

# Calibration and test of an aneroid mini-bomb combustion calorimeter

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## Abstract

A new mini-bomb combustion calorimeter designed at the University of Lund was improved, installed and calibrated at the University of Porto. This calorimeter is suitable for high precision combustion calorimetry with samples of mass about (10 to 40) mg. The energy equivalent of the calorimeter,  $\epsilon_{\text{cal}} = (1946.45 \pm 0.11) \text{ J} \cdot \text{K}^{-1}$ , was obtained from 15 independent calibration experiments with benzoic acid SRM 39i. Anthracene, succinic acid, acetanilide, and 1,2,4-triazole were used as test compounds, with excellent agreement with the literature values.

	$-\Delta_{\text{c}}H_{\text{m}}^{\circ}$ kJ · mol <sup>-1</sup>	$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr})$ kJ · mol <sup>-1</sup>
Anthracene	7062.6 ± 2.1	124.3 ± 2.8
Succinic acid	1490.2 ± 0.7	-941.3 ± 0.9
Acetanilide	4226.2 ± 1.1	-208.2 ± 1.6
1,2,4-Triazole	1326.1 ± 0.4	110.3 ± 0.5

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## 1. Introduction

Combustion calorimetry is the most widely used technique for determining the standard molar enthalpies of formation in the condensed phase of organic compounds containing C, H and also O, N, S, F, Cl, Br, I atoms, because they can be oxidised completely and the final state of the combustion reaction is well characterised. However, a severe limitation for traditional macro-bomb combustion calorimetry is the large amount of substance necessary for

each experiment. Considering a typical number of six independent combustion experiments, one can conclude that this technique is prohibitive for a large group of compounds that are very difficult to obtain and purify in large quantities or that are very expensive. To solve this problem, several authors [1–12] developed mini-combustion calorimeters that need amounts of substance as small as few milligrams per experiment. This enables a broader application of combustion calorimetry on the study of new organic compounds that are made every day and, as a consequence, improve and increase relationships between molecular structure and energy. Nowadays, some of the most interesting problems in molecular energetics arise from quite small

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molecular energy differences, typically of few  $\text{kJ} \cdot \text{mol}^{-1}$ . As a consequence, the design, construction and set up of any new mini-bomb combustion calorimeter must be done with the main objective of achieving an overall uncertainty as small as possible similar to the typical uncertainty obtained in modern macro-bomb combustion calorimetry. There are, however, some difficulties deriving from such miniaturisation of the calorimeters, such as the extremely high sensitivity towards sample impurities, increased care in handling and better control of all variables that could influence the results.

The mini-bomb combustion calorimeter was originally designed and constructed at the University of Lund by S. Sunner and M. Månsson and formerly installed at the thermochemistry laboratory of the University of Manchester (UK). A similar mini-bomb combustion calorimeter has been described by Diogo and Minas da Piedade [6]. The calorimeter has now been reconstructed, modernized at the University of Porto with a new set up, where significant changes have been made in order to improve quality of temperature measurement and overall long time system reproducibility. The calorimeter will be described in detail, with the complete experimental procedure, as well the results of the calibration and tests performed with organic compounds containing C, H, O and N, namely: anthracene, succinic acid, acetanilide, and 1,2,4-triazole.

## 2. Experimental

### 2.1. Calorimetric system

The overall calorimetric system is schematically represented in figure 1. It is an aneroid isoperibol type calorimetric system based in a cylinder copper block with 18.0 cm length, 7.51 cm external diameter and weighing 3802.8 g.

The thermal insulation of the thermostat bath is assured by a 2 cm thick polystyrene layer that surrounds completely a system of 9  $\text{dm}^3$  of distilled water that circulates around the whole calorimeter, including the swing-away lid.

Inside a cylindrical cavity within the thermostatic bath, a copper block with a hollow cylindrical form is placed as shown in figure 2. It has a copper cover with the same external diameter, which contains a propeller and a gas valve. The cover is adjusted tightly to the copper block by three screws, pressing it towards a Viton O-ring in the copper block. The mini-bomb and its support are placed inside a concentric cylindrical hole in the block of 43.9 mm in diameter. There are also nine small cylindrical holes situated around the central one, each of 8.9 mm diameter, in the copper block.

The body of the mini-bomb is made of stainless steel, with an internal free volume of 18.185  $\text{cm}^3$ . The internal

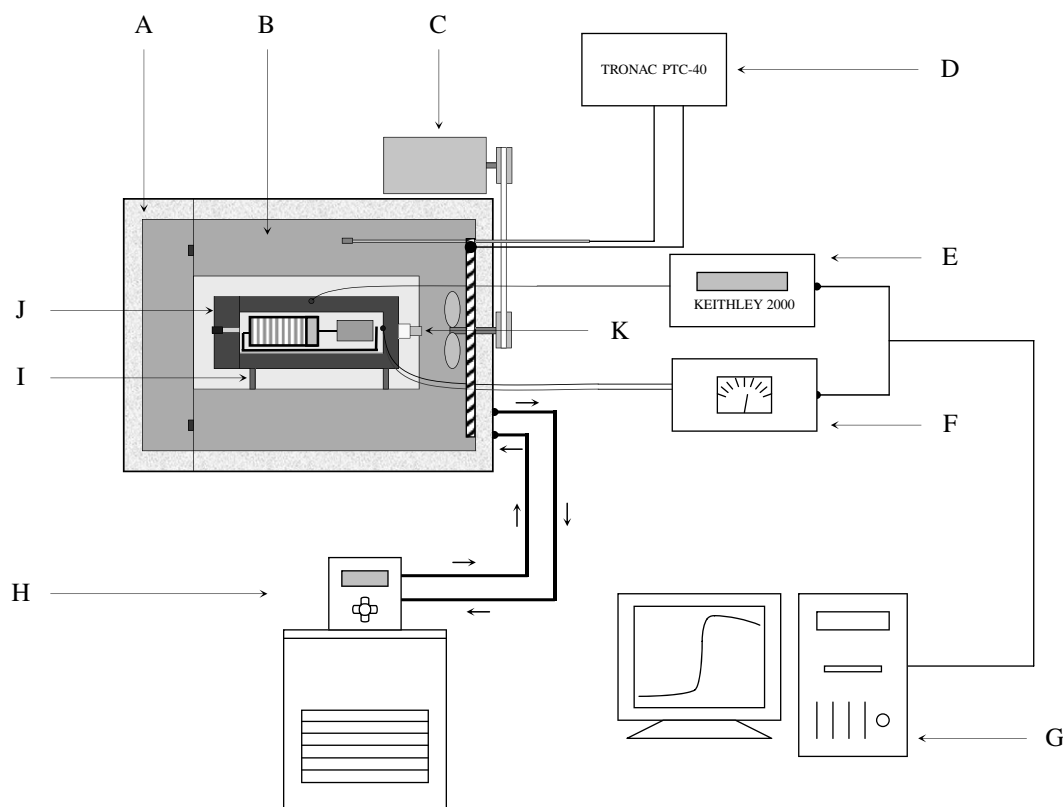


FIGURE 1. Schematic flow-sheet of the set up of the mini-bomb calorimeter. A – isolating polystyrene; B – water bath thermostat; C – thermostat stirring motor (1500 rpm); D – temperature controller (Tronac PTC40); E –  $6\frac{1}{2}$  Digits multimeter (Keithley 2000); F – firing unit; G – personal computer and monitor; H – water-cooling source (Julabo F12-ED); I – insulating calorimeter block support; J – calorimeter block with the bomb; K – DB25 wire connector.

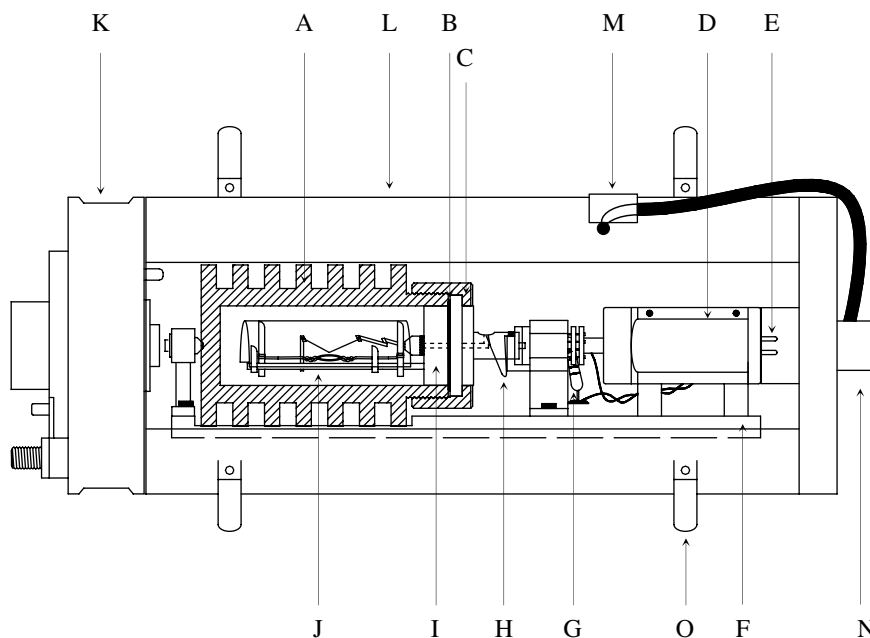


FIGURE 2. Schematic representation of the bomb, DC motor and the support. A – bomb body; B – Viton O-ring; C – retaining stainless steel ring; D – DC motor; E – electrical terminals; F – bomb and motor support; G – resistor in parallel with the firing circuit; H – firing electrical contact; I – head of the bomb; J – platinum support and electrodes; K – head of the calorimeter block; L – calorimeter block body; M – thermistor; N – DB25 electrical connector; O – thermal insulator.

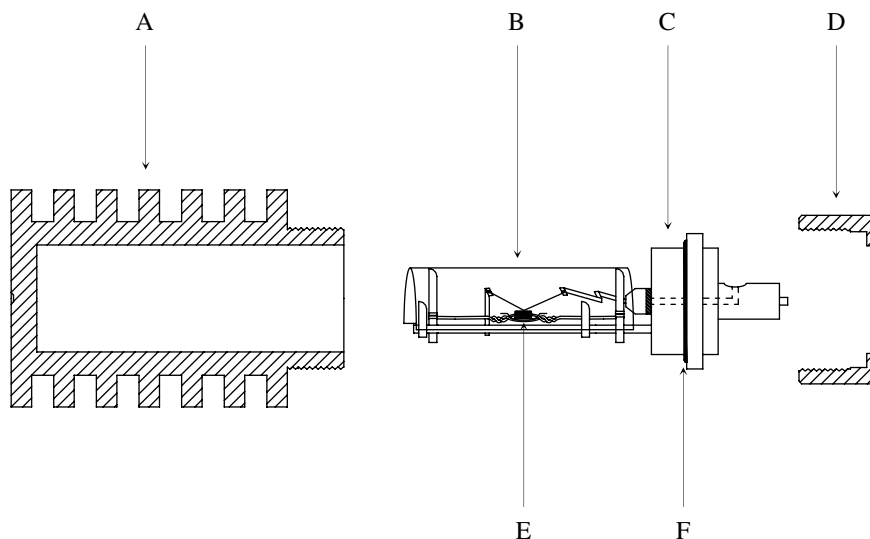


FIGURE 3. Details of the bomb assembling. A – bomb body; B – Platinum sheet; C – bomb head; D – retaining ring; E – crucible with pellet; F – Viton O-ring.

contents of the bomb represented in figure 3 (electrodes, crucible, sheet, and support) are all made of platinum. The platinum sheet is 50  $\mu\text{m}$  thick and has an approximate area of 14  $\text{cm}^2$ . This platinum sheet is placed above the crucible in an inverted U-shaped form to concentrate the heat when the sample ignites, thus helping to prevent the formation of carbon, which would occur if the combustion zone reached the inner wall. The crucible, made of platinum 50  $\mu\text{m}$  thick, has a circular plate form of 7 mm in diameter. There is one gas valve at the top of the head as well as an

insulated electrode, through which a potential discharge through the ignition wire from the 2000  $\mu\text{F}$  condenser attached to the calorimetric system is made with a resistance of 22  $\text{k}\Omega$  in parallel to complete the discharge from the condenser. Throughout the experiment, the mini-bomb is operated in a horizontal position.

After assembly, the mini-bomb is positioned in the support that connects to a DC motor that can be used for rotation and is adjusted to the ignition electrical contact of the ignition circuit.

A vacuum line system (glass line and a rotary pump, Edwards model Speedivac 2) is used to evacuate the interspaces between the copper block and the stainless steel mini-bomb before filling it with helium. The helium (mass fraction purity 0.9999) at a pressure of 0.2 MPa is used to fill the free interspaces in the copper block to improve heat conduction.

## 2.2. Temperature measurement and control

The temperature of the water bath that circulates around the whole calorimeter block is maintained and regulated at  $(298.820 \pm 0.001)$  K by a TRONAC precision temperature controller, model PTC-40. A thermostatic water circulator (Julabo, model F12-ED) is used as a cooling source, at  $T = (296.15 \pm 0.02)$  K, to the main bath of the calorimeter system.

The measurement of the calorimeter temperature is made with a stable bean type thermistor ( $R = 4$  k $\Omega$  at  $T = 298.15$  K) that is placed in a depression in the copper block. The thermistor was calibrated *in situ* with a small size Pt100, class 1/10 from Lab Facility using an  $8\frac{1}{2}$  digits precision ohmmeter (SOLARTRON model 7081). The above Pt100 had been previously calibrated against a SPRT (25  $\Omega$ ; Tinsley, 5187A) temperature, in accordance to the International Temperature Scale of 1990, ITS-90. The temperature was fitted to the resistance by the following equation:

$$T/\text{K} = \frac{B}{\ln(R/\Omega) - A}, \quad (1)$$

where  $T$  is temperature in Kelvin,  $R$  the measured resistance of the thermistor in ohms and  $A$  and  $B$  empirical constants:  $A = -1.9078269$ ,  $B = 3050.5514$  K.

## 2.3. Data acquisition and control

The resistance of the thermistor is measured in four wire measurement mode by a  $6\frac{1}{2}$  digits multimeter (Keithley model 2000) and the data are collected and monitored in a PC by a modified version of LABTERMO program [13]. The LABTERMO program is also used to monitor the voltage across the 2000  $\mu\text{F}$  condenser ignition circuit and start the combustion at a pre-defined time of the experiment.

The temperature of the calorimeter block is recorded every 10 s and the time–temperature plot visualised in real time. The initial, main and final periods have durations of (3000, 2000 and 2000) s, respectively, giving a total experiment time of 7000 s per experiment. Despite having 300 data points, only the final 150 data points are considered to define the initial period. To determine the adiabatic temperature change during the process, the Regnault–Pfaundler method [14] is used, where the initial and final periods are fitted to quadratic functions, following the methodology previously described [13].

Some typical results obtained in a combustion experiment are listed in table 1.

TABLE 1

Example of some relevant physical parameters obtained for one combustion experiment

Parameter	Value
Fitted quadratic function for the initial period	$-2.092879 \cdot 10^{-9}(t/s)^2 + 4.799805 \cdot 10^{-5}(t/s) + 297.994351$
Fitted quadratic function for the final period	$2.599612 \cdot 10^{-10}(t/s)^2 - 7.660028 \cdot 10^{-6}(t/s) + 298.529579$
Mean temperature ( $T_m/\text{K}$ )	298.46495
Cooling constant [ $k/(\text{s}^{-1})$ ]	$1.07472 \cdot 10^{-4}$
Convergent temperature ( $T_\infty/\text{K}$ )	298.45073
Temperature correction ( $\Delta T_{\text{corr}}/\text{K}$ )	-0.003056
Adiabatic temperature change ( $\Delta T_{\text{ad}}/\text{K}$ )	0.381276

## 2.4. Experimental procedure

The platinum crucible, sheet and head fittings are cleaned by heating in a propane flame. All the parts of the mini-bomb are previously dried and the mass of each piece of the mini-bomb and the calorimeter block checked and compared to the reference values.

The compound is pressed into a pellet form and the surface is cleaned with a stream of oxygen. The apparent mass of the sample and auxiliary substance is determined with a Mettler Toledo micro-balance, model UMT2, with a sensitivity of  $\pm 10^{-7}$  g, by placing them successively in the platinum crucible. Then, the crucible is put into its support in the head of the mini-bomb where a platinum wire (Goodfellow, 99.9%, diameter 0.080 mm) with approximately 20 mm length was previously attached to the electrodes terminals (see figure 3). The wire is forced down with a clamp to assume a V shape with the edge immediately above the pellet, and after that, the platinum sheet is placed carefully above this assembly, attaching the edges to the support. 0.050 cm<sup>3</sup> of water are placed inside the body of the mini-bomb and the head with a Viton O-ring is then tightly adjusted to it by means of a stainless steel screw-ring. An adapter is placed in the gas valve to fill the sealed mini-bomb with oxygen to 3.04 MPa and purge it. This procedure is repeated twice before filling the mini-bomb with oxygen to a pressure of 3.04 MPa and closing the valve. After this, the mini-bomb is placed in its support, and this assembly is introduced in the copper block and this block is sealed with its cover. Then, the helium gas line is connected to the valve in the copper block cover through an adapter and the block is evacuated, followed by filling it with 0.2 MPa with helium, and repeated evacuation for purging, and finally filling with helium up to 0.2 MPa and closing the valve. The propeller in the cover of the block can be set to work to improve helium circulation in the interior of the block, but it was shown [6] that no extra benefits were gained with this procedure, which would introduce a stirring heat effect to take into account. The temperature at which the recording starts is about  $T = 298.036$  K so that the initial temperature of the main period is as close as possible to  $T = 298.15$  K.

At the end of the experiment, the gases in the bomb are released and the bomb is then opened to check for the presence of any traces of carbon or other signs of incomplete combustion. In case of carbon formation solely in the crucible, its mass is determined in the microbalance mentioned above and accounted in the energy of the process. In case of carbon formation in parts other than the crucible, the experiment is rejected. After careful inspection, the contents and interior of the mini-bomb are washed with water to a flask to be analysed by ionic chromatography.

### 2.5. Nitric acid analysis

To determine the amount of nitric acid formed during the reaction, the solutions are diluted to 50.00 cm<sup>3</sup> in volumetric flasks (except for the 1,2,4-triazole combustion experiment solutions that were diluted to 100.0 cm<sup>3</sup> volumetric flasks due to a high HNO<sub>3</sub> amount) and analysed by ionic chromatography in a Dionex System 2000i/SP Ion Chromatograph equipped with a Dionex Ionpac<sup>®</sup> AS4 Column. The standard concentration solutions are prepared by dilution of a stock solution of standard 0.1000 mol · dm<sup>-3</sup> HNO<sub>3</sub> Titrisol<sup>®</sup> Merck.

### 2.6. Calibration and test compounds

The calibration of the mini-bomb was made with benzoic acid (NIST SRM 39i) with a massic energy of combustion under certificate conditions of  $-(26434 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$  [15]. Anthracene, succinic acid, acetanilide, and 1,2,4-triazole were used as test compounds. Anthracene and succinic acid are secondary and tertiary standards, respectively, and acetanilide is recommended as a reference substance for compounds with low nitrogen content, whereas 1,2,4-triazole is recommended as a reference substance for compounds with a high nitrogen content [16]. Anthracene, succinic acid, and acetanilide were previously purified by sublimation at reduced pressure, benzoic acid and the 1,2,4-triazole were used without any additional purification. With the exception of the benzoic acid (NIST SRM 39i) sample, the purities of the compounds were determined by Gas Chromatography (Agilent 4890D) and this yielded a minimum of 0.9995 mass fraction for all samples.

It was found in the first experiments that burning anthracene alone led to the formation of considerable amounts of carbon. Therefore, dried *n*-hexadecane (Aldrich, mass fraction purity 0.999) was used as an auxiliary substance.

Throughout the literature, several reports [17,18] refer to the difficulty in igniting succinic acid. This behaviour was confirmed in the first experiments. Several different experimental conditions were tested, from changing the amount of mass used, using well pulverised and non-pulverised sample and increasing the initial oxygen pressure inside the mini-bomb to 3.55 MPa. Since none of these solved the problem, auxiliary substances were used. Dried *n*-hexadecane was used first, but the sample ignited very poorly, as after the experiment a large amount of carbon was produced. Finally, a very thin pellet of standard benzoic acid (NIST SRM 39i) was placed above the succinic acid one and in these experimental conditions the sample ignited completely with no traces of carbon residue.

Acetanilide and 1,2,4-triazole burned completely without any trace of carbon. The sample of 1,2,4-triazole used was the same of Roux *et al.* [19]. In the paper they emphasise the stability of this compound several years after being purified, fact that led to immediate use in the combustion experiments without any former purification process.

Table 2 list some relevant physical–chemical information about the test compounds.

The relative atomic masses used throughout this paper were those recommended by the IUPAC Commission in 2001 [25].

## 3. Results

### 3.1. Calibration

Table 3 lists the results of 15 calibration experiments, where symbols have the following meaning:  $m(\text{BA})$  is the mass of benzoic acid;  $m(\text{Pt})$  is the combined mass of the platinum sheet and crucible;  $T_i$  and  $T_f$  are the initial and final temperature of the main period, respectively;  $\Delta T_{\text{ad}}$  is the adiabatic temperature change due to the reaction ( $\Delta T_{\text{ad}} = T_f - T_i - \Delta T_{\text{corr}}$ , with  $\Delta T_{\text{corr}}$  being the correction to the temperature change caused by heat exchange between the calorimeter and the surroundings);  $\Delta U(\text{BA})$  is the change in internal energy due to the combustion of benzoic acid. Due to small deviations from the certificate conditions, the certificate energy of combustion of benzoic acid was corrected using the formula given by Coops *et al.* [14] to be  $-(26432.3 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$ ;  $\Delta U(\text{ign})$  is the energy of ignition calculated from the initial and final difference in potential between the terminals of the 2000  $\mu\text{F}$  condenser.  $\varepsilon_c$  is the energy equivalent of the contents; and  $\varepsilon_{\text{cal}}$  is the energy equivalent of the calorimeter minus contents. The

TABLE 2  
Physical–chemical data for the studied compounds

Compound	CAS number	$M/(\text{g} \cdot \text{mol}^{-1})$	Density	$-(\frac{\partial U}{\partial p})_T/(\text{J} \cdot \text{MPa}^{-1} \cdot \text{g}^{-1})$	$C_p/(\text{J} \cdot \text{K}^{-1} \cdot \text{g}^{-1})$
Anthracene	120-12-7	178.2330	1.283 [20]	0.1 <sup>a</sup>	1.188 [23]
Succinic acid	110-15-6	118.0890	1.572 [20]	0.098 [21]	1.295 [24]
Acetanilide	103-84-4	135.1652	1.22 [20]	0.067 [22]	1.39 [22]
1,2,4-Triazole	288-88-0	69.0658	1.394 [19]	0.0944 [19]	1.15 [19]

<sup>a</sup> Estimated.

TABLE 3  
Experimental calibration results obtained with the calibration combustion experiments with benzoic acid (NIST SRM 39i)

Experiment	1	2	3	4	5	6	7	8
$m(\text{BA})/\text{mg}$	33.6513	33.5462	30.4643	29.3323	28.9001	25.0039	31.3457	24.5521
$m(\text{Pt})/\text{g}$	2.2020	2.2020	2.2020	2.2020	2.2020	2.2022	2.2023	2.2023
$T_i/\text{K}$	298.0939	298.0224	298.0110	298.0220	298.0256	298.06524	298.0018	298.0694
$T_f/\text{K}$	298.5372	298.4783	298.4342	298.4306	298.4278	298.41688	298.4366	298.4154
$\Delta T_{\text{ad}}/\text{K}$	0.457158	0.455770	0.414014	0.398648	0.392722	0.339780	0.425796	0.333757
$\Delta U(\text{BA})/\text{J}$	889.481	886.704	805.243	775.320	763.897	660.912	828.540	648.968
$\Delta U(\text{ign})/\text{J}$	0.907	0.855	0.916	0.882	0.907	0.891	0.911	0.906
$(\varepsilon_{\text{cal}} + \varepsilon_c)/(\text{J} \cdot \text{K}^{-1})$	1947.659	1947.384	1947.178	1947.086	1947.444	1947.740	1948.001	1947.147
$\varepsilon_c/(\text{J} \cdot \text{K}^{-1})$	1.025	1.025	1.021	1.020	1.020	1.014	1.023	1.014
$\varepsilon_{\text{cal}}/(\text{J} \cdot \text{K}^{-1})$	1946.63	1946.36	1946.16	1946.07	1946.42	1946.73	1946.98	1946.13
Experiment	9	10	11	12	13	14	15	
$m(\text{BA})/\text{mg}$	20.4955	20.1569	23.9532	25.2033	24.1777	20.9304	26.9143	
$m(\text{Pt})/\text{g}$	1.7043	1.7072	1.8495	1.9145	1.9145	1.9116	1.9116	
$T_i/\text{K}$	298.1071	298.1459	298.1699	298.1585	298.1685	298.1989	298.1429	
$T_f/\text{K}$	298.3988	298.4247	298.4918	298.4974	298.4938	298.4824	298.5043	
$\Delta T_{\text{ad}}/\text{K}$	0.278579	0.274041	0.325529	0.342545	0.328796	0.284680	0.365928	
$\Delta U(\text{BA})/\text{J}$	541.743	532.794	633.139	666.181	639.072	553.239	711.407	
$\Delta(\text{ign})/\text{J}$	1.004	0.984	0.639	1.035	1.036	1.115	1.074	
$(\varepsilon_{\text{cal}} + \varepsilon_c)/(\text{J} \cdot \text{K}^{-1})$	1948.270	1947.803	1946.917	1947.820	1946.824	1947.288	1947.052	
$\varepsilon_c/(\text{J} \cdot \text{K}^{-1})$	0.942	0.942	0.966	0.976	0.975	0.970	0.978	
$\varepsilon_{\text{cal}}/(\text{J} \cdot \text{K}^{-1})$	1947.33	1946.86	1945.95	1946.84	1945.85	1946.32	1946.07	

$$\langle \varepsilon_{\text{cal}} \rangle = 1946.45 \pm 0.11 \text{ (0.0057\%)} \text{ J} \cdot \text{K}^{-1}$$

$m(\text{BA})$  is the mass of benzoic acid burnt in each experiment;  $m(\text{Pt})$  is the mass of the platinum fittings;  $T_i$  and  $T_f$  are, respectively, the initial and final temperature rise  $\Delta T_{\text{ad}}$  is the corrected temperature rise;  $\Delta U(\text{BA})$  is the energy of combustion of the benzoic acid;  $\varepsilon_{\text{cal}}$  is the energy equivalent of the empty bomb;  $\varepsilon_c$  is the energy equivalent of the contents.

quantity  $\varepsilon_{\text{cal}}$  refers to the calorimeter with empty interior of the mini-bomb with the platinum electrodes and crucible support. The uncertainty associated to  $\varepsilon_{\text{cal}}$  is the standard deviation of the mean and represents only 0.0057% of the energy equivalent,  $\varepsilon_{\text{cal}} = (1946.45 \pm 0.11)$ .

### 3.2. Test compounds

Typical combustion results are listed in table 4, where  $\varepsilon_i$  and  $\varepsilon_f$  are the energetic equivalent of the contents in the initial and final states, respectively;  $\Delta U(\text{IBP})$  is the internal

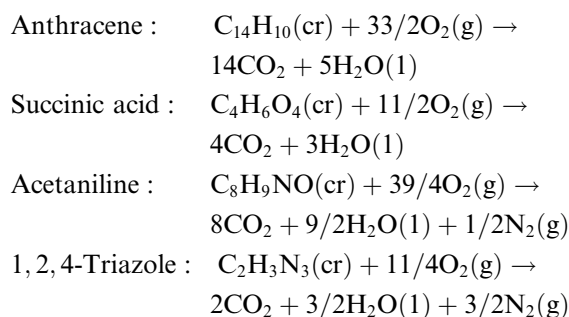
TABLE 4  
Typical combustion results at  $T = 298.15 \text{ K}$  ( $p^\circ = 0.1 \text{ MPa}$ ) for the test compounds

	Anthracene	Succinic acid	Acetanilide	1,2,4-Triazole
$m(\text{cpd})/\text{mg}$	20.7743	24.3277	24.8448	35.6547
$m'(\text{BA})/\text{mg}$		12.2355		
$m''(n\text{-hexadecane})/\text{mg}$	4.7880			
$m(\text{Pt})/\text{g}$	1.7077	1.8493	1.8461	1.8461
$T_i/\text{K}$	297.9584	298.1269	298.1063	298.1415
$T_f/\text{K}$	298.4949	298.4746	298.5026	298.4938
$\Delta T_{\text{ad}}/\text{K}$	0.539129	0.324647	0.400065	0.354815
$\varepsilon_i(\text{cont.})/\text{J}$	1.012	1.043	1.031	1.037
$\varepsilon_f(\text{cont.})/\text{J}$	1.058	1.082	1.065	1.064
$-\Delta U(\text{IBP})^a/\text{J}$	1049.032	631.331	778.022	689.830
$m' \cdot \Delta_c u^\circ(\text{BA})/\text{J}$		323.434		
$m'' \cdot \Delta_c u^\circ(n\text{-hexadecane})/\text{J}$	225.813			
$\Delta U(\text{HNO}_3)/\text{J}$	0.000	0.000	1.355	3.863
$\Delta U(\text{ign})/\text{J}$	0.917	0.929	1.109	1.177
$\Delta U_{\Sigma}/\text{J}$	0.526	0.566	0.427	0.479
$-\Delta_c U/\text{J}$	822.693	307.331	776.240	685.488
$-\Delta_c u^\circ/(\text{J} \cdot \text{K}^{-1} \cdot \text{g}^{-1})$	39601.5	12633.0	31243.6	19225.7

$m(\text{cpd})$  is the mass of compound burnt in each experiment;  $m'(\text{BA})$  is the mass of benzoic acid burnt in each experiment;  $m''(n\text{-hexadecane})$  is the mass of  $n$ -hexadecane burnt in each experiment;  $m(\text{Pt})$  is the mass of the platinum fittings;  $T_i$  and  $T_f$  are, respectively, the initial and final temperature rise;  $\Delta T_{\text{ad}}$  is the corrected temperature rise;  $\varepsilon_i$  is the energy equivalent of contents in the initial state;  $\varepsilon_f$  is the energy equivalent of contents in the final state;  $\Delta U(\text{IBP})$  is the energy change for the isothermal combustion reaction under actual bomb conditions;  $\Delta_c u^\circ(\text{BA})$  is the massic energy of combustion of the benzoic acid;  $\Delta_c u^\circ(n\text{-hexadecane})$  is the massic energy of combustion of the  $n$ -hexadecane;  $\Delta U(\text{HNO}_3)$  is the energy correction for the nitric acid formation;  $\Delta U(\text{ign})$  is the electrical energy for ignition;  $\Delta U_{\Sigma}$  is the standard state correction;  $\Delta_c U$  is the energy of combustion of the compound;  $\Delta_c u^\circ$  is the standard massic energy of combustion.

<sup>a</sup>  $\Delta U(\text{IBP})$  already includes the  $\Delta U(\text{ign})$ .

energy change for the isothermal bomb process, calculated as  $\Delta U(\text{IBP}) = \varepsilon_{\text{cal}} \cdot \Delta T_{\text{ad}} + \varepsilon_i \cdot (T_i - 298.15) + \varepsilon_f \cdot (298.15 - \Delta T_{\text{ad}} - T_i) + \Delta U(\text{ign})$ ;  $\Delta U(\text{HNO}_3)$  is the energy of formation of the nitric acid from  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}(\text{l})$  based in the value  $\Delta_f U_{\text{m}}^{\circ}(\text{HNO}_3, 0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ aq}) = -59.7 \text{ kJ} \cdot \text{mol}^{-1}$  [26];  $\Delta U_{\Sigma}$  is the correction energy to the standard state, corresponding to the sum of items (81), (82), (83), (84), (85), (87), (88), (89), (90), (93), and (94) referred by Hubbard *et al.* [27];  $\Delta_c u^{\circ}(n\text{-hexadecane})$  is the massic energy of combustion of *n*-hexadecane, determined in this laboratory as being  $-(47161.9 \pm 3.2) \text{ J} \cdot \text{g}^{-1}$ ;  $\Delta_c u^{\circ}$  is the standard ( $p^{\circ} = 0.1 \text{ MPa}$ ) massic energy of combustion corresponding to the following combustion reactions:



The individual values of the standard massic energy of combustion for each compound are listed in table 5, as well as the mean value of  $\Delta_c u^{\circ}$  and standard deviation of the mean.

Table 6 gathers the derived molar quantities from the mean standard massic energy of combustion for each compound, in which,  $\Delta_c U_{\text{m}}^{\circ}$  and  $\Delta_c H_{\text{m}}^{\circ}$  are the standard molar energy and enthalpy of combustion, respectively, and

$\Delta_f H_{\text{m}}^{\circ}(\text{cr})$  is the standard molar enthalpy of formation in the crystalline phase. As recommended [28,29] the uncertainties associated with these molar quantities are twice the overall standard deviation of the mean, and they include the uncertainties associated with the calibration experiments (uncertainties of massic energy of combustion of benzoic acid and energetic equivalent of the calorimeter) and auxiliary substances, when used. For the calculation of  $\Delta_f H_{\text{m}}^{\circ}(\text{cr})$  from the derived  $\Delta_c H_{\text{m}}^{\circ}$ , the following values were used:  $\Delta_f H_{\text{m}}^{\circ}(\text{H}_2\text{O}, \text{l}) = -(285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$  [30];  $\Delta_f H_{\text{m}}^{\circ}(\text{CO}_2, \text{g}) = -(393.51 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$  [30].

#### 4. Discussion

As mentioned above, there are several mini-combustion calorimeters described throughout the literature. Table 7 lists the performance of recent mini-combustion calorimeters, with different operating conditions, as well as the energetic equivalent and uncertainty interval. The % error is the standard deviation found in calibration experiments. It is apparent that many are capable of producing results of the standard made by macro-combustion calorimeters but the experimental methods are more difficult. It is expected that further improvements will be made in this area whereas the technique for macro-combustion calorimetry is unlikely to be improved.

Long time stability was found for the energetic equivalent obtained in this calorimeter. That was verified from over than 70 successful calibration experiments that were done during the last 3 years where no statistical evidence for a time-drift of the mean value of the energetic equivalent was found. The obtained uncertainty interval

TABLE 5

Standard massic energies of combustion, at  $T = 298.15 \text{ K}$ , of all the experiments considered for each compound

	Anthracene	Succinic acid	Acetanilide	1,2,4-Triazole
$-\Delta_c u^{\circ}/(\text{J} \cdot \text{g}^{-1})$	39578.7 39600.2 39590.0 39580.3 39589.7 39598.8 39584.9 39600.0 39601.5	12633.0 12631.4 12627.9 12626.7 12631.0 12630.4	31243.4 31248.2 31247.9 31237.1 31240.4 31245.0 31243.6	19225.7 19225.0 19229.7 19235.0 19231.8 19220.9 19225.5 19224.7
$-\langle \Delta_c u^{\circ} \rangle/(\text{J} \cdot \text{g}^{-1})$	$39591.6 \pm 3.0$	$12630.1 \pm 1.0$	$31243.7 \pm 1.5$	$19227.3 \pm 1.6$

TABLE 6

Standard ( $p^{\circ} = 0.1 \text{ MPa}$ ) massic energy of combustion, standard molar energy and enthalpy of combustion and derived standard molar enthalpy of formation, at  $T = 298.15 \text{ K}$ , for each studied compound

Compound	$-\Delta_c u^{\circ}$ $\text{J} \cdot \text{g}^{-1}$	$-\Delta_c U_{\text{m}}^{\circ}$ $\text{kJ} \cdot \text{mol}^{-1}$	$-\Delta_c H_{\text{m}}^{\circ}$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_{\text{m}}^{\circ}(\text{cr})$ $\text{kJ} \cdot \text{mol}^{-1}$
Anthracene	$39591.6 \pm 3.0$	$7056.5 \pm 2.1$	$7062.7 \pm 2.1$	$124.4 \pm 2.8$
Succinic acid	$12630.1 \pm 1.0$	$1491.5 \pm 0.7$	$1490.3 \pm 0.7$	$-941.2 \pm 0.9$
Acetanilide	$31243.7 \pm 1.5$	$4223.1 \pm 1.1$	$4226.2 \pm 1.1$	$-208.1 \pm 1.6$
1,2,4-Triazole	$19227.3 \pm 1.6$	$1327.9 \pm 0.4$	$1326.0 \pm 0.4$	$110.3 \pm 0.5$

TABLE 7  
Some recent micro-combustion calorimeters found throughout the literature

Author	Calorimeter type	m/mg	Number of calibration experiments	$\varepsilon_{\text{cal}}/(\text{J} \cdot \text{K}^{-1})$	% Error	Year	Reference
This work	Aneroid isoperibol	10 to 40	15	$1946.45 \pm 0.11$	0.0057		
Camarillo and Flores	Isoperibol	40	9	$1283.8 \pm 0.6$	0.047	2006	[12]
Rojas-Aguilar	Isoperibol	20	13	$687.45 \pm 0.34$	0.049	2002	[11]
Dávalos and Roux	Isoperibol	80	10	$2083.74 \pm 0.48$	0.023	2000	[10]
Sakiyama and Kiyobayashi	Isoperibol	10 to 20	7	$1371.78 \pm 0.29$	0.021	2000	[9]
Xu-wu and Jun	Isoperibol	10	6/5/6	$456.20 \pm 0.05/$ $420.81 \pm 0.08/$ $419.29 \pm 0.08$	0.011/ 0.019/ 0.019	2000	[8]
Nagano	Aneroid isoperibol	5	5	$67.8330 \pm 0.0024$	0.0035	1999/2001	[7,31]
Diogo and Piedade	Aneroid isoperibol	10 to 50	9	$1809.82 \pm 0.28$	0.015	1995	[6]
Beckhaus et al.	Aneroid isoperibol	60 to 90		$1333.50 \pm 0.17$	0.013	1984	[5]
Metzger et al.	Adiabatic semi-micro	50	8	$4168.98 \pm 2.23$	0.053	1983	[4]
Parker et al.	Aneroid isoperibol	20	8	$2261.6 \pm 0.7^a$	0.031	1975	[3]
Månsson	Isoperibol	10	5	$583.45 \pm 0.07$	0.012	1973	[2]
Mackle and O'Hare	Aneroid isoperibol	10 to 20	10	$75.251 \pm 0.021^a$	0.028	1963	[1]

<sup>a</sup>  $\varepsilon_{\text{cal}}$  in  $\text{J} \cdot \Omega^{-1}$ .

TABLE 8  
Standard massic energy of combustion and standard molar enthalpy of combustion of anthracene at  $T = 298.15 \text{ K}$

Author	$-\Delta_c u^\circ$ $\text{J} \cdot \text{g}^{-1}$	$-\Delta_c H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$	Reference
This work	$39591.6 \pm 3.0$	$7062.7 \pm 2.1$	
Nagano	$39604.2 \pm 3.1$	$7065.0 \pm 1.1$	[31]
Metzger et al.	$39597 \pm 10$	$7063.8 \pm 5.3$	[4]
Coleman and Pilcher	39617.6	$7067.5 \pm 1.7$	[32]
Mackle and O'Hare	$39561 \pm 4$	$7054.8 \pm 4.3$	[1]
Bender	39569.3	$7058.8 \pm 2.9$	[33]

TABLE 9  
Standard massic energy of combustion and standard molar enthalpy of combustion of succinic acid at  $T = 298.15 \text{ K}$

Author	$-\Delta_c u^\circ$ $\text{J} \cdot \text{g}^{-1}$	$-\Delta_c H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$	Reference
This work	$12630.1 \pm 1.0$	$1490.2 \pm 0.7$	
Sabbah et al.	$12638.0 \pm 1.6$	1491.2	[16]
Rojas-Aguilar and Valdés-Ordoñez	12652.3	$1492.9 \pm 0.8$	[34]
Rojas and Valdés	$12622 \pm 13$	$1489.3 \pm 1.6$	[17]
Coley et al.	12640	$1491.4 \pm 4.2$	[35]
Vanderzee et al.	$12639.3 \pm 2.3$	1491.3	[21]
Wong and Westrum Jr.	$12634.3 \pm 0.8$	1490.7	[36]
Wilhoit and Shiao	$12634.0 \pm 4.2$	1490.7	[37]
Bills and Cotton	$12636.1 \pm 2.1$	1490.9	[38]
Good et al.	$12634.8 \pm 1.7$	1490.8	[39]
Cass et al.	12635.7	$1490.9 \pm 0.3$	[40]
Pilcher and Sutton	12638.3	$1491.2 \pm 0.3$	[41]
Huffman	$12632.8 \pm 1.1$	$1490.5 \pm 0.4$	[42]

( $\pm 0.0057\%$  of the energetic equivalent) is of the same order than the typical energetic equivalent uncertainties intervals obtained in macro-bomb calorimetry and is certainly one of the smallest found in the literature in mini- and micro-bomb combustion calorimetry.

TABLE 10  
Standard massic energy of combustion and standard molar enthalpy of combustion of acetanilide at  $T = 298.15 \text{ K}$

Author	$-\Delta_c u^\circ$ $\text{J} \cdot \text{g}^{-1}$	$-\Delta_c H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$	Reference
This work	$31243.7 \pm 1.5$	$4226.2 \pm 1.1$	
Sabbah et al.	$31234.0 \pm 5.0$	4224.8	[16]
Rojas and Valdés	$31217.1 \pm 8.4$	$4222.5 \pm 1.1$	[17]
Finch and Payne	31245.2	$4226.4 \pm 3.6$	[43]
Sato-Toshima et al.	$31233.7 \pm 3.4$	$4224.8 \pm 1.0$	[44]
Finch et al.	$31218 \pm 11$	4222.7	[45]

TABLE 11  
Standard massic energy of combustion and standard molar enthalpy of combustion of 1,2,4-triazole at  $T = 298.15 \text{ K}$

Author	$-\Delta_c u^\circ$ $\text{J} \cdot \text{g}^{-1}$	$-\Delta_c H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$	Reference
This work	$19227.3 \pm 1.6$	$1326.1 \pm 0.4$	
Sabbah et al.	$19204.2 \pm 4.1$	1324.5	[16]
Roux et al.	$19200.3 \pm 3.4$	1324.2	[19]
Sabbah and Perez	19173.9	$1322.4 \pm 1.0$	[46]
Jiménez et al.	$19203.1 \pm 1.2$	$1324.4 \pm 0.3$	[47]
Faour and Akasheh	$19267 \pm 17$	$1328.9 \pm 1.2$	[48]

The results obtained by several authors for the study of combustion of anthracene, succinic acid, acetanilide, and 1,2,4-triazole, respectively, are presented in tables 8 to 11.

The enthalpies of combustion obtained in this work for the test compounds are in all the cases in good agreement with the results available in the literature.

The results obtained with the four test compounds indicate that the mini-bomb calorimeter is working with an adequate accuracy and with an overall uncertainty near the same order of magnitude than the uncertainties obtained in macro-bomb combustion calorimetry.



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