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by

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COMBUSTION-MANOMETRIC METHOD FOR SIMULTANEOUS DETERMINATION OF CARBON AND HYDROGEN

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ABSTRACT

A combustion-manometric method[1] was used to determine small amounts of carbon and hydrogen in various materials. In this method, the sample is burned at 1000° C in a fused-silica furnace containing Alundum chips and cupric oxide to support the sample and ensure complete oxidation. The water formed from the hydrogen in the sample is collected in a trap cooled by an ethanol-dry ice mixture, and then measured manometrically at 100° C. The carbon dioxide produced from the carbon in the sample passes through the first trap, is collected in a second capillary trap cooled by liquid nitrogen, and is measured manometrically at room temperature.

Several materials, including tantalum, plutonium, and (uranium, plutonium) dioxide, have been analyzed for carbon and hydrogen in this manner. For 100-mg samples, the standard deviations are ± 5 ppm in determining 5 to 50 ppm carbon and 10 relative % at higher concentrations. For the determination of hydrogen in 100-mg samples, relative standard deviations are 1 to 2% above 11 ppm, 5% at the 11-ppm level, and 60% at the 5-ppm concentration level. This method applies equally well to any material that oxidizes completely at 1000° C in the presence of oxygen, but does not form volatile products other than carbon dioxide and water.

INTRODUCTION

Holt's combustion-manometric method[1] was applied to the simultaneous determination of small amounts of carbon and hydrogen in sintered uranium-plutonium dioxide reactor fuels and other materials. Conventional combustion-gravimetric methods did not provide the required sensitivity unless large samples, greater than 5 g, were analyzed. Vacuum fusion,[2-5] extraction,[5] and combustion methods have been used for the determination of hydrogen alone, and commercial analyzers are available for determining carbon and hydrogen.[6-8] Experience with the capillary trap method for measuring carbon[9] has been so satisfactory that extension to include manometric measurement of hydrogen, as is the case in Holt's method,[1] offered the most promise. The method is sensitive, and a small sample is adequate. Initial tests of the method led to modification of the combustion tube. Then the method was applied to analysis of mixed oxide fuels and other materials.

APPARATUS AND REAGENTS

Apparatus:

Aluminum foil envelopes, Fold a 12-mm square piece of 0.5-mil aluminum foil into an envelope with one end open. Analyze several envelopes for carbon and hydrogen. The foil used in this work had a carbon content of 0.12 μg/mg and a hydrogen content of 0.03 μg/mg.

Bubbler, borosilicate glass, two required, see Fig. 1.

Bunsen burner

Dewar, 250-ml capacity, three required.

Dosing stopcock, four-way, capillary, having two bores of different volume.

Drying tower, Fill the bottom quarter of a borosilicate glass tube, 750 mm long and 50 mm in diam, with silica gel. Then fill succeeding quarters with Ascarite, indicating silica gel, and anhydrous magnesium perchlorate. Put glass wool plugs in both ends of the tower to prevent escape of dust from the reagent.

Dumper, borosilicate glass, see Fig. 2. A solenoid fitted around the outside of the top tube raises the iron rod and attached glass seal magnetically when an electric current is passed through the coil.

Furnace, nickel, filled with cupric oxide. Fill a 16-in. length of 1.125-in.-diam nickel tube with wire-form cupric oxide. Place a copper wool plug in each end of the furnace tube to contain the cupric oxide.

Furnace, resistance, tube-type, 1-1/4-in. i.d., Hevi Duty Type 70 or equivalent, one 12-in. and one 8-in. furnace required.

Furnace tube, fused-silica. See Fig. 3.

Heat gun, Claude Michael, Inc., Model 1750 X or equivalent. Modify the standard heat gun by connecting the heating coil leads to a 7.5-A variable transformer.

Heating tapes, heavy insulated Briskeat or equivalent, 2-ft length, for heating apparatus from furnace exit to valve V_1, two required.

Inert atmosphere enclosure, similar to that designed by Smith et al.[10]

Manometer and capillary trap, borosilicate glass, for measuring carbon dioxide, see Fig. 4.

Manometer and swivel assembly, borosilicate glass, for measuring water, see Fig. 5.

Manometric apparatus, connected as shown in Fig. 6.

Manostat bottles, 2-ℓ, two required.

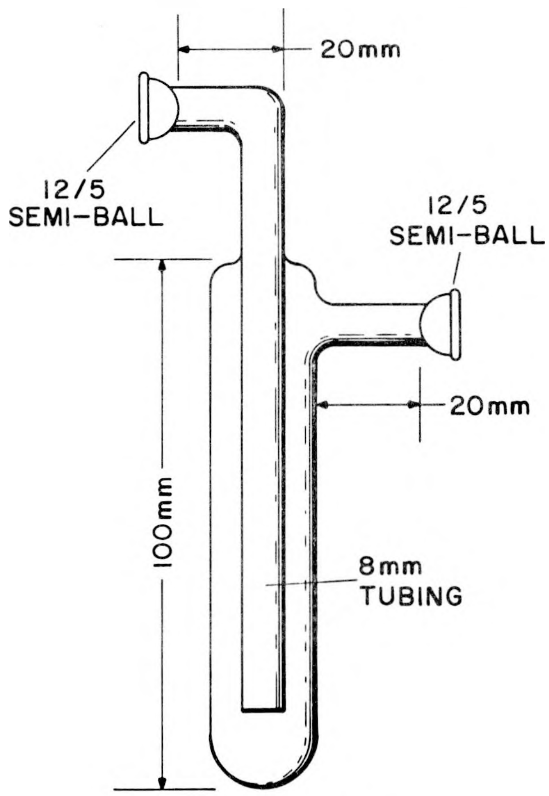

Fig. 1. Bubbler.

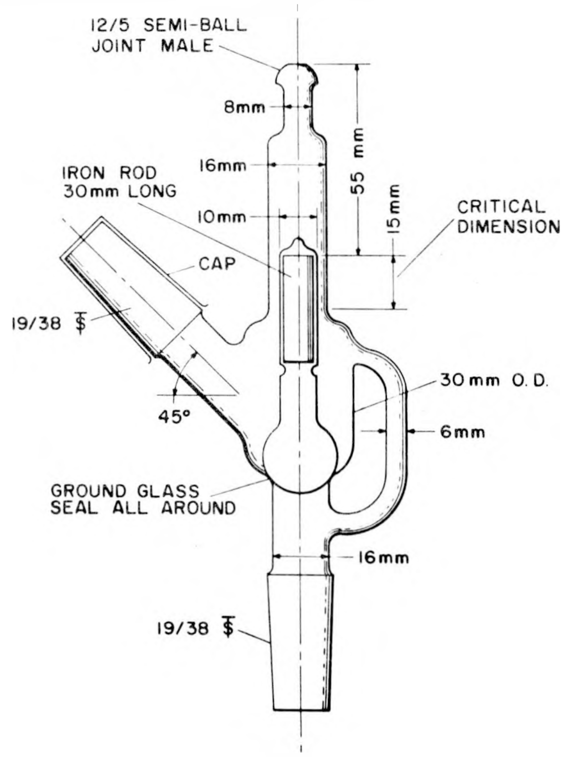

Fig. 2. Sample dumper.

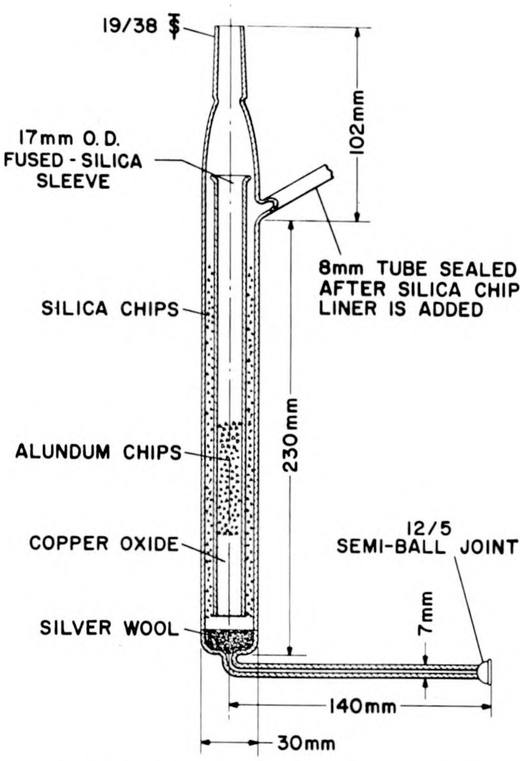

Fig. 3. Fused-silica furnace tube.

Meter sticks, two required.

Mixer mill, Spex Industries, Model 8000II or similar.

Pyrometer, graduated from 0 to 1000° C, Sim-Ply-Trol Assembly Products, Inc., or equivalent with Chromel-Alumel thermocouples, four required.

Sleeve, borosilicate glass. See Fig. 7.

Thermometer, alcohol, graduated from -100 to + 50° C.

Thermometer, mercury, graduated from -20 to + 110° C.

Trap, mercury, see Fig. 1.

U-Tube, borosilicate glass, for trapping water, see Fig. 8.

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

Variable transformers, 7.5-A, five required.

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

Reagents:

Alcohol, ethyl, denatured.

Alundum, chips.

Ascarite, 8- to 20-mesh.

Cupric oxide, wire-form, reagent grade.

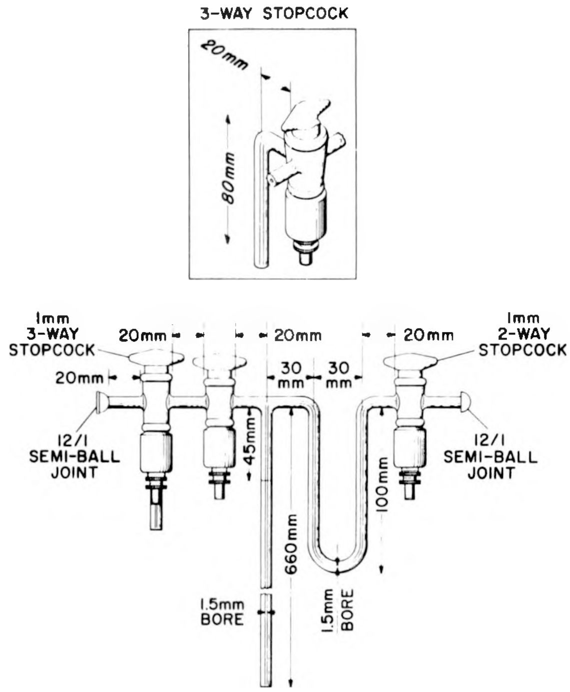

Fig. 4. Manometer and capillary trap for measuring carbon.

Hydrogen, tank.

Magnesium perchlorate, anhydrous, reagent grade.

Mercury, triple distilled.

Nitrogen, liquid.

Octoil, vacuum pump fluid.

Oxygen, tank.

Silica gel, 6- to 16-mesh.

Silica gel, indicating, 6- to 16-mesh.

Silicone oil, Dow Corning 200 fluid or similar.

Wool, copper.

Wool, glass.

Wool, silver.

SAMPLE PREPARATION

Inspect the sample for obvious impurities such as lint, and remove any foreign material. Remove any surface contamination from metal samples by mechanical polishing, and wash the sample in methyl chloroform or suitable solvent to remove oils. For a metal sample, weigh a 100-mg portion to ± 0.1 mg and transfer it to a clean 1-dram vial. Grind all oxide samples in a stainless steel mixer-mill capsule in a carbon-free inert atmosphere prior to analysis. Accurately weigh 50 to 100 mg of the powdered sample into a weighed aluminum foil envelope having a known carbon content, fold

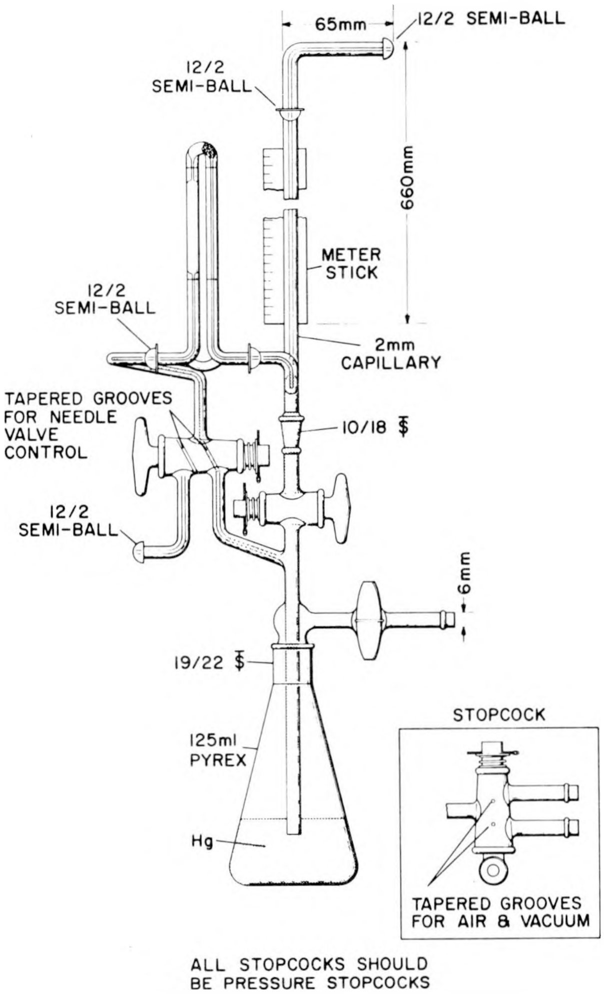

Fig. 5. Manometer and swivel assembly for measuring water.

the open end of the envelope to enclose the sample, and place it in a clean 1-dram vial.

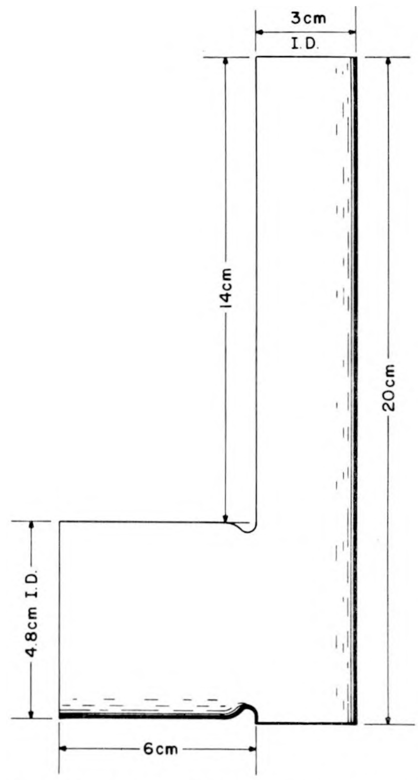

Fig. 7. Borosilicate glass sleeve.

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.

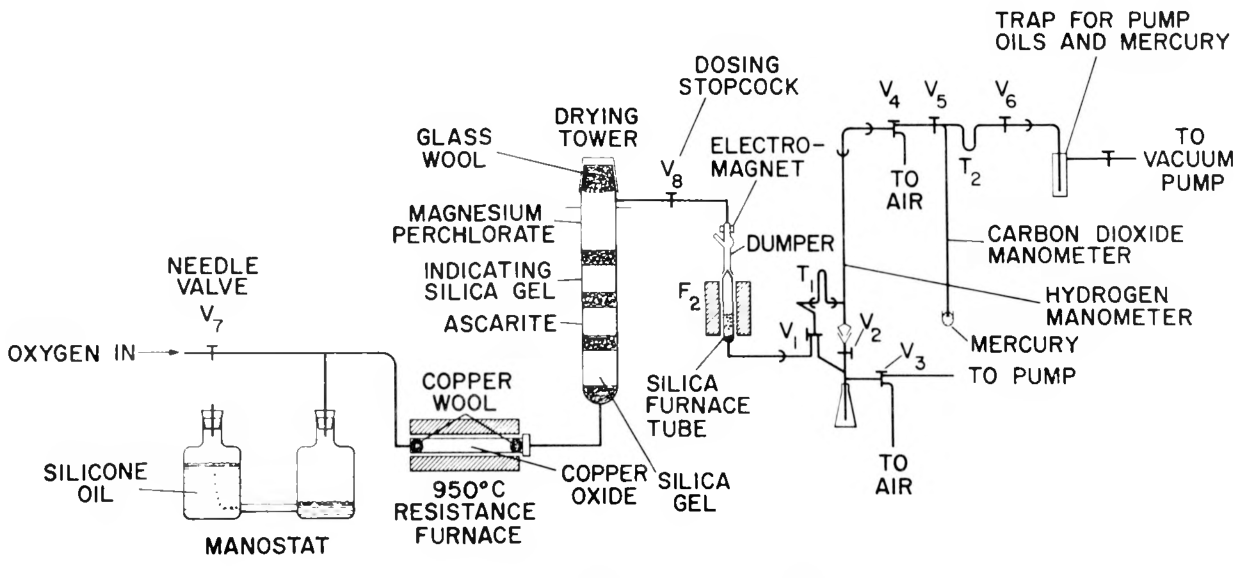

Fig. 6. Manometric apparatus.

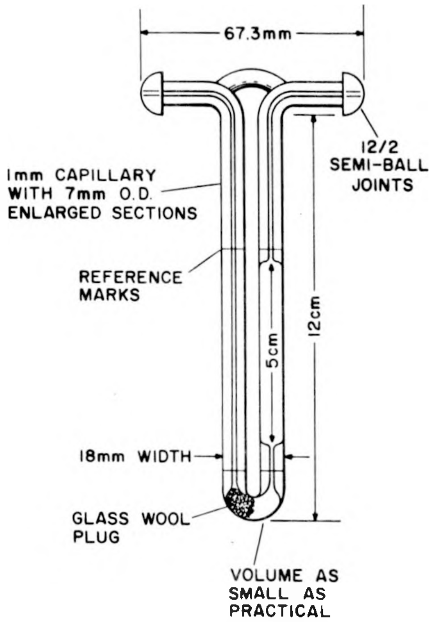

Fig. 8. U-tube for trapping water.

Sample Analysis

1. Calibration of Manometer for Measuring Carbon Dioxide. Determine the cross-sectional area (S), of the manometer by weighing the mercury that fills a measured length of the capillary tube. Calculate the cross-sectional area using

$$S = \frac{m}{\rho \ell}, \tag{1}$$

in which

m = mass of mercury in g,
ρ = density of mercury in g/mm^3,
ℓ = length of mercury in mm.

Determine the volume, V_o, of the U-trap as follows. Connect a leveling bulb filled with mercury to the bottom of the manometer with a rubber tube. Open the manometer valve, V_6 (Fig. 6), to the atmosphere. Raise the mercury to the zero mark on the manometer. Read the atmospheric pressure, h, on a barometer. Close valve V_6 to seal the trap from the atmosphere, and lower the leveling bulb to near the bottom of the manometer. Note the manometer reading, x_1, open V_6 to the atmosphere, and read the new level, x_2. Calculate V_o from

$$V_o = S\,x_1\,(h - x_2 + x_1)/(x_2 - x_1). \tag{2}$$

2. Calibration of Manometer for Measuring Water. Introduce known amounts of hydrogen into the fused-silica furnace through the dosing stopcock and measure, by the method to be described later, the pressure of the water formed. Add various amounts of hydrogen to obtain data for a calibration "curve" of the form y = a + bx. Use either of the two measuring volumes of the hydrogen manometer to obtain one or two "curves."

3. Dosing Stopcock Calibration. Determine the volume of either bore of the dosing stopcock by weighing the amount of mercury contained in that bore. Calculate the volume from

$$V = \frac{m}{\rho}, \tag{3}$$

in which

V = volume of bore in cm^3,
m = mass of mercury in g,
ρ = density of mercury in g/cm^3.

Calculate the amount of hydrogen introduced into the system from the dosing stopcock, having a bore of volume V, by

$$g = 0.02362\,\frac{(PV)}{(T)}, \tag{4}$$

where

g = mass of hydrogen in g,
P = atmospheric pressure in atm,
V = volume of bore in cm^3,
T = temperature in °K.

4. Sample Analysis.

a. Turn on the oxygen source and adjust the flow with needle valve V_7 (Fig. 6) until the oxygen bubbles very slowly from the manostat bottles.

b. Open valves V_8, V_1, and V_4.

c. Turn on the vacuum pump and slowly open valve V_6.

d. Adjust the flow of oxygen to 100 ml/min by partially opening needle valve V_5. Measure the flow of gas by passing the pump exhaust gas through a wet test meter.

e. Close valve V_1 so that a positive pressure is created in the furnace tube, and remove the cap from the sample dumper.

f. Load the sample into the dumper, and replace the cap with a slight twist to seat it firmly.

g. Open valve V_1 and allow oxygen to flush the line for 1 min.

h. Immerse trap T_2 in liquid nitrogen. Turn the hydrogen swivel trap, T_1, to its down position, and immerse it in an ethyl alcohol-dry ice mixture.

i. Actuate the sample dumper to drop the sample into the furnace, and burn the sample for 10 min at 1000° C.

j. Close valve V_1 and completely open valve V_5 to the vacuum pump.

k. Close valves V_5 and V_6, remove the liquid nitrogen from the capillary trap, warm the trap to room temperature, and read the manometer to ± 0.5 mm. (This reading is an indirect measure of the carbon dioxide pressure.)

l. Calculate the micrograms of carbon in the sample using

$$w = 0.000641\,(V_o x + S\,x^2), \tag{5}$$

where

w = weight of carbon in μg,
x = sample pressure in mm,
V_o = volume of U-trap in mm^3,
S = cross section of manometer in mm^2.

m. Open valves V_1, V_2, V_5, and V_6 to the vacuum pump.

n. Slowly open valve V_3 to air and push the mercury up into the manometer as shown in Fig. 5.

o. Close V_3, remove the alcohol-dry ice bath, and swivel trap T into its "up" position.

p. Place the glass sleeve over the U-trap, insert the heat gun into the sleeve, and turn on the blower and heating element. (Note: This resistance-type heat gun should rapidly heat the trapped water to 100° C and maintain the gas at this temperature throughout the measurement.)

q. When the gas begins to heat, again open V_3 to the air and slowly push the mercury farther up into the swivel assembly. (When the gas is at 100° C, the mercury level should be even with the reference marks on the trap.) Close V_3 when the mercury reaches the calibration mark.

r. Read the manometer to ± 0.5 mm as a measure of the pressure of the trapped water.

s. Turn off the heat gun, remove the glass sleeve, open V_3 to the vacuum, and slowly draw mercury back into the reservoir. (Design of the outward projection of the swivel assembly as shown in Fig. 5 is critical to ensure smooth operation at this point.)

t. Close V_2 and V_1 to the silica furnace.

u. Adjust V_5 so that the flow of oxygen through the system is again 100 ml/min, and flame the line from V_1 to the mercury trap to remove the water from the system.

v. From the hydrogen calibration curve, obtain the micrograms of hydrogen present in the sample.

w. Determine a blank before and after each analysis by repeating steps a through v, omitting step t, the addition of the sample.

EXPERIMENTAL

The apparatus is similar to that designed by Holt,[1] except for the design of the fused-silica furnace tube. As shown in Fig. 3, a fused-silica liner surrounded by quartz chips was added to the reaction furnace tube. This liner did not significantly reduce the furnace capacity, but permitted combustion of metal samples weighing as much as 1 g without danger of cracking the furnace due to the violence of reaction.

Two minor changes were made in the hydrogen swivel assembly and manometer to facilitate operation and maintenance. First, the outward projection of the swivel assembly was designed with a 30° angle to the horizontal, as opposed to horizontal. This change allowed the mercury to flow smoothly back into the reservoir after measurement of the water. Secondly, a small right-angle connection was added to connect the manometer for measuring water to the U-trap for collecting carbon dioxide. This modification reduced breakage during disassembly of the apparatus for cleaning.

RELIABILITY

The calibration of the carbon-measuring manometer was verified by determination of carbon in 10 samples of calcite. The average amount of carbon found, based on the stoichiometric amount of carbon in the samples, was 98% with a relative standard deviation of 4%. The inherent precision of the apparatus for measuring hydrogen was estimated by repeatedly injecting known quantities of hydrogen into the apparatus from the dosing stopcock. The manometer for measuring water pressures had two different volumes, thus permitting accurate measurement of two ranges of hydrogen

Table I

Precision of Hydrogen Measurements
(100-mg Samples)

Manometer Range	Hydrogen, μg	Std. Dev., μg	Rel. Std. Dev., %
High	1.13	0.14	13
High	2.75	0.13	5
High	5.66	0.13	2
High	10.4	0.13	1
Low	1.13	0.06	5
Low	2.46	0.04	2
Low	5.66	0.05	1

quantities. The high range was used for 4 to 16 μg, and the low range for 0 to 6 μg. An estimate of the precision was based upon 26 measurements at various hydrogen levels (Table I).

The method was further tested by repeated analyses of tantalum and plutonium samples for hydrogen or carbon, or both. The results were compared with those obtained by the combustion gravimetric method (Table II). Two samples of sintered (uranium, plutonium) dioxide powders were then analyzed (Table III). Unfortunately, the available quantities of these samples were not sufficient for analyses by the combustion-gravimetric method.

The results obtained by the two methods for carbon and hydrogen in plutonium agree well, as do the values for hydrogen in tantalum. The accuracy and speed of the two methods are comparable for measuring low (ppm) concentrations of carbon and hydrogen, but the combustion-manometric method has the advantage of requiring only a small sample. The combustion-gravimetric method is preferred for measuring large concentrations of these elements.

Table III

Analysis of Sintered $(U, Pu)O_2$ for Carbon and Hydrogen
(100-mg Samples)

Sample	No. Det'ns.	Carbon, ppm	Hydrogen, ppm
$(U, Pu)O_2$ (I)	14	40 ± 9[a]	31 ± 4[a]
$(U, Pu)O_2$ (II)	8	25 ± 5[a]	13 ± 4[a]

[a]Estimated standard deviation for a single determination.

ACKNOWLEDGMENTS

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Table II

Determination of Hydrogen and Carbon in Tantalum and Plutonium
(100-mg Samples)

	Gravimetric			Manometric		
Sample	No. of Det'ns.	C, ppm	H, ppm	No. of Det'ns.	C, ppm	H, ppm
Ta	3	a	< 20	9	40 ± 7[b]	12 ± 5[b]
α Pu	15	15 ± 8[b]	10 ± 4[b]	12	20 ± 7[b]	11 ± 3[b]

[a]Sample not analyzed for carbon by this method.

[b]Estimated standard deviation of a single determination.