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Macro Determination of Oxygen in Metal Oxides by Inert Gas Fusion

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ABSTRACT

The inert gas fusion method was extended to the direct determination of oxygen in metal oxides on a milligram scale to take advantage of increased precision in measurement data. Sample sizes, depending on the molecular weights of the oxides, ranged from 50 to 200 mg. About 100 mg of CO_2, produced by the procedure, was collected in absorption weighing tubes and measured on a standard analytical balance. In the analysis of pure oxides (Fe_2O_3, SiO_2, Al_2O_3, Cr_2O_3, UO_2, Ta_2O_3, and TiO_2) average recoveries of 99 to 100% of the theoretical oxygen content were obtained, with standard deviations from the means of about 0.5%. The same degree of precision was obtained in the analysis of standard samples of refractory oxide mixtures, glass, and silica brick. The temperature of the covered graphite crucible was controlled to prevent the loss of sample by entrainment during the carbon-reduction of the oxides.

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by Inert Gas Fusion

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As experimental work expands in scientific fields
involving refractory nuclear fuels, ceramics, meteorites,
rocks, and other solid substances containing mixtures
of metal oxides, the need increases for a precise method
by which the oxygen content may be measured directly
rather than by difference. Preferably the method should
be applicable in a macro range, so that the sample size
might be large enough to favor homogeneous sampling of
heterogeneous materials, and that the measurement data
might contain enough significant figures to afford good
precision in the calculated results.

Two methods in current use for the direct determination
of oxygen in oxides are the bromine trifluoride method
with its various modifications (1-4,8), and the inert gas
fusion method. A recent paper by MacDonell, Prosman, and
Williams (6), in which they cited a number of references
to published applications of the inert gas fusion method

to low concentrations of oxygen in metals and alloys,
describes their work in determining oxygen in glasses,
refractories, and refractory oxides. These authors con-
fined their investigation to a sample-size range of 2 to
10 mg., using conductimetric equipment for measurement
of the CO_2 produced by the procedure.

This paper describes the extension of the inert
gas fusion method toward the macro range. Sample sizes,
depending on the molecular weights of the oxides, ranged
from 50 to 200 mg. The quantity of CO_2 produced by the
procedure was about 100 mg. It was collected in weighing
tubes and measured on a standard analytical balance.

Most of our investigations were confined to the
analysis of oxides found in stony meteorites, as Fe_2O_3,
SiO_2, Al_2O_3, Cr_2O_3, MgO and CaO. Other analyzed oxides
have included UO_2, Ta_2O_5, and TiO_2. MgO and CaO were
the only oxides tested that gave considerable difficulty.
Although our own experience (5) as well as that of
MacDonell, Prosman, and Williams (6), has shown that
acceptable results for oxygen can be obtained on MgO when
the sample is quite small, we were unsuccessful in the
analyses of 100 mg. quantities of MgO and CaO by the
method, as applied to the other oxides.

The chief modifications made to the inert gas fusion
procedure, as it is usually applied to micro quantities

of oxygen in metals, were the control of the rate of
formation of CO in the graphite crucible, the oxidation
of CO to CO_2 by hot copper oxide rather than by rapidly-
depleted iodine-pentoxide oxidizers, and the gravimetric
(rather than manometric or conductometric) measurements
of the CO_2.

EXPERIMENTAL

Apparatus. As illustrated in Figure 1, the analytical
train consisted of a source of pure inert gas (helium or
argon), a water-cooled fused-silica furnace tube contain-
ing a covered graphite crucible inductively heated by a
10-kw. generator, a combined dust and cold trap, a copper
oxide furnace, a desiccating tube, a weighing tube, and
an exhaust bubbler. As a convenient accessory, a mano-
metric train (also shown in Figure 1) was attached, to be
operated either in series with or in place of the gravi-
metric train. It consisted of a Schutze reagent (10)
tube, a capillary trap manometer, and a vacuum line.

Although argon was used as the carrier gas for most
of the analyses, helium was substituted when it was
necessary to remove interfering gaseous impurities from
the gas stream by immersing the dust trap in liquid
nitrogen. This was necessary for oxide mixtures containing
sulfides or phosphides.

The fused silica furnace tube has been described previously (5). The tantalum tube and fused silica shield included in the earlier description were omitted in this procedure. For convenience, a longer tungsten rod was installed for supporting the crucible at about the mid-section of the furnace tube.

Figure 2 illustrates the crucible and lid. Sixteen holes, 1/16-inch in diameter and equally spaced, were drilled radially into the side of the lid as shown. To facilitate easy assembly and disassembly, the lid was made to fit loosely in the crucible and its lower edges were slightly rounded. The crucible and lid were fabricated from a 3/4-inch diameter extruded graphite rod, grade AUC, supplied by the National Carbon Co., N. Y. Suitable tongs were fabricated for reaching in from the top of the furnace tube to remove the crucible and lid.

The dust trap following the furnace tube was constructed of a 2 mm. 4-way stopcock (for by-passing when necessary), an enlarged section (18 mm. o.d.) containing a glass wool dust filter, and standard taper joints to facilitate cleaning. The U-tube section was 12 inches long and 2 inches in over-all width. This trap served to remove metal dust produced in the reduction reaction. When metal oxide-sulfide or metal oxide-phosphide mixtures were analyzed, the trap was immersed in liquid nitrogen

for the removal of gaseous impurities such as CS and CS_2, which otherwise would interfere in the measurement of CO. (Quantitative recoveries of oxygen in known mixtures of FeS and Fe_2O_3 indicated that there was no loss of oxygen as oxides of sulfur under the conditions of the procedure.)

The silica tube (3 cm. o.d. x 25 cm. long) containing wire-form CuO was maintained at 450° C. Oxygen was introduced via the 3-way stopcock at the entrance of the tube for reoxidation of reduced copper.

The CO_2 weighing tube (Schwartz absorption type, with ball and socket side tubes), manufactured by Corning Glass Works #98250, was filled to 3/4 its volume with Ascarite, followed by 1/4 volume of Anhydrone. Glass wool plugs were inserted at each end, and glass wool or exploded mica was interspersed with the Ascarite to minimize clogging of gas flow after several hundred milligrams of CO_2 had been absorbed. It was attached to a by-passing 4-way stopcock by ball-joint linkages for convenient installation and support. The ball joints touching the weighing tube contained no grease. The tube was preceded by an identical one filled with Drierite and Anhydrone, and was followed by an exhaust bubbler by which the rate of gas flow was monitored.

The components of the manometric train shown in the diagram are modified units of equipment described earlier by Smiley (9).

Platinum capsules, into which oxide samples were weighed before dropping into the crucible, were 0.344 inch in length and were made from 0.180-inch o.d. tubing, 0.005 inch in wall thickness. One end of each capsule was closed by a metal-spinning process. After weighing in the sample, the other end was closed by crimping with pliers.

The output power of a 10-kw. induction heating generator, manufactured by Induction Heating Corp., N. Y., controlled by a Variac transformer on the 220 volt, single-phase circuit, feeding the primary coils of the input transformer. The power was continuously variable in a range sufficient to produce crucible temperatures of 600 to 2100° C.

Procedure. Place a crucible and lid, which have been previously baked out for 5 minutes at 2000° C. in an inert atmosphere, on a tungsten wire support in the furnace tube and add 7 grams of platinum. Heat for 10 minutes at about 2000° C. with inert gas flowing through the train and out the bubbler, but by-passing the weighing tube. Heat an additional 10 minutes with the gas stream flowing through the weighing tube. Disconnect and weigh the weighing tube, using established techniques common to gravimetric carbon analysis.

Remove the optical-window cap on the furnace tube

and, with inert gas flowing out, reach in with appropriate tongs and remove the crucible. Replace the cap on the furnace tube and set the crucible in an appropriately designed glass holder, placed on a clean sheet of aluminum foil on the laboratory bench. Lift the crucible lid; introduce a weighed sample, contained in a platinum capsule; and then return the closed crucible to the tungsten support in the furnace tube. Locate the supporting member of a viewing mirror (for optical pyrometer readings) over the furnace tube cap in such a way as to hold it down securely during the subsequent procedure.

Manipulate the stopcocks to direct a stream of about 150 cc./minute through the reaction tube, dust trap, CuO furnace, desiccating tube, weighing tube, and bubbler. Or, instead of using the bubbler, the manometric train may be operated in series with the gravimetric train, as a precaution against incomplete removal of CO_2 in the weighing tube. In this case, the gas flow should be throttled at the inlet stopcock of the capillary manometer.

Cautiously, increase the power to the induction heating coil until the temperature of the crucible lid is raised to a point which by previous calibration corresponds to a temperature inside the crucible of about 1770° C. (melting point of platinum). (The calibration

is conveniently made by temporarily using a lid with a vertical, 52-mil. peep hole drilled in it. Simultaneous readings can be made of the inside temperature and of the lid temperature for various settings of the Variac that controls the input voltage to the induction heater.) If, before such a temperature is reached, smoke is seen to be evolved from the crucible, immediately decrease the input power until the smoking is diminished almost to extinction. Hold at this setting for 20 minutes. Raise the temperature of the lid about 100° C. and hold for 5 minutes. Finally boost the power such as to produce a temperature of about 2000° C. inside the crucible, and hold for 5 minutes. Shut off the power to the work coil and turn off the cooling water to the furnace tube. (This is to ensure that the inside walls will be warm when the furnace tube is subsequently opened for the addition of the next sample.) Allow the line to flush 5 minutes before removal of the weighing tube.

Wipe the weighing tube, first with a damp cloth and then with chamois leather. Remove static charge on the tube by exposing it to a Tesla spark coil. Let it hang in the open air for 10 minutes before weighing. From the total amount of CO_2 that is measured, deduct the prevailing blank (usually about 0.3 mg.) that is obtained by proceding through all the steps of the analysis, using an

empty platinum capsule for the sample.

RESULTS

It was necessary to adjust and control the crucible temperature more precisely in the determination of milligram amounts of oxygen than is normally required for microgram quantities by the inert gas fusion method. To illustrate the need for the control of the rate at which CO is produced inside the crucible, it may be pointed out that an oxide sample of sufficient size to produce the conveniently weighable quantity of 100 mg. of CO_2 is converted to about 350 cc. of CO, not including the volume of gaseous metal vapor, which must escape from the interior of the crucible (at 1600° C.) through the holes in the lid. Certainly, if the temperature is raised too high or too rapidly, the gas pressure inside the crucible can increase sufficiently to dislocate the lid and to blow unreacted sample particles out of the crucible. The effect of crucible temperature control on the analysis of UO_2 is illustrated in Table I. The values in the first column were obtained by following the unmodified procedure for analyzing oxygen impurity in metals by the inert gas fusion method ([7],[9]), making little effort to adjust the temperature for a controlled rate of reduction. The other column gives results obtained by following the procedure of this method.

Table I. Effect of Temperature Control on

Recovery (%) of Oxygen in UO_2

Complete Reduction at 1900° C. [a]	Partial Reduction at 1750° C. [b]
86.1	101.0
85.2	100.8
46.2	100.6
99.2	100.3
88.4	99.8
	100.5
	100.3
	99.7
	101.7
	100.3
	100.4

Average	81	100.5
Std. dev.	± 20	± 0.6

[a] Completed within 10 minutes.

[b] Twenty minutes at 1750° C. and 10 minutes at 1900° C.

Several attempts were made to carry out the reaction with no lid on the crucible. The obvious advantage to such an arrangement would be to allow an unobstructed view of the sample, during reduction, by which the temperature and the progress of the reaction could be monitored. However, it proved to be impractical to adjust the temperature of the crucible precisely enough to effect a suitably rapid reduction reaction without entailing loss of sample by entrainment of oxide particles in the effluent gas, and/or by spattering of the molten bath by bubble formation from CO produced beneath the surface of the liquid metal. In Table II a comparison is made of the results obtained on Fe_2O_3 and SiO_2, with and without a lid. By covering the crucible the precision was considerably improved for both oxides, and the accuracy was greatly improved for SiO_2.

Table III shows recovery percentages on Al_2O_3, Cr_2O_3, Ta_2O_5, and TiO_2. Although the average recovery values for some of these oxides and for Fe_2O_3 and SiO_2 of Table II show definite bias, the precisions are such that corrective bias factors can be applied to reduce the relative error to within 1%.

Four samples of iron oxide-sulfide mixtures were analyzed to investigate the interference of sulfides in

Table II. Effect of Crucible Cover on Recovery (%)

of Oxygen in Fe_2O_3 and SiO_2

Without Cover		With Cover	
Fe_2O_3	SiO_2	Fe_2O_3	SiO_2
101.1	93.5	95.1	97.7
94.3	87.8	97.3	97.5
96.7	91.3	97.6	96.6
96.8		97.1	98.1
97.2		97.0	97.2
97.6		96.9	98.0
88.4		96.7	97.9
		97.7	98.4
		97.2	98.4
		97.0	

	Without Cover		With Cover	
	Fe_2O_3	SiO_2	Fe_2O_3	SiO_2
Average	96	91	97.0	97.8
Std. dev.	± 4	± 3	± 0.7	± 0.6

Table III. Recovery (%) of Oxygen in Pure Oxides

Al_2O_3	Cr_2O_3	Ta_2O_5	TiO_2
99.1	99.2	100.7	99.9
98.9	98.6	99.6	99.6
98.8	98.0	101.4	99.8
99.6	98.7	100.5	100.1
100.2		100.3	100.1
99.6		101.4	99.5
99.8		100.7	
98.9			
99.5			
99.0			
99.3			

	Al_2O_3	Cr_2O_3	Ta_2O_5	TiO_2
Average	99.3	98.6	100.7	99.8
Std. dev.	± 0.4	± 0.5	± 0.6	± 0.3

the determination of oxygen in oxide mixtures such as stony meteorites. The FeS/Fe_2O_3 ratio was varied from 1/5 to 1/9. The average recovery of oxygen from the theoretical amount present in the mixtures was 100.5% with a standard deviation from the mean of ± 0.8.

During the course of the investigation more and more effort was devoted toward operation at the minimum temperature effective in the reduction of a given oxide within a 20-minute period. As might be expected, this minimum varied from one oxide to another, being con- siderably lower for Fe_2O_3 and Cr_2O_3 than for Al_2O_3. Also it was noted that the visual detection of smoke during the reduction of the oxides of iron or chromium was usually accompanied by low results, whereas the complete reduction of Al_2O_3 always produced plentiful swirls of white smoke. This may be explained on the basis of the higher volatility of aluminum metal. It is largely boiled out of the crucible as white "smoke" whereas iron and/or chromium remain in the crucible, alloyed with the platinum flux. When smoke appears in the case of these two metals, 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.

With these added precautions in mind, more oxides of iron and chromium were analyzed. Table IV shows the

Table IV. Improved Recovery Data Obtained on Fe_2O_3 Samples by
Reacting at Lower Temperatures Than Prescribed by the
General Procedure

Batch No.	Oxygen Content (%)		Deviation[b]	Recovery (%)
	Calculated[a]	Inert Gas Fusion Analysis		
1	29.9	29.8	- 0.1	99.7
2	29.9	29.8	- 0.1	99.7
		29.9	0.0	100.0
3	29.9	30.0	+ 0.1	100.3
		30.0	+ 0.1	100.3
4	30.0	30.1	+ 0.1	100.3
		30.2	+ 0.2	100.7
5	29.8	29.7	- 0.1	99.7
		29.9	+ 0.1	100.3
6	29.8	29.7	- 0.1	99.7
		29.6	- 0.2	99.3
7	29.8	29.8	0.0	100.0
		30.0	+ 0.2	100.7
8	29.8	29.9	+ 0.1	100.3
		30.2	+ 0.4	101.3

100.2 ± 0.4
S.D.

[a]Calculated by difference (from average of duplicate, volumetric iron analyses).

[b]Deviation from calculated value.

later results on Fe_2O_3 with a mean recovery value of 100.2 ± 0.4%, S.D., as compared to the previous mean of 97.0 ± 0.7%, S.D., Table II. Six samples of Cr_2O_3, also reduced more slowly at lower temperatures, (not tabulated) averaged 100.0 ± 0.4% recovery.

Pure silica was not reanalyzed by the improved technique, although it is presumed that about the same accuracy and precision might be expected as was obtained in the analysis of NBS #102 silica brick (93.9% SiO_2, 1.96% Al_2O_3, 2.29% CaO), Table V, in which the average "recovery," based on chemical analysis supplied by the National Bureau of Standards, was 99.4% with a relative standard deviation of ± 0.5%. Other results on mixed oxides are shown in Table V. The major constituents of NBS #76 are: 54.7% SiO_2, 37.7% Al_2O_3, 2.4% Fe_2O_3, 2.2% TiO_2, and 1.54% K_2O; and of NBS #77: 32.4% SiO_2, 59.4% Al_2O_3, 2.9% TiO_2, and 2.11% K_2O. The direct oxygen results on NBS #93 (80.6% SiO_2, 12.8% B_2O_3, 1.9% Al_2O_3, and 4.2% Na_2O) differed more from the calculated value (based on chemical analyses of the other elements) than did the results of the other standard materials. The average value of 52.3% may be low due to gettering by the relatively large concentration of alkali metal in the sample. Generally, gettering is not a problem associated with inert gas fusion, as it is with vacuum

Table V.   Analysis of Standard Oxide Mixtures

	NBS No. 76 alumina refractory	NBS No. 77 alumina refractory	NBS No. 93 high-boron glass	NBS No. 102 silica brick
	48.5	47.5	52.0	51.7
	48.7	47.6	52.3	52.0
	48.6	47.4	52.0	51.6
Series of results (% oxygen)	48.7	47.5	52.4	51.3
	48.4	47.3	52.2	51.7
	48.5		52.6	
Average (% Oxygen)	48.6	47.5	52.3	51.7
Rel. Std. Dev. (%)	± 0.3	± 0.3	± 0.5	± 0.5
Calcd. from NBS analysis (% Oxygen)	49.2	47.8	53.8	52.0

fusion. Where there is an appreciable quantity of alkali metal or alkaline earth metal being evolved with CO from the hot zone of a graphite crucible, however, there appears to be a potential difficulty that is hard to overcome. Presumably gettering was the major cause of our failure to get acceptable recoveries of oxygen in milligram amounts of MgO and CaO by this method.

DISCUSSION

A few experiments were made to investigate the necessity of using a metal bath in the crucible. In some bathless runs the sample was covered with graphite chips, and in others the sample was confined to a covered crucible made of very porous graphite. Most recoveries obtained under these conditions were low by more than 20%. As might be expected, the reagents (oxide and carbon) interacted much slower in "dry" contact than when wetted by flux in a liquid bath. Furthermore, there was probably more loss by entrainment in the absence of liquid metal which may be presumed to wet down the sample particles and retain them by surface tension.

When the reduction reaction produced swirls of smoke emanating from the crucible, most of the tiny metal particles making up this smoke were swept away by the

carrier gas to be filtered out on the glass wool in the
dust trap. A considerable amount also settled out on
the glass surfaces between the crucible and trap imparting
a dirty appearance to the glass line in that area. Other
than in appearance, however, this deposit apparently had
no detrimental effect upon the analyses of the oxides
reported in this paper.

Another phenomenon observed during the reduction
of Al_2O_3 samples was a green corona discharge in the
reaction tube extending from the crucible to the top end
of the tube. This was not observed for the other oxides
and was apparently unrelated to the success of the
method.

It was noted that in the analysis of iron oxides
it was desirable to prevent the platinum-to-iron weight ratio
in the bath flux from dropping below 10. With excessive
iron concentrations there was a tendency for iron vapor
to condense on the cooler surfaces of the lid, thereby
plugging up the vent holes and causing the lid to stick
to the crucible at the termination of the heating period.

The photograph in Figure 3 illustrates the condition
of a graphite crucible, containing 15 grams of platinum,
after it had been used in the analysis of oxide samples
which produced a total of 0.3968 grams of CO_2. The

irregularity of the inside diameter of the crucible
resulted from the depletion of graphite in the reaction

$$MO + C \rightarrow M + CO \;.$$
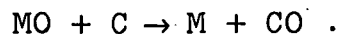
The bubble, visible in the center of the melt, doubtless
contained entrapped CO which had not completely emerged
at the conclusion of the analytical run. Such a
quantity of CO was insignificant, however, when compared
to the total weighable quantity converted to CO_2 for
gravimetric measurement.

Exposure of the crucible and of the upper section
of the furnace tube to the atmosphere during the time
(about 1.5 minutes) required to load the sample was found
to have little effect on the over-all blank of the pro-
cedure. Atmospheric contamination was found to increase
the final gravimetric measurement by only about 0.2 mg.,
an amount which is small compared to the quantities of
about 100 mg. usually measured for each sample.

Most of the gravimetric measurements in this inves-
tigation were made with weighing tubes having 12/5
ground ball joints for connection to the analytical
train. Near the end of the work, however, these were
replaced by ball joints of the same size but with rubber
O-rings embedded in the center of the face of the male
section, and with the female section smooth (unground).

As a result of this change an improvement in the precision of weight data was noted. It is probable that there had been minor misfits in the ungreased, ground ball joints that had connected the regular-type weighing tubes to the analytical train. The o-rings eliminated this potential source of error.

It may be concluded that although a general procedure is applicable to the analysis of a variety of oxides, minor modifications to the procedure may be necessary to give the best results for specific oxides. The ultimate degree of accuracy and precision attainable by this method clearly depends upon the art of the analyst in successfully carrying out the oxide-reduction step without the loss of sample.

ACKNOWLEDGMENT

1-30-64/jcw

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FIGURE LEGENDS

Figure 1.   Analytical Train

Figure 2.   Crucible and Lid, Diagram

Figure 3.   Crucible and Lid After Use

Table I.   Effect of Temperature Control on

                  Recovery (%) of Oxygen in UO_2.

Table II.   Effect of Crucible Cover on Recovery

                  (%) of Oxygen in Fe_2O_3 and SiO_2.

Table III.   Recovery (%) of Oxygen in Pure

                  Oxides.

Table IV.   Improved Recovery Data Obtained on

                  Fe_2O_3 Samples by Reacting at Lower

                  Temperatures Than Prescribed by the

                  General Procedure.

Table V.   Analysis of Standard Oxide Mixtures
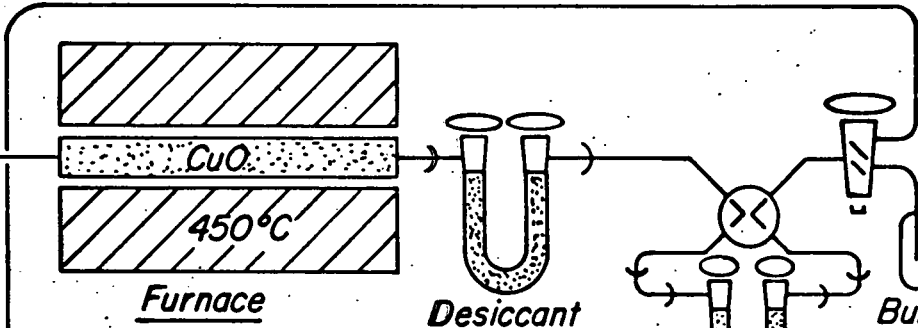
Water-Cooled Quartz Furnace Tube

$O_2 \rightarrow$

CuO

450°C

Furnace

Desiccant

Weighing Tube

Bubbler

Crucible

Dust Trap

Schutze Reagent

Capillary Manometer

To Vacuum

Inert Gas

ANALYTICAL TRAIN

(16) $\frac{1}{16}$ Dia. Holes

$\frac{3}{16}$

$\frac{1}{8}$

$\frac{1}{4}$ Dia.

$\frac{5}{8}$ Dia.

$\frac{3}{8}$ Dia.

1"

0.052" Dia. Hole

$\frac{3}{4}$

$\frac{1}{4}$ Dia.

CRUCIBLE and LID