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U. S. DEPARTMENT OF COMMERCE

# National Bureau of Standards

## Certificate

FOR

STANDARD SAMPLE 39f

### BENZOIC ACID

(Calorimetric or Acidimetric Use)

#### MATERIAL

This lot of benzoic acid was prepared to insure material of high purity and uniformity. Although it is known to contain a small amount of impurity, its heat of combustion has been found to be the same, within the estimated uncertainty of the measurements, as that of specially purified samples of benzoic acid. On the basis of titration, a purity of 100.03 percent is indicated. It has also been found that this material will not absorb moisture from the atmosphere. The heat of combustion and the acidimetric value of the sample will not change with time if adequate precautions are taken to avoid the introduction of impurities.

#### CALORIMETRIC STANDARD

The quantity of heat evolved by combustion of Standard Sample 39f of benzoic acid has been found to be 26.4284 int. kj/g mass<sup>1</sup> (weight in vacuo) with an estimated uncertainty of 0.0026 int. kj/g, when the sample is used under the following conditions:

- A. The combustion reaction is referred to 25° C.
- B. The sample is burned in a bomb of constant volume in pure oxygen at an initial absolute pressure of 30 atm 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.

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

- 1. The material should be made into a briquet and weighed in this form in the crucible in which it is to be burned.
- 2. The conditions stated above under 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 heat 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  $t$ ,

<sup>1</sup>The value given here is higher by 0.036 percent than that given in the certificate for Standard Sample 39 e. The difference is not due to difference in material, but to an error in the previous value. There is no measurable difference in heat of combustion between Standard Samples 39 e and 39 f. In cases where an error of 0.036 percent is significant, the results of calibration experiments with benzoic acid, which were originally calculated on the basis of the data given in the certificate for Sample 39 e can be reduced to the basis of the data given in this certificate by the procedure described in J. Research NBS 29, 247 (1942) RP1499.

$m_s$  = mass of sample in grams,  
 $m_w$  = mass, in grams, of water placed in bomb before combustion,  
 $V$  = volume of bomb in liters,  
 $t$  = temperature to which the reaction is referred, in degrees centigrade.

3. The charge should be fired by passing electric current through a short length of iron wire (about No. 34 B. & S. gage). Correction should be made for the heat of combustion of the iron wire (6.63 kj/g of iron) and for the electric energy used in igniting the wire. The correction for the energy used in firing the charge (heat of combustion of iron wire plus electric energy) may be determined by blank calorimetric experiments in which only the iron wire is burned. A battery of 3 to 5 storage cells or 6 to 10 dry cells in series is suitable for ignition, although a toy transformer with a secondary voltage of about 10 is more convenient if alternating current is available.

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. The correction for the formation of aqueous nitric acid is 59 kj/mole, or 0.94 kj/g of HNO<sub>3</sub>.

If the heat of combustion of the sample in calories per gram is desired, the following conversion factor may be used:

$$1 \text{ calorie} = 0.0041833 \text{ int. kj.}$$

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 International Steam Tables calorie (I. T. cal.), which is defined by the relation

$$1 \text{ I. T. cal} = 3.600/860 \text{ int. kj.}$$

The Btu used in modern steam tables is defined by means of the relation:

$$1 \text{ I. T. cal/g} = 1.8 \text{ Btu/lb.}$$

In the ordinary use of 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) may be omitted and the heat evolved expressed as 26.449 int. kj (kw-sec)/g weight against brass weights in air (6,323 cal/g weight in air, or 6,318 I. T. cal/g weight in air, or 11,373 Btu/lb weight 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 length of the iron wire and the temperature rise of the calorimeter are about the same in the calibration of the calorimeter as in the determination of heats of

combustion. In determining the heating values of fuels it is desirable to follow a standardized procedure such as that specified by the American Society for Testing Materials in their Standard D-271-43 for coal or Standard D-240-39 for fuel oil.

Methods of calculating heats of reaction at a constant pressure of 1 atm., from bomb calorimetric data, are given by Washburn.<sup>2</sup>

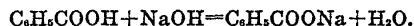
#### ACIDIMETRIC STANDARD

The following directions should be followed in the standardization of a 0.1 *N* solution of sodium hydroxide:

<sup>2</sup>E. W. Washburn, *Standard states for bomb calorimetry*, BS J. Research 10, 525 (1933) RP546.

Prepare a solution of sodium hydroxide that is approximately 0.1 *N* and free from carbon dioxide. Transfer 1.0000 g of benzoic acid to a 300-ml flask that has been swept free from carbon dioxide, and add 20 ml of alcohol (95 percent). Stopper the flask, and allow to stand until the sample has dissolved. Add 3 drops of a 1-percent solution of phenolphthalein, and titrate as a current of air that is free from carbon dioxide is passed through or over the solution in the flask.

Determine the volume of standard alkali required to obtain the same end point in a solution containing the same quantities of alcohol, water, and indicator as were used in the titration of the benzoic acid. Subtract the volume required from that used in the first titration, and calculate the normality of the sodium hydroxide solution on the basis of the equation



LYMAN J. BRIGGS, *Director*.

WASHINGTON, November 30, 1944.

Supplementary Note: The value 26.4284 int. kj per gram mass (weight in vacuum) given on the other side of this sheet for the heat of combustion of benzoic acid under the specified conditions is based in part on the use of the value 1.260 g/cm<sup>3</sup> at 25° C for the density of benzoic acid in reducing weight in air to weight in vacuum. This value of density was derived from the value 1.266 g/cm<sup>3</sup> at 15° C given in International Critical Tables, Vol. I p.208 (1926). Measurements reported in the literature by two different observers indicate that the true value of the density of benzoic acid is very nearly 1.320 g/cm<sup>3</sup> at 25° C, and this value has been confirmed by independent determinations made at this Bureau. Using this value for the density, the value obtained for the heat of combustion of standard sample 39f under the specified conditions is 26.4294 int kj per gram mass, and this value may be considered as the one derived correctly from the experimental data on this sample.

It may be noted that in using the sample to calibrate a bomb calorimeter, the same result would be obtained with either value of heat of combustion per gram mass, provided the corresponding value of density was used in reducing weight in air to mass.

Washington, February 12, 1946.