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J. H. Edgerton
H. G. Davis

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J. H. Edgerton and H. G. Davis

Date Issued: JAN 15 1957

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ABSTRACT

The determination of microgram quantities of carbon in alloys by the low-pressure combustion method is based on the combustion of the specimen in oxygen at 135 mm pressure, freezing out the carbon dioxide, pumping out the excess oxygen, and then measuring the carbon dioxide in the gas phase with a known volume by means of a McLeod gage. The recommended concentration range is from 0.003 to 0.3 milligrams of carbon in a 0.3-gram sample, i.e., from 0.001 to 0.1% carbon.[2] The relative standard deviation of the method is 10%. The unique features of the apparatus is the use of a Toepler pump to transfer the carbon dioxide to the McLeod gage.

DETERMINATION OF MICROGRAM QUANTITIES OF CARBON BY LOW-PRESSURE COMBUSTION

J. H. Edgerton and H. G. Davis

INTRODUCTION AND SUMMARY

The determination of microgram quantities of carbon in metals and alloys by low-pressure combustion involves combustion of the sample in an atmosphere of pure oxygen, absorption of the carbon dioxide in a cold trap and subsequent release of the carbon dioxide, after evacuation of the oxygen, into a McLeod gage. The amount of carbon dioxide in the sample is calculated from the increase in pressure in the McLeod gage.

Various forms of the low-pressure microcombustion method have been described by a number of workers.[1,2,3] The method is claimed to have considerable advantages over other methods for carbon. The blanks for the system are much smaller than those generally obtained in direct combustion and the other methods, i.e., of the order of 0.0005% carbon for a 0.3-g sample.

The low-pressure method eliminates the need for large samples and is more sensitive than gravimetric or volumetric methods because the evolved carbon dioxide is determined by the measurement of its pressure in a calibrated volume by means of a McLeod gage.[3] Induction heating is used for the combustion of the sample,[1] and a palladium catalyst is used in conjunction with liquid traps to purify the oxygen[2] that is required

for the apparatus. The procedure for its use and examples of its application are included.

This apparatus gave results which compare favorably with those obtained in a microcombustion train. The low concentration of carbon involved and ability to use small sample size make this a very desirable method. The relative standard deviation is 10%; however, this is satisfactory with such low concentrations and the sample size of 0.3 g. Once the apparatus is put into operation, the determinations are rapid. Practically no maintenance of the apparatus is required between analyses. Eight samples can be loaded, one at a time, through the specimen arms by means of a glass chute; it is not necessary to change the furnace system until twenty to thirty samples have been analyzed.

APPARATUS

1. Low-pressure Combustion Apparatus. This apparatus is shown in detail in Fig. 1.
2. RCA electronic power generator, 1-kw
3. Dewar Flasks, wide-mouth, borosilicate glass. At least five are needed.
4. Optical Pyrometer, Leeds and Northrup Cat. No. 8622.

REAGENTS

1. Oxygen, cylinder of commercial grade.
2. Carbon Dioxide, solid, commercial grade.

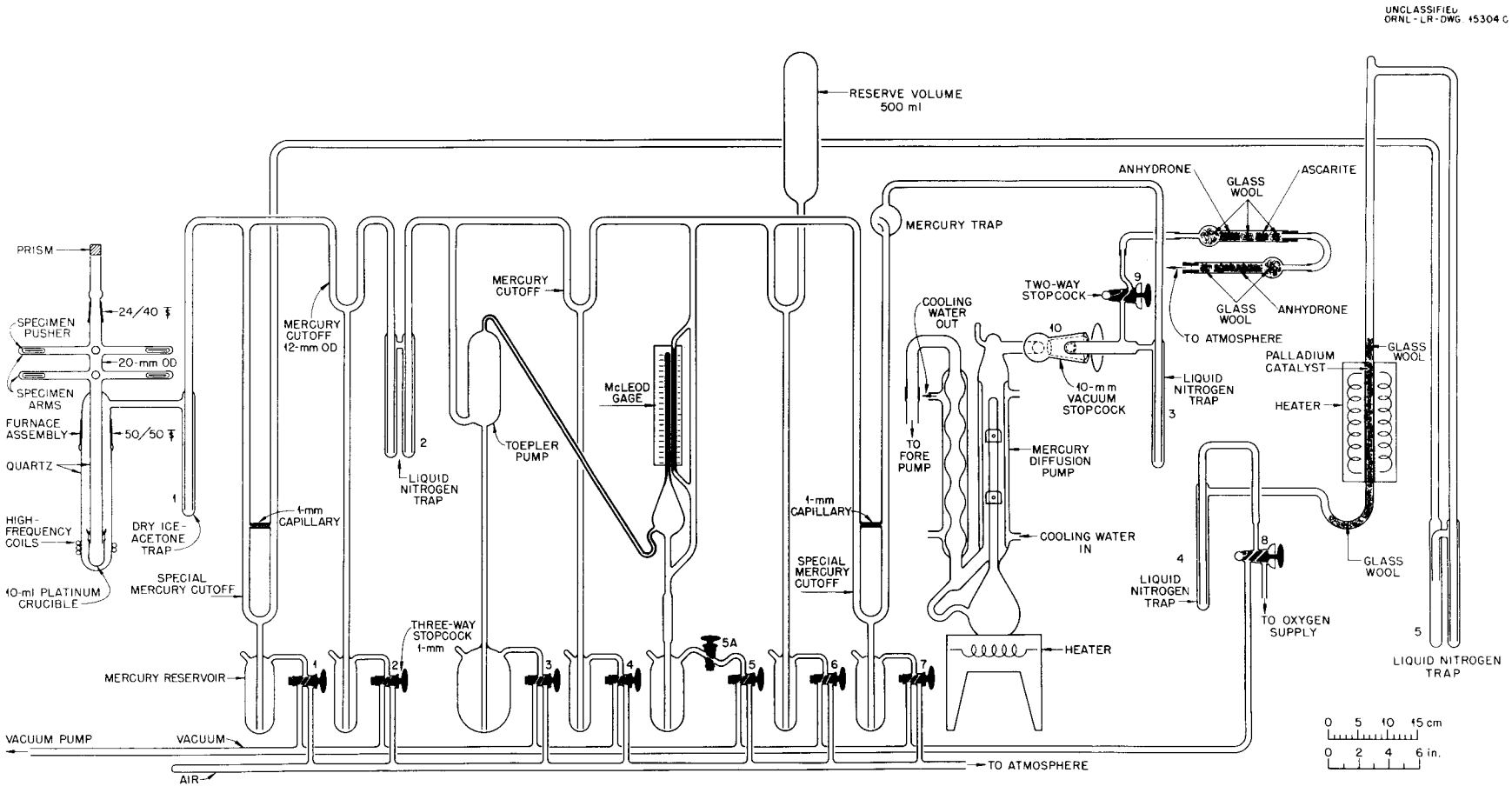

Fig. 1. Apparatus for Determination of Carbon by Low-Pressure Microcombustion.

3. Liquid Nitrogen, commercial grade.
4. Acetone, reagent grade.
5. Palladium on asbestos, for use as a catalyst.
6. Apiezon Wax "W" and "L", available from James G. Biddle Company, Philadelphia, Pa.

PROCEDURE

The platinum crucible is suspended in place by the platinum wires and the furnace tube is sealed in place with Apiezon "W" wax. The samples are loaded one at a time into the specimen arms by means of a glass chute. The top of the furnace is sealed on with Apiezon "W" wax. After these joints have cooled, all stopcocks are closed, a Dewar flask that contains liquid nitrogen is placed over trap T_3 and the manifold pump is turned on. After the manifold pump has been running for a few seconds, i.e., until it is quiet, the fore pump is turned on. After the fore pump has run for approximately three minutes, stopcock No. 10 is opened until the mercury begins to rise slowly in the cutoff tubes. Stopcocks Nos. 1, 3, 5, and 7 are manipulated in order to keep the mercury below the cutoff points during evacuation. When there is no further rise of the mercury, stopcock No. 10 is opened completely. The system is evacuated in this manner until a reading of 30 to 40 mm on the McLeod gage is obtained. At this point, the heater for the mercury diffusion pump is turned on and the Variac is adjusted to a low setting so that the heat can be increased very gradually and thus prevent possible cracking of the diffusion pump. The

heater for the palladium catalyst is turned on and is allowed to come to operating temperature (400° C).

When the pressure in the system is such that the mercury, when raised into the capillary of the McLeod gage, will rise completely to the top of the gage, Dewar flasks that contain liquid nitrogen are placed around the traps T_4 and T_5 in the oxygen purification train, and a dry ice-acetone slurry is placed around the dry ice-acetone trap T_1. The crucible is heated by the induction heater to a temperature that is 200° C higher than the final operating temperature and is then outgassed at that temperature for twenty minutes. With the crucible at that temperature, stopcock No. 10 is closed and stopcock No. 8 opened slowly in order to allow the oxygen to pass through the traps that are surrounded by liquid nitrogen and over the palladium catalyst. From the purification train, the oxygen passes into a manifold and then into the No. 1 cutoff where it is admitted to the system through the capillary in the cutoff until a pressure of approximately 100 mm is obtained. Cutoffs No. 1 and 7 are closed. The platinum crucible is held at 1350° temperature in this atmosphere of oxygen for 30 minutes. The induction heater is turned off, stopcock No. 10 is opened, and the oxygen and other gases are evacuated. When the system shows no pressure reading on the McLeod gage, stopcock No. 10 is closed, oxygen is again admitted to the system, and cutoffs Nos. 1 and 7 are closed.

The platinum crucible is heated to operating temperature (1300-1400° C), and a Dewar flask of liquid nitrogen is placed around trap T_2. The sample is pushed into the crucible by means of a magnetic pusher. After complete combustion of the sample, the mercury in cutoff No. 7 is lowered just below the capillary, and stopcock No. 10 is opened so that a slow evacuation takes place. When the system is nearly evacuated, stopcock No. 10 is opened fully and the No. 7 cutoff is lowered below the major cutoff point. When the system shows no pressure reading on the McLeod gage, cutoffs Nos. 2, 4, 5, 6 and 7 are closed. The Dewar flask of liquid nitrogen is lowered away from trap T_2 and the CO_2 is allowed to expand in the Toepler pump. When the trap T_2 is at room temperature, the CO_2 is pumped from the Toepler pump into the McLeod gage and the pressure of it is measured. If the mercury in the closed capillary stops below the scale and a reading is impossible cutoff 6 is lowered to just below the cut-off point. The CO_2 is released from the McLeod gage and allowed to expand into the 500-ml volume. After two minutes is allowed in order for the system to come to equilibrium, the CO_2 is again measured. A blank is determined in this manner and is subtracted from the reading of the sample. The percent carbon is calculated by the method of Yeaton.[4]

CALCULATION[4]

"Assume that all the gas from any particular phase of

the analysis is compressed into the capillary of the McLeod gage. The volume of the gas in such a case is equal to the cylindrical volume of the capillary or $\pi r^2 h$ where 'h' is the length of the capillary in which the gas is contained, and 'r' is the radius of the capillary. Since the pressure 'p' expressed in mm Hg of the gas is also equal to 'h', the differential in height between the mercury columns, the 'Pv' product may be expressed as

$$Pv = \pi r^2 h^2$$

now the ideal gas law states that Pv = NRTk where 'N' is the number of mols of gas present, 'R' is the gas constant in suitable units, and 'Tk' is the temperature in °K. Then, since the molecular weight M X the numbers of mols of gas N is equal to the weight of the gas in grams G by substituting and solving the above equations we have

$$G_{\text{grams of gas}} = \frac{M \quad r^2 h^2}{R \ Tk}$$

or for practical purposes we may combine constants and convert to per cent directly

$$\text{Gas}_{\%} = \frac{K \quad h^2}{\text{wt. of sample in grams}}$$

$$\text{where} \quad K = \frac{100 \ M \ \pi r^2}{R \ Tk}$$

$$\%\ \text{Carbon} = \frac{(h_s^2 - h_b^2) \ \text{X} \ 1.153 \ \text{X} \ 10^{-5} \ \text{X} \ 100}{W}$$

h_s = McLeod gage reading in mm of sample.
h_b = McLeod gage reading in mm of blank.
$1.153 \text{ X } 10^{-5}$ = Factor for carbon based on volume of capillary and ideal gas laws.
W = Weight of sample in grams."

RESULTS

Results of a series of determinations of carbon in a U. S. Bureau of Standards 55a iron sample are shown in Table I. Figure 1 illustrates the apparatus used in this experiment.

TABLE I

Results Obtained by Low-Pressure Microcombustion with Bureau of Standards 55a Iron Sample

Determination	Carbon Weight % (a)(b)(c)(d)
1	0.013
2	0.011
3	0.013
4	0.012
5	0.013
6	0.014
7	0.012
8	0.012
9	0.012

(a) Bureau of Standards certificate value was 0.014% carbon.
(b) Ignition for 20 min. at 1300° C in 135 mm oxygen.
(c) The blank was 0.0005% carbon.
(d) The standard deviation is 8.76×10^{-4}.

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