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MACRODETERMINATION OF OXYGEN IN URANIUM DIOXIDE COMPOSITES BY INERT-GAS FUSION

by

Harvey T. Goodspeed and Dewitt Pettis

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Chemistry Division

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ABSTRACT

This report describes an inert-gas fusion method for the macrodetermination of oxygen in uranium dioxide composites. Sample sizes ranged around 300 mg. About 100 mg of CO_2 produced by the procedure was collected in absorption-weighting tubes and measured on a standard analytical balance. As an initial check on the method, it has been applied with success to oxygen determinations for various standard materials other than UO_2 composites. When applied to uranium dioxide composites, the method gives results that again appear to be completely satisfactory when temperature is taken to be the critical factor and therefore controlled.

Average recoveries of 99.9 and 100.1% of the theoretical oxygen content were obtained in the analysis of U_3O_8 and UO_2 standards, with standard deviations from the means of about 0.3%. The same degree of precision was obtained in the oxygen analysis of known samples of W- UO_2 composites. Results obtained in the oxygen analyses of composites of UO_2 and other metal oxides are presented in tabular form.

INTRODUCTION

Two methods in current use for the direct determination of oxygen in oxides are the bromine trifluoride method, with its various modifications,¹⁻³ and the inert-gas fusion method.⁴

In every version of the procedure used for the determination of oxygen in metal oxides by inert-gas fusion, the temperature was initially held for a time at a given precalibrated setting⁴ and then raised in two steps.

By a later approach to the procedure, the initial temperature and the time the crucible was kept at this temperature were governed by the ratio of the uranium dioxide to the composite material.

This report describes the procedure used and the results obtained in the determination of oxygen in composites of UO_2 and other metal oxides.

PROCEDURE

The procedure described here is basically the same as that in Ref. 4, the major change being in temperature control. In this report, the power to the induction heating coil was set so that the temperature of the crucible lid (shown in the upper part of Fig. 1) was raised to a point which, by a previous calibration, corresponds to a temperature of about 1650°C inside the crucible. The procedure is as follows:

120-7099

Fig. 1. Cross Section of Carbon Crucible and Lid

1650°C) will vary with each oxide sample depending upon the ratio of UO_2 to the composite material.

4. Increase the input power to raise the temperature of the lid about 150°C , and maintain this level for 10 min.

1. Manipulate the stopcocks to direct a flow of argon gas of about 150 cc/min through the reaction tube, the CuO furnace, the desiccating tube, the weighing tube, and the manometric train,⁵ which is operated in series with the gravimetric train as a precaution against incomplete removal of CO_2 in the weighing tube. Throttle the gas flow at the inlet stopcock of the capillary manometer. Figure 2 shows the relationship of the components involved in this step.

2. Apply power to the induction heater to raise the temperature of the crucible lid, watching closely for the appearance of smoke from the crucible. Then immediately decrease the input power until the smoking diminishes almost to extinction.

3. Maintain this power and temperature level for 15 min. The initial temperature inside the crucible (1550 to

5. Finally, boost the power to produce a temperature of about 2000°C inside the crucible, and hold this level for 5 min.

6. Disconnect and weigh the weighing tube, using the technique described in Ref. 4.

7. From the total amount of CO_2 measured, deduct the prevailing blank (usually about 0.3 mg) obtained by proceeding through steps 1-6 above, using an empty platinum capsule for the sample.

120-7100 Rev. 1

Fig. 2. Schematic Diagram of Manometric and Gravimetric Trains

RESULTS

During the investigation, more and more effort was devoted toward operation at the minimum temperature effective in the reduction of a given oxide within a 15-min period. As might be expected, this minimum varied from one oxide to another, being slightly lower for tungsten- UO_2 than for U_3O_8 . The oxide samples that produced more than 150 mg of CO_2 frequently smoked when the temperature was increased after the 15-min initial temperature period. These phenomena were usually accompanied by low results. When smoke appears during the reduction reaction, it may be assumed that CO is being released too rapidly and that some of the oxide dust particles are being carried away by entrainment.⁴ With these precautions in mind, some UO_2 composites were analyzed. Tables I-VII illustrate the precision obtained for oxygen analysis by following this procedure.

TABLE I. Recovery Data on U_3O_8 (NBS Sample 950a)

Oxygen Content, %	Recovery, %	Oxygen Content, %	Recovery, %
15.20	100.0	15.18	99.9
15.21	100.1	15.19	99.9
15.28	100.5	15.25	100.3
15.16	99.7	15.18	99.9
15.23	100.2		
Av. 100.1			
Std. Dev. ± 0.3			

TABLE II. Percentage of Oxygen in UO_2

Sample	Method of Analysis		Deviation from Mean
	Oxidation to U_3O_8	Macro Inert-gas Fusion	
Oxide No. 1	12.37 ^a	12.38	+0.02
	12.32 ^a	12.32	-0.04
		12.39	+0.03
		12.33	-0.03
		12.34	-0.02
		12.37	+0.01
		12.36	± 0.00
		Av. 12.36	Std. Dev. ± 0.03
Oxide No. 2			Rel. Std. Dev. $\pm 0.2\%$
	11.85 ^b	11.85	+0.01
		11.84	± 0.00
		11.82	-0.02
		Av. 11.84	Std. Dev. ± 0.02
			Rel. Std. Dev. $\pm 0.2\%$

^aBy ANL Chemical Engineering Division.^bBy ANL Chemistry Division.

TABLE III. Recovery Data Obtained on Tungsten- UO_2 Composites.

Sample ($\text{W}^a + \text{UO}_2^b$)	Oxygen Content, %		Recovery, %
	Calculated	Macro Inert-gas Fusion	
No. 1	8.70	8.67	99.7
No. 2	10.21	10.22	100.1
No. 3	9.39	9.38	99.9
No. 4	9.10	9.11	100.1
No. 5	10.89	10.88	99.9
No. 6	9.62	9.60	99.8
			Av. 99.9
			Std. Dev. ± 0.2

^a0.28% oxygen (inert-gas fusion method).^b11.85% oxygen (oxidation to U_3O_8 and inert-gas fusion methods).TABLE IV. Analysis of
Thorium Oxide-Uranium
Oxide Composites

Sample	Oxygen, %	Difference between Duplicates, %
No. 1	11.81 11.80	0.01
No. 2	11.91 11.80	0.11
No. 3	11.91 11.88	0.03
No. 4	11.69 11.70	0.01
No. 5	11.83 11.78	0.05
Av. Diff.		0.04
Rel. Std. Diff.		0.5%

TABLE V. Analysis of
 ZrO_2 - UO_2 Composites

Sample	Oxygen, %	Difference between Duplicates, %
ZrO ₂ (5 m/o) + } UO ₂ (95 m/o) }	12.15 12.19	0.04
ZrO ₂ (10 m/o) + } UO ₂ (90 m/o) }	12.55 12.52	0.03
ZrO ₂ (5 m/o) + } UO ₂ (95 m/o) }	12.09 12.12	0.03
ZrO ₂ (10 m/o) + } UO ₂ (90 m/o) }	12.30 12.25	0.05
Av. Diff.		0.04
Rel. Std. Diff.		0.3%

TABLE VI. Analysis of Rare-earth Oxides- UO_2 Composites

Sample	Oxygen, %	Difference between Duplicates, %
$\text{SmO}_2 + \text{UO}_2$	12.30 12.24	0.06
$\text{SmO}_2 + \text{UO}_2$	12.09 12.16	0.07
$\text{Eu}_2\text{O}_3 + \text{UO}_2$	12.01 12.01	0.00
$\text{Eu}_2\text{O}_3 + \text{UO}_2$	12.05 12.05	0.00
$\text{Gd}_2\text{O}_3 + \text{UO}_2$	12.09 12.06	0.03
$\text{Gd}_2\text{O}_3 + \text{UO}_2$	12.21 12.27	0.06
$\text{Gd}_2\text{O}_3 + \text{UO}_2$	11.90 11.77	0.13
$\text{Gd}_2\text{O}_3 + \text{UO}_2$	12.08 12.06	0.02
$\text{Gd}_2\text{O}_3 + \text{UO}_2$	11.86 11.84	0.02
$\text{Gd}_2\text{O}_3 + \text{UO}_2$	12.29 12.30	0.01
Av. Diff. 0.04 Rel. Std. Diff. 0.5%		

TABLE VII. Analysis of Al_2O_3 - UO_2 Composites

Sample	Oxygen, %	Difference between Duplicates, %
No. 1	12.23 12.28	0.05
No. 2	12.34 12.14	0.20
No. 3	12.61 12.43	0.18
No. 4	11.93 11.86	0.07
No. 5	11.85 11.83	0.02
No. 6	12.55 12.74	0.19
No. 7	12.00 12.05	0.05
No. 8	12.44 12.54	0.10
Av. Diff. 0.11 Rel. Std. Diff. 1.1%		

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