TechNotes

Bulletin No.101

Calibration of Oxygen Bomb Calorimeters

Procedures for standardization of Parr oxygen bomb calorimeters.

Energy Equivalent

The calibration of an oxygen bomb calorimeter has traditionally been called the standardization. During the standardization process, a known amount of heat is introduced into the calorimeter by the combustion of benzoic acid. This standardization produces the energy equivalent of the calorimeter for a specific temperature rise.

Before a material with an unknown heat of combustion can be tested in a bomb calorimeter, the **energy equivalent (EE or E)** or heat capacity of the calorimeter must first be determined. This value represents the sum of the heat capacities of the components in the calorimeter, notably the metal bomb, the bucket, the water in the bucket and the jacket. Since the system changes slightly with use, energy equivalents are determined empirically at regular intervals by burning a sample of a standard material with a known heat of combustion under controlled and reproducible operating conditions. By international agreement in the 1920's, benzoic acid was selected as the chemical standard to be used in calibrating bomb calorimeters. Today, it remains as the sole chemical primary standard for this type of calibration.

Desirable Properties for Test Substances:

Test substances for bomb combustion calorimetry should satisfy the following requirements.

- It must be readily available in pure form.
- It must be stable.
- It must not be hydroscopic.
- It must not be volatile.
- It must be easily brought into a form suitable for combustion.
- It should offer no unusual difficulties during combustion in the bomb.
- The value for the heat of combustion is characterized with suitable accuracy.

While contrary to some of the above requirements, in certain cases the following apply.

- It is advantageous for tests involving materials that are difficult to handle or ignite that the test substance poses similar handling or ignition difficulties.

- It is advantageous for tests involving substances whose combustion chemistry is complex that the test substance yields similar combustion products under the same experimental conditions.

For example, 2,2,4-Trimethyl-pentane (iso-octane) is widely used as a test substance for oxygen bomb combustion work with volatile liquids.

The amount of heat introduced by the reference sample is determined by multiplying the heat of combustion of the standard material by the weight of the sample burned. Then, by dividing this value by the temperature rise produced in the test, we obtain a resultant energy equivalent for this particular calorimeter.

Example:

Consider a standardization test in which 0.9914 grams of standard benzoic acid (heat of combustion 6318.4 cal/g) produced a temperature rise of 2.639°C. The energy equivalent (W) of the calorimeter is then calculated as follows:

$$W = \frac{(0.9914g)(6318.4cal/g)}{2.639^\circ C} = 2374cal/^\circ C$$

Note: For simplicity, the corrections usually applied for heats introduced by the fuse and by acid formation are omitted from the above example.

It is important to note that the energy equivalent for any calorimeter is dependent upon a set of operating conditions, and these conditions must be reproduced when the fuel sample is tested if the energy equivalent is to remain valid. For instance, the addition of one gram of water in the calorimeter will alter the energy equivalent value by one calorie per degree Celsius. Less obvious but equally important are the changes resulting from different bombs or buckets with unequal masses, different operating temperatures, different thermometers, or even the biases imposed by different operators.

After the energy equivalent has been determined, the calorimeter is ready for testing fuel samples. Samples of known weight are burned and the resultant temperature rise is measured and recorded. The amount of heat obtained from each sample is then determined by multiplying the observed temperature rise by the energy equivalent of the calorimeter. Then, by dividing this value by the weight of the sample we obtain the calorific value (heat of combustion) of the sample on a unit weight basis. Continuing the above example:

Assume a fuel sample weighing 0.9936 gram produced a temperature rise of 3.234°C in a calorimeter with an energy equivalent of 2416 cal/°C. The gross heat of combustion (H_g) is determined by multiplying the temperature rise by the energy equivalent, and dividing this product by the weight of the sample:

$$Hg = \frac{(3.234^\circ C)(2416cal/^\circ C)}{0.9936g} = 7863cal/g$$

Note: Again, for simplicity, corrections for acids and fuse have been omitted.

Standard Test Methods

Standard Test Methods have been written, tested, and published by a number of international standards organizations including the American Society for Testing and Materials (ASTM), International Organization for Standardization (ISO), British Standards Institution (BS), and Deutsches Institute for Nurmung (DIN). Each of these methods contains procedures for both the initial standardization and the continuing verification of that standardization. Laboratories should calibrate (standardize) their calorimeters in accordance with the details spelled out in the test method they are using.

Recommended Standardization Procedure

CALIBRATION RUN LIMIT 10
USE BOMB 1
EE MAX. STD. DEVIATION 0.0
HEAT OF COMBUSTION OF STANDARD 6318.4
BOMB SERVICE INTERVAL 500

If a standard method is not being used, the following standardization procedure is recommended.

Initial standardization:

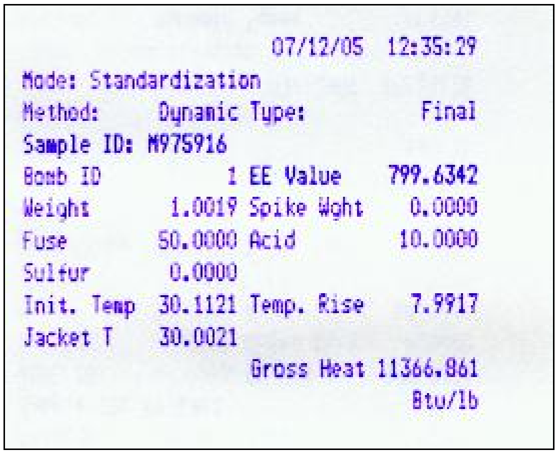
1) Determine the average energy equivalent as the average of 10 tests.
2) To be acceptable, the relative standard deviation of this series of tests shall be 0.17% or less for 6400, 6300, and 6200 Calorimeters, 0.34% or less for 6100 Calorimeters, 0.50% or less for 1341 Calorimeters and 0.67% or less for 6725 Calorimeters. (Review TechNote 100 “Precision and Accuracy” for additional information).

BOMB EE VALUE 928.3655
RUNS, EE VAL 10
REL. STD. DEV. 0.0375%
BOMB FIRE COUNT 0
PROTECT EE VALUE Off
MANUAL EE ENTRY 928.3655

3) If these criteria are not met, the source of the problem must be found and corrected and the entire series repeated until an acceptable energy equivalent is determined.

The calibration of any instrument should reflect as closely as practicable, the current state of the measuring system. To this end, the Parr 6000 Series Calorimeters support the calculation and automatic maintenance of a rolling average of the energy equivalent. A calibration run limit of no less than five tests is recommended when using a rolling average method.

It is important that the E value NOT be protected in order for the instrument to automatically update the E value when new final standardization tests become available. The rolling average method keeps the E value current, by analyzing a sample of benzoic acid run every tenth test in standardization mode. The following type of test report is issued when a standardization test is performed:



```
                     07/12/05  12:35:29
Mode: Standardization
Method:     Dynamic Type:         Final
Sample ID: M975916
Bomb ID           1 EE Value   799.6342
Weight       1.0019 Spike Wght   0.0000
Fuse        50.0000 Acid        10.0000
Sulfur       0.0000
Init. Temp  30.1121 Temp. Rise   7.9917
Jacket T    30.0021
                    Gross Heat 11366.861
                                  Btu/lb
```

Not only is an E value provided and incorporated into the rolling average, but a gross heat value is back calculated using the current average instrument calibration factor. This gross heat value can be quickly compared against the accepted value of 11373 Btu/lb in order to assess the degree of overall control on the measurement process.

In order for the standardization test to be incorporated in to the rolling average, the test must be final, not preliminary. The Operating Instruction Manuals for each calorimeter provide details on fixed corrections which will create a final test if a more rigorous determination of the corrections is not required.

Periodic Heat Capacity Checks

The calorimeter heat capacity value (energy equivalent) shall be checked on a regular basis. Renewed determination of the heat capacity is required whenever significant alterations have been made to the instrument or to the test conditions. The optimum frequency for checking the heat capacity or instrument calibration will depend on the stability of the measurement system and the risk involved when the system departs from statistical control. Since all data obtained during the period last-known-in-control to first-known-out-of-control are suspect, such intervals may need to be minimized.

There are several empirical approaches to making a decision on how frequently the instrument calibration should be checked. The experience of the laboratory may indicate the expected frequency of occurrence of trouble, in which case reference sample measurements, at least three in number, should be equally spaced within such an interval. Another approach is the "length of run" concept. In this, recognizable breaks in the production (of data) process are identified which could cause significant changes in precision or bias. Such breaks could include:

change of work shift
rest periods
change, modification, or adjustment of apparatus
use of new calibration standards
significantly long down-times
use of a new lot of reagents

At least three reference samples should be measured during any of these periods when the periods are considered to be potentially significant.

Periodic checks of the instrument calibration are a risk-reducing procedure. However, if it involves more than ten percent of a laboratory's measurement effort, either the quality control process may need improvement or too much effort is being exerted in this direction. If less than five percent of effort is devoted to such measurements, the laboratory may be taking too high a risk of producing unacceptable data, or may not even know the quality of the data it is producing. The above statements are made with a laboratory making a significant number of high-quality routine measurements in mind. If a laboratory's program involves occasional or one-of-a-kind measurements, the amount of quality assurance effort required, including the number of measurements of reference materials to be made may be significantly more than that indicated above.

TechNote Bulletin No. 100 “Precision and Accuracy” discusses the determination of acceptable results from a calorimeter in detail and should be reviewed.

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