

National Bureau of Standards

Certificate

Standard Reference Material 1656

Thianthrene

Combustion Calorimetric Standard

This Standard Reference Material (SRM) consists of thirty grams of thianthrene which was purified by three recrystallizations and determined to be at least 99.7% pure. SRM 1656 is intended for use in checking calorimetric apparatus, analytical procedures, and the calculations utilized in the oxygen-bomb calorimetry of organic sulfur compounds.

The certified value for quantity of heat evolved by combustion of a sample of this material in an oxygen-bomb calorimeter is:

$$33.480 \pm 0.009 \text{ MJ/kg.}$$

The uncertainty of the certified value is two times the overall standard deviation of the mean. The overall standard deviation of the mean was computed from the standard deviations of the mean from the thianthrene measurements, the calibration measurements and the uncertainty of the certified value for SRM 39i (Benzoic Acid) which was used in the calibration measurements.

The certified value is for the following reaction at 25 °C:



Bomb Conditions:

- (1) The SRM should be thoroughly dried either in a vacuum oven or at elevated temperatures; the dried sample may be stored at room temperature in a closed container. The dried material should be compressed into a pellet before placing it in the bomb.
- (2) The mass of water (in grams) initially placed in the bomb should be a minimum of 30 times the volume of the bomb (in cubic decimeters).
- (3) The material in pellet form is burned in a bomb of constant volume filled with pure oxygen at a pressure of 3 MPa at room temperature. The bomb should not be purged of air which should be included with the 3 MPa of oxygen to ensure the oxidation of sulfur to the hexavalent state.
- (4) The bomb must be rotated to form a homogeneous sulfuric acid solution inside the bomb. The rotation should be initiated 1-2 minutes after ignition of the sample and the total time of rotation should be at least 1 minute.

(over)

Recommended Procedures:

- (1) The ignition energy must be accounted for in each experiment.
- (2) The quantity of nitric acid is taken as the difference between the total acid produced and the theoretical quantity of sulfuric acid calculated from the mass of the sample.
- (3) The energy evolved by the actual bomb process, ΔU_B , must be corrected to that of the ideal process, ΔU_0° , by the method of Hubbard, Scott and Waddington [1,2] and Månsson and Hubbard [3]. For a detailed description of procedures for the combustion bomb calorimetric measurement of organic sulfur compounds, the reader should consult the chapter by Waddington, Sunner, and Hubbard [4].

The measurements were performed and analyzed in the Chemical Thermodynamics Division by D. R. Kirklin, under the technical direction of E.S. Domalski.

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- [1] W.N. Hubbard, D.W. Scott and G. Waddington, "Reduction to Standard States (at 25 °C) of Bomb Calorimetric Data for Compounds of Carbon, Hydrogen, Oxygen and Sulfur," *J. Phys. Chem.* **58**, 152 (1954).
- [2] W.N. Hubbard, D.W. Scott and G. Waddington, Chapter 5, "Standard States and Corrections for Combustions in a Bomb at Constant Volume," *Experimental Thermochemistry*, F.D. Rossini, Editor, Interscience Publishers, Inc., New York, 1956, pp. 75-128.
- [3] Månsson, M., and Hubbard, W.N., Chapter 5, *Combustion Calorimetry*, S. Sunner and M. Månsson; Editors, (Pergamon Press, New York, 1979).
- [4] Waddington, G., Sunner, S., and Hubbard, W.N., Chapter 7, "Combustion in a Bomb of Organic Sulfur Compounds," *Experimental Thermochemistry*, F.D., Rossini, Editor, Interscience Publishers, Inc., New York, 1956, pp. 149-179.

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