DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate

FOR

STANDARD SAMPLE No. 39d

BENZOIC ACID

(Calorimetric or Acidimetric Use)

TREATMENT OF MATERIAL

The sample as issued by the bureau may be considered free from moisture. After long standing, particularly if the container has been opened, there is a possibility that the material may contain some moisture. If there is any doubt as to the integrity of the sample, fusion may be resorted to. 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. In one case, material which had stood in the laboratory for about two years showed differences before and after fusion of 6 to 7 parts in 10,000 when tested for acid equivalent.

ANALYSIS [a]

Purity of fused sample on basis of titration.[b]	Sulphur	Chlorine	Nonvolatile matter at 600° C	[c] Density $\frac{15}{4}$
Per cent 99. 98	*Per cent* 0. 001	*Per cent* <0. 001	*Per cent* 0. 003	1. 266

[a] By Aaron Isaacs. [b] Compared with HCl which was standardized by weighing AgCl. [c] International Critical Tables 1, p. 208.

CALORIMETRIC STANDARD

The total heat of combustion at constant volume of benzoic acid No. 39d, per gram weight in air against brass weights, has been found to be 6,329 calories $_{20°}$.

The total heat of combustion at constant volume of a substance containing only the elements carbon, hydrogen, and oxygen is defined as the number of heat units liberated by the combination in an inclosure of constant volume. of unit quantity of the substance, with oxygen, to form gaseous carbon dioxide and liquid water, the substance and the oxygen being initially at the same temperature, and the products of combustion being cooled to the initial temperature. A discussion of this definition may be found in B. S. Scientific Paper 230.

In using the standard sample. it is desirable to observe the following procedure:

1. If the material has not been fused, it should be made into a briquet and weighed in this form. The charge should not be too large for complete combustion in the bomb in which it is to be burned, usually from 1.0 to 1.5 g. The charge should be placed in the bomb immediately after weighing.

2. The charge should be fired by a short length of iron wire of about No. 34 B. & S. gage (about 0.15 mm diameter) and a correction (1,600 calories per gram) should be applied for the heat of combustion of the wire. A battery of 3 to 5 storage cells or 6 to 10 dry cells in series should be used for ignition. A toy transformer with secondary voltage of about 10 is more convenient, if alternating current is available.

3. The charge should be burned in pure oxygen or in commercially pure oxygen, containing preferably not over 5 per cent of nitrogen and no combustible gases. To secure complete combustion the total quantity of oxygen should be not less than three times that required to combine with the combustible charge. This usually requires a pressure of from 20 to 40 atmospheres in the bomb.

4. The formation of nitric acid as a result of combustion yields 230 calories per gram of acid formed and a correction for the heat so produced should be applied.

Most fuels can be burned without briqueting, and platinum wire may be used for ignition in place of iron wire; otherwise the conditions specified above, as well as the details of observing and of computing results, should be as nearly as possible identical in fuel combustions and in calibration observations.

ACIDIMETRIC STANDARD

The following directions should be used for 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 per cent). Stopper the flask, and allow to stand until the sample has dissolved. Add 3 drops of a 1 per cent 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.

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

George K. Burgess

Director.

ıshington, D. C.
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