LA-4849

c. 3

Determination of $^{18}O/^{16}O$ Atom Ratio in Plutonium Dioxide Enriched in ^{16}O

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

Printed in the United States of America. Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.95

LA-4849
UC-23
ISSUED: February 1972

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

Determination of $^{18}O/^{16}O$ Atom Ratio in Plutonium Dioxide Enriched in ^{16}O

by

Carolyn S. MacDougall
Maynard E. Smith
Glenn R. Waterbury

DETERMINATION OF $^{18}O/^{16}O$ ATOM RATIO IN PLUTONIUM DIOXIDE ENRICHED IN ^{16}O

by

Carolyn S. MacDougall, Maynard E. Smith, and Glenn R. Waterbury

ABSTRACT

Mass spectrometry is used to measure the $^{18}O/^{16}O$ atom ratio in plutonium dioxide enriched in ^{16}O isotope, after the oxygen has been separated as carbon monoxide by reacting the refractory oxide with carbon at 2000° in an inductively heated graphite crucible. The carbon monoxide is trapped on silica gel that is cooled in liquid nitrogen and is separated from any nitrogen present on a gas chromatographic column before being analyzed in a mass spectrometer. The $^{18}O/^{16}O$ atom ratio is calculated from the ratio of the $^{12}C^{18}O$ to $^{12}C^{16}O$ peak heights.

As plutonium oxide standards having known $^{18}O/^{16}O$ atom ratios were not available, the mass spectrometric method was tested by comparing the measured $^{18}O/^{16}O$ atom ratios with results obtained from neutron-count analyses that indicated the approximate maxima for these ratios. The results from both methods were generally about equal and, more important, the mass spectrometric results were always lower than the maxima indicated by the neutron counts. At an $^{18}O/^{16}O$ ratio of 5×10^{-5}, the standard deviation of the method was 5×10^{-6}. This method, which should apply equally well to any oxide that yields carbon monoxide upon reaction with carbon at 2000°, has been applied to the measurement of ^{18}O in plutonium oxides in which the ^{238}Pu enrichment was 80% or greater and in various cladding materials surrounding these plutonium oxides.

INTRODUCTION

The successful use of $^{238}PuO_2$ as an energy source for heart pacers or artificial hearts required that it have the lowest possible neutron emission rate. Neutron emission from this fuel is due primarily to spontaneous fission of the ^{238}Pu isotope and to (α, n) reactions with impurities. Oxygen-18 is among the isotopes that react significantly with alpha particles of > 0.86-Mev energy to produce neutrons. Because of the large oxygen contents of oxide fuels, the ^{18}O concentration in the oxygen must be kept extremely low.

Chemical[1-3] and vacuum fusion[4] methods for determination of ^{18}O in organic compounds have been reported. Most of the analyses were for relatively high ^{18}O concentrations, of about the natural abundance. For the present application, ^{18}O concentrations of ~ 10 ppm relative to the ^{16}O in the sample ($^{18}O/^{16}O$ atom ratio of 1×10^{-5}) were expected. Favorable experience with inert-gas fusion led to a choice of this method for separating the oxygen from the plutonium dioxide and cladding materials. In this method the sample is reacted with carbon in an inductively heated graphite crucible at 2000°, and the carbon monoxide that forms is swept to the analysis system by inert gas, thereby eliminating the need for an elaborate vacuum system. The carbon monoxide is easily measured mass spectrometrically with the required sensitivity after a chromatographic column separation from nitrogen impurity. Use of inert-gas-fusion separation and chromatographic purification of the carbon monoxide in conjunction with a high-sensitivity mass spectrometer for measuring the $^{12}C^{18}O$-to-$^{12}C^{16}O$ atom ratio provided the required sensitivity and reliability in determining the ^{18}O contents.

APPARATUS AND REAGENTS

Apparatus:

Adapter. To one end of a 15-in. length of 0.375-in.-diam, 0.125-in.-wall surgical rubber tubing, attach a ₸ 12/30 inner taper, borosilicate glass joint. To the other end, attach a ₸ 12/30 outer taper.

Balance, analytical, Cahn Gram Electrobalance or equivalent.

Ball bearings, 0.125-in., chrome-steel.

Capsule, stainless-steel, mixing, see Fig. 1.

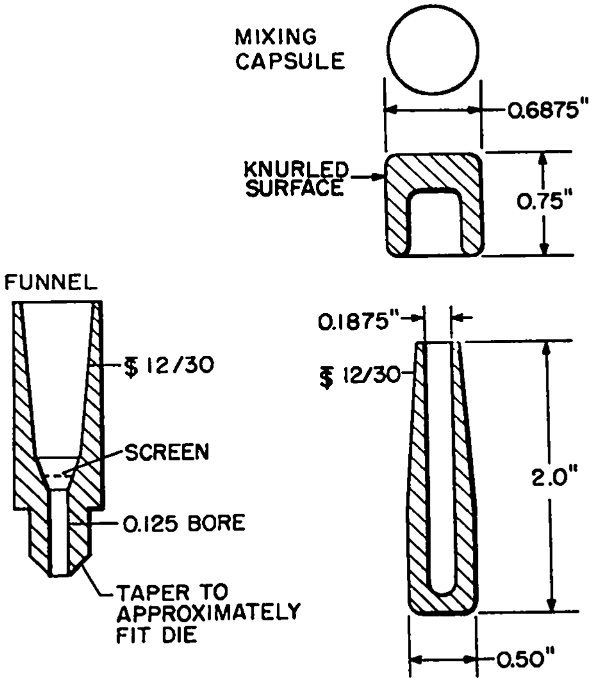

Fig. 1. Mixing capsule and funnel.

Crucible, graphite, AUC grade, for heating samples, with 9 g platinum, see Fig. 2.

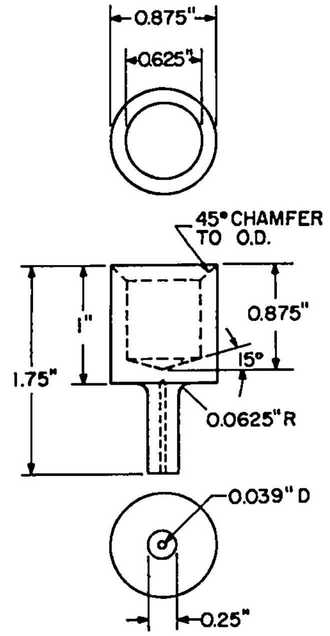

Fig. 2. Graphite crucible.

Dewar flasks, vacuum, borosilicate glass. One 2.93-in.-i.d. by 6-in.-high, and one 3.25-in.-i.d. by 9.5-in-high.

Die, with accessories, for making 0.125-in.-diam pellets, see Fig. 3.

Engraver, Vibrograver or similar, for vibrating die and accessories during powder transfers to ensure nearly quantitative transfers.

Funnel, for pouring powdered sample into die, see Fig. 1.

Funnel, guide tube, for putting pellet into crucible. Silver solder a 0.625- by 0.375-in. reducing coupling to a 10-in. length of 0.375-in.-diam stainless steel tubing.

Furnace tube, fused-silica, see Fig. 4.

Gas chromatograph, Varian Aerograph Series 200 or similar. Use a 6-ft, 0.25-in.-diam column filled with molecular sieve.

Hammer, ball-peen, 12-oz.

Heating tape, heavy insulated, Briskeat or equivalent tape, 4-ft-long, for baking out purification tubes and traps, three required.

Induction heater, R. F. generator, 20-kV, Lepel Type T-751-32 or equivalent.

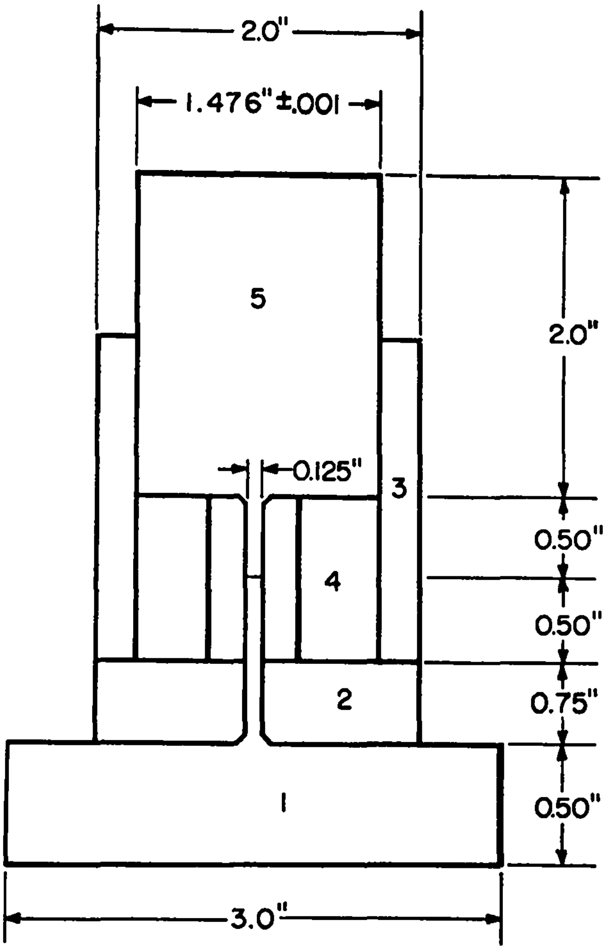

Fig. 3. Pellet die. (1) bottom stensor, (2) slotted spacer, (3) brace, (4) sleeve, (5) top stensor.

Inert-atmosphere enclosure, with gloves, argon-filled, capable of maintaining oxygen and moisture concentrations of < 2 ppm in the argon[5].

Inert-gas-fusion apparatus, a helium-purification system, fused-silica furnace tube, induction heater, valves, and traps; assembled as shown in Fig. 5.

Mass spectrometer, CEC Model 21-621 or equivalent, with 500-μ A ionizing current capability, equipped with a valve to shut off the expansion volume.

Mortar, diamond, plattner and pestle, E. A. Sargent and Co., Cat. No. S-62325 or equivalent mortar.

Pellet press, Carver Model B or similar.

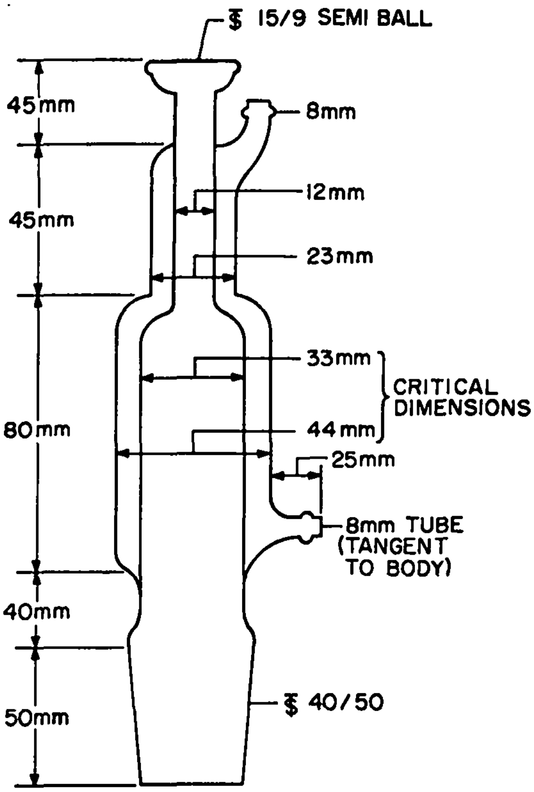

Fig. 4. Furnace tube.

Recorder, strip-chart, Honeywell Brown Electronic Model Y 153 x 62 V2-X-(16) or similar, one for gas chromatograph and one for mass spectrometer.

Rod, crucible support, tungsten, 0.040-in.-diam.

Sample inlet system, to chromatograph, see Fig. 6.

Transformer, 12-V, equipped with second timer, to heat collection trap No. 1.

Trap, collection No. 1, containing silica gel. See Fig. 7.

Trap, collection, No. 2, containing silica gel, wrapped with heating tape. See Fig. 8.

Tube, purification. See Fig. 9.

Tube, U, 6-in.-high, 1.75-in. between arms, made from 0.25-in. stainless steel tubing, fitted

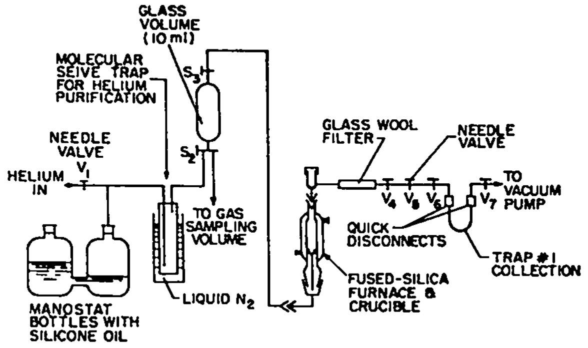

Fig. 5. Inert-gas-fusion assembly.

with 0.25-in. Swagelock quick disconnects, to fit inert-gas-fusion apparatus. See Fig. 5.

Tubing cutter, 0.125- to 1.125-in. capacity, to open sample containers.

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

Variable transformer, 7.5-A, to control temperature of heating tapes, three required.

Vials, flint glass, 1-dram, to transfer sample pellets from inert-atmosphere enclosure to reaction furnace. Remove paper lining from cap and replace with aluminum liner.

Wet test meter, Precision Scientific Co., or similar instrument.

Reagents:

Graphite, National Carbon Co., grade SP-1.

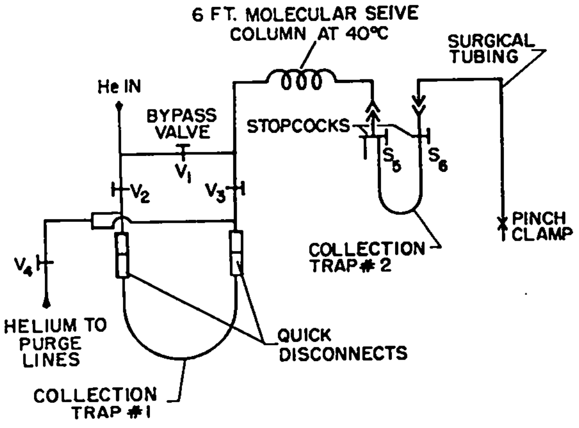

Fig. 6. Sample inlet to chromatograph.

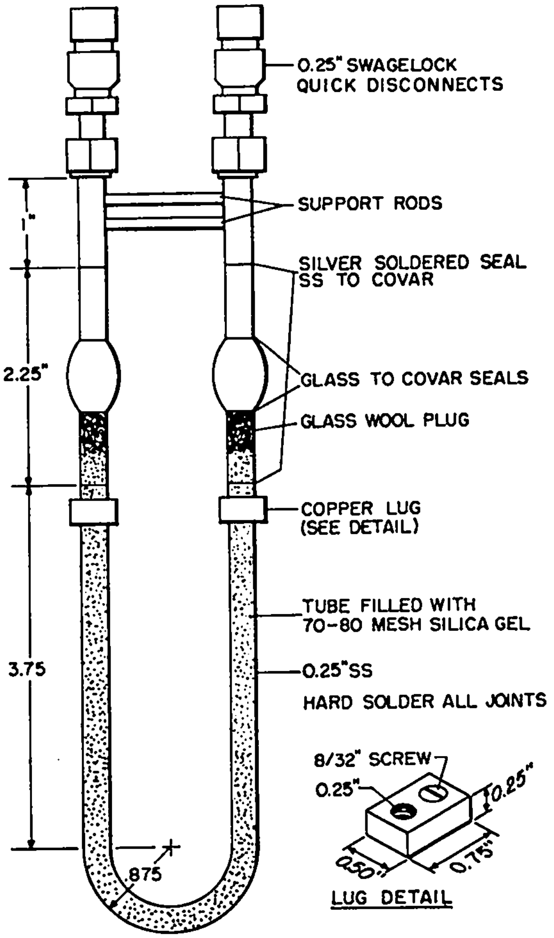

Fig. 7. Collection trap No. 1.

He, tank.

Molecular sieve, Linde 5A or equivalent.

Nitrogen, liquid.

Platinum, metal.

Silica gel, 70 to 80 mesh.

SAMPLE PREPARATION

Prepare the samples for analysis in an inert-atmosphere enclosure. For oxide samples received in air-tight, welded, tantalum cylinders, as is usual, hold the cylinder upright and cut off its top with a tubing cutter. If the sample is powdered, weigh out and transfer 50 mg into a clean aluminum sample container, using a clean microspatula. If the sample is a pellet, crush it in a diamond mortar and treat it as a powdered sample. To the oxide in the container, add ~ 10 mg of SP-1 graphite, and transfer the mixture to the mixer capsule.

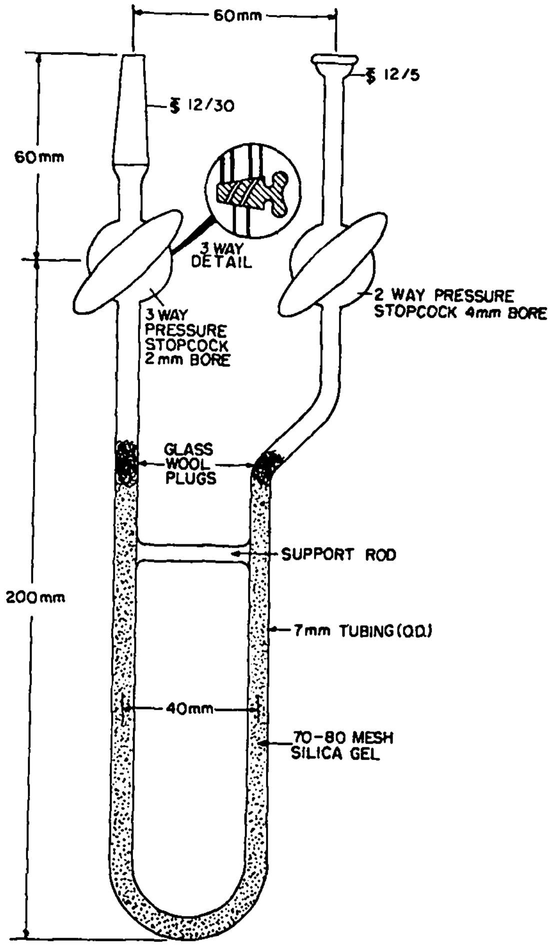

Fig. 8. Collection trap No. 2.

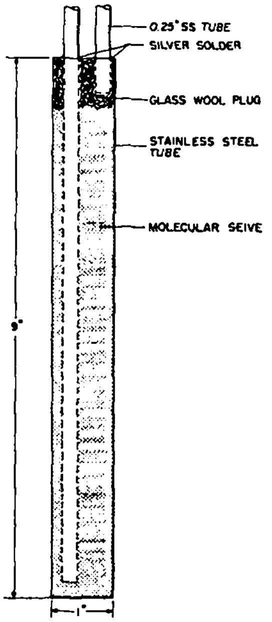

Fig. 9. Purification tube - 5A molecular sieve.

Add one 0.125-in. chrome-steel ball bearing, and manually shake the mixer capsule for about 30 sec. Carefully remove the cap from the capsule and pour the sample through the loading funnel into the 0.125-in. pellet die, using the vibrograver to vibrate the die and funnel to ensure quantitative transfer. Place the die in the pellet press and apply 2000-lb-gage pressure. Remove the pellet from the die and place it in a clean 1-dram vial for transfer to the fusion furnace. For cladding samples containing at least 0.05% oxygen, transfer a 1.0-g piece to a clean 1-dram vial for transfer to the fusion furnace. Do not attempt analyses of samples containing less than 0.5% oxygen. Cleanliness is absolutely necessary in all phases of sample preparation to prevent contamination with ^{18}O.

RECOMMENDED PROCEDURE

CAUTION: Health and safety rules for handling of radioactive materials must be rigidly followed, and adequate protection for the operator must be ensured by the use of suitable glove boxes and protective clothing.

I. APPARATUS CONDITIONING

1. Cool the molecular sieve trap with liquid nitrogen (see Fig. 5), and turn on the vacuum pump.
2. Turn needle valve V_1 until helium bubbles slowly from the manostat bottles, and open stopcocks S_2, S_3 and valves V_4, V_7 and V_6 in that order.
3. Adjust V_5 until the gas flow is 100 ml/min as measured with a wet test meter connected to the exhaust side of the vacuum pump.
4. Turn on the induction heater, slowly raise the crucible temperature to 2000° in about 30 min, and allow the apparatus to outgas for 30 min.
5. Examine the gas chromatograph to be sure that the gas flow is 100 ml/min and the column temperature is 40°.

II. SAMPLE FUSION

1. Close valves V_7 and V_6 (see Fig. 5) in that order.
2. Make certain that the helium purge gas is flushing collection trap No. 1 on the gas chromatograph through valve V_4, Fig. 6.

3. Use the quick disconnects to remove the U-tube from the inert-gas-fusion apparatus (Fig. 5), and replace it with collection trap No. 1.

4. Open valves V_7 and V_6 in that order, and allow the line to flush for 2 min with the induction generator on.

5. Turn off the induction generator, allow the crucible to cool, and close valves V_7 and V_4 in that order.

6. Remove the cap from the furnace, carefully insert the guide tube, and drop the pellet or cladding sample through the funnel into the crucible.

7. Remove the funnel, replace the furnace tube cap, open valves V_4 and V_7 in that order, and allow the line to flush for 2.5 min.

8. Cool collection trap No. 1 with liquid nitrogen, preset the induction generator to provide a crucible temperature of 1000°, and turn on the induction generator.

9. Increase the induction generator power to heat the pellet gradually from 1000° to 2000° in 5 min, continue heating the pellet for another 10 min, and then close valves V_7 and V_6 in that order.

10. Open valve V_4 (see Fig. 6) and close valves V_2 and V_3 of the chromatograph to ensure exclusion of air from the trap during the transfer.

11. Disconnect collection trap No. 1 from the line, keep it immersed in liquid nitrogen, transfer it to the sample inlet on the chromatograph, and turn off the chromatograph helium purge gas.

12. Replace the U-tube in the inert-gas-fusion apparatus, open V_7 and V_6, and allow the line to flush for at least 30 min with the induction generator on to flush out the line.

III. CHROMATOGRAPHIC SEPARATION OF NITROGEN FROM CARBON MONOXIDE (See Fig. 6.)

1. Open stopcock S_5 to the atmosphere, close stopcock S_6, and close the rubber tube with a pinch clamp.

2. Close V_4 and remove the liquid nitrogen from collection trap No. 1.

3. Turn on the recorder, and cool collection trap No. 2 with liquid nitrogen.

4. Attach the transformer leads to copper lugs on the trap, and turn on the power.

5. Wait ~ 10 sec until the trap heater shuts off, open valves V_3 and V_2, and close V_1.

6. Allow the line to flush into the air to vent the eluted nitrogen until the first evidence of the carbon monoxide peak appears on the recorder in ~ 7 min.

7. Quickly open stopcock S_5 to trap No. 2, open stopcock S_6, and remove the clamp from the rubber tube.

8. Collect the gas in trap No. 2 for 5 min, and then close stopcocks S_6 and S_5 in that order.

9. Remove trap No. 2 while it is immersed in liquid nitrogen, and transfer it to the mass spectrometer.

10. Close valves V_2 and V_3, and open V_1.

IV. MASS SPECTROMETRY

1. Connect the liquid-nitrogen-cooled trap No. 2 to the mass spectrometer inlet by means of the surgical tube adapter.

2. Evacuate the system up to the trap for 15 min.

3. Open stopcock S_5 and allow the trap to evacuate for 2.5 min to remove the helium.

4. Close stopcock S_5, remove the liquid nitrogen and the tubing adapter, reconnect the trap directly to the mass spectrometer, and again evacuate the system up to the trap.

5. Use power from a preset variable transformer connected to the heating tape to heat trap No. 2 to 200°, and allow 10 min for equilibration of the system.

6. Close off the 3-liter expansion volume of the mass spectrometer, and allow the sample to enter the sample block.

7. Turn on the recorder, and set the input sensitivity to "High" and the ionizing current to "500 μA."

8. Admit sample to the analyzer and scan from the $m/e = 27$ to the $m/e = 32$ peak.

9. Turn the ionizing current to "0," evacuate residual sample from the sample block, and shut off the recorder.

10. Return collection trap No. 2 to the chromatograph, turn on the helium flush gas, and bake the trap for 15 min at 250° by connecting the heating tape to a preset variable transformer.

V. CALCULATIONS

Calculate the $^{18}O/^{16}O$ atomic ratio by dividing the m/e = 30 peak height by the m/e = 29 peak height and multiplying by the m/e = 29 to m/e = 28 peak height ratio which is determined empirically.

$$\frac{^{18}O}{^{16}O} = \frac{(m/e = 30}{(m/e = 29} \times \frac{(m/e = 29)}{(m/e = 28)}. \qquad (1)$$

EXPERIMENTAL

Reaction of the Oxide with Carbon

A 100% yield of carbon monoxide from the sample is not necessary for the success of this method, as there is no evidence of preferential reaction of either oxygen isotope. The sensitivity of ^{18}O measurement depends, however, upon the quantity of carbon monoxide recovered. Calculations of the amount of carbon monoxide produced from a 50-mg sample of oxide indicated that this sample size is adequate. Test samples of this size wrapped in platinum foil and heated in a graphite crucible produced erratic yields. When the 50-mg oxide samples were intimately mixed with 10 mg of carbon and the mixture was pelletized, adequate and reproducible yields of carbon monoxide resulted. Cladding materials containing 0.05% oxygen or more yield the minimum usable amount of carbon monoxide from a 1-g sample.

Measurement of the $^{18}O/^{16}O$ Atom Ratio

Because mass spectrometric techniques already existed for measuring ^{18}O in oxygen gas, the problem here was to release the oxygen from the refractory oxide in a form suitable for measurement without isotopic exchange or contamination. Practical methods for decomposing the oxide and liberating uncontaminated oxygen gas were not known to exist. The most-tested and promising method for separating the oxygen was to react the oxide with carbon at 2000°. This produced carbon monoxide that could be analyzed with the mass spectrometer. Unfortunately, nitrogen impurity in the sample interfered with the measurement. It was obvious that the carbon monoxide must either be purified to remove nitrogen or be converted to another form that could be analyzed without interference from nitrogen.

Conversion of carbon monoxide to carbon dioxide by disproportionation is possible according to

$$2CO \xrightleftharpoons{\text{(Catalyst)}} CO_2 + C. \qquad (2)$$

The ratio of the m/e = 46 to the m/e = 44 peak height for the carbon dioxide could be used to determine the $^{18}O/^{16}O$ ratio. These peaks are not subject to interference from most contaminants, including nitrogen. Several catalysts were tried in attempting to effect the disproportionation. Use of a nickel catalyst at 300 or 500° accomplished about 13% conversion, but the reagent blank was high, being equal to 40% of the carbon dioxide produced. This blank was not eliminated by reduction of the metal catalyst with hydrogen. Use of platinized asbestos at 250° caused conversion of ~ 80 to 90% of the carbon monoxide with a reagent blank equal to 10% of the carbon dioxide produced. Palladized charcoal did not appear promising because it contains organic compounds that volatilized on heating.[6]

Because of difficulties encountered in producing carbon dioxide from carbon monoxide, a chromatographic separation of the nitrogen from the carbon monoxide and mass spectrometric analysis of the purified carbon monoxide was considered. This approach had an additional advantage because the mass spectrometer sensitivity was greater for measuring carbon monoxide than carbon dioxide. Using a 6-ft molecular sieve column at 40°, the optimum time interval for separating the nitrogen from the carbon monoxide was determined to be 5 min between the desorption and the start of the collection of carbon monoxide. A 5-min collection time maximized the sample-to-background ratio.

Maximum sensitivity and stable sample pressures in the mass spectrometer inlet were attained by evacuating the excess helium from the chilled collection trap after separation of the nitrogen and carbon monoxide. Air contamination of the sample was avoided by evacuating the vacuum lines leading to the trap for 15 min using an oil-diffusion pump backed by a mechanical pump. The mass spectrometer inlet vacuum system was convenient for this purpose. The trap was then evacuated for 2.5 min using the same vacuum manifold. The blank caused by the evacuation of the trap was reproducible and corresponded to 1-μm pressure.

This preconcentration of the sample magnified any contamination. Therefore, the helium supply to the chromatograph had to be purified by passage through a liquid nitrogen-cooled molecular sieve trap. Of course, any leak in the apparatus was immediately detected by the gas chromatograph or the mass spectrometer because of the increased nitrogen background. Because of the high partial pressure of the carbon monoxide ($^{12}C^{16}O$, m/e =28), the height of the 28 peak was calculated from measurement of another carbon monoxide peak ($^{13}C^{16}O$, m/e = 29).

RELIABILITY

Samples of plutonium oxides having accurately known low ^{18}O contents were not available. Therefore several other materials were used in testing the method. One material was $^{238}PuO_2$ made from natural oxygen. Repeated analyses of this oxide showed that the average $^{18}O/^{16}O$ ratio was 0.0020, which is the accepted natural-abundance value. To test the accuracy of the method at lower ^{18}O concentrations, a sample of oxygen gas having an $^{18}O/^{16}O$ ratio of 1.46×10^{-4}, as measured on the mass spectrometer, was injected into the apparatus at the entrance to the hot, reaction furnace tube, and the carbon monoxide formed was purified and analyzed. The $^{18}O/^{16}O$ ratio of the resultant carbon monoxide was 1.49×10^{-4}, in good agreement with the original value. Attempts to extend the measurement of the $^{18}O/^{16}O$ ratio to the 10-ppm level on oxygen samples were prevented by crucible reactions peculiar to the corrosive action of oxygen gas. This analysis of the oxygen gas sample indicated that at the 150-ppm level, ^{18}O isotope exchange was negligible, if indeed it occurred at all in the analysis apparatus.

To extend the tests to lower ^{18}O concentrations and at the same time avoid complications observed in working with oxygen gas, a sample of carbon monoxide was prepared from $^{238}PuO_2$ depleted in ^{18}O. The ^{18}O concentration in this carbon monoxide was determined mass spectrometrically to be 63 ppm. This carbon monoxide was injected into the apparatus at the entrance of the hot reaction furnace and analyzed for ^{18}O according to the normal procedure. The average of four analyses was 63 ppm, showing that isotopic exchange with carbon monoxide, the actual product of the basic reaction, did not occur during the analytical procedure.

The next materials used were ^{238}Pu dioxides whose neutron emission rates had been determined radiochemically. As the emitted neutrons originate mainly from spontaneous fission of ^{238}Pu and from (α, n) reactions on various impurities, one can assume as a first approximation for relatively pure oxides that neutron emissions in excess of the constant rate from the spontaneous fission stem from ^{18}O, and to a much lesser extent from ^{17}O, impurities. This assumption is supported by the facts that the oxygen content is higher (11.8%) and that the ^{16}O used in preparing the oxide must be extremely pure to eliminate introduction of significant quantities of ^{18}O and ^{17}O. However, estimation of ^{18}O content from neutron emission rates is subject to error because of other impurities, especially light elements such as fluorine which have large cross sections for (α, n) reactions. These errors introduce a positive bias, and the ^{18}O estimate must be considered as the maximum content. Repeated measurements of the ^{18}O were made on a sample of $^{238}PuO_2$ having a maximum possible concentration of 63 ppm of ^{18}O relative to the total oxygen content. The average of 14 analyses was 53 ppm of ^{18}O, and the standard deviation of the method was 4 ppm. Neutron-count rates measured during and after the mass spectrometry were equal, indicating that the sample was not contaminated by the analytical operations.

Further tests of the method were made by analyzing various samples of $^{238}PuO_2$ (Table I) and comparing the results with the maximum $^{18}O/^{16}O$ ratios calculated from the neutron counts. In each case, the calculated maximum was higher than the measured value, as expected. This difference indicated the presence of other impurities that contributed to the neutron emission rate.

Although this method has been used almost exclusively in the measurement of ^{18}O in plutonium dioxide, other materials have been analyzed recently. These include plutonium dioxide (50%)-tantalum pentoxide (50%) mixtures, plutoniun dioxide-molybdenum cermets, tantalum metal, tantalum-tungsten (10%) alloys, and tantalum-tungsten (8%)- hafnium (2%) alloys. One-gram samples of the metals containing as little as 500 ppm total oxygen are analyzed with no sacrifice in precision. Neutron counting of the metals was not possible, and data could not be compared. No obvious difficulties occurred. Erratic results were obtained for samples containing less than 500 ppm of oxygen which should be considered the lower limit for the method.

TABLE I

$^{18}O/^{16}O$ Ratios in $^{238}PuO_2$ Materials

		O^{18}/O^{16} ratio x 10^{-6}	
Sample No.	Neutrons/ sec g	Neutron-Count Data	Mass-Spectrometric Data
1	2730	62	53
2	3100	130	70
3	2630	36	25
4	3610	232	220
5	3890	288	280
6	4130	336	150
7	2880	86	35
8	3530	216	190
9	3240	158	150
10	3290	170	160
11	2620	36	15
12	3320	176	95
13	2790	175	65

ACKNOWLEDGMENTS

We gratefully acknowledge the assistance and helpful suggestions of Charles F. Metz and thank L. J. Mullins and members of the Plutonium Technology Group for the $^{238}PuO_2$ and L. D. Allen for the preparation of the oxygen gas mixtures. Neutron-count rates were measured by J. Bubernak and M. Lew of the Radiochemical Section.

REFERENCES

1. I. Sheft, A. F. Martin, and J. J. Katz, J. Am. Chem. Soc., 78, 1557 (1956).
2. M. Anbar and S. Guhman, Inter. J. Appl. Radiation and Isotopes 5, 233-5 (1959).
3. P. D. Boyer, D. J. Graves, C. H. Sveller, and M. E. Dempsey, Anal. Chem., 33, 1906-1909 (1961).
4. R. N. Clayton and S. Epstein, J. Geology, 66, 352-71 (1958).
5. M. E. Smith, J. M. Hansel, and G. R. Waterbury, Los Alamos Scientific Laboratory Report LA-3344 (1965).
6. G. Fester and G. Brude, Ber., 56B, 2245 (1923).

KT/wg: 269 (50)