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AEC RESEARCH AND DEVELOPMENT REPORT

PRECISE DETERMINATION OF OXYGEN IN REFRACTORY OXIDES BY INERT GAS FUSION - GAS CHROMATOGRAPHY

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PRECISE DETERMINATION OF OXYGEN IN REFRACTORY OXIDES BY INERT GAS FUSION - GAS CHROMATOGRAPHY

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ABSTRACT

A commercial instrument employing inert gas fusion-gas chromatography has been modified to quantitatively determine the oxygen content of actinide oxides and other refractory oxides. The instrument gives a relative precision of 0.4% for samples containing 0.5 to 7.0 mg of oxygen.

The method requires 12 minutes per determination, permits flexibility in the choice of sample size, and requires only a single daily analysis to ensure that the calibration curve is satisfactory.

CONTENTS

INTRODUCTION

Studies of the oxides of curium at the Savannah River Laboratory require a direct oxygen analysis precise to at least 1%.

The "LECO"* Nitrox-6 Analyzer was selected to analyze curium oxide and other refractory oxides containing 0.5 to 7.0 mg of oxygen. This inert gas fusion-gas chromatography analyzer has been used by Coyle and Gannon(1) to determine oxygen in columbium and tantalum. MacDonell, Prosman, and Williams(2) have used an inert gas fusion method to analyze glasses, refractories, and refractory oxides containing 55% oxygen with a relative precision of ±2%. Their work cites references to other applications of inert gas fusion for analysis of metals and alloys with a low oxygen content.

This paper describes the use of the "LECO" Nitrox-6 Analyzer, which was modified to analyze highly α-active material, and to improve the relative precision from 3.4%(3) to 0.37% for samples containing 1 mg of oxygen and 0.39% for 7 mg of oxygen. With this instrument, one operator can analyze a sample in 12 minutes, and only a single daily standard analysis is required to ensure that the equipment, method, and calibration curve are satisfactory.

ANALYSIS OF SAMPLE

To determine the total oxygen content of an oxide, a sample is dissolved in molten platinum contained in a graphite crucible heated inductively to 2250°C. The oxygen is then quantitatively reduced to carbon monoxide. An inert carrier gas transfers the carbon monoxide and all other evolved gases through a glass wool filter and a porous stainless steel filter, and to a cold trap where they are stored until gas evolution is complete. All gases are then eluted from the trap, separated by gas chromatography, and passed through a thermal conductivity detector. The electrical output of the detector is integrated to give only the carbon monoxide content. By comparing the integrator output, which is in counts, to a previously prepared calibration curve, the oxygen content of the original sample can be found.

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* Trademark of Laboratory Equipment Corporation, St. Joseph, Michigan.

APPARATUS

A "LECO" Nitrox-6 Analyzer, modified to analyze α-active material, is used.(3) In the modified analyzer, the furnace section was removed from the RF generator and mounted in a glove box (Figure 1). A filter was added in the gas line between the fusion furnace and gas chromatograph to improve the precision;

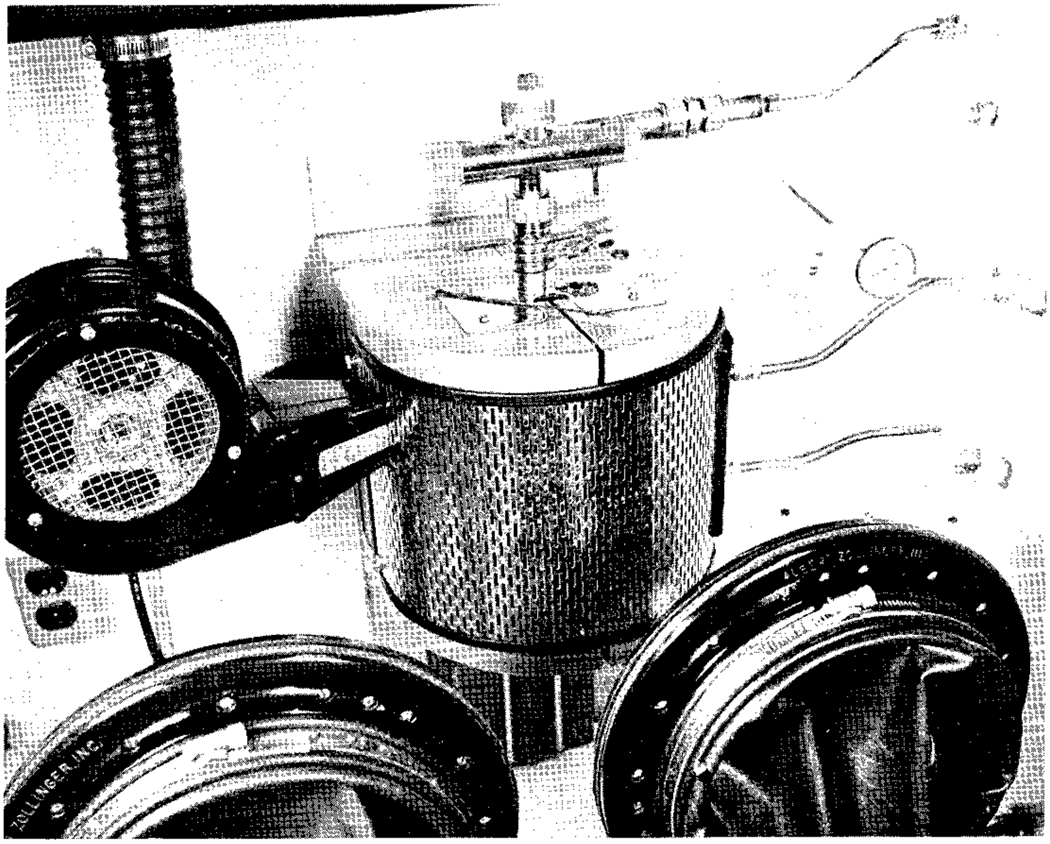

FIG. 1 GLOVED BOX LAYOUT FOR INDUCTION FURNACE

another filter was added as a safety factor for containment. Helium carries the furnace-evolved gases through the filters to the gas chromatographic unit of the Nitrox-6 Analyzer located outside the golve box (Figure 2).

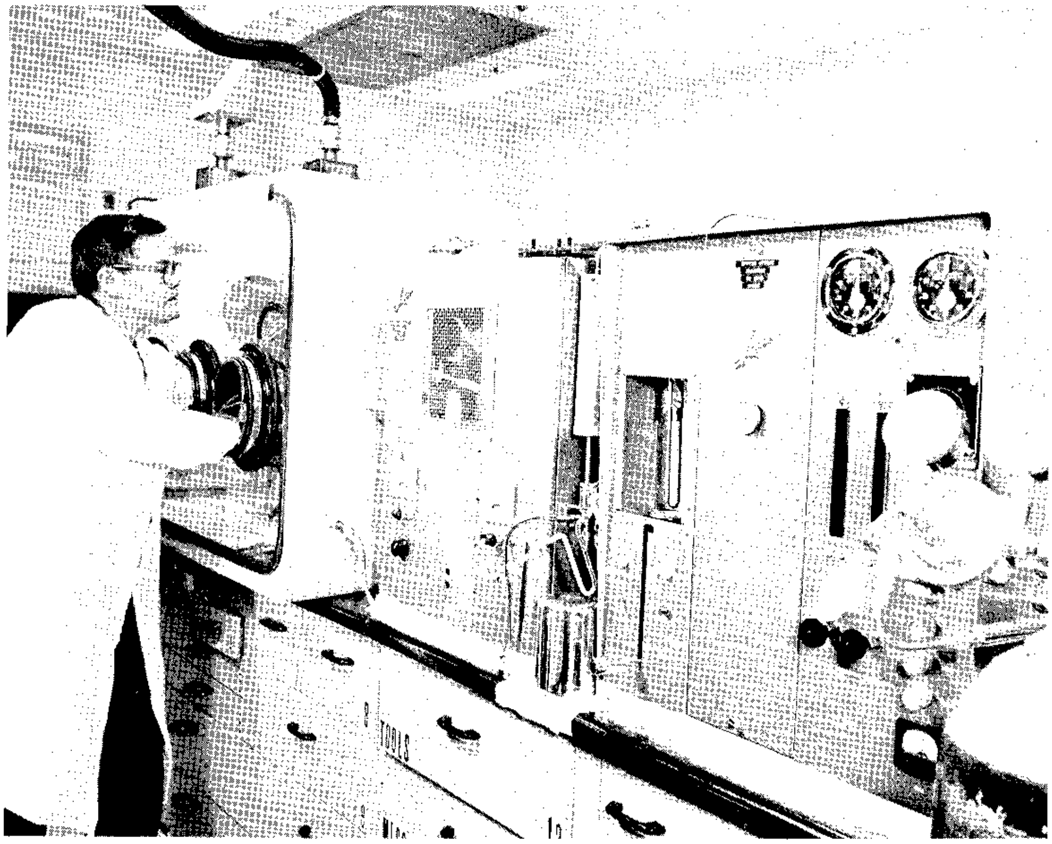

FIG. 2 EQUIPMENT ARRANGEMENT FOR O_2 ANALYSIS IN CURIUM OXIDE

CALIBRATION

Uranium oxide (U_3O_8) from the National Bureau of Standards was used to prepare a calibration curve and to determine the precision. The data obtained for a typical calibration is shown in Table I.

Table I
U_3O_8 Calibration Data

Theoretical Oxygen, mg	Instrument Response, counts	Calculated Oxygen, mg
0.502	125	0.507
0.528	130	0.526
0.833	211	0.830
1.036	265	1.033
1.102	284	1.105

The calculated oxygen values were obtained from the equation of the straight line as determined by least squares fit to the theoretical oxygen vs. counts data points. The standard deviation is ±0.0037 mg, corresponding to a relative standard deviaof 0.37%, for 1 mg of oxygen. Further calibration data have given a standard deviation of ±0.027 mg, corresponding to a relative standard deviation of 0.39%, for 7 mg of oxygen.

EVALUATION

To confirm the quantitative removal of oxygen from U_3O_8, spectrographically pure thorium oxide (ThO_2) and lanthanum oxide (La_2O_3) were analyzed. These results are summarized in Table II.

Table II

Oxygen Analysis of Thorium and Lanthanum Oxide

Sample	Theoretical Oxygen, mg	Measured Oxygen, mg	% Recovery
ThO_2	1.217	1.213	99.7
ThO_2	0.748	0.749	100.1
ThO_2	0.743	0.749	100.8
La_2O_3	0.772	0.779	100.9
La_2O_3	0.783	0.786	100.4
La_2O_3	1.116	1.117	100.1

The average percent recovery of oxygen from ThO_2 was 100.2 and that from La_2O_3 was 100.5.

As a further test of the general applicability of the method, samples of oxides of neptunium, plutonium, niobium, platinum, and chromium were analyzed. Reproducibility of data was satisfactory. In addition, an organic standard, NBS cystine, was analyzed successfully.

ANALYSIS OF CURIUM OXIDE

Six samples of curium oxide were analyzed. These results are summarized in Table III.

Table III

Oxygen Analysis of Curium Oxide

Sample	Nominal Formula	Oxygen Found, %
1	CmO_2	15.15, 15.28
2		12.09
3	Cm_2O_3	10.34, 10.30
4		11.09, 11.10
5		9.38, 9.41
6		8.92, 8.99

Sample 2, which approaches the expected composition CmO_2 (11.59% oxygen), was prepared by calcination of curium oxalate followed by further heating in a reducing atmosphere; Sample 5, which approaches the expected composition Cm_2O_3 (8.96% oxygen), was prepared by cycling calcined curium oxalate several times between room temperature and 1200°C; Sample 6, prepared similarly to Sample 5, contained the theoretical amount of oxygen. Emission spectrographic analysis of the sample revealed no significant level of metallic impurities that might be present as oxides.

REFERENCES

1. F. T. Coyle and W. C. Gannon. "Oxygen and Nitrogen Determination in Columbium and Tantalum by Inert Gas Fusion Employing Chromatographic Detection." 8th Conference on Analytical Chemistry in Nuclear Technology, Gatlinburg, Tenn., October 6-8, 1964.
2. H. L. MacDonell, R. J. Prosman, and J. P. Williams. Anal. Chem. 35, 579 (1963).
3. LECO Nitrox-6 Nitrogen Analyzer, Form 1102B, Laboratory Equipment Corporation, St. Joseph, Michigan.