a mixture from oxides prepared by careful oxidation of pure uranium and plutonium metals. However, one possible drawback of this oxide mixture is its possible difference in behavior during analysis from that of the sintered oxide fuel. The oxide mixtures we used were not heated to the sintering temperatures used in preparing fuel pellets because of the possibility of changing the O/M ratio. Possible contamination of the oxide, reaction between the oxide and the containment vessel, or loss of sample during high-temperature sintering would cause O/M-ratio changes that could not be reliably calculated from the oxide weight. If these problems in preparation of a sintered reference material could be overcome and a sintered mixed oxide standard having an accurately known O/M ratio could be prepared, that standard would be preferred in testing methods for determining O/M ratios.

VI. FUEL INHOMOGENEITY

Variations in O/M ratios may exist originally along the axis or radius of an unirradiated fuel pellet, and they are expected after significant burnup which has been shown to cause fuel and fission-product migration.[34, 35] Analysis of a complete fuel pellet gives an average O/M ratio that may differ from that of the fuel near the pellet surface in contact with the containment vessel or at other locations on the fuel cross section. From the standpoint of reactivity with the cladding, the O/M ratio at the pellet surface is more informative than an average value. To obtain this ratio, the sampling problem must be solved. The capability may already exist to obtain a small, accurately pinpointed sample by microcoring or drilling. Alternatively, a small lathe might be used to obtain a thin surface sample. Sampling must be done in an inert atmosphere under conditions that protect the sample from oxidation or reduction. In addition, sample contamination by the cutting devices must be avoided.

An even greater problem is reliable remote measurement of O/M ratios of small irradiated samples. In the thermogravimetric analysis of a 5-mg sample, a weighing error of 1 μg would change the O/M ratio by 0.003. Such small weighing errors will be difficult to obtain under remote conditions.

One further question about fuel homogeneity can be raised. What actually happens to the fuel when it is removed from the reactor and thermally cooled? Is the fuel or oxygen distribution changed by the cooling and, if so, what might be done to "hold" the fuel in conditions like those found in the reactor until the fuel can be analyzed? This is a problem common to all analyses of reactor fuel, and no answers are available at this time.

VII. DATA INTERPRETATION

One further problem in determination of O/M ratios is that of interpreting the data obtained by various methods. For example, we used three methods to determine O/M ratios of uranium-plutonium oxide samples. Two were the thermogravimetric methods described previously but run at 1000°C, and the third consisted of determination of oxygen by inert-gas fusion,[1] coulometric determination of uranium and plutonium,[2] and calculation of the O/M ratio from these results. As shown in Table VII, the results agree very well in some cases, but not in others. The reasons for these differences are unknown, and the question arises as to which data are correct. We calibrated each method by analyzing "standards" along with the samples. The variance in results shows that sintered samples may act differently from the calibration standards. Therefore, a better way of making a standard reference material may need to be developed. Note that there is little difference in results (0.003 and 0.001) obtained using the two thermogravimetric methods for the sintered samples, whereas there is a difference of 0.006 (Table IV) for the mixed uranium-plutonium oxide reference material. This could possibly be an effect of differences in surface area of the two materials, or, as stated previously, the sintered samples may act differently from the unsintered oxide mixture. Recently published data[36] indicate that this may be true.

VIII. SAMPLE HANDLING

The handling of samples before analysis also presents a problem. Some hypostoichiometric dioxides seem very active, gaining weight rapidly when exposed to air. Drying these samples produces no weight loss so we assume that the weight gain is due to oxidation. Therefore, it may be necessary to protect hypostoichiometric dioxide fuels in an inert atmosphere at all times before analysis for O/M ratios.

ACKNOWLEDGMENT

We thank C. F. Metz, under whose supervision this work was done, and the uranium- and plutonium-metal fabrication groups for the high-purity uranium and plutonium metals used in this work.

TABLE VII

OXYGEN-TO-METAL RATIOS OBTAINED BY THREE METHODS

Sample	Thermogravimetric Methods		Determination of U, Pu, and O
	He-6% H_2	Moist Ar-8% H_2	
A	1.999	-	1.993
B	1.962	-	1.993
C	1.997	2.000	1.993
D	1.990	1.991	1.968

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