National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 39j

Benzoic Acid
(Calorimetric Standard)

This Standard Reference Material (SRM) is intended for use in the calibration and standardization of adiabatic, isoperibol, and aneroid bomb calorimeters. It was refined by fractional freezing to give a material of high homogeneity and purity and conforms to the American Chemical Society specification for reagent-grade benzoic acid. Mass spectrometric and coulometric measurements indicate a purity of 0.999996 mol/mol. The heat of combustion does not differ significantly from that of SRM 39i and earlier lots, on the basis of comparison experiments with earlier standard samples. SRM 39j is supplied in a unit consisting of 30 g of crystalline material.

The quantity of energy evolved by combustion of SRM 39j, benzoic acid, when burned under the standard bomb conditions is given below, where g is the gram mass (mass in vacuum). The reduction of weight in air to mass in vacuum was made using the value $1.320 \text{ g} \cdot \text{cm}^{-3}$ for the density of benzoic acid at 25 °C.

$$\text{Certified Value: } 26\ 434 \text{ J} \cdot \text{g}^{-1} \pm 3 \text{ J} \cdot \text{g}^{-1}$$

Uncertainty: The uncertainty is given for the certified quantity of energy detailed in Table 1. It is calculated according to the ISO and NIST Guides [1]. The uncertainty for the heat of combustion, $\Delta_c u_{39j}$, of the benzoic acid, was calculated from the relative standard deviation of the mean (coefficient of variability) of the four components shown in equation 2 as described in detail under "Determination of Overall Uncertainties".

NOTICE AND WARNINGS TO USERS

Handling and Storage: SRM 39j is stable when stored in its original container, with the cap tightly closed under normal laboratory conditions of temperature and humidity. This SRM will not absorb moisture from the atmosphere if the relative humidity does not exceed 90 %. The heat of combustion of the sample will not change with time if adequate precautions are taken to avoid the introduction of impurities.

Expiration of Certification: The certified value is valid **indefinitely**, provided the material is handled and stored in accordance with the instructions given in this certificate (see section "Handling and Storage"). Past experience with benzoic acid has shown no degradation of this material with time. Samples from the earliest lots of SRM 39 have shown no change to date.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of the technical measurements leading to certification were performed by D.R. Kirklin of the NIST Chemical Kinetics and Thermodynamics Division.

Material characterization was performed by A. Cohen (ret.), K.W. Pratt, M.J. Welch, and E.V. White of the NIST Analytical Chemistry Division.

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See Certificate Revision History on Last Page

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Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Source and Preparation of Material[1]: Benzoic acid was manufactured by Velsicol (Rosemont, IL) by oxidizing toluene to benzoic acid using cobalt naphthenate as a catalyst. The product was purified by distillation and supplied as a low-odor quality material to Universal Preservache (Brooklyn, NY). Harrell Industries (Rock Hill, SC) obtained three separate batches of this material and further purified it according to NIST specifications using fractional freezing (cooling molten benzoic acid and drawing off liquid) then grinding the product to specified size 125 μm to 600 μm (30 mesh to 140 mesh) using a Stokes granulator (an oscillating drum which pressed the crystals through a stainless steel screen of specified mesh).

Sample Characterization: The SRM 39j benzoic acid sample lot was analyzed, by several methods, for impurities and other properties relating to purity. Benzoic acid samples in various matrices were analyzed by infrared spectroscopy, ultraviolet spectroscopy, mass spectrometry, and gas chromatography/mass spectrometry. No impurities were detected by these techniques. An insoluble matter of 21.1 μg/g $\pm$ 0.5 μg/g was measured from a methanol solution of the SRM 39j sample. An acidimetric assay by coulometry of the dried sample yielded a value of 0.999 996 mol/mol $\pm$ 0.000 072 mol/mol [1]. The preliminary drying steps yielded values less than 0.01 weight % for the moisture content. SRM 39i was used as a control sample for all of these measurements and in all cases the new SRM 39j is of equal or better quality than the SRM 39i sample.

Homogeneity and Certification Under Actual Bomb Conditions: Fifteen bottles of SRM 39j were randomly selected to determine the measurement order. An analysis specimen was selected from each bottle and pressed into pellet form. Seven analysis specimens were selected from each of the two bottles of SRM 39i used as a calibrant specimen. A measurement with a SRM 39i specimen was performed between two SRM 39j measurements, alternating specimens from bottle one and then bottle two of the SRM 39i, for a total of fourteen calibrant runs and 15 certification runs.

The NIST adiabatic aneroid bomb calorimeter was used to make these measurements. Approximately 0.287 g of benzoic acid were burned in Ultra High Purity (UHP) oxygen. This quantity of sample was necessary to produce a three degree temperature rise in the calorimeter. The benzoic acid pellet was weighed into a platinum crucible and then placed in contact with a 2 cm platinum fuse. Three tenths (0.3) of a mL of water was placed in the bomb. The bomb has an internal volume of 0.096 L. The bomb was sealed and filled to 3.1 MPa (450 psia) of UHP oxygen. The oxygen was slowly released to purge the bomb of the one atmosphere of air that was initially in the bomb. The bomb was refilled to 3.1 MPa (450 psia) of UHP oxygen. The charged bomb was placed inside the adiabatic calorimeter jacket and the calorimeter jacket evacuated with a vacuum pump. The calorimeter was heated to 25 °C and allowed to equilibrate overnight. On the following day, time vs. temperature measurements were made for a 75 min experiment time. The sample was ignited after the first 25 min period. A measured calorimeter temperature rise was determined for each of the 29 benzoic acid samples.

The preceding procedure is an example of the actual bomb conditions. In actual practice, the experimental results are referenced to standard bomb conditions which are given below.

Standard Bomb 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 3.0 megapascals 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.

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[1]Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

INSTRUCTIONS FOR USE

In the use of SRM 39j, the following procedure should be observed:

1. The benzoic acid should be made into a pellet and weighed in this pelleted 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 possible. If it is necessary to depart from these conditions, the value given for the energy evolved should be multiplied by the following factor.

$$1 + 10^{-6}[200\,(P - 3.0) + 42\,(m_s/V\text{-}3) + 30\,(m_w/V\text{-}3) - 45\,(t - 25)] \tag{1}$$

where:

P = initial absolute pressure of oxygen, in megapascals 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 chromel (0.15 mm dia.), or platinum (0.08 mm dia.) fuse wire. The correction for the energy used in firing the charge (electrical energy plus energy of combustion of the chromel wire, and of any other combustible ignition aids used) may be determined by blank calorimetric experiments on the fuse alone.

4. The charge should be burned in pure oxygen, or in commercially pure oxygen containing not more than 100 µg/g of nitrogen and 20 µg/g of hydrocarbon. The amount of nitric acid formed in the combustion may be determined by titration with 0.1 mol/L solution of sodium hydroxide. The correction for the formation of aqueous nitric acid is 59 kJ·mol^{-1} of HNO_3.

Determination of Overall Uncertainties: The calculation of the total uncertainty is based upon the ISO and NIST Guides [1]. The uncertainty for $\Delta_c u$ of the benzoic acid, was calculated from the relative standard deviation of the mean (coefficient of variability) of the four components shown in equation 2. The square root of the sum of the squares of the four components was determined to calculate the uncertainty for $\Delta_c u_{39j}$ according to equation 2, which follows.

$$s\{\Delta_c u_{39j}(39j,cr)\} = (\Delta_c u_{39j}) \ \text{x} \ [\{s(<\varepsilon_{std}>)/\varepsilon_{std}\}^2$$

$$+ \ \{s(<\Delta_c u_{39j}>)/\Delta_c u_{39j}\}^2 + \{s(<\Delta_c u_{39i}>)/\Delta_c u_{39i}\}^2 + (0.00005)^2]^{\frac{1}{2}} \tag{2}$$

The first two components were derived from the mean and the standard deviation of the mean of the calibration measurements with SRM 39i and the certification measurements for the proposed SRM 39j. The third component was derived from the uncertainty of the measurements [2] for the certification of the calibration standard, SRM 39i. The total uncertainty for the certification of the previous lot, SRM 39i, was calculated using the mean and standard deviation of the mean of the calibration and certification measurements reported by Churney and Armstrong [2]. An estimated uncertainty of five thousands (0.005) of one percent was used for systematic errors associated with SRM 39j measurements.

Calculations 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 Hubbard, Scott, and Waddington [3].

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 in item two under Standard Bomb Conditions and the buoyancy correction may be omitted.

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 (see section "ASTM Standard Test Methods Applicable to the Use of SRM 39j").

Table 1. Components of the Overall Uncertainty for SRM 39j[a]

$<\varepsilon_{std}>$	-2516.481 $J \cdot K^{-1}$ $\pm$	0.054 $J \cdot K^{-1}$		Type A[b]
$<\Delta_c u_{39j}>$	-26434.79 $J \cdot K^{-1}$ $\pm$	0.65 $J \cdot g^{-1}$		Type A
$<\Delta_c u_{39i}>$[3]	-26433.67 $J \cdot K^{-1}$ $\pm$	0.63 $J \cdot g^{-1}$		Type A
Systematic Component	0.005 % of $<\Delta_c u_{39j}>$			Type B[c]

The total uncertainty is equal to twice the calculated value of 1.70.

[a] The "$\pm$" precedes the standard deviation of the mean.
[b] Type A uncertainties are evaluated by statistical methods [1].
[c] Type B uncertainties are evaluated by other means [1].

ASTM Standard Test Methods Applicable to the Use of SRM 39j

D 3180-89   Standard Test Material for Calculating Coal and Coke Analyses from As-Determined to Different
             Bases
D 5865-02   Standard Test Method for Gross Calorific Value of Coal and Coke; Annu. Book ASTM Standard
D 240-00   Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter
D 4809-00   Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter

REFERENCES

[1]   ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed., International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.
[2]   Churney, K.L.; Armstrong, G.T.; *Studies in Bomb Calorimetry. A New Determination of the Energy of Combustion of Benzoic Acid in Terms of Electrical Units*; J. Res. Nat. Bur. Stand., Vol. 72A, pp. 453–465 (1968).
[3]   Hubbard, W.N.; Scott, D.W.; Waddington, G.; *Reduction to Standard States* (*at 25°*) *of Bomb Calorimetric Data for Compounds of Carbon, Hydrogen, Oxygen and Sulfur*; J. Phys. Chem., Vol. 58, No. 2, pp. 152–162 (1952).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751, email srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.