

DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate

FOR

STANDARD SAMPLE No. 39e

BENZOIC ACID

(Calorimetric or Acidimetric Use)

MATERIAL

This lot of benzoic acid was prepared to insure material of high purity and uniformity. It is not, however, to be considered as entirely free from impurity. As issued by the Bureau the moisture content is so low that no perceptible change in calorimetric or acidimetric value results from drying the material at 110 C or from fusing it. After long standing, particularly if the container has been opened, the material may have absorbed some moisture, in some cases enough to cause changes approaching 0.1 percent. If the amount of moisture absorbed is appreciable, it may be detected by making observations with both the original material, and the material after drying or fusing. The acid should be fused in a covered glass or platinum vessel placed in an air bath. The temperature during fusion must not rise above 140 C; it is best to keep it below 130 C (melting point about 122 C) and to cease heating as soon as fusion is complete.

ANALYSIS ^a

Purity of dried or fused sample on basis of titration ^b	Sulphur	Chlorine	Nonvolatile matter at 600 C	Heavy metals	Insoluble in diluted NH ₄ OH (1+3)	Density ^c at 25 C
Percent	Percent	Percent	Percent	Percent		g/cm ³
99.99	<0.001	<0.001	0.002	<0.0005	None	1.259

^a By J. I. Hoffman and H. A. Buchheit.

^b Compared with HCl which was standardized by weighing AgCl.

^c International Critical Tables, vol. 1, p. 208, and B.S. Jour. Research, vol. 7, p. 903, 1931.

No attempt was made to determine any water that may be retained in the dried or fused sample. The 1933 International Atomic Weights were used in calculating results.

CALORIMETRIC STANDARD

The quantity of heat evolved by combustion of standard sample no. 39e of benzoic acid has been found to be 26.419 international kilojoules per gram mass (weight in vacuo) with an estimated uncertainty of 0.006 international kilojoules per gram, when the sample is used under the following conditions:

- The reaction is referred to 25 C.
- The sample is burned in a bomb of constant volume in pure oxygen at an initial absolute pressure of 30 atmospheres at 25 C.
- The weight of the sample burned amounts to 3 grams per liter of bomb volume.
- The bomb before combustion contains 3 grams of liquid water per liter of bomb volume.

Methods of calculating heats of reaction at a constant pressure of one atmosphere, from bomb calorimetric data, are given in Bureau of Standards Journal of Research, vol. 10, p. 525, 1933 (RP546, "Standard States for Bomb Calorimetry").

In using the standard sample it will be advantageous to observe the following procedure:

- If the material has not been fused it should be made into a briquet and weighed in this form.

- 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:

$$1 + 10^{-6}[25(P-30) + 49(m_s/V-3) + 38(m_w/V-3) - 36(t-25)]$$

where

P = initial oxygen pressure in atmospheres.

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.

- 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 (6.64 kilojoules per gram 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 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.

[OVER]

4. The charge should be burned in pure oxygen, or in commercially pure oxygen containing not more than 5 percent nitrogen and no combustible gases. The amount of nitric acid formed in the combustion may be determined by titration with 0.1 normal aqueous NaOH. The correction for the formation of aqueous nitric acid is 62 kilojoules per mole, or 0.98 kilojoules per gram of HNO₃.

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

1 calorie=0.004185 kilojoules or 0.004183, international kilojoules.

The calorie thus defined has been used in most of the recent thermochemical work done in the United States and is equal to the 15° calorie within the accuracy with which the specific heat of water at 15° is known.

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 26.440 international kilojoules (kilowatt-seconds) per gram weight against brass weights in air at a pressure of one standard atmosphere (6,320 calories per gram 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

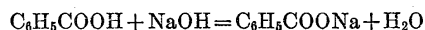
follow a standardized procedure such as that specified by the American Society for Testing Materials in their Standard D-271-30 for coal or Standard D-240-27 for fuel oil.

ACIDIMETRIC STANDARD

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

Prepare a solution of sodium hydroxide free from carbon dioxide. Transfer 1.0000 g of benzoic acid to a 300-ml flask which 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 free from carbon dioxide is passed through or over the solution in the flask.

Determine the effect of the alcohol and of the dilution on the end point by titrating a blank containing the same quantities of alcohol, water, and indicator. 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 following equation:



For discussions regarding the use of benzoic acid in acidimetry see articles by George W. Morey (Jour. Am. Chem. Soc., 34, p. 1027, 1912) and E. R. Weaver (Ibid., 35, p. 1309, 1913).

Lyman J. Briggs,
Director.

WASHINGTON, D.C.
October 16, 1933.