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New concepts in bomb calorimeter design and operation[1]

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Abstract

Advances in computer technology over the last 15 years have led to a significant evolution in combustion calorimetric instrumentation and methodology. Today highly automated combustion calorimeter systems are commercially available, that free the operator from many of the tasks related to manually handling the bomb or other system components. In addition to the obvious time savings offered by these automated systems, test results are much less dependent upon operator technique since the instrument itself performs the majority of the tasks in a repeatable manner. This paper will highlight some of the more innovative aspects of the Parr 1271 and 1281 calorimeters, contrasting them to more traditional approaches, where applicable. © 1998 Elsevier Science B.V.

Keywords: Automated combustion calorimeter; Bomb calorimeter; Combustion calorimeter; Dynamic method

1. Introduction

Bomb calorimetry – a procedure that determines the heat of combustion of materials – is a fundamental test of great significance to anyone concerned with:

- Production and/or utilization of solid and liquid fuels.
- Incineration of waste and refuse materials.
- Foods, animal nutrition and energy balance studies.
- Explosives, heat powders, rocket fuels and related propellants.
- Thermodynamic studies.

The addition of microprocessor technology to commercial bomb calorimetric systems occurred in the late 1970’s. These initial ‘‘add-on’’ systems permitted existing calorimeter technology to operate in a semi-automatic fashion. Today, most contemporary commercial combustion calorimeters utilize an isoperibol design that incorporates microprocessor technology into the thermometry, process control, data acquisition, computation and reporting functions of the instrument. The models 1271 and 1281 calorimeters continue this evolutionary process by adding fully automatic bomb and water handling capabilities to calorimeter operations.

2. A new oxygen bomb

At the heart of these new calorimeters is a completely new oxygen combustion bomb built to traditional commercial construction and performance standards, but differing considerably from prior bomb

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designs. In this new patented design, the bomb head is sealed into the cylinder with a 1/16 turn, using a modified breech-block closure. The bomb is installed in the 1271 Calorimeter (Fig. 1) in an inverted position with the head at the bottom of the cylinder where a controlled pneumatic system rotates the head to develop the seal. This same bomb closure concept is used in the 1281 Calorimeter, but installed in the more conventional manner with the head at the top of the cylinder and sealed by hand.

These 340 ml bombs will safely burn samples liberating up to 33 kJ as prescribed in most standard test methods. Each bomb is individually tested to 200 bar, $\approx 2\frac{1}{2}$ times the maximum pressure developed in a normal combustion, in accordance with ASTM and ISO recommended test procedures.

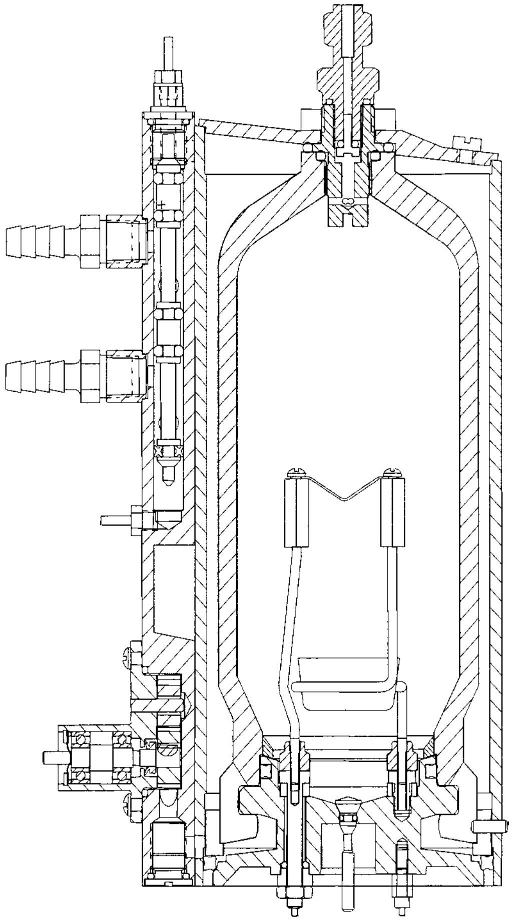

Fig. 1. 1271 Calorimeter bomb and bucket assembly.

The standard construction material for these bombs is Carpenter 20Cb3 stainless steel. This alloy contains twice the nickel of the 300 series austenite stainless steel and it is stabilized with the addition of molybdenum and columbium to provide outstanding resistance to the hot mixed nitric and sulfuric acids produced when burning samples which contain sulfur. Alternate bombs of the same design but made of a special alloy with enhanced resistance to chlorides are offered for testing halogenated solvents, wastes and other related materials.

3. New capabilities

The new technology incorporated into the 1271 and 1281 calorimeters free the operator from the tasks of:

- Manually sealing the bomb.
- Filling the bomb with oxygen.
- Measuring and handling the water in the calorimeter bucket.
- Exhausting the bomb at the end of the test.
- Removing the bomb and bucket from the calorimeter.
- Opening and washing the bomb.
- Drying the bomb and bucket.

In the 1271 Calorimeter, a pneumatic system opens and closes the bomb automatically. In the 1281 Calorimeter, the operator opens and closes the bomb using the patented quick-turn closure, and removes only the head of the bomb for reloading. With these new developments, the operator's involvement with the test is reduced to simply massing the sample and inserting into the bomb head along with a short auxiliary cotton fuse. As a result, two thing occur:

- The time required for the operator to prepare the calorimeter for the next run drops from ≈6 min to <1 min per test.
- Test results are much less dependent upon operator technique since the calorimeter now performs the bulk of the required tasks in a highly repeatable manner.

The unique design features and unprecedented degree of automation offered in these calorimeters causes them to differ in certain procedural details from the basic calorimeter designs prescribed in current ASTM, ISO, BS and DIN standards. The basic fundamental requirements in each of these methods has been carefully reviewed and extensive testing has confirmed that the results obtainable with either of these calorimeters will meet or exceed the precision and accuracy limits specified in the most widely used and popular standard test methods.

4. Calorimeter operating diagrams

Figs. 2–5 illustrate the principal operating components and how they are utilized in the operation of the 1271 Calorimeter. During all operating phases, water is circulated from the closed water system through an isothermal jacket that completely surrounds the calorimeter bomb and bucket. This isothermal jacket maintains the surroundings of the calorimeter at a constant temperature, namely 30°C. The water in the water-handling system is maintained by an immersion heater and a supply of cold water from a water chiller. Both, the heating and cooling control loops are maintained by the calorimeter controller and are updated every two seconds.

To begin a test the operator first fits the massed sample and combustion capsule into the loop electrode of the bomb head. Next, a 10 cm cotton thread used as an auxiliary fuse is looped over the heating wire, twisted into a single strand and allowed to touch the sample. The operator then presses START key at the controller keyboard to begin the test. The controller then prompts the operator for a sample ID number and the sample mass. At the same time,

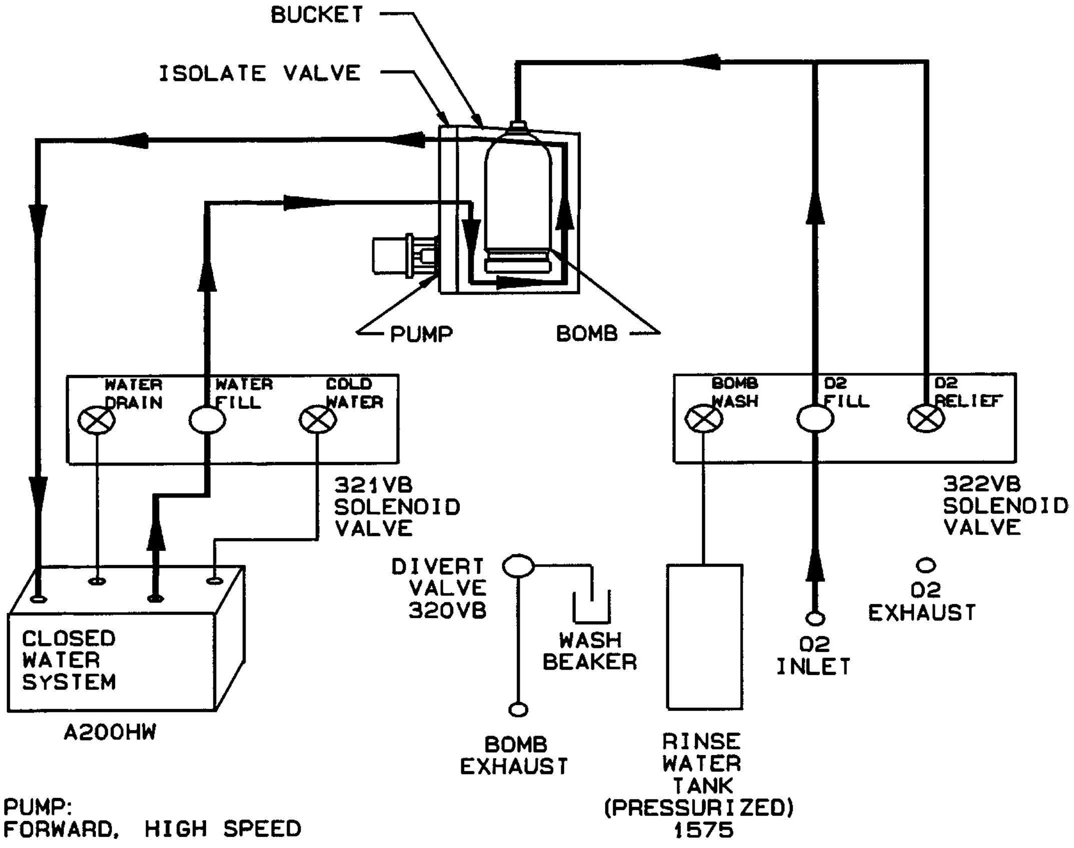

Fig. 2. Fill.

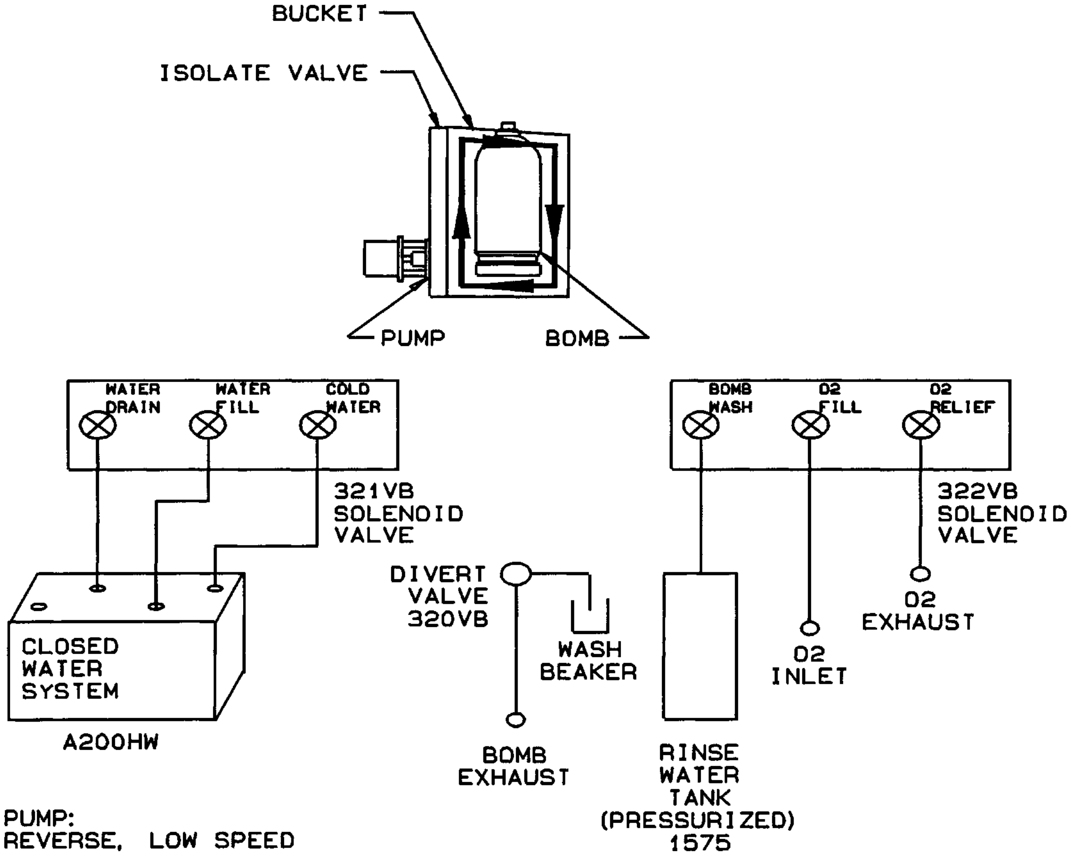

Fig. 3. Pre/post-period.

the bomb head is automatically inserted into the cylinder and locked in place with a 1/16-turn rotation. The loader rod is withdrawn and a thermal shield swings into place which not only thermostats the head area but also connects the ignition circuit to the bomb head.

4.1. Fill

The fill sequence begins by checking the bomb-ignition circuit for continuity. The water-fill solenoid opens and water is pumped from the closed water system into, and through the bucket that surrounds the bomb. The calorimeter bucket holds $\approx$400 cm^3 of water. Overflow from the bucket is returned to the closed water system. The sloped top of the bucket and the location of the water exit point excludes air from within the bucket during the fill process and guarantees a consistent volumetric fill. Because the jacket and bucket are both filled with water from the closed water system, initial equilibrium is achieved quickly. At the same time, the oxygen fill solenoid is opened and oxygen is admitted to the bomb, filling it to 3.0 MPa over a period of one minute.

4.2. Pre/post-period

At the completion of the fill sequence, the pre-period begins. The isolate valve located in the pump block of the calorimeter bucket is forced down, pneumatically, which blocks the entry and exit points and isolates the water in the bucket from the rest of the system.

A small gear pump fitted into a cavity of the pump block then circulates the water trapped within the bucket. The active portion of the temperature probe

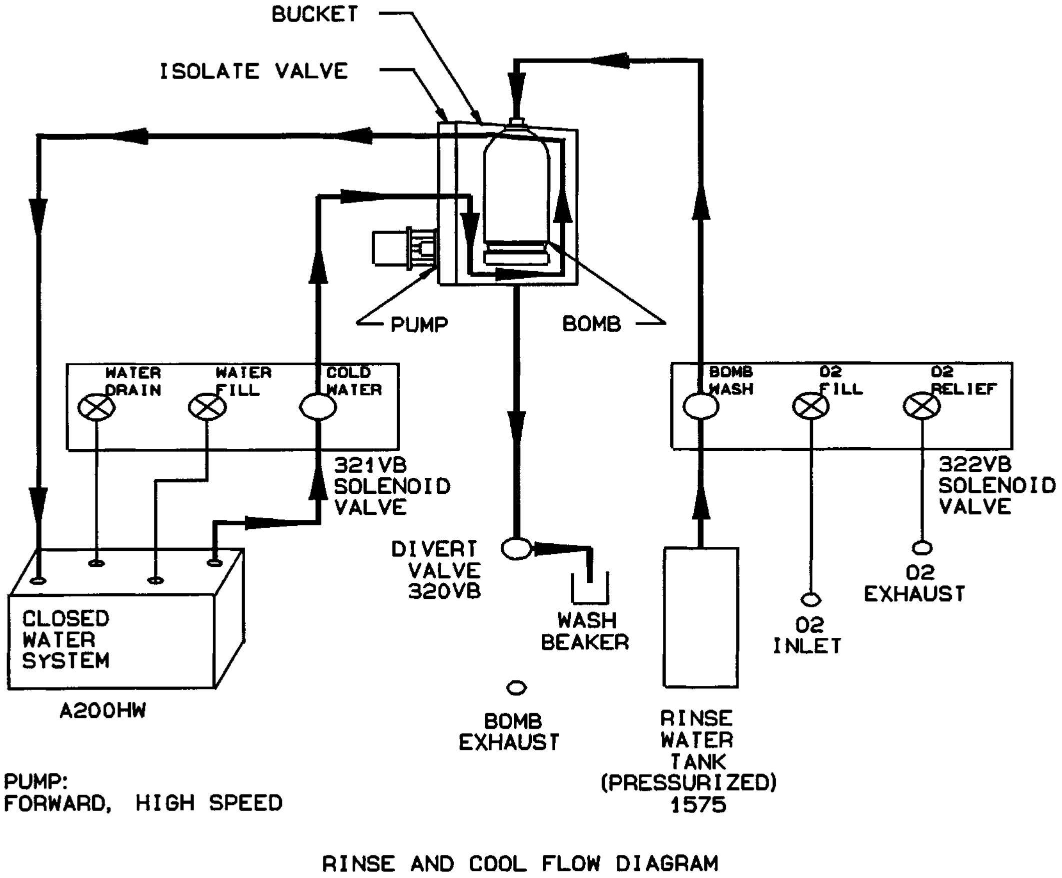

Fig. 4. Cool/rinse.

used to monitor the calorimeter temperature is inserted directly in the water flow path. Water continues to circulate from the closed water system through the jacket surrounding the bucket. The oxygen filling valve closes and the pressure in the filling line is vented. The check valve at the top of the bomb cylinder closes and isolates the bomb from the oxygen filling line. The controller then monitors the operating temperature until it confirms that the initial equilibrium has been established. Once the initial equilibrium is confirmed, the controller initiates the firing sequence. There are no changes to the water-circulation pattern, as shown in this figure, from the pre-period through the bomb firing and the post-period. An audible warning of five short beeps is sounded indicating the bomb is about to be fired. Current from a storage capacitor is passed through the heating wire to ignite the auxiliary cotton thread which, in turn, ignites the sample. The controller then monitors the temperature rise in the bucket in order to establish that some minimum temperature rise actually occurs. If no temperature rise occurs, a misfire is reported and the test-abort sequence is initiated. After firing, the controller monitors the temperature rise and determines the final calorimeter "delta *T*" using either an extrapolation technique (dynamic method) or the classical equilibrium criteria, as established by the user. In either case, real-time corrections are made for the small, systematic heat transfer that takes place from the calorimeter bucket to the jacket, which is maintained at a fixed temperature. Once the final temperature rise is determined, it is recorded and the test report issued. The typical temperature rise for this calorimeter is on the order of 10 K.

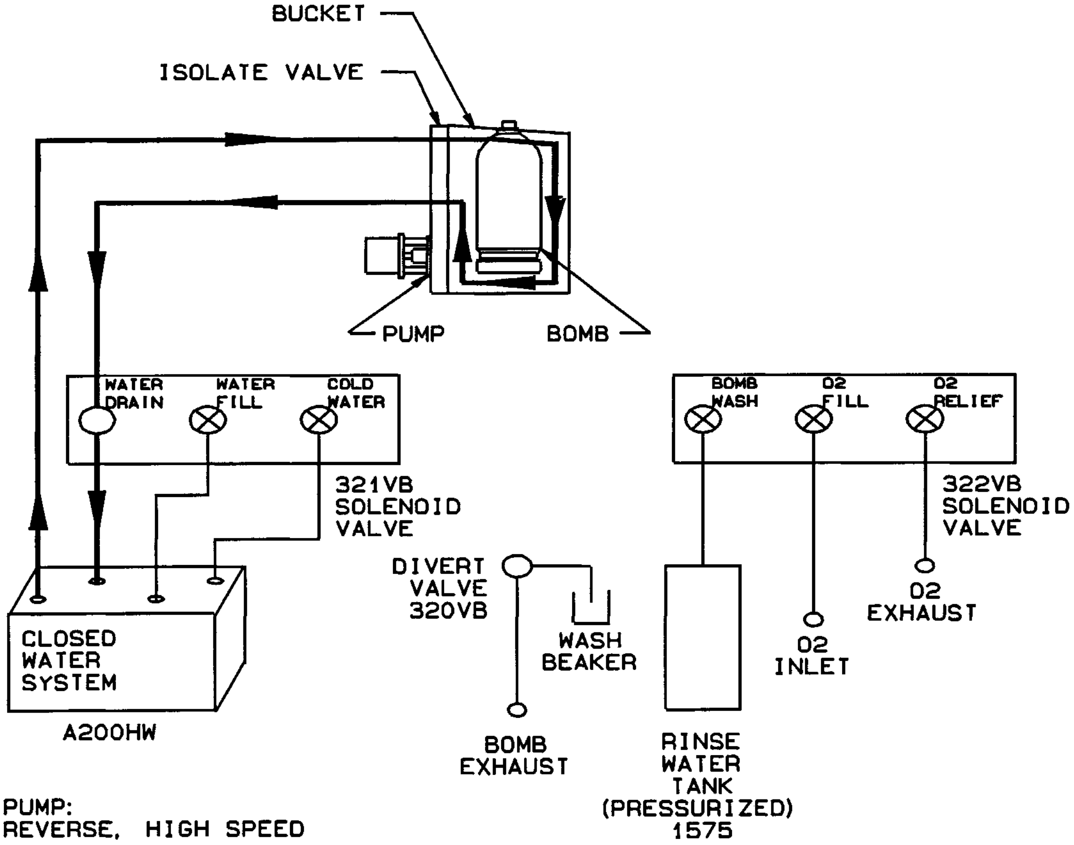

Fig. 5. Drain.

4.3. Cool/rinse

At the completion of the post-period, the rinse and cool sequence begins. The isolate valve is driven to the up position, pneumatically, and water from the cooler via the closed water system is circulated through the bucket to cool the bomb back to the initial temperature. The check valve in the bomb head is lifted and opened by the penetration of the loader rod into the head. The residual pressure is released through the hollow loader rod and the bomb exhaust line. Once the residual combustion gases are vented, the divert valve is activated and distilled water from the pressurized rinse-water tank is admitted through the bomb wash solenoid valve to the top of the bomb. The bomb wash water completely wets the interior of the bomb and is collected in a beaker (or other suitable container) placed at the side of the instrument. In order to meet various operational and analytical requirements, the user may configure the rinse pattern and the volume of water used. At the end of the rinse sequence, the bomb is partially filled with oxygen and quickly exhausted in order to flush residual water from the interior of the bomb and the oxygen fill line.

4.4. Drain

At the completion of the bomb cool sequence, the drain sequence begins. The water in the bucket is pumped out of the bucket and back to the closed water system using the small gear pump. Once the bucket is pumped dry, the bomb head is opened and lowered for the preparation of the next sample.

5. The 1281 Calorimeter

The 1281 Calorimeter, illustrated in Fig. 6, employs many of the same basic parts and uses the same fundamental operating concepts as the more automatic 1271 Calorimeter. The 1281 Calorimeter is designed for users who want a calorimeter with all of the new technology provided in the 1271 Model but who do not require a fully automated bomb closing mechanism and provision for expansion to a dual calorimeter system. All of the principal components of the calorimeter, including the calorimeter controller and the water handling system, are built into a single console that is 45 cm wide, 53 cm deep and 40 cm high.

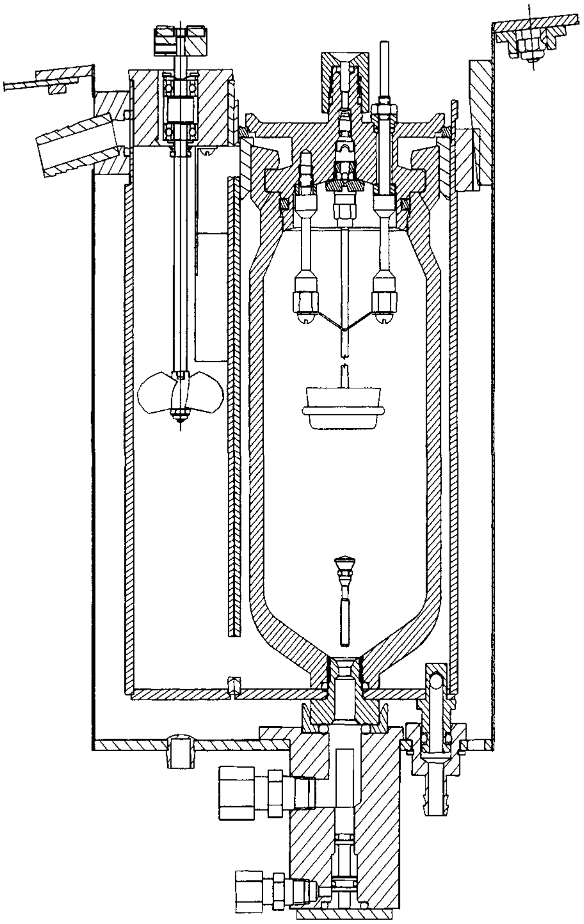

Fig. 6. The 1281 Calorimeter bomb and bucket assembly.

Oxygen (during the fill sequence) and water (during the rinse sequence) are admitted to the head of the bomb. Residual combustion gas and bomb rinses are passed out of the bottom of the cylinder at the end of the test. As with the 1271 Calorimeter, the bucket is filled volumetrically in a manner which forces out all air from the bucket chamber, ensuring a repeatable amount of water from test to test. The water in the bucket is circulated using a simple, propeller type, stirring mechanism that is magnetically coupled to the drive motor.

6. The dynamic test method

The dynamic test method is used to shorten the post-period of a test by as much as 50%, without sacrificing any of the precision associated with traditional ANSI/ASTM calorimetric test methods. To use this method successfully requires an understanding of the calorimeter's thermal response (cf. Fig. 7). A single-pole RC (resistor–capacitor) time constant can be used to model the response time of the calorimeter. In this model, capacitance is equivalent to thermal mass or heat capacity and resistance is equivalent to the inverse of the thermal conductivity of the system. This information is utilized to generate a correction factor that augments the raw response of the temperature sensor. This correction factor is larger when the temperature is changing rapidly. In other words, the faster the temperature changes, the higher the final temperature value is likely to be. The first order, RC time constant, is determined experimentally by fitting calorimeter temperature vs. time data to the model response of the calorimeter.

Fig. 8 illustrates the time rate of change of the calorimeter temperature after firing, corrected for the small systematic heat transfer that takes place between the bucket and the jacket. The area under this curve is the temperature rise for the calorimetric test. By applying the calorimeter model to the trailing edge of this curve, it is possible to accurately complete the integration in half the time it takes for the test to finish using the traditional equilibrium treatment. For more than a decade, this time-saving technique has been successfully applied on three generations of Parr calorimeters. It is so widely accepted and used that it

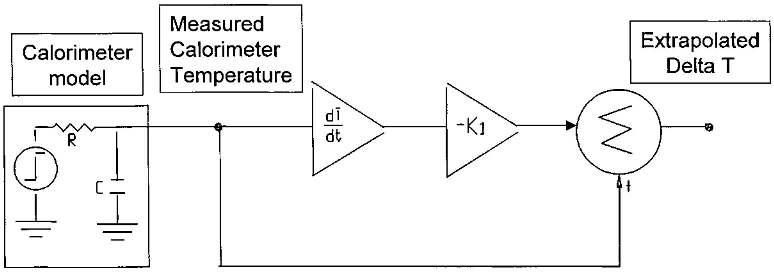

Fig. 7. The dynamic method.

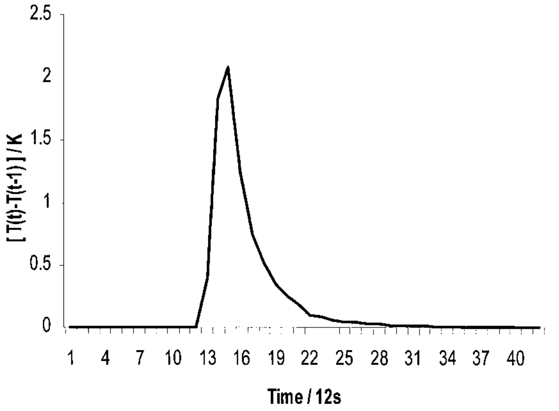

Fig. 8. Plot illustrating the typical time rate of change of the calorimeter temperature during a test run.

has become the de-facto standard operating mode for the majority of fuel testing applications [1,2].

Table 1 illustrates heat of combustion values obtained for calorimetric standard-grade benzoic acid (CAS Reg. No. 0065-85-0) using the 1281 Calorimeter operated in both, the classical equilibrium method [3–5] and the dynamic method. The precision of the test results for each of the test methods is comparable (<0.1% RSD). For either test method, the calorimeter exhibits no significant bias or trends over the 13 kJ range illustrated here. Most importantly, for routine commercial testing the results using the dynamic method are obtained with a calorimeter post-period that is <60% of the post-period time recorded using the equilibrium method.

Table 1
The 1281 calorimeter test data using benzoic acid as the test sample

Test method [a]	Sample mass/g [b]	T_{sum}/K [c]	T_{extrap}/K [d]	Post-period time/s [e]	$-\Delta u_c/(\mathrm{J\ g^{-1}})$ [f,g,h]
Equilibrium	1.0042	7.9538	0.0000	384	26461
Equilibrium	1.0174	8.0530	0.0000	384	26446
Equilibrium	0.9110	7.2172	0.0000	384	26441
Equilibrium	1.2032	9.5191	0.0000	384	26471
Equilibrium	1.4628	11.5402	0.0000	384	26433
Dynamic	1.0033	7.8540	0.0892	216	26449
Dynamic	0.9920	7.7853	0.0754	228	26470
Dynamic	0.9168	7.1709	0.0910	216	26438
Dynamic	1.2143	9.5263	0.0741	228	26455
Dynamic	1.4371	11.2780	0.0866	228	26493

[a] Calorimeter firmware revision is 010697–970331.
[b] Mass against brass weights in air.
[c] Actual accumulated temperature rise for the best.
[d] Extrapolated portion of the total temperature rise. Total temperature rise for the test is $T_{sum}+T_{extrap}$.
[e] Time between firing and when the test report is issued.
[f] Calorimeter calibration factor is 3372.2 J/K.
[g] Calorimetric corrections used for all tests (nitric acid+fuse)=250 J.
[h] Accepted value [6] for benzoic acid is 26454 J g^{-1}.

7. Conclusion

The models 1271 and 1281 oxygen bomb calorimeters bring an unprecedented degree of automation to routine heat-of-combustion measurements. The novel design features of these calorimeters permit rapid and precise measurements with a minimum of operator intervention. Application of the dynamic test method to these calorimeter systems offers a further reduction in the analysis time without any unfavorable impact on the precision or accuracy of the results.

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