

**Bulletin No. 104****Calorimeter Applications****There are six major applications  
for oxygen bomb calorimeters**

The history of bomb calorimetry reaches back into the late 1800's. The general principles of modern calorimetric methods were started by the eminent French scientist and statesman, Berthelot (1827-1907), the pioneer in using oxygen under pressure to affect combustion. His original calorimeter bomb of 1881 was lined with platinum to withstand the action of the gases resulting from the combustion. It was modified in 1892 by Mahler, who had the instrument maker Golaz of Paris make a bomb with porcelain enamel deposited on the steel, to replace the expensive platinum lining. Modifications of the Berthelot and Mahler calorimeters were made by Fischer, Hempel and others, including Williams of Boston and W. O. Atwater (1844-1907) of Wesleyan University, Middletown, Connecticut.

Professor S.W. Parr at the University of Illinois developed the peroxide bomb calorimeter in 1899. At that time there were very few satisfactory calorimeters available, and these were all of the oxygen bomb type that required expensive noble-metal linings as well as a source of compressed oxygen and considerable technical experience in their operation. Professor Parr sought to construct a simple calorimeter which could be sold at low cost and which would be suitable for use by semi-skilled operators in fuel producing industries where there was a definite and growing need for data on heating values. Instead of using compressed oxygen as the oxidizing medium in his apparatus, he proposed to use sodium peroxide. This material could be obtained in powdered form and,

when mixed with a fuel sample and ignited in a small calorimeter bomb, it yielded the large amount of oxygen necessary to affect the desired complete combustion. The thousands of these calorimeters placed in service during the nearly half a century of production provide ample evidence of their general acceptance. In 1911, Parr introduced an oxygen bomb calorimeter and after fifteen years of research to eliminate the metallic lining, he produced a new acid-resistant alloy, Ilium.

Today, there are six major applications for oxygen bomb calorimeters:

1. Solid and Liquid Fuel Testing
2. Waste and Refuse Disposal
3. Food and Metabolic Studies
4. Propellant and Explosive Testing
5. Fundamental Thermodynamic Studies
6. Educational Training

### **Solid and Liquid Fuel Testing**

Fuels such as coal and oil, are traded based on the calorific value of the material. Regulations have been established with regards to the total calorific content of the coal, the quality or purity of the coal, and the classification of the coal. The gross calorific value of the coal is also used to evaluate the effectiveness of the beneficiation process in use at the plant. ISO 1928, ASTM D5865, BS1016, and DIN 51900 are the most common methods for determining the gross calorific value of coal and coke.

Liquid fuels such as gasoline, kerosene, diesel, and gas turbine fuels are also tested by bomb calorimetry. The heat of combustion (HOC) of the fuel will provide a measure of the energy available from a fuel. The mass heat of combustion (essential for airplanes and hydrofoils) and the volumetric heat of combustion (essential for automobiles and ships) can also be determined with

the HOC value. ASTM D240 and D4809 are common methods for this sort of work.

Increased interest in biomass as a source of renewable and clean energy highlights another potential market for calorimeters. Biomass resources are potentially the world's largest and most sustainable energy source - a renewable resource comprising 220 billion oven-dry tonnes (about 4 500 EJ) of annual primary production (Hall & Rao, 1999).

### **Waste and Refuse Disposal**

“The United States generates more than 5 million tons of organic hazardous waste that requires thermal treatment each year. The cement industry currently uses over one million tons of hazardous waste a year as an alternative fuel - replacing expensive and non-renewable fossil fuels such as coal” (CKRC, 2004). The waste industry, like the coal industry, is driven by government regulations such as the Environmental Protection Agency in the United States. EPA Method 5050, Bomb Preparation Method for Solid Waste, is one example of such a method.

The Kyoto Protocol to reduce human-made greenhouse gas emissions was agreed upon by 150 countries in December 1997. With increased interest in international cooperation regarding the reduction of greenhouse gases, the number of countries implementing regulations regarding incineration will increase.

### **Food and Metabolic Studies**

Researchers have found bomb calorimetry to be of value when studying the effects of diet, not only in laboratory animals, but also humans. The gross energy (G.E.) content of a food is determined by bomb calorimetry. The digestible energy (D.E.) content of a food is the amount of energy in the food which is able to be absorbed. The metabolizable energy (M.E.) content of a food represents

the amount of energy in the food which the animal actually utilizes. One such study is that of González-Cossío, et al. which determines a link between lactation and malnutrition. Another metabolic study was performed by Rammerstorfer et al. at the Texas Agricultural Experiment Station to characterize physiological responses of reining horses during an exercise simulating reining horse performances.

Other applications of this nature involve preparing samples for analysis through the use of an oxygen bomb. Tissue and vegetative matter is broken down during the combustion process in a closed system allowing the user to analyze the resulting products. W.H. Hill performed multiple analysis of this nature.

### **Propellant and Explosive Testing**

Chemical explosives can be classified as low or high explosives. Low (or deflagrating) explosives are used primarily for propelling; they are mixtures of readily combustible substances that when ignited undergo rapid combustion (Columbia Electronic Encyclopedia). Propellants are often materials such as gun powders, smokeless powders or liquid fuels. Generally, propellants burn in a predictable manner at a controlled rate.

High (or detonating) explosives (e.g., TNT) are used mainly for shattering; they are unstable molecules that can undergo explosive decomposition without any external source of oxygen and in which the chemical reaction produces rapid shock waves. In an explosion, the reaction products fill a much greater volume than that occupied by the original material and exert an enormous amount of pressure (Columbia Electronic Encyclopedia).

These types of applications are generally found in government operations and their private sector suppliers and contractors. Recently however, the automotive industry has become active in this market. Air bags are inflated with a violent reaction of sodium azide. Other economic and passenger friendly compounds

are being researched. Examples of explosive compounds are listed in the following table:

**Table UCRL-52821**

<b>Compound</b>	<b>Heat of Detonation (cal/g)</b>
2,4,6-Trinitrotoluene (TNT)	1093 +/- 11
Pentaerythritol Tetranitrate (PETN)	1490 +/- 5
Cyclotetramethylene Tetranitramine (HMX)	1334 +/- 9
Cyclotrimethylene Trinitramine (RDX)	1452 +/- 15
Ethylenedianine Dinitrate (EDN)	1163 +/- 20
Hydrazine nitrate (HN)	1247 +/- 25
Hexanitrobenzene (HNB)	1653 +/- 17

There are various test methods which cover the testing of explosives. These include:

- Naval Ordnance 9375
- OS 6765B
- Mil – Std 286B
- Mil-P- 46994

Parr offers the Dynamic Pressure Recording System which monitors the pressure associated with the fast decomposition associated with propellants and explosives. More information on this application can be found in Tech Note 106.

### **Fundamental Thermodynamic Studies**

There are many areas of study in this category related to bomb calorimeters:

- Standard Reaction Enthalpy
- Enthalpy Change for Isomerization
- Heats of Formation – Hess's Law
- Heats of Reaction

The standard enthalpy of combustion  $\Delta H_c^\theta$  is the heat content change which occurs when one mole of a substance is completely burned in oxygen, under standard conditions. The standard enthalpy of formation  $\Delta H_f^\theta$  is the heat content change when one mole of a compound is formed from its elements in their standard states, under standard conditions. Parr has many articles relating to this topic and there is much more research being done in this area.

### **Educational Training**

As can be seen by the number of markets, the field of calorimetry is still active and therefore is taught in universities across the globe. Many schools will find the 6765 Semimicro/ Solution Combination Calorimeter to be an attractive option as it allows for both oxygen bomb calorimetry studies as well as thermodynamic studies to be taught. Another attractive option, due to its low cost and basic components, is the 1341 Plain Jacket Calorimeter. Additionally, the 6772 Calorimetric Thermometer provides schools with the ability to interface their calorimeters directly with a PC and therefore teach data analysis to students; an important skill for the 21<sup>st</sup> century.

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