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Thermochimica Acta 437 (2005) 126–133

thermochimica acta

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Enthalpies of combustion and formation of fullerenes by micro-combustion calorimetry in a Calvet calorimeter

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Received 8 February 2005; received in revised form 19 June 2005; accepted 21 June 2005

Abstract

A set of micro-combustion bombs has been adapted to a Setaram C80 Calvet calorimeter. The calorimetric constant of the micro-bomb in the measurement fluxmeter was determined by combustions with benzoic acid NIST 39*j*, giving an uncertainty of less than 0.03% for calibration. The experimental methodology of applying this micro-combustion device to the measurement of the energy of combustion of graphite, C_{60} and C_{70} is described. Accuracy of better than 0.08% is obtained in some cases.

Keywords: Fullerene; Micro-combustion calorimetry; Heat flux calorimetry; Enthalpy of combustion; Enthalpy of formation

1. Introduction

Despite the improvements in the methods of isolation and purification of fullerenes by chromatographic techniques [1–5], these allotropes of the carbon still available in small quantities, especially those having more than seventy carbon atoms. Commercial samples of purity larger than 98% are very expensive and available in not more than a few milligrams.

In this perspective, a thermochemical study involving the measurement of the energy of combustion of fullerenes would not be possible without the development of micro-combustion methods, from which, the combustion energy of a compound is measured with a similar precision as in conventional combustion calorimetry but using a sample mass of only a few milligrams. A set of combustion micro-bombs have been developed and associated with a commercial Setaram C80 Calvet calorimeter and in a previous paper, the measurement of energy involved in the combustion of masses less than 8 mg of organic compounds was examined [6]. Now, prior to measurement of the enthalpy of combustion of the larger fullerenes, we have verified the accuracy of our micro-combustion assembly, by applying it to the measurement of the enthalpy of combustion of fullerenes C_{60} and C_{70}, which have been previously studied in our laboratory [7,8], and whose combustion energy value is now well known. Although there are no recommended values for the energies of combustion of these fullerenes at present, enough combustion data are available to compare our experimental results employing the Calvet calorimeter.

Our results show the viability of applying this technique not only in the study of C_{60} and C_{70}, but that it can be extended to the thermochemical study of the higher fullerenes. In the same way, results have shown that for a reliable comparison, a revision of the assignment of uncertainties associated to previous values of enthalpies of combustion must be considered.

2. Experimental

The energies of combustion of the fullerenes were measured with a micro-bomb set associated to a Setaram C80 Calvet calorimeter operating in isothermal mode. The sen-

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doi:10.1016/j.tca.2005.06.029

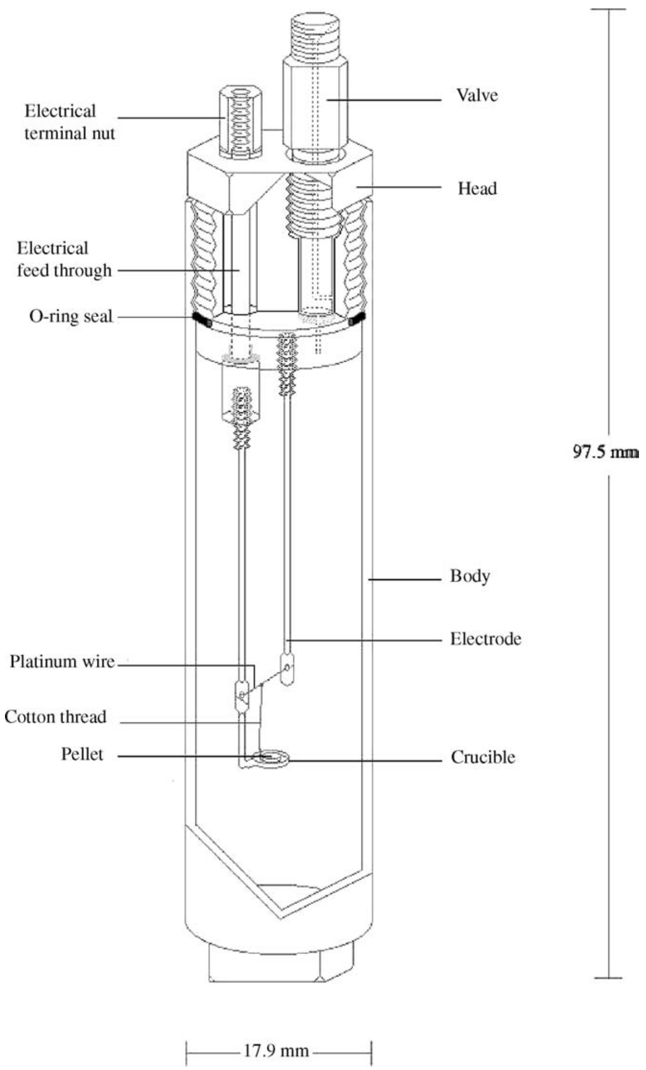

Fig. 1. Micro-combustion bomb. The body is a high pressure Setaram vessel of 8.5 cm^3 of volume. The head, electrical feedthrough and valve are manufactured in stainless steel. Electrodes assemblies and crucible are made in gold and platinum.

sors of the calorimeter are two fluxmeters with a detection limit in power of 2 μW and a calorimetric resolution of 0.1 μW, which are assembled inside of a calorimetric block with a temperature control of at least ±0.001 K. An adequate temperature control in the environmental conditions of our laboratory is attained maintaining the calorimetric block at $T = 303.15$ K.

A schematic diagram of the micro-combustion bomb developed in our laboratory is shown in Fig. 1. The body of the micro-bomb is a cylindrical Setaram high pressure stainless steel vessel. The head of the bomb was manufactured in our laboratory and, is a stainless steel hexagonal screw with the appropriate locknuts for the assembly of a valve for filling with oxygen and a complete electrode assembly. In the extremity of a platinum electrode, a 4.5 mm diameter platinum crucible is soldered. A second platinum electrode is directly screwed to the head of the bomb. Both platinum electrodes are assembled by means of respective gold screws. An O-ring seal fitted to the base of the micro-bomb's head guarantees no oxygen leakage.

The fullerenes whose combustion energies were measured, are commercial Strem products. The C_{60} has a mass fraction purity ≥0.9995 while for the C_{70} it is >0.99. The absence of larger fullerenes and solvents in these samples was verified by ^{13}C N.M.R. and I.R. spectroscopy [7,8]. Graphite, is the Aldrich product for spectroscopy, catalog number 49,658–8, with a mass fraction purity >0.9999.

Table 1 summarizes the required physical, chemical and thermochemical properties of the compounds studied. The chemical composition of the cotton and the Vaseline was determined by elemental analysis [6,7]. Massic heat capacities, densities and data of $-(\partial U/\partial P)_T$ for graphite, both fullerenes and the others substances were taken from previous calorimetric studies [7–16]. Calculation of the molar masses is based on data of atomic masses recommended by the IUPAC [17]. The energies of combustion of solid Vaseline and cotton were previously measured in our laboratory [6,7].

Looking for an improvement on the accuracy of the measurements and, in contrast to that previously reported [6], only the micro-combustion bomb located in the measurement fluxmeter was utilized to quantify the energy of combustion of the fullerenes studied in the current work. The calorimetric constant of the measurement micro-combustion bomb was determined using NIST 39*j* benzoic acid. Throughout the calibration experiments, the best conditions in mass of substance, time for thermal stabilization and time lapse for data acquisition were optimized to get adequate amplitude of the signal and, linear initial and final periods to assure a complete curve in each experiment. In order to test the accuracy of our set of micro-bombs and calorimeter in measurements of the energy of combustion of the allotropes of carbon and, to optimize the quantities of substance utilized in each experiment, the energy of combustion of the graphite was measured previous to measurements on C_{60} and C_{70}.

The allotropes of carbon burned in this study were pelletized using a Parr pellet press and, a 2.38 mm stainless steel punch and die set. Combustion experiments with pellets of graphite between 5 to 7 mg provided evidence that in our experimental conditions, the completeness of combustion for this substance was not achieved. These tests also showed that ignition and better combustion of the sample was achieved by distributing about 1.3 mg of solid Vaseline in the crucible directly under the sample of graphite.

The masses of graphite, fullerenes and all the others substances involved in each combustion experiment were measured using a Sartorius 4503 microbalance sensitive to 1 μg (precision: ±1 μg), and the corrections for apparent mass to mass were applied. For all the calibration and measurement experiments, 1.1×10^{-3} mol of demineralized water was placed in the bomb to ensure a well-defined thermodynamic equilibrium at the end of the combustion. Because the micro-bomb has only one valve, the flushing to remove air must be

Table 1
Physical, chemical and thermochemical properties at $T = 298.15$ K required for the combustion experiments of the fullerenes

Substance	Formula	M (g mol^{-1})	ρ (g cm^{-3})	$-(\partial U/\partial P)_T$ (J g^{-1} MPa^{-1})	c_p (J K^{-1} g^{-1})	$-\Delta_c u^o$ (J g^{-1})
Graphite	C	12.011	2.26 [9]	0.010[a]	0.729 [7]	
Buckminsterfullerene	C_{60}	720.642	1.67 [9]	0.007 [10]	0.724 [7]	
C_{70}	C_{70}	840.749	1.69 [11]	0.006 [12]	0.790 [8]	
Cotton	$CH_{1.823}O_{0.881}$ [6]	27.943	1.50 [13]	0.289 [13]	1.294 [14]	16609.4 ± 38.0 [6]
Vaseline	$CH_{2.059}$ [7]	14.086	0.84 [7]	0.060 [13]	3.491 [7]	46403.7 ± 6.0 [7]
Benzoic acid	$C_7H_6O_2$	122.122	1.32 [15]	0.120 [15]	1.190 [14]	26434 ± 3.0 [16]

[a] Estimated value.

carefully done by successively charging the bomb with oxygen to 1.5 MPa then, relieving the pressure to the atmosphere. The procedure is repeated ten times to assure total absence of nitrogen. After this, the bomb is charged to $p = 3.04$ MPa. The oxygen used was research grade, mole fraction 0.99998, Air Liquid products. The micro-bomb serving as reference is charged exactly in the same way as described above.

Once the micro-bombs have been charged, a 30 cm long and thermally isolated stainless steel rod is fixed to the ignition nuts. This rod is the tool used to descend each micro-combustion vessel into its respective fluxmeter and simultaneously it carries the electrical wires for ignition out of the calorimeter. A perforated plug in Teflon acts as a guide for the steel rod and electrical wires and, closes the lid of the calorimeter.

The ignition of the sample is attained through a 11 mm long cotton thread knotted to the same long platinum wire attached to the electrodes of the micro-bomb and, by an electrical current supplied by a Parr ignition unit, 2901EE. The electric firing energy was also determined using the C80 calorimeter and, the resulting average energy from ten ignition experiments was of (1.383 ± 0.082) J. This quantity was taken into account in the calculation of the calorimetric constant of the micro-bomb and in the computation of the energy of combustion of graphite and of the fullerenes.

From introduction of the charged micro-bombs into the fluxmeters, until a complete thermal stabilization of the calorimetric device is achieved, a period of 80 min is required, after which, data acquisition begins. Five minutes are enough to get an initial stable baseline, then ignition of the sample is carried out. The energy of combustion of the fullerene utilized in an experiment is enough to produce a sharp curve with a maximal amplitude of 900 mW. After ignition, data acquisition continues for 115 min more, in order to get the complete calorimetric register, even if the analysis of initial and final baseline showed that for a maximal quantity of energy of 380 J involved in some of the combustions experiments, the transfer of heat was complete in less than 90 min. At the end of the combustion experiment, the difference between initial and final baseline was not more than 0.01 mW, which introduced a maximal uncertainty in the measurement of the area under the combustion curve of ±0.069 J.

After each combustion experiment, analysis of the gas phase is required, The volume of gas produced by the combustion is not enough for conventional Dräger analysis. Under these conditions, a Dräger detection tube was connected directly to the valve of the micro-bomb by a 15 cm of Tygon tubing, and the valve was very slowly opened to release the mixture of gases through the detection tube in order to get a qualitative check for CO, NO and NO_2. Employing this procedure, no evidence of nitrogen oxides was found but, for the reasons given below, in some experiments traces of CO were detected.

Even with the use of Vaseline as a combustion aid, complete combustion of a mass of graphite or fullerene up to 5 mg was not possible under our experimental conditions. In all the experiments where a similar mass was utilized, unburned traces were detected on the bottom of the crucible and on the electrode that supports it. A careful quantification of these residues was required. This was carried out after each combustion by disassembling the electrode-crucible set and drying it at $T = 323$ K for around 1 h. The item was then weighted, and cleaned by putting it in the flame of a Bunsen burner until total volatilization of the carbon traces. After this procedure, the clean electrode-crucible assembly was left to cool and weighted again and the mass of residues was deduced by difference. Experiments where unburned residues were detected on the crucible also showed traces of CO during the analysis of the gas phase.

Given that the methodology developed in the current work is intended to be applied to the study of larger fullerenes, which are commercially available in masses of not more than 10 mg, is clear that combustion experiments involving 5 mg samples are not viable, given the number of experiments necessary. In order to improve this point, another set of combustion experiments were performed, but employing masses of graphite and fullerenes of around 2 mg or less. The applied methodology was the same, except that in each experiment a spiral platinum wire was utilized on the bottom of the crucible, this item reduces thermal contact between the pellet and the crucible during combustion and, despite the small masses of sample utilized, completeness of combustions could be achieved.

Corrections for apparent mass to mass, corrections to the standard state, and calculations of the thermodynamic quantities were performed with computer software written in the laboratory and with assistance from reference [18].

Table 2
Masses and energetic quantities for the combustion experiments of graphite and fullerenes at $T = 303.15\,\mathrm{K}$ ($p^{\mathrm{o}} = 0.1\,\mathrm{MPa}$)

	~5 mg samples			~2 mg samples		
	Graphite	C_{60}	C_{70}	Graphite	C_{60}	C_{70}
m(substance)/mg	6.702	4.813	4.872	2.508	2.020	2.110
m(vaseline)/mg	2.105	1.196	1.331	1.198	0.585	0.503
m(cotton)/mg	0.296	0.239	0.239	0.325	0.292	0.323
m(unburned residues)/mg	0.031	0.017	0.006	0.052		
m(platinum)/mg	3.140	3.373	3.223	3.156	3.399	3.405
A/J	−318.910	−230.704	−238.839	−141.509	−104.681	−104.336
ΔU_{IBP}/J	−322.600	−233.373	−241.602	−143.159	−105.902	−105.552
ΔU_{ign}/J	−1.383	−1.383	−1.383	−1.383	−1.383	−1.383
ΔU_{W}/J	0.213	0.146	0.150	0.082	0.063	0.065
ΔU_{corr}/J	−1.016	−0.557	−0.197	−1.704		
$m\ \Delta_{\mathrm{c}}u^{\mathrm{o}}$ (vaseline)/J	−97.680	−55.499	−61.763	−55.592	−27.146	−23.341
$m\ \Delta_{\mathrm{c}}u^{\mathrm{o}}$ (cotton)/J	−4.916	−3.970	−3.970	−5.398	−4.850	−5.365
$m\ \Delta_{\mathrm{c}}u^{\mathrm{o}}$ (substance)/J	−219.424	−172.932	−174.533	−82.408	−72.460	−75.398
$\Delta_{\mathrm{c}}u^{\mathrm{o}}$ (compound)/($\mathrm{J\,g^{-1}}$)	−32740.08	−35930.19	−35823.69	−32858.05	−35871.29	−35733.65

m(substance), mass of substance; *m*(vaseline), mass of vaseline utilized to promote the combustion, *m*(unburned residues), mass of unburned residues detected on the crucible after combustion, *m*(cotton), mass of cotton thread; *m*(Pt), mass of platinum wire for ignition; *A*, area of the combustion curve; ΔU_{IBP}, energy of the isothermal bomb process; ΔU_{ign}, ignition energy; ΔU_{W}, correction to standard state; ΔU_{corr}, correction in energy for the unburned residues, for which a value of $32762.5\,\mathrm{J\,g^{-1}}$ was considered; $\Delta_{\mathrm{c}}u$(vaseline), massic energy of combustion of the vaseline; $\Delta_{\mathrm{c}}u$(cotton), massic energy of combustion of cotton; $\Delta_{\mathrm{c}}u^{\mathrm{o}}$(substance) massic energy of combustion of the substance. The initial mols of water inside of the bomb in all experiments were 0.0011, equivalent to $0.02\,\mathrm{cm^3}$.

3. Results and discussion

For the measurement of the energy of combustion of graphite and the fullerenes, previous calibration of the measurement micro-bomb was performed by 16 combustion experiments using about 6.7 mg of NIST 39*j* benzoic acid with a massic energy of combustion under certificate conditions of $\Delta_{\mathrm{c}}u = -(26{,}434 \pm 3)\,\mathrm{J\,g^{-1}}$. given that our experimental conditions differ from the certified ones, the value of energy of combustion given above was multiplied by the factor:

$$f = 1 + 10^{-6}[20(p - 3.0) + 42(m_{\mathrm{s}}/V_{\mathrm{b}} - 3) + 30(m_{\mathrm{w}}/V_{\mathrm{b}} - 3) - 45(T - 298.15)], \qquad (1)$$

as recommended in the references [19] and [20]. Considering a pressure *p*, of 3.0 MPa; an average mass, m_{s}, of 6.7 mg for the sample; an initial mass of water into the bomb,

Table 3
Summary of the massic energy of combustion of the graphite and fullerenes at $T = 303.15\,\mathrm{K}$ ($p^{\mathrm{o}} = 0.1\,\mathrm{MPa}$)[a]

Graphite	C_{60}	C_{70}
~5 mg samples		
−32740.08	−35930.19	−35823.69
−32644.54	−35921.99	−35808.08
−32889.53	−35898.70	−35790.33
−32845.23	−35926.75	−35828.84
−32937.25	−35984.94	−35804.40
−32720.34	−35904.89	−35780.09
−32762.94	−35902.66	−35833.63
−32765.42		−35786.34
−32688.50		
−32744.34		
$\langle\Delta_{\mathrm{c}}u^{\mathrm{o}}(\mathrm{cr}, 303.15)\rangle = -(32773.82 \pm 28.72)\,\mathrm{J\,g^{-1}}$	$\langle\Delta_{\mathrm{c}}u^{\mathrm{o}}(\mathrm{cr}, 303.15)\rangle = -(35924.30 \pm 11.15)\,\mathrm{J\,g^{-1}}$	$\langle\Delta_{\mathrm{c}}u^{\mathrm{o}}(\mathrm{cr}, 303.15)\rangle = -(35806.93 \pm 7.20)\,\mathrm{J\,g^{-1}}$
~2 mg samples		
−32858.05	−35871.29	−35733.65
−32835.55	−35993.42	−35772.41
−32819.53	−35892.22	−35778.17
−32801.80	−35979.67	−35820.49
−32812.55	−35992.00	−35805.42
−32771.00		
−32824.45		
$\langle\Delta_{\mathrm{c}}u^{\mathrm{o}}(\mathrm{cr}, 303.15)\rangle = -(32817.56 \pm 10.30)\,\mathrm{J\,g^{-1}}$	$\langle\Delta_{\mathrm{c}}u^{\mathrm{o}}(\mathrm{cr}, 303.15)\rangle = -(35945.72 \pm 26.43)\,\mathrm{J\,g^{-1}}$	$\langle\Delta_{\mathrm{c}}u^{\mathrm{o}}(\mathrm{cr}, 303.15)\rangle = -(35782.03 \pm 14.96)\,\mathrm{J\,g^{-1}}$

[a] The uncertainty associated to each average value represents the standard deviation of the mean.

m_w, of 20 mg; a volume of the bomb, V_b, of 8.5 cm^3 and, $T = 303.15$ K; results in an energy of combustion for the benzoic acid of $-(26\ 425.1 \pm 3)$ J g^{-1}, which was used in the calculations of the calorimetric constant of the micro-bomb located in the measurement fluxmeter, providing an average value of $k_m = (1.01157 \pm 0.00027)$. The uncertainty associated with this calorimetric constant represents the standard deviation of the mean and implies a precision better than 0.03% for the calibration with benzoic acid.

Detailed quantities of mass and energy involved in each experiment for the combustion of the graphite and each fullerene are given in Table 2; where, A is the area of the combustion curve; ΔU_{ign}, is the energy supplied to ignite the sample; ΔU_W, is the correction to the standard state and $\Delta U_{unburned}$; is the correction in energy for the mass of unburned residue. In the case of the experiments of C_{60} and C_{70} involving samples of around 2 mg, no unburned traces were detected after combustion. In all cases the internal energy change for the isothermal bomb process at $T = 303.15$ K is calculated as $\Delta U_{IBP} = A \times k_m$, where k_m is the constant of the measurement micro-bomb.

The corresponding average standard massic energies of combustion of the graphite and each fullerene at $T = 303.15$ K, reported in Table 3 are related to the ideal combustion reactions:

$$C(cr) + O_2(g) = CO_2(g), \tag{2}$$

$$C_{60}(cr) + 60O_2(g) = 60CO_2(g), \tag{3}$$

$$C_{70}(cr) + 70O_2(g) = 70CO_2(g). \tag{4}$$

The uncertainty associated with each of the experimental results of massic energy of combustion represents one standard deviation of the mean. On the other hand, the overall uncertainty $\sigma(\Delta_c U_m^o)_\Sigma$, accompanying the molar energy of combustion was calculated following the procedure described in references [21] and [22], using the formula:

$$\sigma(\Delta_c U_m^o)_\Sigma = \left[\sum_{i=1}^{5}\left(f_i \frac{\sigma_i}{q_i}\right)^2\right]^{1/2} \Delta_c u^o(C_n). \tag{5}$$

In this expression, f_i represents different rapports between the rough mean values of the energetic quantities involved in a set of combustion experiments, defined as

$$f_1 = f_2 = \frac{[\Delta U_{IBP} - m\Delta_c u(\text{vas})]}{m\Delta_c u(C_n)};$$

$$f_3 = \frac{m\Delta_c u(\text{vas})}{m\Delta_c u(C_n)};\ f_4 = \frac{m\Delta_c u(\text{cot})}{m\Delta_c u(Cn)};\ f_5 = 1.$$

On the other hand, q_i corresponds to the values of the constant of calibration and, the standard massic combustion energies of the substances involved in a set of measurements, and are characterized as

$$q_1 = k_m;\quad q_2 = \Delta_c u^o(\text{benzoic acid});$$

$$q_3 = \Delta_c u^o(\text{vas});\quad q_4 = \Delta_c u^o(\text{cot});\quad q_5 = \Delta_c u^o(C_n).$$

Finally, σ_i symbolizes the uncertainty associated to each value q_i. The final uncertainty associated to the average standard molar energy of combustion shown in Table 4 is twice the overall uncertainty calculated in this way.

The standard enthalpies of combustion at $T = 298.15$ K reported also in Table 4 were derived from the results of standard enthalpies of combustion at $T = 303.15$ K by use of the equation:

$$\Delta_c H_m^o(cr, T = 298.15\ K) = \Delta_c H_m^o(cr, T = 303.15\ K) - \int_{T=298.15\ K}^{T=303.15\ K} \Delta c_{p,m} dT, \tag{6}$$

where the value of $\Delta c_{p,m}$ for the combustion process was calculated from data of heat capacity of each allotrope of carbon reported in Table 1 and, the molar heat capacities at constant pressure of (29.387 ± 0.003) J K^{-1} mol^{-1} and (37.220 ± 0.002) J K^{-1} mol^{-1}, respectively for O_2(g) and CO_2(g) at $T = 300$ K [23]. Analysis of propagation of errors as is described in reference [24], shows that due to the low dispersion of the heat capacities data, the uncertainty associated to the average value of enthalpy of combustion at $T = 298.15$ K remains unchanged with respect to that at $T = 303.15$ K.

The derived standard molar enthalpies of formation in the condensed state at $T = 298.15$ K shown in the Table 4 were calculated using the standard molar enthalpy of formation of CO_2(g) at $T = 298.15$ K of $-(393.51 \pm 0.13)$ kJ mol^{-1} [23].

Results in Table 4 shows that the largest uncertainty is that associated to the average value of the molar standard enthalpy of combustion of graphite, resulting from experiments employing masses of more than 5 mg of this substance. This fact can be explained if difficulties for complete oxidation of the sample are considered. This corresponds precisely to the set of experiments where the largest masses of unburned residues (among 30–56 μg) were detected after each combustion experiment.

For the fullerenes, the maximal uncertainty is 0.14% for the set of experiments of C_{60} employing masses of around 2 mg. In these particular cases, even that no residues were detected after experiment, we presume that the dispersion in the results is due to the low mass employed so, a manipulation of the sample without loss of mass is hard to perform. It is also important to remember that these are overall uncertainties, involving the uncertainty in the calibration of the calorimetric system, and in the energy of combustion of the cotton and the Vaseline.

For each substance, no matter whether 5 or 2 mg of substance are utilized in a combustion experiment, the result is essentially the same. The results are then unrelated to the mass of substance employed in a set of experiments. The only consequence of employing a minimal mass of substance is that the precision suffers, but without a lost of accuracy.

Table 4
Resulting molar standard energies of combustion[a], enthalpies of combustion and enthalpies of formation for graphite and the fullerenes (p^o = 0.1 MPa)

	Graphite	C_{60}	C_{70}
∼5 mg samples			
$\Delta_c U_m^o$ (cr, T = 303.15 K)/(kJ mol^{-1})	−393.65 ± 0.73	−25888.56 ± 22.57	−30104.64 ± 22.05
$\Delta_c H_m^o$ (cr, T = 303.15 K)/(kJ mol^{-1})	−393.65 ± 0.73	−25888.56 ± 22.57	−30104.64 ± 22.05
$\Delta_c H_m^o$ (cr, T = 298.15 K)/(kJ mol^{-1})	−393.64 ± 0.73	−25888.30 ± 22.57	−30104.06 ± 22.05
$\Delta_f H_m^o$ (cr, T = 298.15 K)/(kJ mol^{-1})	0	2277.70 ± 27.44	2558.36 ± 28.59
∼2 mg samples			
$\Delta_c U_m^o$ (cr, T = 303.15 K)/(kJ mol^{-1})	−394.17 ± 0.37	−25904.00 ± 42.02	−30083.70 ± 32.73
$\Delta_c H_m^o$ (cr, T = 303.15 K)/(kJ mol^{-1})	−394.17 ± 0.37	−25904.00 ± 42.02	−30083.70 ± 32.73
$\Delta_c H_m^o$ (cr, T = 298.15 K)/(kJ mol^{-1})	−394.17 ± 0.37	−25903.74 ± 42.02	−30083.12 ± 32.73
$\Delta_f H_m^o$ (cr, T = 298.15 K)/(kJ mol^{-1})	0	2293.14 ± 44.82	2537.42 ± 37.45

[a] The uncertainty accompanying the average value of energy of combustion represents twice the overall uncertainty computed from Eq. (5).

A comparison with several results of the standard molar enthalpy of combustion of the C_{60} and C_{70} reported in the literature is given in Table 5. Concerning C_{60}, to our knowledge there are nine reported values where the enthalpy of combustion of this substance was measured by conventional or by micro-bomb combustion calorimetry. Sample masses ranged from 7 to 500 mg, in about six experiments. None of these previous studies were performed by combined micro-combustion method and Calvet calorimetry.

The values of the standard molar enthalpy of combustion of the C_{60}, determined in this work as −(25,888.30 ± 22.57) kJ mol^{-1} and −(25,903.74 ± 42.02) kJ mol^{-1} are in very good agreement with the results reported by Diogo and Minas da Piedade [10], Kiyobayashi and Sakiyama [25] and Beckhaus et al. [26]. Furthermore, considering the associated uncertainties, at least one of our values overlaps with those obtained also by Beckhaus [11] in a second measurement of the enthalpy of combustion of this substance and, with the result reported by Xu-wu [29]. From a review of data avail-

Table 5
Comparison of results for the C_{60} and C_{70} at T = 298.15 K (p^o = 0.1 MPa)

	Calorimetric procedure	Number of experiments	$m(C_n)$ (mg)	$-\Delta_c H_m^o$ (cr, 298.15 K)[a] (kJ mol^{-1})	$\Delta_f H_m^o$ (cr, 298.15 K)[b] (kJ mol^{-1})
C_{60}					
Steele et al. [9]	Macro-combustion	2	Not specified	26032.9 ± 14.0 (15.2)	2422.3 ± 16.0 (21.8)
Diogo and Minas da Piedade [10]	Macro-combustion	6	9	25888.7 ± 12.1 (12.1)	2278.1 ± 14.4 (19.8)
Beckhaus et al. [11]	Macro and micro-combustion	5	32	25937.0 ± 32.0 (32.5)	2327.0 ± 32.9 (36.1)
Kiyobayashi and Sakiyama [25]	Micro-combustion	5	14	25881.8 ± 13.0 (15.1)	2273.4 ± 15.2 (21.7)
Beckhaus et al. [26]	Micro-combustion	6	35	25890.8 ± 10.9 (12.8)	2280.2 ± 13.4 (20.2)
Kolesov et al. [27]	Macro-combustion	8	88	25965.0 ± 24.0 (17.1)	2355.0 ± 25.2 (23.1)
Xu-wu et al. [28]	Macro-combustion	5	500	25970.2 ± 9.7 (14.4)	2359.6 ± 12.5 (21.3)
Xu-wu et al. [29]	Micro-combustion	5	7	25947.1 ± 20.0 (26.7)	2336.0 ± 21.5 (31.0)
Rojas-Aguilar [7]	Micro-combustion	6	16	25899.1 ± 28.4 (39.0)	2288.5 ± 29.5 (42.0)
Diky and Kabo [30]				25956.0 ± 12.0	2346.0 ± 12.0
This work	Micro-combustion	7	5	25888.3 ± 22.6	2277.7 ± 27.4
This work	Micro-combustion	5	2	25903.7 ± 42.0	2293.1 ± 44.8
C_{70}					
Beckhaus et al. [11]	Macro and micro-combustion	7	40–260	30101 ± 20 (21)	2555 ± 22 (28)
Pimenova et al. [12]	Macro-combustion	5	50	29985 ± 37 (37)	2439 ± 37 (41)
Kiyobayashi and Sakiyama [25]	Micro-combustion	3	12	29920 ± 16 (18)	2375 ± 18 (25)
Xu-wu et al. [29]	Micro-combustion	5	9	29953 ± 22 (27)	2407 ± 22 (32)
Diogo et al. [31]	Micro-combustion	4	7–15	30124 ± 13 (13)	2578 ± 16 (23)
Pimenova et al. [32]	Macro-combustion	9	50	29998 ± 32 (37)	2452 ± 33 (41)
Rojas-Aguilar [8]	Micro-combustion	7	16	30100 ± 57 (65)	2554 ± 58 (67)
Diky and Kabo [30]				30101 ± 22	2555 ± 22
This work	Micro-combustion	8	5	30104 ± 22	2558 ± 29
This work	Micro-combustion	5	2	30083 ± 33	2537 ± 37

[a] The number in parenthesis is the overall uncertainty computed from Eq. (5).

[b] The number in parenthesis represents the final uncertainty on the enthalpy of formation, computed according to reference [22].

able until 1999, Diky and Kabo [30] suggested a value of enthalpy of combustion of $-(25{,}956 \pm 12)\,\mathrm{kJ\,mol^{-1}}$ for the C_{60}; our result from combustion of samples of 2 mg, differs only 0.2% respect to that one.

Concerning to the enthalpy of combustion of C_{70}, seven previous reported values from the literature are given in Table 5. These values were obtained from conventional or micro-bomb combustion procedures, using sample masses ranging from 9 to 260 mg, in about six experiments. The uncertainty associated with these results is also twice the standard deviation of the mean. The values of the standard molar enthalpy of combustion of C_{70} was determined in this work as $-(30{,}104.06 \pm 22.05)\,\mathrm{kJ\,mol^{-1}}$ and $-(30{,}083.12 \pm 32.73)\,\mathrm{kJ\,mol^{-1}}$. Our results are among the higher values, but are still consistent with the results of Beckhaus et al. [11], Diogo et al. [31] and, are in excellent agreement respect to the review of Diky and Kabo [30], who suggested as reliable a value of enthalpy of combustion of $-(30{,}101 \pm 22)\,\mathrm{kJ\,mol^{-1}}$, for this fullerene.

The results obtained in this work for C_{60} as well as for C_{70} are practically identical to those previously attained in this laboratory by isoperibolic calorimetry [7,8].

A reliable comparison of results is difficult, because different researchers compute their respective uncertainties in different ways. Some authors do not consider error associated with the energy of combustion of the auxiliary material and calibration. In order to compare errors in a consistent manner, we recalculate it from data available in each article using the Eq. (5) given in this work; the recalculated overall uncertainty associated with each value of enthalpy of combustion is shown in Table 5 as the number in parenthesis after each combustion datum. Examined in this manner, with the exception of the work of Diogo et al. [10,31] and Kolesov and Pimenova [27,32], authors currently underestimated the spread associated with their enthalpy of combustion and formation values.

4. Conclusion

A set of micro-bombs associated with a Calvet heat flux calorimeter, were calibrated and the combustion energy of three allotropes of carbon have been measured. Under the current conditions of manipulation and operation, the uncertainty of this device is 0.03% for calibration with calorimetric standard benzoic acid. Energy of combustion of graphite was measured with a maximal deviation of 0.17% compared to the recommended value. This fact shows the reliability of the apparatus in the measurement of the energy of combustion of allotropes of carbon. The energy of combustion of fullerenes C_{60} and C_{70} were measured, the results obtained are in good agreement with previous values reported in the literature. In some of these measurements, an overall uncertainty less than 0.080% was attained, which is remarkable given that masses less than 2 mg were employed. Furthermore, the accuracy can be improved by attaining a complete combustion of the sample in all experimental runs. Despite these problems inherent to micro-combustion procedure of the fullerenes, we have demonstrated that the accuracy and precision of the device to measure the energy of combustion of these substances is acceptable for the current version of our calorimetric assembly and experimental procedure. We hope in a very short time, to apply this device in the themochemical study of larger fullerenes.

Acknowledgment

The authors are grateful to the CONACYT (Mexico) for financial support (project G32710-E). Thanks go to Mrs. Teresa Contreras for secretarial assistance. M.M.H. thanks CONACYT for his scholarship.

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