



# Parr Instrument Company

## Introduction to Bomb Calorimetry



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## Scope

The information presented here is intended to give Parr Calorimeter users an overview of the basic principals involved in measuring the heat of combustion (calorific value) of solid and liquid fuels, foodstuffs and other combustible materials in a bomb calorimeter. Although this paper does not attempt to cover all of the technical aspects of bomb calorimetry, it will serve as a useful supplement to the operating manuals furnished with Parr Calorimeters and Oxygen Combustion Apparatus. Users who want a more detailed coverage of the theoretical aspects of bomb calorimetry and experimental thermochemistry will want to consult other references such as those listed on pages 10-11.

## Related Instructions

The following Parr publications are also available to further your understanding of bomb calorimetry and Parr Calorimeters:

No.	Description
204M	1341 Plain Jacket Calorimeter
205M	1108 Oxygen Combustion Vessel
584M	6100 Compensated Calorimeter
585M	6200 Isoperibol Calorimeter
587M	6400 Automatic Isoperibol Calorimeter
592M	6725 Semimicro Calorimeter

## Customer Service

Questions concerning the installation or operation of this instrument can be answered by the Parr Customer Service Department:

1-309-762-7716 • 1-800-872-7720 • Fax: 1-309-762-9453  
 E-mail: [parr@parrinst.com](mailto:parr@parrinst.com) • <http://www.parrinst.com>

## Terminology

Calorimetric measurements involve the use of various temperature and energy units. In order to avoid errors and confusion in the interpretation of these data, their relationships should be well understood.

**Calorimetry** is the science of measuring quantities of heat, as distinct from "temperature". The instruments used for such measurements are known as **calorimeters**. In this publication we are concerned only with **oxygen bomb calorimeters**, which are the standard instruments for measuring calorific values of solid and liquid combustible samples.

The **calorific value** (heat of combustion) of a sample may be broadly defined as the number of heat units liberated by a unit mass of a sample when burned with oxygen in an enclosure of constant volume. In this reaction the sample and the oxygen are initially at the same temperature and the products of combustion are cooled to within a few degrees of the initial temperature; also the water vapor formed by the combustion is condensed to the liquid state. A more exact definition would specify the temperature at which the reaction begins and ends. However, the change in the heat of combustion with possible variations in the initial temperature is so small that this specification is not necessary. Also, the initial and final temperatures are not the same – differing by the amount of temperature rise in the calorimeter – but the effect of this difference is small and usually it is neglected. Thus the term **calorific value** (or heat of combustion) as measured in a bomb calorimeter denotes the heat liberated by the combustion of all carbon and hydrogen with oxygen to form carbon dioxide and water, including the heat liberated by the oxidation of other elements such as sulfur which may be present in the sample.

The **heat energy** measured in a bomb calorimeter may be expressed either as **calories** (cal), **British thermal units** (BTU) or **Joules** (J), with the International Steam Table calorie as the basic unit in this system. One **calorie** equals 4.1868 absolute Joules, and is roughly equivalent to the heat energy required to raise the temperature of one gram of water one degree Celsius at 15 °C. The **British thermal unit** equals 251.996 calories and is roughly equivalent to the heat energy required to raise one pound of water one degree Fahrenheit at 60 °F. These and other energy relationships are shown in the table below.

### Calorific Values

1 calories	=	4.1868 Joules
1 BTU	=	1055.06 Joules
1 BTU	=	251.996 calories
1 BTU / lb	=	2.326 Joules / gram
1.8 BTU / lb	=	1.0 calories / gram

### Note About Nomenclature

*Historically, burning a sample enclosed in a high pressure oxygen environment is known as Oxygen Bomb Calorimetry and the vessel containing the sample is known as an Oxygen Bomb. The terms bomb and vessel are used interchangeably.*

## Characteristics of Bomb Calorimeters

Heats of combustion as determined in an oxygen bomb calorimeter are measured by a substitution procedure in which the heat obtained from the sample is compared with the heat obtained from combustion of a similar amount of benzoic acid or other standardizing material whose calorific value is known. These measurements are obtained by burning a representative sample in a high-pressure oxygen atmosphere within a metal pressure vessel or "bomb". The energy released by this combustion is absorbed within the calorimeter and the resulting temperature change within the absorbing medium is noted. The heat of combustion of the sample is then calculated by multiplying the temperature rise in the calorimeter by a previously determined energy equivalent or heat capacity determined from previous tests with a standardizing material. Corrections must be applied to adjust these values for any heat transfer occurring in the calorimeter, as well as for any side reactions which are unique to the bomb combustion process.

Four essential parts are required in any bomb calorimeter:

1. A bomb or vessel in which the combustible charges can be burned.
2. A bucket or container for holding the bomb in a measured quantity of water, together with a stirring mechanism.
3. An insulating jacket to protect the bucket from transient thermal stresses during the combustion process.
4. A thermometer or other sensor for measuring temperature changes within the bucket.

**The bomb** must be a strong, thick-walled metal vessel which can be opened for inserting the sample, for removing the products of combustion and for cleaning. Valves must be provided for filling the bomb with oxygen under pressure and for releasing residual gases at the conclusion of a test. Electrodes to carry an ignition current to a fuse wire are also required. Since an internal pressure up to 1500 psig can be developed during combustion, most oxygen bombs are constructed to withstand pressures of at least 3000 psig.

In the moist, high-pressure oxygen environment within a bomb, nitrogen present will be oxidized to nitric acid, sulfur present will be oxidized to sulfuric acid, and chlorine present will be released as a mix-

ture of chlorine and hydrochloric acid. These acids combine with the residual high temperature oxygen to form a corrosive vapor which will etch ordinary metals. Therefore the bomb must be made of materials which will not be attacked by these combustion products. Parr oxygen bombs are made of complex high-chromium-nickel alloys which have proven to be particularly well suited for this purpose, as demonstrated by the many thousands of these bombs which are still in service after having been used for many years.

The **calorimeter bucket** must be carefully designed with sufficient capacity to hold the bomb completely submerged in water, with a probe to read temperature and a stirrer included to promote rapid thermal equilibrium without introducing excessive heat in the form of mechanical energy. Buckets are commonly made with a highly polished outer finish to minimize the absorption and emission of radiant heat.

The bomb and bucket are held in a calorimeter jacket which serves as a thermal shield, controlling any heat transfer between the bucket and the surroundings. The jacket will minimize the effects of drafts, radiant energy and changes in room temperature during a test, but it may not completely eliminate all heat leak. Therefore it is necessary to have a means for establishing precisely the amount of heat transferred during a test, or controlling the transfer so that it is uniform from one test to another.

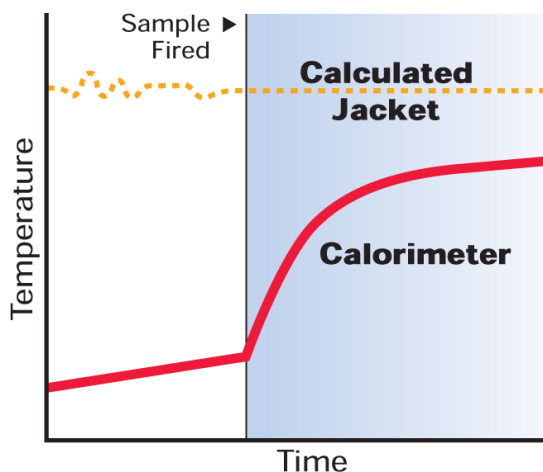
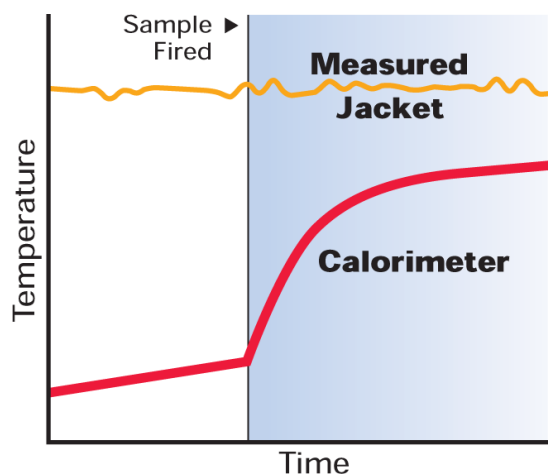
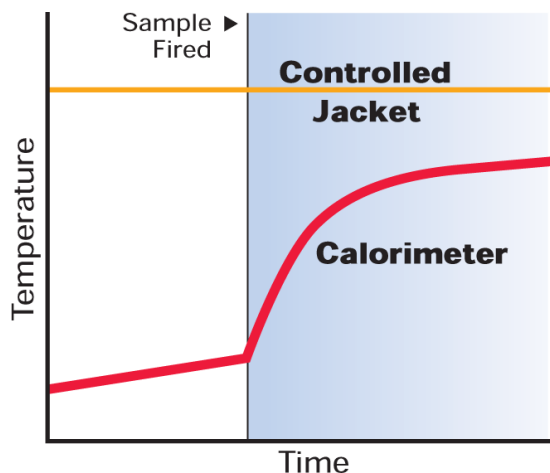
Several types of **jacketing systems** are used in oxygen bomb calorimeters. The simplest of these is the uncontrolled or plain insulating jacket. With this type of jacket it is assumed that the jacket temperature will remain constant throughout the test without employing an auxiliary temperature control system. Because of their simplicity, plain jacket calorimeters are recommended mainly as a low cost instrument for users who make only occasional calorific tests, or whose workload does not justify the purchase of a temperature controlled model. A plain jacket calorimeter requires no permanent connections. It can be set up and ready to operate in a few minutes, and when not in use it is easily disassembled for storage.

For best precision, the temperature of the calorimeter jacket must be closely controlled. This usually requires a water-filled jacket equipped with a means for adjusting the jacket temperature, either by an immersion heater or by hot and cold water

injections. With a temperature controlled jacket the calorimeter can be operated either in an **adiabatic** or **isoperibol mode**. In an adiabatic system the jacket temperature is adjusted continuously during a test to keep it equal at all times to the temperature in the bucket. Thus, by maintaining a zero differential between the jacket and bucket, there will be no heat transfer between the jacket and bucket, there will be no heat transfer between these components and the calculations and corrections required for an uncontrolled or isoperibol system can be eliminated. This type of jacketing was the dominate method for bomb calorimetry since Parr introduced the first practical adiabatic jacket nearly 100 years ago.

With the introduction of microprocessor based calorimeter controllers, isoperibol operation has become an extremely attractive option. In this type of system the jacket temperature is controlled and held constant throughout the determination while the bucket temperature is rising. A correction must then be applied to account for the heat leak resulting from the changing differential between bucket and jacket temperatures. Previously this method was largely reserved for high precision research since the required temperature measurements and calculations made it much less convenient than the adiabatic method. But with a microprocessor controller that will automatically monitor the temperatures and apply the required corrections, this limitation is removed. Calorimeters equipped with constant temperature jackets and automatic isoperibol computing capability are now available, offering excellent precision and operating speed without requiring the extensive jacket heating and cooling associated with adiabatic operation.

Precise **temperature measurements** are essential in bomb calorimetry. Mercury-in-glass thermometers, platinum resistance thermometers, quartz oscillators and thermistor systems have all been used successfully to measure the temperature rise in the bucket. Whatever system is used must provide excellent resolution and repeatability, with an accuracy of 0.001 °C or better specified in most standard test methods. Interestingly, high single-point accuracy is not a requirement since we are dealing here with **temperature changes**, not absolute values. When using an electrical temperature measurement system the temperature rise can be taken directly in ohms or other electrical units without conversion to temperature degrees, provided the same system is used when standardizing the calorimeter.



## Calorimeter Selection

The principal factors affecting selection of a calorimeter for a specific application deal with the precision required and the anticipated workload, and not with the type of sample to be tested. The same calorimeters are used for all oxygen-combustible samples; solids and liquids alike. Special sample holders and specific techniques may be required for holding volatile liquid samples to prevent evaporation loss during weighing operations, and certain additives may be required to obtain complete combustion of slow-burning samples, but with only a few exceptions, all can be burned in the same oxygen bomb using the same calorimeter system. Specially constructed, extra high strength bombs are available for burning explosives and similar hazardous materials, and bombs with a platinum lining or made of special corrosion resistant materials are available for use with samples which liberate unusual amounts of fluorine, chlorine or other corrosive combustion products.

Until recently, adiabatic calorimeters were the preferred choice in most industrial laboratories. Modern adiabatic jackets with microprocessor controls can approach the theoretical goal of eliminating all heat leaks, providing excellent precision in calorimetric tests, but specialized jackets and control systems are required. Tests may be slower and may require more externally supplied heating and cooling medium than an isoperibol system.

Isoperibol calorimeters with their controlled constant temperature jackets are an excellent choice for all calorific tests provided they are equipped with microprocessor controls to monitor the test and to compensate for heat flow within the calorimeter. With their less demanding requirements for externally supplied heating and cooling mediums, isoperibol systems offer opportunities for significant savings in energy and installed accessory equipment. Isoperibol calorimeters with microprocessor control are also the preferred choice for laboratories in which large numbers of samples are tested daily on a routine basis, giving the user the ability to complete as many as 7 tests per hour with excellent repeatability.

Because uncontrolled or plain jacket calorimeters lack the speed and convenience offered by adiabatic and isoperibol systems, plain calorimeters are used primarily for student instruction and by users who make only occasional tests, or whose workload does not justify the purchase of a more expensive automatic system.

## Standardization

Before a material with an unknown heat of combustion can be tested in a bomb calorimeter, the **energy equivalent** 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 and the water in the bucket. Since the exact amount of each of the metals used in the bomb and bucket is difficult to determine and continually changing 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. Benzoic acid is used almost exclusively as a reference material for fuel calorimetry because it burns completely in oxygen; it is not hygroscopic and is readily available in very pure form.

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. For example:

Consider a standardization test in which 1.651 grams of standard benzoic acid (heat of combustion 6318 cal/g) produced a temperature rise of 3.047 °C. The energy equivalent (W) of the calorimeter is then calculated as follows:

$$W = \frac{(1.651)(6318)}{3.047} = 2416 \text{ cal / } ^\circ\text{C}$$

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. It is readily apparent that a difference of one gram of water in the calorimeter will alter this 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.

## The Fuel Test

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 sample:

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 then determined by multiplying the temperature rise by the energy equivalent, and dividing this product by the weight of the sample:

$$H_g = \frac{(3.234)(2416)}{0.9936} = 7863 \text{ calories / gram}$$

Again, for simplicity, we have omitted corrections for acids and fuse.

To convert the heat of combustion to BTU per pound, we multiply by 1.8

$$(7863)(1.8) = 14,153 \text{ BTU / lb}$$

## Calorimetric Corrections

Precision in bomb calorimetry is dependent upon a repeatable set of operating conditions, applied uniformly to all standardization and determination tests. Those factors which cannot be held constant will require corrections to compensate for their effects. In addition, any differences between the combustion as it takes place in the bomb in relation to the process in a power plant or other application must also be taken into account.

The burning **fuse wire** in the bomb contributes additional heat to the bomb combustion. Since the amount of fuse wire consumed in each test may vary, the energy contributed by the fuse must be determined for each test and a correction applied to compensate for this variance. Similarly, if any **spiking material** or combustion aid is used to promote complete combustion of a sample that is difficult to burn, the heat produced by the combustion aid must be subtracted from the total energy release.

Since combustion in the bomb takes place in an atmosphere of nearly pure oxygen at high temperature and pressure, several reactions occur which would not develop when burning the same material under normal atmospheric conditions. These side reactions are important because they generate an appreciable amount of heat which cannot be credited to the sample, and for which a correction must be made.

In normal combustion all sulfur in a fuel is oxidized to sulfur dioxide and discharged with the stack gases. But when the same material is burned in an oxygen bomb, the oxidation is carried further to trioxide which then reacts with moisture in the bomb to form **sulfuric acid**. Likewise, in normal combustion nitrogen in the air is not affected. But when a fuel sample is burned in an oxygen bomb, some of the molecular nitrogen trapped in the bomb is oxidized and combined with water vapor to form **nitric acid**. ASTM and ISO test methods contain procedures for calculating the correction which must be applied to account for the heat liberated in the formation of these acids. While these methods are consistent within themselves, they are not exactly the same and users must review their individual procedure before making any changes in the method used to compute these corrections. Other elements such as phosphorus and chlorine in the sample may also introduce side reactions unique to the bomb, but in most cases these components are not present in sufficient quantities to significantly affect the results.

## Basis for Report

The results of a calorimetric test are originally expressed in terms of the state of moisture in the sample that was burned in the calorimeter. That is, if a weighed quantity of air-dried coal is used for the test, the original results will be in terms of heat units per weight of air-dry sample. This value is easily converted to other moisture content of the test sample and using conversion formulas published in ASTM Standard Method D3180 or in other standard references on fuel technology.

## Gross and Net Heats of Combustion

The results obtained from tests in a bomb calorimeter represent the gross heat of combustion of a sample, which includes the heat of vaporization given up when the newly formed water vapor produced by oxidation of hydrogen is condensed and cooled to the temperature of the bomb. In nearly all industrial applications this water vapor escapes as steam in the flue gases and is not available for useful work. To compensate for this loss we can calculate the net heat of combustion by subtracting the latent heat of vaporization from the gross value obtained from the calorimeter, but this requires a knowledge of the hydrogen content of the sample. If the hydrogen content is known, the net heat of combustion can be calculated as follows:

$$H_n = H_g - (91.23)(H)$$

where,

$H_n$  = net heating value, BTU / lb

$H_g$  = gross heating value, BTU / lb

H = weight percent hydrogen in the sample

Because of the difficulty in accurately determining the hydrogen content of the sample, and the fact that the hydrogen content of most fuels is fairly low, the gross heat of combustion is usually reported in preference to the net value in most applications.

Users interested in high precision calorimetry will understand that test results obtained in a bomb calorimeter express calorific values obtained at constant volume. This differs from the usual conditions under which fuels are burned at constant pressure rather than constant volume. If the sample contains elements which normally would increase in volume after combustion, a correction must be applied to account for the heat equivalent of this work. This value is so small as to be negligible in routine work, and it usually is disregarded.

## Chemical Analysis

Because samples are completely oxidized during combustion in an oxygen bomb and because the combustion products are quantitatively retained within the bomb, procedures have been developed for determining sulfur, halogens and other elements in conjunction with the heat of combustion. Perhaps the most common of these auxiliary tests is the one for sulfur in fuels.

During the combustion process in the bomb, sulfur in the sample is oxidized to sulfur trioxide which, in turn, combines with the moisture in the bomb to condense as sulfuric acid. The inner surfaces of the bomb are then washed with distilled water and the washings are collected. After appropriate neutralization and preparation, the sulfate present can be determined by adding barium chloride to produce a barium sulfate precipitate. The bomb washing technique can also be used to determine chlorine, bromine, iodine, fluorine, arsenic, mercury, phosphorus, boron, lead, selenium, and other metals in combustible materials. Parr Manual 207M, Analytical Methods for Oxygen Bombs, provides more information on this method and other analytical methods associated with combustion bombs.

## Safety Considerations

Combustion reactions in an oxygen bomb calorimeter need not be considered unusually hazardous as they are carried out routinely in thousands of laboratories. Nevertheless, since they do involve nearly explosive reactions at high pressures, constant vigilance is required to ensure safe operation. Care must be taken when charging the bomb to be sure that the amount of sample placed in the bomb and the charging pressure do not exceed the limits prescribed for the bomb being used.

It is extremely important that the bomb be maintained in good repair at all times. Any bomb that is leaking oxygen from a valve, from an electrode or from any other seal should never be fired. The combined flame front and high pressure oxygen released under such conditions can ignite the bomb itself in the area of the leak. Each bomb should also be subjected to hydrostatic and proof tests on a regular basis to confirm that it has not been weakened by corrosion or wear, and that it is suitable for continued service.



Summarizing these basic safety rules, laboratory supervisors should insist upon strict compliance with the following instructions:

1. Do not use too much sample. The standard 1108 Oxygen Combustion Vessel cannot be expected to withstand the effects of combustible charges which liberate more than 8000 calories frequently. This generally limits the total weight of combustible material (sample plus firing oil, gelatin or any other combustion aid) to not more than 1.10 gram.
2. Do not charge the bomb with more oxygen than is necessary to obtain complete combustion. As a rule, it is best to use the lowest gas pressure that will give complete combustion. Lower pressures permit higher gas temperatures and greater turbulence, both of which help to secure better combustion. The range of charging pressures for the 1108 Oxygen Combustion Vessel falls between 20 and 35 atmospheres, and should never exceed 40 atmospheres.
3. Keep all parts of the bomb – especially the o-rings, insulated electrode assemblies and valves – in good repair at all times. Do not fire the bomb if gas bubbles are leaking from the bomb when it is submerged in water.
4. Stand back from the calorimeter for at least 15 seconds after firing and, above all, keep clear of the top of the calorimeter. If the bomb should explode it is most likely that the force of the explosion will be directly upward.
5. Proceed with caution and use only a fraction of the allowable maximum sample when testing new materials that may burn rapidly, or that may have explosive characteristics.

## Standard ASTM Test Methods

The American Society for Testing and materials (ASTM) has developed a series of standard methods for testing both solid and liquid fuels in an oxygen bomb calorimeter. Copies of these methods are available on the ASTM website at [www.astm.org](http://www.astm.org) or by contacting the Society at the address shown below.

### ASTM International

100 Barr Harbor Drive  
P.O. Box C700  
West Conshohocken, PA 19428-2959  
(610) 832-9585

- ASTM D346 / D346M, "Standard Practice for Collection and Preparation of Coke Samples for Laboratory Analysis"
- ASTM D2013 / D2013M, "Standard Practice for Preparing Coal Samples for Analysis"
- ASTM D3176, "Standard Practice for Ultimate Analysis of Coal and Coke"
- ASTM D3180, "Standard Practice for Calculating Coal and Coke Analyses from As Determined to Different Bases"
- ASTM D129, "Standard Test Method for Sulfur in Petroleum Products (General High Pressure Decomposition Device Method)"
- ASTM D240, "Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter"
- ASTM D720, "Standard Test Method for Free-Swelling Index of Coal"
- ASTM D808, "Standard Test Method for Chlorine in New and Used Petroleum Products (High Pressure Decomposition Device Method)"
- ASTM D1412, "Standard Test Method for Equilibrium Moisture of Coal at 96 to 97 Percent Relative Humidity and 30 °C"
- ASTM D2361, "Standard Test Method for Chlorine in Coal (Withdrawn 2008)"
- ASTM D2961, "Standard Test Method for Single-Stage Total Moisture Less than 15% in Coal Reduced to 2.36-mm (No. 8 Sieve) Topsize"
- ASTM D3173, "Standard Test Method for Moisture in the Analysis Sample of Coal and Coke"
- ASTM D3174, "Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal"
- ASTM D3175, "Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke"
- ASTM D3177, "Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke (Withdrawn 2012)"
- ASTM D3684, "Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method"
- ASTM D4809, "Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)"
- ASTM D5865, "Standard Test Method for Gross Calorific Value of Coal and Coke"

## **International Standard Test Method**

- ISO 1928, "Solid mineral fuels - Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value"

## **Australian Standard Test Method**

- AS1038.5, "Coal and coke - Analysis and testing - Gross calorific value"

## **British Standard Test Method**

- BS1016, "Methods for analysis and testing of coal and coke. Total moisture of coal"

## **German Standard Test Method**

- DIN 51900-2, "Testing of solid and liquid fuels - Determination of the gross calorific value by the bomb calorimeter and calculation of the net calorific value - Part 2: Method using isoperibol or static, jacket calorimeter"

## **Japanese Industrial Standard Method**

- JIS M 8814, "Coal and coke -- Determination of gross calorific value by the bomb calorimetric method, and calculation of net calorific value"

## **Additional References**

Jessup, R.S., "Precise Measurement of Heat Combustion with a Bomb Calorimeter"; U.S. Bureau of Standards Monograph No. 7 (1970), US Government Printing Office, Washington, D.C.

Rossini, F.D., "Experimental Thermochemistry – Measurement of Heats of Reaction"; Interscience-Wiley, New York (1956).

Skinner, H.A. "Experimental Thermochemistry, Vol. 2"; Interscience-Wiley, New York (1962).



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