Journal of Thermal Analysis and Calorimetry, Vol. 71 (2003) 137–145

DETERMINATION OF AN AMOUNT OF GAS BY WEIGHING UNDER VACUUM CONDITIONS AND UNCERTAINTY ANALYSIS

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Abstract

For the determination of the calorific value of gases, a mass determination system for the gas burnt in the calorimeter was developed. Contrary to classical methods, which weigh the gas bottle offline, the method applied here weighs the amount of gas online and continuously. For this purpose, a commercial analytical balance with a readability of 10 μg across the entire weighing range of 205 g was modified for use under vacuum conditions.

Since the gas bottle has to be permanently connected to the calorimeter by a steel capillary, an additional force is exerted to the balance. The influence of this force is investigated and determined by a special weighing procedure.

In addition, an automatic calibration technique must be developed to ensure the traceability of the results to the national standard of mass. This allows an uncertainty analysis according to the Guide to the Expression of Uncertainty in Measurement (GUM) to be performed.

Keywords: calibration of micro balances, gas calorimeter, gas mass determination, micro balance, uncertainty analysis, vacuum

Introduction

In calorimetric determination of the calorific values of gases by gas calorimetry a known quantity of fuel gas is burnt and the energy released is measured as a temperature rise in the calorimeter cell. Gas calorimeters are used to determine the specific superior calorific value H_s (heat of combustion) of pure gases (methane, ethane, propane, butane), synthetic natural gases (mixtures of up to 11 components) and natural gases (mixtures of aliphatics, aromatics, olefins, inert gases, nitrogen and carbon dioxide). However, all calorimeters commonly known require calibration which is carried out using calibration gases and the tabulated calorific values specified in ISO 6976 [1]. Since most of the calorific values given in ISO 6976 were derived from measurements performed in the thirties and sixties of the last century, traceability to national standards is difficult or even impossible due to lack of sufficient data in the publications. The uncertainty can only be estimated at approximately 0.1%.

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1418–2874/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

However, the use of modern equipment and automatic data acquisition allow an estimated uncertainty of less than 0.05% (two standard deviations) to be reached in the determination of H_s. A major task to be fulfilled in order to reduce the uncertainty is the development of a weighing technique that allows the mass of the burnt gas to be determined with an uncertainty of less than 0.01%. Different weighing techniques were compared, and it was found that the use of a balance in vacuum offers the possibility of reaching this aim.

On the basis of preliminary investigations, this paper describes the proposed design of the weighing system with a custom-made calibration technique and a container specially designed for this project. Additionally, based on the calibration of the weighing system, the expected uncertainty according to GUM [2] for the developed weighing procedure is compared with a conventional weighing procedure (in air).

Weighing system–Design considerations

Precise and accurate weighing of the amount of gas burnt is essential to obtain repeatable and traceable results with the gas calorimeter. For this purpose, an electronic balance (Mettler AT201) capable of weighing up to 205 g and reading to 10^{-5} g, is used. The electronics of the balance was modified to adapt it to operation under vacuum conditions. The whole weighing system can be controlled and monitored from outside the vacuum chamber. Since the electric motor of the calibration system was not vacuum resistant, it had to be replaced by a custom-made mechanical calibration system.

Therefore a tray of non-magnetic stainless steel (permeability μ_r=1.044) was mounted on the weighing pan, on which five calibration weights can be placed in a sequential calibration procedure. These weights are placed using a positioning finger. Moving the finger downwards, the calibration weights are placed on the tray one after another. This is done by an eccentric which is powered by a stepping motor accom-

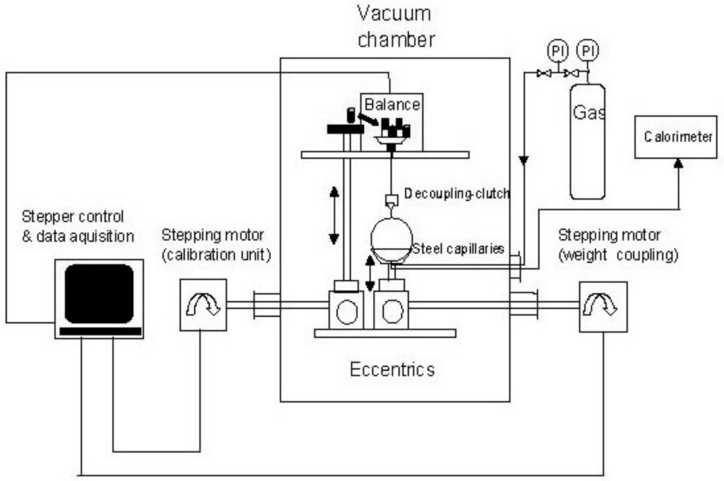

Fig. 1 Basic flow chart of the weighing apparatus

modated outside the vacuum chamber, and controlled by an external computer as can be seen in Fig. 1.

The gas is stored in a special gas container of spherical shape made of a high-grade steel to permit an operating pressure of about 25 bar at a weight of about 100 g. This gas container is located under the balance and is permanently connected to the gas supply via a capillary. For the unloading of the gas, a second capillary is connected to the calorimeter. A coupling technique allows the gas container to be removed from the balance. This is done by a second eccentric powered by a second stepping motor. The gas container is lifted, and the clutch decouples the sphere from the balance. Adsorption vacuum pumps serve to evacuate the chamber to a residual pressure of about 1 mbar. The room where the whole arrangement is located is air-conditioned at a constant temperature of ϑ=25±1°C.

Weighing procedure and uncertainty analysis

Restoring forces

As there is a slight movement of the weighing pan (by some micrometers), the capillaries exert an additional restoring force on the balance, which has to be corrected. Previous investigations have shown that this influence is of a systematic nature. Different materials were tested and a stainless steel capillary showed the best settling time for the balance to obtain stable results. The restoring force F_r can be described by the following equation [3]

$$F_r = \frac{3EI_y}{I^3} w \tag{1}$$

where E is the Young's modulus, I is the length of the capillary and w is the movement of the capillary. The areal moment of inertia I_y can be described by

$$I_y = \frac{\pi d_m^3 s}{8} \tag{2}$$

where π is the ratio of the circumference to the diameter d_m of the capillary and s is the wall thickness. In Eqs. (1) and (2) all parameters except for w are constant and can be combined to form c_r, so that the following linear equation can be established.

$$F_r = c_r w \tag{3}$$

Hence the restoring force F_r depends only on the movement of the balance. Calibration in the range of the mass determined therefore allows the influence of the restoring force to be determined and the weighing results to be corrected.

Buoyancy forces

Buoyancy forces F_b act on the movable parts of a balance whenever a gas surrounds it. These forces are given by

$$F_b = \rho_g v_i g \tag{4}$$

where ρ_g is the density of the gas, g is the gravity constant and v_i is the volume of the movable system under consideration. In the system described, the influence of buoyancy forces is prevented by weighing in vacuum. Two main corrections to the weighing result are therefore avoided:

1) A correction for the difference between the true air density and the conventional value of $\rho_{air}=1.2$ kg m^{-3}.
2) Linear expansion of the gas container. The initial volume will decrease due to the pressure reduction of approximately 10 bar during an experiment using 2 g of gas for combustion in the calorimeter.

The influence of buoyancy forces on the described system can be neglected at pressures of less than 1 mbar in the vacuum chamber because the change in mass is smaller than $1\cdot10^{-7}$ g. This value is one hundredth of the readability of the balance.

Residual mass in capillary

An additional uncertainty occurs due to the use of a capillary: the amount of gas inside the capillary is not measured by the balance. Due to the difference in pressure before and after a calorimetric experiment, the mass inside the capillary changes. Assuming ideal behavior of the gas this quantity Δm can be described by

$$\Delta m = \frac{(p_1 - p_2)V_{cap} M}{RT} \tag{5}$$

where p_i are the pressures before (1) and after (2) the experiment, V_{cap} is the internal volume of the capillary, R is the ideal gas constant, T is the temperature and M is the molar mass of the gas used for the calorimetric experiment. This leads to a correction of (3 to 4)$\cdot10^{-5}$ g to be included in the weighing result.

Standard deviation of the balance and uncertainty of mass standards

A calibration provides the possibility of determining the correlation between the value measured by a balance and the true value. This determination is performed by comparing a known mass standard traceable to the national standard of mass with the indication of the balance. The relative standard deviation $u_{rel,\,w}$ of the balance can then be calculated as follows [4]

$$u_{rel,\,w} = 2\sqrt{\frac{1}{m_n^2}\left(s_w^2 + \frac{d^2}{12}\right) + u_{m_n}^2} \tag{6}$$

where m_n is the mass of the mass standard and d is the scale interval of the balance. Equation (6) includes the standard deviation s_w as well as the uncertainty due to rounding errors which are dependent on the scale interval. The contribution is assumed to follow a rectangular distribution [4]. The coverage factor in Eq. (6) (k=2) indicates that the result is expressed as the expanded uncertainty. The value of the coverage factor k is taken from a t-table with a coverage probability of 95%. In addition, the influence of the uncertainty of the mass standard, u_{m_n}, is taken into account. This uncertainty was determined by comparison with the national standard of the Mass Laboratory of Physikalisch-Technische Bundesanstalt. The standard deviation s_w is calculated by the following equation

$$s_w = \sqrt{\frac{1}{n-1}\sum_i (I_i - \bar{I})^2} \tag{7}$$

where n is the number of weighings, I_i is the result of one weighing and $\bar{I}$ is the mean value calculated by

$$\bar{I} = \frac{1}{n}\sum_i I_i \tag{8}$$

In addition to the relative standard deviation the results of a weighing need to be corrected if non-linearity of the characteristics curve occurs. The set of calibration weights of the balance therefore includes two masses of equal weight to calculate the effective deviation from linearity in the range of the amount of gas taken off the gas container.

Weighing procedure

A special weighing procedure has been developed to determine the systematic deviations as described above and the relative uncertainty of the weighings. The weighing procedure consists in placing five weights one after another on the weighing pan.

One of these five weights compensates the weight of the gas container so that the balance works in a small weighing range, which leads to a small standard deviation of the weighing results. After the calorimetric experiment, the mass of the gas taken off the container is substituted by putting the substitution weight on the pan.

Attainable uncertainty and comparison with a conventional weighing procedure

In the majority of cases, a physical value is not measured directly but rather as a function of N different input values. The uncertainty is determined using a mathematical model for which the uncertainties of the N different input values must be specified. According to Gauss' law of error propagation and the 'ISO Guide to the expression of uncertainty in measurement' [2], the combined uncertainty of a physical value (in the described system the mass of gas burnt in the calorimeter m_{gas}) can then be calculated according to the following equation

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial y}{\partial x_i}\right)^2 u^2(x_i) \tag{9}$$

where y is the mathematical model relating the value of mass to the input quantities x_i, $u_c(y)$ is the combined standard uncertainty for y and $u(x_i)$ is the uncertainty for the input value x_i.

Uncertainty analysis of the procedure by weighing against a dummy gas container

One way of determining the amount of gas for a calorimetric experiment is to use a dummy gas container. This way will in the following be called Method I. This technique makes buoyancy corrections unnecessary, because after each weighing of the actual gas container a dummy gas container of equal volume is weighed. The difference in mass due to buoyancy is in this way experimentally subtracted [5].

However, an uncertainty of the volume due to manufacture-related differences in size and a linear expansion, as already discussed, had to be introduced into the mathematical model. Equation (10) is the model equation to calculate the amount of gas taken for the experiment.

$$m_{gas}=m_{11}-m_{12}+m_{21}-m_{22}+\rho_{air}(V_{dummy}-V_{gas\text{-}container}) \qquad (10)$$

where m_{11} and m_{12} are the masses of the dummy gas container before and after a calorimetric experiment, m_{21} and m_{22} are the masses of the gas container before and after a calorimetric experiment, ρ_{air} is the air density, V_{dummy} is the volume of the dummy and $V_{gas\text{-}container}$ is the volume of the gas container.

The gas container and the dummy are assumed to be of spherical shape. The volumes can be calculated as follows

$$V_{gas\text{-}container}=\frac{\pi}{6}d_1^3 \qquad (11)$$

$$V_{dummy}=\frac{\pi}{6}d_2^3 \qquad (12)$$

The diameters d_i of the spheres depend on the pressure and can be calculated by the following equation

$$d_i=d_{i,0}(1+k_1p) \qquad (13)$$

where $d_{i,0}$ is the diameter when there is no pressure difference between the interior and exterior of the gas container, k_1 is a material constant which is the reciprocal value of Young's Modulus, and p is the gauge pressure inside the gas container. With the aid of Eqs (11) to (13) the decrease in volume of the gas container is taken into account as described previously.

The standard deviation of the balance was determined by experiments using a 100 g calibration weight of known uncertainty. Use of Eq. (6) has led to a relative uncertainty of $u_{rel,w}=1\cdot10^{-4}\%$, which was taken as the uncertainty of each weighing (m_{11}, m_{12}, m_{21}, m_{22}) in the model Eq. (10). All uncertainties of the values further used in the mathematical model as input values in Eq. (10) are summarised in Table 1. The relative uncertainty for 2 g of gas taken off the container can then be calculated to be $u_{rel,gas}=2\cdot10^{-2}\%$.

Table 1 Uncertainties of input values, Method I

Input value	Definition	Unit	Mean value	Expanded uncertainty	Coverage factor
ρ_{air}	Density of air (ϑ=25°C, p=1.01325 bar)	kg m^{-3}	1.20	0.12	2
d_{10}	Diameter of dummy (without pressure load)	m	0.08	$2.0\cdot10^{-3}$	2
d_{20}	Diameter of gas container (without pressure load)	m	0.08	$2.0\cdot10^{-3}$	2
p_1	Pressure before calorimetric experiment	bar	25	0.25	2
p_2	Pressure after calorimetric experiment	bar	15	0.15	2

Uncertainty analysis for the new weighing scheme

The mathematical model for the weighing method developed – in the following called Method II – in which the gas container is permanently connected to the balance in an evacuated chamber connected to the calorimeter via a capillary, is given by Eq. (17).

$$m_{gas}= m_1-(m_2-m_{subst})-m_r+m_{cap} \tag{17}$$

where m_1 and m_2 are the masses of the gas container before and after the calorimetric experiment, m_{subst} is the mass substituted after the calorimetric experiment, m_r is the difference in the weighing result due to the restoring force of the capillary and m_{cap} is the residual mass in the capillary. The residual mass in the capillary is calculated by Eq. (5).

The standard deviation of the balance was determined by experiments using a 2 g calibration weight of known uncertainty and a preload of 100 g. Equation (6) gave a relative uncertainty of $u_{rel,\,w}$=1.3·10^{-3}%, which was taken as the uncertainty for each weighing (m_1, m_2) in the model Eq. (17). The influence of the capillary was investigated experimentally. For a weight of 2 g it was found that the systematic influence of the capillary was equivalent to $m_r = 4\cdot10^{-5}$ g. The expanded uncertainty was determined to be $u_{m_r}=3.5\cdot10^{-6}$ g.

Table 2 Uncertainties of input values Method II

Input value	Definition	Unit	Mean value	Expanded uncertainty	Coverage factor
p_1	Pressure before calorimetric experiment	bar	25	0.25	2
p_2	Pressure after calorimetric experiment	bar	15	0.15	2
V_{cap}	Internal volume of the capillary	m^3	$1.4\cdot10^{-9}$	$1.4\cdot10^{-10}$	2
T	Thermodynamic temperature	K	298.15	2	2

All further uncertainties of the values used in the mathematical model for the new weighing technique are summarised in Table 2. The relative uncertainty for 2 g of gas taken off the container can then be calculated to $u_{\text{rel, gas}}=4.4\cdot10^{-3}\%$.

Comparison and discussion of the results

Figure 2 shows the calculated values of the relative uncertainty, based on the mass of gas, for the two weighing methods. In comparison with the conventional Method I the relative uncertainty of the new method is smaller by a factor of approximately 4.

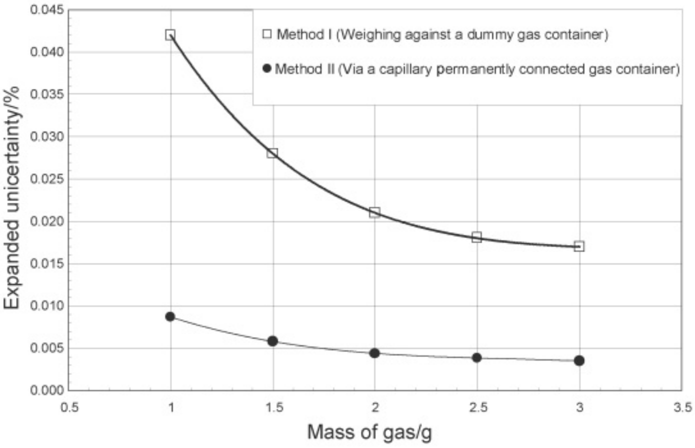

Fig. 2 Comparison of uncertainties of the two methods at various gas masses

From the uncertainty analysis it can be seen that the relative uncertainties of both weighing techniques decrease when more gas is burnt in the calorimeter. This development is mainly caused by the fact that the absolute (expanded) uncertainty has been divided by the mass of gas in order to represent the relative uncertainty. The absolute (expanded) uncertainties ($k=2$) expressed in absolute masses are constant ($u_{\text{Method I}}=4.2\cdot10^{-2}$ g, $u_{\text{Method II}}=8.8\cdot10^{-3}$ g).

However, there is a limit to the amount of gas which can be burnt in the calorimeter. Only masses of up to 3 g should be considered for a calorimetric experiment, because otherwise the temperature increase in the calorimeter is too large.

Although the influence of the restoring force of the capillary accounts for 18% of the expanded uncertainty, Method II provides the possibility of a more accurate determination of the mass of gas. The smaller uncertainty of the weighing technique developed can mainly be attributed to the fact that only two weighings need to be carried out in a small weighing range of 2 g. The relative standard deviation of the balance is small in this weighing range. In contrast to that, use of Method I requires 4 weighings in a larger weighing range (100 g) so that the relative uncertainty in relation to the gas mass is higher.

To complete the discussion, this uncertainty analysis has also shown that by use of Method I the influence of linear expansion and the assumed difference in size of the gas container and the dummy does not significantly affect the weighing result and can therefore be neglected. This allows the conclusion to be drawn that the principle of Method I (determination of a small amount at high load of the balance) is the reason for the higher uncertainty compared with Method II.

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Part of this work was financially supported by Advantica Technologies (formerly BG Technology), Reta Gas Italia (formerly SNAM) and Ruhrgas within the GERG (Groupe Européen de Recherches Gazières) project 'Feasibility Study for the Design of a Reference calorimeter'.

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