U. S. Department of Commerce
C. R. Smith
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

Standard Reference Material 39i

Benzoic Acid

Calorimetric Standard

This sample of benzoic acid was refined by fractional freezing to give a material of high homogeneity and purity. It conforms to the American Chemical Society specification for reagent-grade benzoic acid. Freezing point measurements on macro-samples indicate a purity of about 99.997 mole percent. The material as issued contains on the order of 0.002 percent moisture, and will not absorb moisture from the atmosphere if the relative humidity does not exceed 90 percent. The heat of combustion of the sample will not change with time if adequate precautions are taken to avoid the introduction of impurities. Sample 39i is more compact and free-flowing than sample 39h and earlier lots due to the difference in method of preparation; however, the heat of combustion does not differ significantly from that of earlier lots, on the basis of preliminary comparison experiments with earlier standard samples.

The quantity of energy evolved by combustion of Standard Reference Material 39i, benzoic acid, when burned under the standard bomb conditions listed below is

$$26434\ \mathrm{J\ g^{-1}} \quad [1,2,3]$$

with an estimated uncertainty of 3 J g^{-1}. These values are based on a comparison of the combustion energy with electrical energy measured in terms of the national standards of resistance, voltage, and time. The combustion energy is within about 1 J g^{-1} of the average of all precise determinations during the past thirty years. The listed uncertainty includes three times the combined estimated standard deviations of the electrical and the chemical measurements made in the comparison, and a small allowance for possible systematic error in equating the energy equivalent of the calorimeter in the two classes of experiments.

Heat measurements leading to the certification of this Standard Reference Material were performed by K. Churney.

The overall direction and coordination of the technical measurements leading to this certificate were performed under the supervision of G. T. Armstrong.

Washington, D. C. 20234
July 15, 1968

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(over)

STANDARD BOMB CONDITIONS:

A. The combustion reaction is referred to 25 °Celsius (centigrade).
B. The sample is burned in a bomb of constant volume in pure oxygen at an initial absolute pressure of 30 atmospheres measured at 25 °C.
C. The number of grams of sample burned is equal to three times the volume of the bomb in liters.
D. The number of grams of water placed in the bomb before combustion is equal to three times the volume of the bomb in liters.

RECOMMENDED PROCEDURE:

In the use of the standard reference material, it will be advantageous to observe the following procedure:

1. The material should be made into a pellet and weighed in this form in the crucible in which it is to be burned.
2. The conditions stated under Standard Bomb Conditions (A,B,C, and D) should be adhered to as closely as practicable. If it is necessary to depart from these conditions, the value given for the energy evolved should be multiplied by the following factor, if this factor is found to differ from unity to a significant extent:

$$1 + 10^{-6}[20(P-30) + 42\,(m_s/V-3) + 30\,(m_w/V-3) - 45(t-25)]$$

where:

P = initial absolute pressure of oxygen, in atmospheres at the temperature t,
m_s = mass of sample, in grams,
m_w = mass of water placed in bomb before combustion, in grams,
V = volume of bomb, in liters,
t = temperature to which the reaction is referred, in degrees C.

3. The charge should be fired by passing electric current through a short length of iron, chromel, or platinum fuse wire (about No. 34 Awg). The correction for the energy used in firing the charge (electrical energy plus energy of combustion of iron or chromel wire, and of any other combustible ignition aids used) may be determined by blank calorimetric experiments on the fuse alone. A battery of 3 to 5 storage cells or 6 to 10 dry cells in series or a transformer with a secondary voltage of about 10 can be used for ignition.
4. The charge should be burned in pure oxygen, or in commercially pure oxygen containing not more than 1 percent of nitrogen and no combustible gases. The amount of nitric acid formed in the combustion may be determined by titration with 0.1 N solution of sodium hydroxide by the use of methyl orange as indicator. Methyl red may be used if the solution is boiled to remove CO_2 before the end point, and under this condition gives a sharper end point. The correction for the formation of aqueous nitric acid is 59 kJ mol^{-1}, or .94 kJ g^{-1} of HNO_3.

CONVERSION TO OTHER ENERGY UNITS. [3]

If the energy of combustion of the standard reference material in calories per gram is desired, the following conversion factor may be used: 1 calorie = 4.1840 J. The calorie thus defined is being used in connection with practically all of the thermochemical work done in the United States.

The results of calorimetric tests of fuels for steam power plants may be expressed in terms of the 1956 International Steam Tables calorie (I.T. cal), which is defined by the relation, 1 I.T. cal = 4.1868 J. The Btu used in modern steam tables is defined by means of the relation, 1 I.T. cal g^{-1} = 1.8 I.T. Btu (lbm* avoidupois)$^{-1}$. Thus 1 I.T. Btu (lbm voirdupois)$^{-1}$ = 2.326 J g^{-1}.

CALCULATION OF STANDARD THERMODYNAMIC QUANTITIES.

Methods of calculating the internal energy and enthalpy of combustion, referred to the thermodynamic standard state, from bomb calorimetric data are given by Prosen [4] and by Hubbard, Scott, and Waddington [4].

CALORIMETRIC TESTING PRACTICE.

In routine testing with the bomb calorimeter, where an accuracy of not better than 0.1 percent is required, as in fuel calorimetry, the use of the factor given under (2) and the buoyancy correction may be omitted and the energy evolved may be expressed in one of the ways listed below:

26.454 kJ (kilowatt seconds) g^{-1}
6,323 cal g^{-1}
6,318 IT cal g^{-1}
11,373 Btu (lbm avoirdupois)$^{-1}$

In the above list, weights are expressed as weight against brass weights in air. Also for work of this order of accuracy, the corrections for the energy used in firing the charge may be omitted if the fuse energy and the temperature rise of the calorimeter are about the same in the calibration of the calorimeter as in the determination of energy of combustion.

In determining the heating value for fuels, it is desirable to follow a standardized procedure such as those specified by the American Society for Testing and Materials [5], or as given in the National Bureau of Standards Monograph 7 [6].

* The abbreviation lbm identifies pound-mass as opposed to lbf which is pound-force. See [3].

[1] g is the gram mass (weight in vacuum). The reduction of weight in air to weight in vacuum was made using the value 1.320 g cm^{-3} for the density of benzoic acid at 25 °C.

[2] The gram (g) is 10^{-3} kilogram and the joule (J) is one newton-meter as defined in the International System of Units (SI). See reference [3].

[3] "ASTM Metric Practice Guide", National Bureau of Standards Handbook 102, (U.S. Government Printing Office, Washington, D.C. 20402, 1967); also available as "ASTM Metric Practice Guide", 2nd edition, (American Society for Testing and Materials, Philadelphia, Pa. 19103, 1966).

[4] Experimental Thermochemistry, Edited by F. D. Rossini, Interscience Publishers, New York, 1956; Chapter 6 by E. J. Prosen; Chapter 5 by Hubbard, Scott, and Waddington.

[5] In the following list of ASTM Standard Methods of Test the last two digits of the ASTM Designation represent the year of last revision. The most recent version should be sought as a matter of good practice.

(a) Laboratory Sampling and Analysis of Coal and Coke. ASTM Designation: D271–64.
(b) Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter. ASTM Designation: D2015–62.
(c) Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter. ASTM Designation: D240–64.
(d) Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High Precision Method). ASTM Designation: D2382–65.

[6] NBS Monograph 7, 1960, Precise Measurement of Heat of Combustion with a Bomb Calorimeter (U.S. Government Printing Office, Washington, D.C. 20402).