

Uncertainty evaluation for the adiabatic temperature rise in isoperibol calorimetry

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Abstract This article describes a practical approach for evaluating the uncertainty of results for determinations of the adiabatic (corrected) temperature rise in isoperibol calorimetry. The methodology is firmly based on the recommendations of the *Guide to the expression of uncertainty in measurement* (GUM). Although developed for a specific modification of the Regnault–Pfaundler method, the approach is sufficiently general to make it applicable to virtually any other scheme for the evaluation of temperature–time curves in temperature-rise calorimetry.

Keywords Adiabatic temperature rise · Calorimetry · Corrected temperature rise · Isoperibol calorimetry · Measurement uncertainty · Uncertainty evaluation

Introduction and background

This study was carried out in support of the development of a new Rossini-type [1–3] combustion calorimeter in the framework of a Groupe Européen des Recherches Gazières (GERG) project. Schley et al. [4] presents the concept and design of the calorimeter, the main measurements and the data evaluation. In all developments—calorimeter, measuring system, data acquisition and evaluation—the consideration of uncertainty sources has been an integral part, and the article gives due account of that.

A major application of the new calorimeter will be high-accuracy measurements of the superior calorific value (SCV) of natural gas components, in particular methane, ethane, propane and other hydrocarbons, with the goal to establish a new collection of SCV reference data with the best possible and well-established uncertainty. Such reference data would among other things significantly improve the calculation of the SCV of natural gas from composition according to the International Standard ISO 6976 [5]. The uncertainty of the calculated SCV is determined by the uncertainty of the component SCVs and the uncertainty of the composition, i.e. the component mole fractions. Due to the lack of reference data with adequate uncertainty for hydrocarbon SCVs, current uncertainty calculations are restricted to composition uncertainty, with the obvious consequences of (i) underestimation of uncertainty, (ii) lack of traceability and (iii) lack of comparability with results of direct measurements of natural gas SCV. Further information is given in [4].

Concerning the uncertainty of calorific value measurements, to date *guide to the expression of uncertainty in measurement* (GUM)-compliant uncertainty statements, based on a comprehensive uncertainty budget, have been the exceptions than the rule. Two such exceptions are given in [6, 7]. Alexandrov [6] describes the development of an isothermal gas calorimeter, designed for a new measurement method, and includes a comprehensive uncertainty budget, which is then applied to measurements of the SCV of methane. Because of the totally different measurement principles—heat compensation measurement instead of temperature-rise measurement—this study could not draw any benefit from these results. In contrast to that, the calorimeter treated in [7] is of the same type as the GERG calorimeter, and the measurement principles are essentially the same. The article reports the results of measurements of

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the SCV of methane including a standard uncertainty calculated from various input uncertainties. However, no details of the uncertainty budget are given, and in particular, there is no information concerning the evaluation of the uncertainty of the adiabatic temperature rise.

The uncertainty of the calorific value of a gas sample measured with the GERG calorimeter is a combination of uncertainties of various different measurements, including those of

- The adiabatic temperature rise in sample combustion,
- The adiabatic temperature rise in electrical calibration,
- The sample mass,
- The mass of unburned gas,
- The amount of energy in electrical calibration.

Each of these uncertainties in turn has a variety of input uncertainties. In order to deal with all of them, the uncertainty budget of the calorific value is decomposed into sub-budgets, following the breakdown of the measurement equation into a sequence of equations for the evaluation of the various constituent measurements.

Among all these measurements and uncertainty budgets, that of the adiabatic temperature rise stands out as being specific to this type of calorimetry and applicable to other measurements in this field. Therefore, a separate publication was decided. The complete uncertainty budget for the measurement of the SCV of methane and other hydrocarbons will be published elsewhere.

Determination of adiabatic (corrected) temperature rise

Notation

Table 1 specifies the symbols attributed to the basic quantities. Evaluation of measured temperature–time data evaluation proceeds by specifying the instants $t_{\text{ini,e}}$ and $t_{\text{fin,s}}$, next evaluating the parameters $T_{\text{ini,e}}$, $T_{\text{fin,s}}$, k , T_{∞} and Θ , and finally calculating ΔT_{ex} and ΔT_{ad} . By default, the symbols $T_{\text{ini,e}}$, $T_{\text{fin,s}}$, k , T_{∞} , Θ , ΔT_{ex} and ΔT_{ad} will be used in a generic sense: description of the mathematical model, and in a specific sense: for values obtained by the dedicated evaluation described in this article. Only when such values are compared with values obtained by an alternative evaluation, an appropriate qualifier is added. For example, $k[\text{sim}]$, $k[\text{ini}]$ and $k[\text{fin}]$ specify values of the cooling constant obtained from the same data by different evaluations: simultaneous regression of the data in the initial and final periods, separate regression of the data in the initial period, and separate regression of the data in the final period, respectively. Similarly, $\Delta T_{\text{ad}}[\text{ded}]$ and $\Delta T_{\text{ad}}[\text{alt}]$ specify results obtained

Table 1 Symbols for basic quantities

Symbol	Quantity
t	Time
$t_{\text{ini,e}}$	Specified end of the initial period (start of the main period)
$t_{\text{fin,s}}$	Specified start of the final period (end of the main period)
T	Temperature
$T_{\text{ini,e}}$	Calorimeter temperature at $t_{\text{ini,e}}$
$T_{\text{fin,s}}$	Calorimeter temperature at $t_{\text{fin,s}}$
T_{J}	Temperature of the calorimeter environment (jacket)
T_{∞}	Convergence temperature of the calorimeter
ΔT_{ad}	Adiabatic (corrected) temperature rise
ΔT_{ex}	Exchange contribution to temperature rise (transfer from the jacket)
k	Cooling constant
u_{M}	Rate of temperature rise due to heat production by combustion or electrical heating (taking place in the main period)
u_{stir}	Rate of temperature rise due to heat production by stirring
Θ	Integral of the temperature-rise curve in the main period

from the same data by the dedicated procedure and an alternative procedure.

Model of isoperibol temperature rise

The basis for the determination of the adiabatic temperature rise is the model of what has been called an “ideal isoperibol temperature-rise calorimeter” in a recent publication [8]. Departures from this model are treated as uncertainty sources. The calorimeter is treated as a single body with a spatially uniform but time-dependent temperature $T(t)$, exchanging heat with an environment (a water jacket with active temperature control) at a uniform, constant temperature T_{J} . The rate of change of the calorimeter temperature is governed by a modification of Newton’s law of cooling:

$$\dot{T}(t) = u_{\text{M}}(t) + u_{\text{stir}} + k(T_{\text{J}} - T(t)). \quad (1)$$

Here we have used the common shorthand notation \dot{X} for the derivatives dX/dt with respect to time. The first term on the right-hand side of this equation, $u_{\text{M}}(t)$, is the rate of temperature change due to heat production by the combustion of a gas sample or electrical heating in a calibration run. These processes are confined to a specified period $[t_{\text{on}} \leq t \leq t_{\text{off}}]$, and thus $u_{\text{M}}(t)$ is assumed to be zero outside this interval. The second term, u_{stir} , is the rate of temperature change due to heat production by the stirrer and any other heat source with constant power. This energy input is assumed to be constant during the entire experiment, and thus u_{stir} is assumed to be constant. Finally, k is the cooling constant of the calorimeter with respect to thermal leakage from the jacket.

If left for a long time, $t \gg t_{\text{off}}$, the calorimeter will reach a final temperature T_∞ above the jacket temperature. This is given by the requirement $\lim_{t \rightarrow \infty} \dot{T}(t) = 0 = u_{\text{stir}} + k(T_J - T_\infty)$ which relates the term u_{stir} to the difference between the convergence temperature T_∞ and the jacket temperature T_J . Substituting this expression into Eq. 1 gives:

$$\dot{T}(t) = u_M(t) + k(T_\infty - T(t)). \tag{1a}$$

In the initial period $[t < t_{\text{on}}]$, the term $u_M(t)$ is zero, and the solution of Eq. 1a is given by:

$$T_{\text{ini}}(t) = T_\infty - C_{\text{ini}} \exp(-kt). \tag{2}$$

The integration constant C_{ini} is obtained by specifying an arbitrary point (t_A, T_A) on the temperature–time curve of the initial period. Then

$$T_{\text{ini}}(t) = T_\infty - (T_\infty - T_A) \exp(-k(t - t_A)). \tag{2a}$$

Likewise in the final period $[t > t_{\text{off}}]$ the solution of Eq. 1a is obtained as:

$$T_{\text{fin}}(t) = T_\infty - (T_\infty - T_B) \exp(-k(t - t_B)). \tag{2b}$$

where (t_B, T_B) is an arbitrary point on the temperature–time curve of the final period.

The target quantity in the evaluation of temperature-rise data, the adiabatic (corrected) temperature rise, i.e. the temperature rise which would have occurred if no thermal leakage to the environment (jacket) had taken place, is given by the integral of the rate of temperature change due to heat production by the combustion of a gas sample or electrical heating in a calibration run

$$\Delta T_{\text{ad}} = \int_{t_{\text{on}}}^{t_{\text{off}}} u_M(t) dt = \int_{t_A}^{t_B} u_M(t) dt, \tag{3}$$

where $[t_A \leq t \leq t_B]$ can be any interval including $[t_{\text{on}} \leq t \leq t_{\text{off}}]$. Solving Eq. 1a for $u_{\text{main}}(t)$ and substituting this expression into the integral on the right-hand side of Eq. 3 gives:

$$\begin{aligned} \Delta T_{\text{ad}} &= T(t_B) - T(t_A) - k \int_{t_A}^{t_B} (T_\infty - T(t)) dt \\ &= T_B - T_A - \Delta T_{\text{ex}}. \end{aligned} \tag{3a}$$

In this equation, ΔT_{ex} is the temperature rise between t_A and t_B due to (i) the heat exchange between the calorimeter and the jacket and (ii) the constant thermal power input from the stirrer and possibly other sources.

Data evaluation

Using Eqs. 2a, 2b and 3a, measurement series of temperature–time points $(t_0, T_0), (t_1, T_1), (t_2, T_2), \dots, (t_N, T_N)$ are evaluated as follows:

- (a) As a first step, an initial time $t_{\text{ini,e}}$ and a final time $t_{\text{fin,s}}$ well outside the “activity” period $[t_{\text{on}} \leq t \leq t_{\text{off}}]$ are chosen as conservative estimates of the upper limit of the initial period and the lower limit of the final period, respectively. How this is done will be described in the next section. Accordingly, the intervals $[t \leq t_{\text{ini,e}}]$, $[t_{\text{ini,e}} \leq t \leq t_{\text{fin,s}}]$ and $[t \geq t_{\text{fin,s}}]$ define the initial period, the main period and the final period.
- (b) Next, a *simultaneous* fit is performed of a function according to Eq. 2a to the data of the initial period, $\{(t_i, T_i), t_0 \leq t_i \leq t_{\text{ini,e}}\}$, and a function according to Eq. 2b to the data of the final period, $\{(t_i, T_i), t_{\text{fin,s}} \leq t_i \leq t_N\}$, using the *same* parameters k and T_∞ . This computation, carried out by ordinary (i.e. unweighted) least-squares regression, yields the values of $k, T_\infty, T_{\text{ini,e}}$ and $T_{\text{fin,s}}$.
- (c) Then the data of the main period, $\{(t_i, T_i), t_{\text{ini,e}} \leq t_i \leq t_{\text{fin,s}}\}$, are evaluated by numerical integration, to compute an approximate value of the integral Θ

$$\Theta = \int_{t_{\text{ini,e}}}^{t_{\text{fin,s}}} T(t) dt. \tag{4}$$

Integration is carried out according to the Simpson rule, based on quadratic interpolation.

- (d) Finally the adiabatic temperature rise is computed as

$$\Delta T_{\text{ad}} = T_{\text{fin,s}} - T_{\text{ini,e}} - kT_\infty(t_{\text{fin,s}} - t_{\text{ini,e}}) + k\Theta. \tag{5}$$

The GERG project included a systematic investigation of twelve evaluation methods, arising from the two basic strategies, integration (Regnault–Pfaundler) and extrapolation (Dickinson/Challoner), by varying the subsequent steps:

- *Initial and final periods* Exponential fit versus approximate linear fit, separate fit versus simultaneous fit,
- *Main period* Integration by the trapezoidal rule, integration by the Simpson rule, equal areas method.

Among these alternatives, the method specified above showed the best performance, among other things with respect to minimising the dependence of the result on the definition of the main period. As another recent publication devoted to this topic, we would like to mention [8], describing an approach for improving the accuracy of evaluations of the adiabatic temperature rise according to both the integration (Regnault–Pfaundler) and extrapolation (Dickinson/Challoner) method, based on a comparison between an exponential-function description of the data in the initial and final periods and an independent third-order polynomial fit. In addition, a dedicated software application Labtermo is introduced.

Supplementary information

This section gives a brief description of (i) the current design of the temperature–time measurement for a run on the GERG calorimeter, (ii) how the limits of the main period are defined and (iii) the tools used for data evaluation.

Combustion measurement design: Before starting a combustion run, the calorimeter is cooled to 22.5 °C and the temperature in the water jacket is set to 27.0 °C. After equilibration of about 2 h, the initial period is started and continued for about 1 h. When the calorimeter temperature has reached 23.48 °C, the argon/oxygen flow is turned on ($t_{\text{ini,e}}$). Some 4–5 min later, when the calorimeter temperature has reached 23.50 °C, sample gas flow and ignition are started simultaneously (t_{on}). Combustion is continued for about 30 min, until the mass of sample gas has reached 1.0 g, resulting in a temperature rise (of about 3 K) to about 26.5 °C. Immediately after the extinction of the flame (t_{off}), the argon/oxygen flow is stopped. After a transition period where the combustion energy is dissipated, typically some 30 min, the final period begins ($t_{\text{fin,s}}$) and continues for about 1 h. The current standard scheme is: equilibration 8,000 s—initial period 4,000 s—main period 4,000 s including a combustion period of 1,500 s—final period 4,000 s.

Calibration measurement design: Calibration runs are designed to match the respective combustion runs as closely as possible, including, e.g. carrier gas flow.

Temperature is measured with a fast-response thermistor sensor. Temperature readings are recorded every 2 s, where each reading is in fact a mean of 2×10^4 single values. Figure 1 shows a plot of a typical data series. At this level of resolution, combustion curves and calibration curves look alike. Higher resolution reveals some characteristic differences (e.g. an overshoot of the calibration curve at the

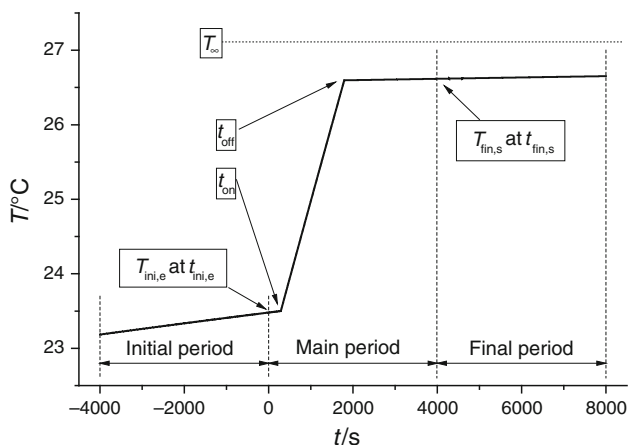


Fig. 1 Plot of a typical temperature-rise data series

end of the heating period) which are, however, not relevant for the purpose of this article.

Definition of the limits of the main period: In theory, the adiabatic temperature rise should be independent of the definition of the limits $t_{\text{ini,e}}$ and $t_{\text{fin,s}}$ of the main period, provided that the interval $[t_{\text{ini,e}} \leq t \leq t_{\text{fin,s}}]$ completely includes the “activity period” $[t_{\text{on}} \leq t \leq t_{\text{off}}]$ where $u_{\text{M}}(t) \neq 0$. In practice, things are not that easy, and care has to be taken to ensure that there are no perturbations of the temperature rise in the initial and final periods. Therefore, the lower limit $t_{\text{ini,e}}$ is defined by the instant when the argon/oxygen flow is turned on (external perturbation). Choosing an earlier instant has no effect on the results for the adiabatic temperature rise. Similar considerations apply to the definition of the upper limit $t_{\text{fin,s}}$, concerning internal perturbations. After the combustion is finished, the dissipation of the released energy requires considerable time, until the system has returned to a state obeying Eq. 2b.

A recognised criterion for the choice of the upper limit was given in [9]. The procedure starts from a set of points which are considered to be definitely within the final period. These are fitted to a least-squares regression line (a straight-line approximation to the exponential curve). Then the starting set is extended by prior points, and new regression lines are computed, until the candidate points are found to depart significantly from the respective regression line.

This approach directly employs the adiabatic temperature rise as an indicator. The upper limit $t_{\text{fin,s}}$ is varied, keeping a constant length of the final period. This is done to avoid different weights of the data of the initial period and the final period in the simultaneous regression. For each choice of $t_{\text{fin,s}}$, the value of ΔT_{ad} is computed. The results typically show a plateau extending over 10–30 min. The limit $t_{\text{fin,s}}$ is chosen to lie well within this plateau. Figure 2 shows plots of the results obtained from a typical data series for a combustion run and a calibration run.

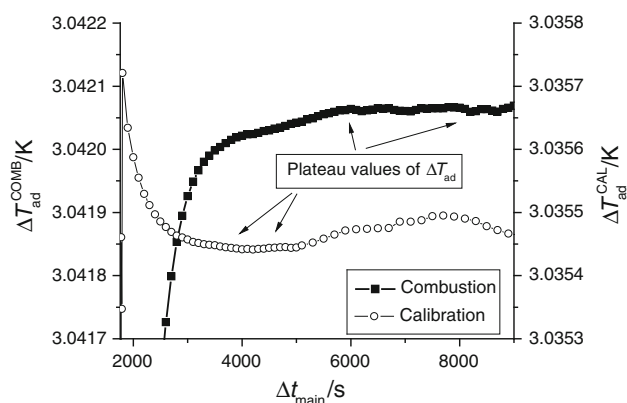


Fig. 2 Dependence of ΔT_{ad} on the duration of the main period

Tools for data evaluation: Simultaneous exponential regression of the data in the initial and final periods is currently carried out using a freeware program (Visual Basic routine for non-linear regression, based on the Levenberg–Marquardt algorithm, available from the website <http://digilander.libero.it/foxes/optimiz/Optimiz1.htm>). The program returns (i) the parameter values k , T_∞ , $T_{\text{ini,e}}$ and $T_{\text{fin,s}}$ and (ii) their variance/covariance matrix. The performance of the program was checked by comparing the output with that of a recognised commercial program [OriginPro 8G.0.63.988 SR6, OriginLab Corporation (Northampton, MA, USA)], for selected measurement series. No relevant differences were observed.

The integral of the temperature–time data over the main period is computed using an in-house Microsoft Excel® application.

Uncertainty sources

For the purpose of this discussion, the uncertainty sources for the determination of the adiabatic temperature rise are subdivided into three different categories: uncertainty due to an error in measuring the temperature–time data, uncertainty due to a departure from the model of the adiabatic temperature rise, and uncertainty due to an error in evaluating the temperature–time data.

Uncertainty due to measurement error

Time measurement

The time basis is provided by a frequency generator (Agilent 33120A). The frequency ($f = 0.5$ Hz, corresponding to $\Delta t = 2$ s) is extremely stable and was calibrated against the atomic clock standard of Germany with a deviation of 18×10^{-6} Hz. The signal of the frequency generator serves as an external trigger signal for the resistance measurement of the thermistor with an Agilent 3458A. The integration time is set to 0.2 s and the measured signal is sampled 20,000 times within this period of time. The time basis of each sampling event has an uncertainty of 5 ns (accuracy of the timer of the Agilent 3458A). The delay time between the trigger pulse and the sampling period has an uncertainty of approximately 50 ns (jitter).

Under these circumstances, the random uncertainty of the time coordinates is much smaller than that of the temperature values and can therefore be neglected. For demonstrating this, a generous upper bound $s_{\text{max}} = 10^{-3}$ s of the standard deviation of the time coordinates will do. With a maximum slope $k(T_\infty - T_0)$ of about 9×10^{-5} K s⁻¹ in the initial and final periods (obtained from $k \approx 2 \times 10^{-5}$ s⁻¹,

$T_\infty - T_0 \approx (27.0 - 22.5)^\circ\text{C}$), $s_{\text{max}} = 10^{-3}$ s translates into $s_{\text{max}} = 0.09$ μK , which is negligible compared to the typical standard deviation of the temperature measurements of 19 μK . During the active part of the main period the slope is larger, $\Delta T = 3$ K in $\Delta t = 1,500$ s, giving $\Delta T/\Delta t = 2 \times 10^{-3}$ K s⁻¹ and $s_{\text{max}} = 2$ μK . But this is still negligible compared to the typical standard deviation of the temperature measurements of 400 μK .

Temperature measurement

Temperature is measured with a fast-response thermistor sensor, which is calibrated off-line against a traceable Pt-25 resistance thermometer. For the purpose of uncertainty evaluation, a distinction is made between random measurement error, time-independent systematic error and drift.

Random measurement error in the initial and final periods is taken into account in the least-squares regression, where the variance/covariance matrix of the parameters k , T_∞ , $T_{\text{ini,e}}$ and $T_{\text{fin,s}}$ is calculated from the residual variance of the temperature values. The conditions for this evaluation are as follows:

- The uncertainty of the time coordinates is much smaller than the uncertainty of the temperature values. This condition is clearly fulfilled.
- The (random) uncertainty of the temperature values is approximately the same throughout both periods. The data are found to conform to this requirement, with a typical standard deviation for both periods of about 19 μK .
- The random variations of the temperature values are approximately uncorrelated. Otherwise the residual variance would require an autocorrelation correction. This is not the case, see “[Random fluctuation of temperature data](#)” section.

Time-independent systematic error is the residual error left by calibration. In the narrow temperature range concerned—about 3 K—this calibration error is approximately constant. As a consequence, due to the shift invariance of the adiabatic temperature rise (see “[Uncertainty calculation](#)” section), the time-independent systematic error does not contribute to the uncertainty of the adiabatic temperature rise.

Drift of the thermistor effects monotonously increasing deviations of measured temperatures from the correct values. These errors are modelled using an “uncertain” drift rate, and the uncertainty contribution is calculated by the propagation of the uncertainty of the drift rate.

Uncertainty due to model error

The model specified in “[Model of isoperibol temperature rise](#)” section assumes that at any instant t the calorimeter

has a spatially uniform temperature $T(t)$. This assumption implies that dissipation of (i) the heat transferred from the jacket to the calorimeter, (ii) the heat produced by the stirrer and (iii) the heat produced by the combustion of the gas sample or by electrical heating in a calibration run, is quick and effective, so that there are no significant departures from a homogeneous temperature distribution. During the initial and final periods, departures from these conditions are negligible. But obviously this does not hold for the main period. Dissipation of the comparatively large amount of “extra” heat produced in the “activity” period takes finite time, and the homogenisation of temperature will therefore be incomplete. However, with the assumptions above, the model has been oversimplified. Starting from the energy balance of the calorimeter, a precursor of Eq. 1 is obtained as follows:

$$\dot{T}_{\text{bulk}}(t) = u_{\text{M}}(t) + u_{\text{stir}} + k(T_{\text{J}} - T_{\text{surf}}(t)). \quad (1\#)$$

Here T_{bulk} is the bulk-averaged temperature of the calorimeter, while T_{surf} is the average surface temperature, governing the heat transfer from the jacket to the calorimeter. For an ideal calorimeter these two temperatures are the same—but this assumption is in fact not necessary. Instead, we may utilise the much weaker assumption that the average surface temperature is the same as the average temperature T_{bath} of the (inner) calorimeter bath. Introducing the convergence temperature yields

$$\dot{T}_{\text{bulk}}(t) = u_{\text{M}}(t) + k(T_{\infty} - T_{\text{bath}}(t)). \quad (1a\#)$$

In the initial and final periods, we can safely assume that T_{bulk} and T_{bath} are the same. In the main period, T_{bulk} and T_{bath} are different, e.g. there is a lag between the rise of the bulk average and the bath average after starting the combustion. However, Eq. 3a for the adiabatic temperature rise remains valid, if all temperatures are taken to be bath averages. Thus, we conclude that the evaluation of temperature-rise data-based Eqs. 2a, 2b and 3a is perfectly valid, provided that the measured temperatures are the same as the bath averages, and the main period is extended up to a point where the dissipation of the “extra heat” is complete. This conclusion also follows from West and Churney’s discussion of the two-body model of a calorimeter [10].

In the GERG calorimeter, temperature is measured at a single site in the bath. This design gives rise to an error source: *deviation of the temperature at the measurement site from the bath average*. This error has two components: (i) fluctuations of the temperature in the volume sampled by the thermistor sensor, and (ii) temporary gradients due to transient flow patterns.

Temperature fluctuations are included, jointly with random measurement error, in the random variations of the temperature values in the main period. The uncertainty is evaluated using the standard deviation of the residuals with

respect to an appropriate curve fitted to the data of the main period. While this standard uncertainty is the same throughout the initial and final periods, in the main period the standard deviation varies, starting from the value in the initial period, then rising to an approximately constant value throughout the “activity period”, and finally decreasing to reach the initial value again before the end of the main period. Typical patterns are 19–440–19 μK for a combustion run and 19–400–19 μK for a calibration run. These data are used to calculate the random uncertainty of the integral Θ . For this purpose, like in the evaluation of the data from the initial and final periods, the random variations of the temperature values should be approximately uncorrelated. Otherwise correlation terms would have to be included in the uncertainty calculation. This is not the case, see “[Random fluctuation of temperature data](#)” section.

Deviations due to temporary gradients are estimated on the basis of measurements and a numerical simulation study, and they are modelled by an “uncertain” control parameter—the level of the deviations. The uncertainty contribution is calculated by the propagation of the uncertainty of the control parameter.

Last, but not least, the model assumes that the cooling constant and the convergence temperature are the same throughout all periods. However, separate regression of the data in the initial and final periods yields significantly different values of both, k and T_{∞} . Analysis of residuals from separate and simultaneous regression indicates that the assumption of constant k and T_{∞} is perfectly valid for single periods, but not quite so for both periods together. These findings suggest that the large temperature rise in the main period effects an appreciable change of k and T_{∞} , while the (comparatively small) temperature rise in the initial and final periods has no such consequence. The immediate question then is which value of k and T_{∞} to use in the calculation of the exchange term ΔT_{ex} . Reasonably, some kind of mean of the values ($k[\text{ini}]$, $k[\text{fin}]$) and ($T_{\infty}[\text{ini}]$, $T_{\infty}[\text{fin}]$) from separate regression should be used, and this is indeed the case for the parameters $k[\text{sim}]$ and $T_{\infty}[\text{sim}]$ from simultaneous regression. However, even with the best possible means, utilising constant values of k and T_{∞} in the calculation of the exchange term ΔT_{ex} implies an error. In order to investigate the level of this error, the exchange term is calculated by an alternative approach, utilising time-dependent parameters k and T_{∞} . The associated uncertainty is estimated by the root mean square of the differences obtained from replicate measurements.

There are various possible reasons for the change of k and T_{∞} in the course of the main period. For example, due to the temperature rise of about 3 K, the viscosity of water decreases by about 8% relative, effecting a significant decrease of the energy input by stirring. This will affect the convergence temperature. The heat capacity of the

calorimeter also undergoes some change during the main period, which will affect the cooling constant. This listing could be continued, but currently the various effects do not provide a quantitative explanation of the observed change of k and T_∞ .

There are a few more model departures which, however, do not require additional action.

- *Additional constant energy input* Other constant energy input than from the stirrer, among other things through the thermistor used to measure the calorimeter temperature, does not compromise the model. Any such input (or loss) will effect a change in the convergence temperature T_∞ . As long as this is determined from the data in the initial and final periods, this does not cause any problems.
- *Change of nominally constant energy input* The energy input from the stirrer changes with the temperature of the calorimeter bath. This will effect a change of the convergence temperature, but this is accounted for in the uncertainty estimate accounting for change in k and T_∞ .
- *Change of heat capacity* Equation 1 is obtained from the heat balance of the calorimeter under the condition of constant heat capacity. Hence the model requires that the heat capacity of the calorimeter does not change during a run. The change of heat capacity due to the change of temperature rise (about 3 K) is indeed negligible. However, the heat capacity also changes due to the enthalpy difference of inlet and outlet gas, in particular due to condensation of water vapour. Changing the heat capacity will change the cooling constant, but this is accounted for in the uncertainty estimate accounting for change in k and T_∞ .

Uncertainty due to evaluation error

Integration uncertainty

Numerical integration using the Simpson rule is affected by the error due to approximating the true curve $\{t, T(t)\}$ by (quadratic) interpolation between equidistant sampling points. The uncertainty referring to this error is obtained from an estimate of the potential remainder given in the literature.

Uncertainty on the limits of the main period

The method used to specify the upper limit was reported in “[Model of isoperibol temperature rise](#)” section. The plateau described there is not totally flat, and the standard deviation of the values on the plateau is used directly as a contribution of the uncertainty on the upper limit to the uncertainty of the adiabatic temperature rise. This number could be expressed as a product of a rather large standard uncertainty $u(t_{fin,s})$ and a small sensitivity coefficient, but this is hardly worthwhile. The contribution of the uncertainty on the lower limit is neglected.

Summary

Table 2 gives a summary of the various uncertainty sources considered.

“[Uncertainty propagation according to GUM](#)” section presents a summary of the standard GUM methodology, while the specific implementation for the evaluation of the adiabatic temperature rise is described in “[Uncertainty evaluation for the adiabatic temperature rise](#)” section.

Table 2 Uncertainty sources

Uncertainty source	Period concerned			Evaluation
	Initial	Main	Final	
Time measurement	X	X	X	None (negligible)
Temperature measurement—time-independent systematic error	X	X	X	None (cancels out)
Temperature measurement—drift	X	X	X	Propagation of uncertainty on the control parameter
Random fluctuation of temperature data	X	X	X	Statistical evaluation
Temperature difference: measurement site—bath average		X		Propagation of uncertainty on the control parameter
Change of cooling constant and convergence temperature		X		Comparison with alternative evaluation
Other constant energy input	X	X	X	None (no consequence)
Change of nominally constant energy input		X		Included in the comparison with alternative evaluation
Change of heat capacity		X		Included (as above)
Numerical integration		X		Estimate of approximation error
Specification of main period limits	X	X	X	Statistical evaluation

Examples referring to current measurements are given in “Examples” section.

Uncertainty propagation according to GUM

The proposed uncertainty evaluation procedure is based on the recommendations of the GUM [11]. An authoritative introduction to this document is given in [12]. This section presents a summary of the standard GUM methodology.

The backbone of the standard GUM methodology is the law of uncertainty propagation, expressing the standard uncertainty of the target quantity as a root sum of squares of contributions from the various uncertainty sources. The basics steps of this recipe are as follows.

A mathematical model of the measurement is set up, expressing the target quantity y as a function of the various input quantities x_1, x_2, \dots, x_n , associated with the relevant uncertainty sources. Often this is just the equation or the algorithm (or the system of equations/algorithms) used to calculate the target quantity from the results of the measurements made. Sometimes, however, an uncertainty source has no counterpart in the evaluation of the measurements. Then an additional input quantity is introduced to complete the mathematical model.

In the next step, the contributions of the various uncertainty sources are quantified as products, $u_k(y) = c_k(y)u(x_k)$, of the standard uncertainty $u(x_k)$ of the respective input quantity x_k and the sensitivity coefficient $c_k(y)$ of the target quantity with respect to changes of the input quantity. Depending on the available data, the standard uncertainties are either determined as standard deviations of measurement series (type A evaluation) or as standard deviations of probability distributions expressing the available information about the value of the input quantity, e.g. a rectangular distribution between an upper and a lower limit (type B evaluation). The sensitivity coefficients

$$c_k(y) = \frac{y(\dots x_k + \Delta x_k \dots) - y(\dots x_k \dots)}{\Delta x_k} = \left(\frac{\partial y}{\partial x_k} \right) \quad (6)$$

can be determined as follows:

- *Experimentally* The target quantity is determined at different values of the input quantity, with all other input quantities unchanged.
- *Numerically* The evaluation algorithm is carried out at different values of the input quantity, with all other input quantities unchanged.
- *Differential calculus* The partial derivative of the mathematical expression for the target quantity (if available) with respect to the input quantity is calculated and evaluated at the current values of the target quantity and the input quantities.

Finally the standard uncertainty $u(y)$ of the target quantity is calculated by the squared addition of the various uncertainty contributions:

$$u^2(y) = u_1^2(y) + u_2^2(y) + \dots + u_n^2(y). \quad (7)$$

In the numerical approach, the uncertainty contributions $u_k(y)$ are conveniently calculated in a single step as finite differences, $u_k(y) = (\partial y / \partial x_k)u(x_k) \approx y(\dots, x_k + u(x_k), \dots) - y(\dots, x_k, \dots)$. Then the standard uncertainty of the target quantity is obtained as a root sum of squares of the differences obtained for the input quantities. This approach can be extended from the propagation of standard uncertainties to the propagation of probability distributions attributed to the input quantities, using a Monte Carlo simulation [13]. This will give a probability distribution for the values of the target quantity, from which, in addition to the mean value and the standard deviation, various other characteristics such as confidence ranges for specified confidence levels are obtained.

Everything said so far refers to *absolute* uncertainties of the target quantity and the input quantities (i.e. uncertainties expressed in the unit of the quantity concerned). If *relative* uncertainties are preferred, the sensitivity coefficients have to be changed accordingly. Then Eq. 7 takes the form

$$u_{\text{rel}}^2(y) = \sum_k u_{k,\text{rel}}^2(y) \quad (7a)$$

with relative uncertainty contributions $u_{k,\text{rel}}(y) = c_{k,\text{rel}}(y)u_{\text{rel}}(x_k)$ and relative sensitivity coefficients

$$c_{k,\text{rel}}(y) = c_k(y) \frac{x_k}{y} = \left(\frac{\partial y}{\partial x_k} \right) \frac{x_k}{y}. \quad (6a)$$

Pythagoras theorem is restricted to uncorrelated uncertainty contributions. Significant correlations between the input quantities (more specifically: between *errors* of the input quantities) have to be quantified, preferably by correlation coefficients, and included in the uncertainty calculation as follows:

$$u^2(y) = \sum_k u_k^2(y) + \sum_k \sum_{l \neq k} r(x_k, x_l)u_k(y)u_l(y). \quad (8)$$

Correlations arise if two input quantities depend upon each other or upon a common third quantity. Such dependency can refer to the quantities themselves but also to their determination. For example, if determined from the same calibration data by least-squares regression, the slope and intercept of a calibration line are correlated, even though these are independent physical quantities.

In the expression of measurement results, the standard uncertainty $u(y)$ may be replaced by an expanded uncertainty, $U(y) = ku(y)$, with a specified coverage factor k . As a default value, $k = 2$ is recommended; this corresponds to a confidence level (coverage probability) of about 95%.

This is a pragmatic recipe. Given appropriate information about the probability distribution of the target quantity, coverage factors for specified confidence levels may be calculated.

Note: Due to the fact that k is the standard notation for the coverage factor, but also for the cooling constant, this symbol will be used for both purposes.

Uncertainty evaluations are conveniently documented in a tabular format known as an “uncertainty budget” (Table 3).

Uncertainty budgets are valuable diagnostic tools for the development and optimisation of measurement procedures. For this purpose, Eq. 7 is re-written as follows:

$$\sum_k \frac{u_k^2(y)}{u^2(y)} = 1. \tag{7b}$$

The variance fractions (variance = squared standard uncertainty) indicate which uncertainty sources are the main contributors to the uncertainty of the target quantity. Only for these sources do efforts to reduce the uncertainty make sense, while this would be a waste for all others.

Uncertainty propagation is also used to evaluate covariances or correlation coefficients for two target quantities, e.g. for the adiabatic temperature rise of a combustion run and that of the associated calibration run. These data are required when evaluating the uncertainty of the calorific value of the gas sample, where both the combustion temperature rise and the calibration temperature rise provide input.

Keeping with the formulas used before, the covariance of two quantities y and z is calculated as the sum of the products of the uncertainty contributions of input quantities common to both,

$$u(y, z) = u_1(y)u_1(z) + u_2(y)u_2(z) + \dots + u_c(y)u_c(z), \tag{9}$$

where x_1, x_2, \dots, x_c are the common input quantities of both y and z . The covariance is related to the correlation coefficient by $u(y, z) = r(y, z)u(y)u(z)$. The latter, taking values between 1 and -1 , specifies the type (positive or negative) and level of correlation.

Equation 9 is valid for independent input quantities. In case of correlated input quantities, covariances are

calculated as follows. Let x_1, x_2, \dots, x_n be the input quantities of y and w_1, w_2, \dots, w_m the input quantities of z . Then

$$u(y, z) = \sum_k \sum_l r(x_k, w_l)u_k(y)u_l(z). \tag{10}$$

Uncertainty evaluation for the adiabatic temperature rise

Preparatory considerations

The mathematical model for the determination of the adiabatic temperature rise is given by the following equations copied from “[Model of isoperibol temperature rise](#)” section:

$$\Delta T_{ad} = T_{fin,s} - T_{ini,e} - kT_{\infty}(t_{fin,s} - t_{ini,e}) + k\Theta, \tag{5}$$

where the quantities $k, T_{\infty}, T_{ini,e}$ and $T_{fin,s}$ are obtained from the data of the initial and final periods by simultaneous regression, using the functions:

$$T_{ini}(t) = T_{\infty} - (T_{\infty} - T_{ini,e}) \exp(-k(t - t_{ini,e})) \tag{2a}$$

and

$$T_{fin}(t) = T_{\infty} - (T_{\infty} - T_{fin,s}) \exp(-k(t - t_{fin,s})). \tag{2b}$$

while the quantity Θ is obtained by numerical integration of the data in the main period

$$\Theta = \int_{t_{ini,e}}^{t_{fin,s}} T(t)dt. \tag{4}$$

The main ingredients for the uncertainty evaluation are given by the results of the analysis of uncertainty sources in “[Uncertainty sources](#)” section.

The standard GUM methodology would embark on Eq. 5 and use uncertainty propagation to express the standard uncertainty of the adiabatic temperature rise by the standard uncertainties of the quantities $k, T_{\infty}, T_{ini,e}$ and $T_{fin,s}$. Due to the fact that these quantities, in turn, share a lot of common input quantities, correlations would have to

Table 3 Format of uncertainty budgets

Input quantity	Symbol	Value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution	Variance fraction
(Name)	X_1	x_1	$u(x_1)$	$c_1(y)$	$u_1(y) = c_1(y)u(x_1)$	$u_1^2(y)/u^2(y)$
(Name)	X_2	x_2	$u(x_2)$	$c_2(y)$	$u_2(y) = c_2(y)u(x_2)$	$u_2^2(y)/u^2(y)$
...
(Name)	X_n	x_n	$u(x_n)$	$c_n(y)$	$u_n(y) = c_n(y)u(x_n)$	$u_n^2(y)/u^2(y)$
Target quantity	Symbol	Value	Standard uncertainty	Coverage factor	Expanded uncertainty	
(Name)	Y	y	$u(y)$	k	$U(y) = ku(y)$	

be taken into account and quantified by estimating the respective correlation coefficients. This would result in an uncertainty propagation equation as follows:

$$u^2(\Delta T_{\text{ad}}|k, T_{\infty}, T_{\text{ini,e}}, T_{\text{fin,s}}, \Theta) = \Sigma \text{Var} + 2\Sigma \text{Cov}, \quad (11)$$

with the variance sum [abbreviation: $L_t = t_{\text{fin,s}} - t_{\text{ini,e}}$]:

$$\Sigma \text{Var} = u^2(T_{\text{fin,s}}) + u^2(T_{\text{ini,e}}) + [\Theta - T_{\infty}L_t]^2 u^2(k) + k^2 L_t^2 u^2(T_{\infty}) + k^2 u^2(\Theta), \quad (11a)$$

and the covariance sum [covariances are symmetric, i.e. $u(a, b) = u(b, a)$]:

$$\begin{aligned} \Sigma \text{Cov} = & -u(T_{\text{fin,s}}, T_{\text{ini,e}}) + [\Theta - T_{\infty}L_t]u(T_{\text{fin,s}}, k) \\ & - kL_t u(T_{\text{fin,s}}, T_{\infty}) + ku(T_{\text{fin,s}}, \Theta) \\ & - [\Theta - T_{\infty}L_t]u(T_{\text{ini,e}}, k) + kL_t u(T_{\text{ini,e}}, T_{\infty}) \\ & - ku(T_{\text{ini,e}}, \Theta) \\ & - kL_t [\Theta - T_{\infty}L_t]u(k, T_{\infty}) \\ & + k[\Theta - T_{\infty}L_t]u(k, \Theta) - k^2 L_t u(T_{\infty}, \Theta). \end{aligned} \quad (11b)$$

In these equations, covariances $u(x, y)$ were used instead of correlation coefficients $r(x, y)$, and the abbreviation $L_t = t_{\text{fin,s}} - t_{\text{ini,e}}$ was used for the length of the main period, to keep the formulas as simple as possible.

There is also an uncertainty on the limits $t_{\text{fin,s}}$ and $t_{\text{ini,e}}$ of the main period. However, considering Eq. 5, it would be unwise to try to include these uncertainties in the uncertainty propagation, because this would result in large uncertainty contributions with almost complete cancellation. Determining small differences of very large numbers is plagued with notoriously high uncertainty and should preferably be left if alternatives are available. Therefore, the contribution of the uncertainty of the limits of the main period should rather be determined separately, and added in quadrature to the variance calculated according to Eq. 11:

$$u^2(\Delta T_{\text{ad}}) = u^2(\Delta T_{\text{ad}}|k, T_{\infty}, T_{\text{ini,e}}, T_{\text{fin,s}}, \Theta) + u^2(\Delta T_{\text{ad}}|t_{\text{ini,e}}) + u^2(\Delta T_{\text{ad}}|t_{\text{fin,s}}). \quad (12)$$

Note: Simple addition in quadrature may appear questionable, because errors in the specification of the limits have a strong impact on the values of the temperatures $T_{\text{ini,e}}$, $T_{\text{fin,s}}$ and the integral Θ . How about the contributions of the associated covariances? In fact, the covariance contributions are already included in the variance contributions of $t_{\text{ini,e}}$ and $t_{\text{fin,s}}$, if these are determined directly. This is true, because then $T_{\text{ini,e}}$, $T_{\text{fin,s}}$ and Θ are not kept constant while varying $t_{\text{ini,e}}$ and $t_{\text{fin,s}}$ but change accordingly, with the consequence that the sensitivity coefficients in the uncertainty contributions of $t_{\text{ini,e}}$ and $t_{\text{fin,s}}$ are not the *partial* derivatives but the *total* derivatives. Transferring covariance contributions into modified

variance contributions by application of the chain rule of differential calculus is a well-known trick to get rid of inconvenient correlations.

The application of Eq. 11 would require the evaluation of 5 variances and 10 covariances—a formidable task. Even worse, there is no real interest in these variances and covariances per se; they are merely lumped together in calculating the variance of the adiabatic temperature rise. In addition to these considerations, for reasons explained in the next section, the correct calculation would imply many cancellations between positive and negative contributions. Therefore, even a single error in a major contribution could easily spoil the result.

Because of these reasons, we will only make restricted use of uncertainty propagation according to Eq. 11. Instead, as far as possible, the variance contributions of the uncertainty sources identified in “[Uncertainty sources](#)” section will be determined directly.

However, the evaluation of the standard uncertainty of single results for the adiabatic temperature rise is not the only task. In addition an estimate of the correlation coefficient between the results of a combustion run and the associated calibration run is required, because these data are jointly used in the determination of the calorific value of the respective gas sample. Another issue requiring correlation coefficients would be the uncertainty of mean values calculated from the results of replicate measurements.

Uncertainty calculation

The model of the adiabatic rise assumes that, in the respective temperature range, the cooling constant is truly a constant. Given this, the adiabatic temperature rise is shift invariant, i.e. the value of ΔT_{ad} does not change if the temperature values $T(t)$ in all three periods are all shifted by a fixed δT according to $T(t) \rightarrow T(t) + \delta T$. This is evident from the model, since the adiabatic temperature rise is calculated from *differences* of temperatures (and the convergence temperature will undergo the same shift). Fortunately it is also true for the adiabatic temperature rise calculated from measured temperature–time series. To confirm this, various measurement series were evaluated with and without an appropriate shift. The results agreed within numerical uncertainty limits.

This shift invariance has a convenient consequence: a constant systematic error of all temperature values in a measurement series has no effect on the result for the adiabatic temperature rise. Therefore, uncertainty contributions from such measurement errors, or other effects resulting in a constant shift are zero and need not be evaluated.

The subsections below deal with the different types of uncertainty sources identified in “[Uncertainty sources](#)”

section. These are random and systematic effects on the series of temperature-rise data and errors made in the evaluation of a given data series.

The uncertainty contributions of the random effects on temperature-rise data are evaluated by statistical methods, utilising the standard deviation of the residuals in the respective periods.

The uncertainty contributions of systematic effects on temperature-rise data are determined directly from the effect on the results for the adiabatic temperature rise. For this purpose effects on temperature-rise data are modelled using a control parameter to specify the level of the effect. This control parameter, in turn, is modelled by a random variable with a specified probability distribution. The mean value of the control parameter, if non-zero, is employed for correcting the temperature-rise data, and for estimating the associated bias of the adiabatic temperature rise obtained. The standard deviation of the control parameter is used for calculating the associated contribution to the uncertainty of the (corrected) adiabatic temperature rise.

Note: At first sight, *systematic* effects with *random* control parameters may appear contradictory. However, in this scenario, ‘systematic’ refers to the behaviour *within* data series, while ‘random’ refers to the behaviour *between* data series.

The uncertainty due to the change of cooling constant and convergence temperature is estimated by a comparison with the results of an alternative evaluation utilising time-dependent parameters.

The uncertainty contributions of evaluation errors are determined directly from appropriate error estimates.

Random fluctuation of temperature data

Initial and final periods Simultaneous exponential regression of the data in the initial and final periods returns the parameter values $k, T_\infty, T_{ini,e}$ and $T_{fin,s}$ and their variance/covariance matrix, i.e. the variances of, and the covariances between these four quantities, resulting from the random fluctuation of the temperature values in both periods. From these data the variance contribution of the random fluctuation in the initial and final periods is calculated as follows (compare “Preparatory considerations” section):

$$u^2(\Delta T_{ad}|random|ini \& fin) = \Sigma Var + 2\Sigma Cov, \tag{13}$$

with the variance sum:

$$\Sigma Var = u^2(T_{fin,s}) + u^2(T_{ini,e}) + [\Theta - T_\infty L_t]^2 u^2(k) + k^2 L_t^2 u^2(T_\infty), \tag{13a}$$

and the covariance sum [$u(a, b) = u(b, a)$]:

$$\begin{aligned} \Sigma Cov = & -u(T_{fin,s}, T_{ini,e}) + [\Theta - T_\infty L_t]u(T_{fin,s}, k) \\ & - kL_t u(T_{fin,s}, T_\infty) \\ & - [\Theta - T_\infty L_t]u(T_{ini,e}, k) + kL_t u(T_{ini,e}, T_\infty) \\ & - kL_t [\Theta - T_\infty L_t]u(k, T_\infty), \end{aligned} \tag{13b}$$

where $L_t = t_{fin,s} - t_{ini,e}$ denotes the length of the main period.

Finally, we would like to address the correlation issue—irrespective of the fact that in the present case the random fluctuation of the temperature data only contributes marginally to the uncertainty of the adiabatic temperature rise. The variance/covariance matrix of the parameter values is obtained from the variance of the residuals. If the residuals are (positively) correlated, their variance will underestimate the actual variance of the temperature fluctuations by a factor $(1 - r_{av})$ where r_{av} is the average of the correlation coefficients for any two residuals. To examine this, the autocorrelation function (ACF) of the residuals was computed, showing only weak short-range correlations. Considering the large number of data points ($n = 2,000$), it is only a tiny fraction of the entire set of $n(n - 1)/2$ correlation coefficients that contributes to the average. Therefore, r_{av} is close to zero, and no correction is required.

Main period The objective is to evaluate the integral Θ defined by Eq. 4. Enumerating the main period data by $(t_i, T_i), i = 0, 1, 2, \dots, m$, and assuming equidistant sampling points, $t_i - t_{i-1} = \Delta t$, the approximation according to the Simpson rule is obtained as follows:

$$\Theta_{Simpson} = \frac{\Delta t}{3} \left[T_0 + 2 \sum_{i=1}^{m/2-1} T_{2i} + 4 \sum_{i=1}^{m/2} T_{2i-1} + T_m \right]. \tag{14}$$

This calculation requires m to be an even number. Assuming uncorrelated random fluctuation of the temperature values with constant standard deviation s_M , the corresponding standard uncertainty of $\Theta_{Simpson}$ is obtained by straightforward uncertainty propagation as follows:

$$u_{rand}(\Theta_{Simpson}) = \sqrt{10m - 2} \frac{\Delta t}{3} s_M \approx \sqrt{10m} \frac{\Delta t}{3} s_M, \tag{15}$$

where the minus 2 were dropped, considering values of m about 2,000. This would give a variance contribution of the random fluctuation in the main period of

$$u^2(\Delta T_{ad}|rand|main) = \frac{10}{9} (\Delta t)^2 k^2 m s_M^2. \tag{16}$$

However, the standard deviation of the temperature values changes in the course of the main period: from a constant high-level s_{MH} during the “activity period”, followed by a monotonic decrease to a constant low level

s_{ML} during the remaining section of the main period. With m_H points in the high-level period, m_T points in the transition period, and m_L points in the low-level period, and with a linear decrease of the variances, an approximate value for the variance contribution of the random fluctuation in the main period is obtained as follows:

$$u^2(\Delta T_{ad}|rand|main) = \frac{10}{9}(\Delta t)^2 k^2 \left[\left(m_H + \frac{m_T}{2}\right) s_{MH}^2 + \left(m_L + \frac{m_T}{2}\right) s_{ML}^2 \right]. \tag{16a}$$

Refined calculations, utilising an improved description of the transition, would only be worthwhile if this were indeed a major variance contribution.

Note: The low-level period includes the 4–5 min between $t_{ini,e}$ and t_{on} .

The final remark concerns the correlation issue. In the main period correlation between residuals has a double effect: (i) The residual variance gives a biased estimate of the actual variance of the temperature fluctuations and requires correction. (ii) Covariances have to be included in the uncertainty propagation for the integral. The investigation of correlations can be restricted to the active period since this provides more than 99% of the uncertainty contribution. For this purpose, we have used the correction factor $[1 + (n - 1)r_{av}]/[1 - r_{av}]$ where again r_{av} is the average of the correlation coefficients for any two residuals, and n the number of data points concerned. In the active period, the ACF of the residuals shows a damped oscillation around zero. We have no explanation for this behaviour and therefore suspect an artefact. To deal with this situation, we calculated average correlation coefficients for different cut-off limits, i.e. using the ACF values up to a specified maximum range and zero for any larger range. Depending on this limit, the average r_{av} takes positive and negative values of about $\pm 10^{-3}$. Thus, we can put the denominator $[1 - r_{av}] = 1$. The numerator $[1 + (n - 1)r_{av}]$ varies between 2 and 0.5. In this situation, we see neither a need nor a justification for a correction factor different from 1. Therefore, no correction is applied.

Systematic effects on temperature data

Drift in temperature measurement Drift effects increasing the error of measured temperatures. Therefore, the drift behaviour of the measurement device—in this case a thermistor sensor—has to be determined, and the measured temperatures have to be corrected to the time of the last calibration. Considering that constant systematic error has no adverse effect on the adiabatic temperature rise, correction to the starting time t_0 of the measurement series will do. Assuming that, in the temperature range concerned,

drift effects an offset increasing with a constant rate, i.e. $T(t_0) \rightarrow T(t) = T(t_0) + R(t - t_0)$, the applicable correction is given by $T(t) \rightarrow T(t_0) = T(t) - R(t - t_0)$. For this purpose the value of the drift rate is required. If the drift rate is known within specified uncertainty limits, the strategy complying with GUM recommendations is to use an appropriate mean for drift correction, and calculate the uncertainty on the correction from the standard uncertainty corresponding to the specification. In the following, two practical cases are considered: (A) drift may be positive or negative, the only available information being a 24-h maximum absolute value $|\Delta T_{max}|$, (B) drift is positive, with a specified 24-h maximum value ΔT_{max} .

Case A As a first step, $|\Delta T_{max}|$ is converted into a positive drift rate R_{max} in appropriate units. Assuming equal likelihood of positive and negative drift, with no preference of values in the specified range $[-R_{max} \leq R \leq R_{max}]$, the drift rate may be treated as a random variable with a rectangular probability distribution between $-R_{max}$ and R_{max} . This distribution has a mean value of zero and a standard deviation of $u(R) = R_{max}/\sqrt{3}$.

Due to the mean value of zero, there is no correction to make. But the uncertainty of the drift rate gives rise to an uncertainty of the adiabatic temperature rise calculated from a measurement series. This uncertainty contribution, or rather the variance contribution, is obtained using the finite difference scheme described in “[Uncertainty propagation according to GUM](#)” section as follows. Given a measurement series $(t_0, T_0), (t_1, T_1), (t_2, T_2), \dots, (t_N, T_N)$, the temperature values are changed according to

$$T_i \rightarrow T_i + \vartheta_{Drift}(t_i) \tag{17}$$

with $\vartheta_{Drift}(t_i) = u(R)(t_i - t_0) = \frac{R_{max}}{\sqrt{3}}(t_i - t_0)$.

The series $\{(t_i, T_i + \vartheta_{Drift}(t_i))\}$ is evaluated, and the difference is calculated between the results obtained on the modified series and the result obtained on the original series.

$$D_{Drift}(\Delta T_{ad}(\{T_i\})) = \Delta T_{ad}(\{T_i + \vartheta_{Drift}(t_i)\}) - \Delta T_{ad}(\{T_i\}). \tag{18}$$

In Eq. 18, the notation for the series was abbreviated from $\{(t_i, T_i)\}$ to $\{T_i\}$ and from $\{(t_i, T_i + \vartheta_{Drift}(t_i))\}$ to $\{T_i + \vartheta_{Drift}(t_i)\}$, and this notation will be used further on.

The difference squared gives the variance contribution of the drift:

$$u^2(\Delta T_{ad}|Drift) = [D_{Drift}(\Delta T_{ad}(\{T_i\}))]^2. \tag{19}$$

Case B As a first step, ΔT_{max} is converted into a drift rate R_{max} in appropriate units. Assuming equal likelihood of drift rates within the specified range $[0 \leq R \leq R_{max}]$, the drift rate may be treated as a random variable with a

rectangular probability distribution between 0 and R_{\max} . This distribution has a mean value of $R_{\max}/2$ and a standard deviation of $u(R) = R_{\max}/2\sqrt{3}$.

In this case, the recommended procedure is to correct the temperature data using the mean drift rate:

$$T_i \rightarrow T_{i,\text{corr}} = T_i - \bar{\vartheta}_{\text{Drift}}(t_i) \quad (20)$$

with $\bar{\vartheta}_{\text{Drift}}(t_i) = \bar{R}(t_i - t_0) = \frac{R_{\max}}{2}(t_i - t_0)$.

For calculating the variance contribution, the *corrected* measurement series is modified according to the standard uncertainty $u(R)$ on the drift rate:

$$T_{i,\text{corr}} \rightarrow T_{i,\text{corr}} + \vartheta_{\text{Drift}}(t_i) \quad (21)$$

with $\vartheta_{\text{Drift}}(t_i) = u(R)(t_i - t_0) = \frac{R_{\max}}{2\sqrt{3}}(t_i - t_0)$.

The series $\{T_{i,\text{corr}} + \vartheta_{\text{Drift}}(t_i)\}$ is evaluated, and the difference is calculated between the results obtained on these two series.

$$D_{\text{Drift}}(\Delta T_{\text{ad}}(\{T_{i,\text{corr}}\})) = \Delta T_{\text{ad}}(\{T_{i,\text{corr}} + \vartheta_{\text{Drift}}(t_i)\}) - \Delta T_{\text{ad}}(\{T_{i,\text{corr}}\}) \quad (22)$$

The difference squared gives the variance contribution of the drift:

$$u^2(\Delta T_{\text{ad}}|\text{Drift}) = [D_{\text{Drift}}(\Delta T_{\text{ad}}(\{T_{i,\text{corr}}\}))]^2 \quad (23)$$

To take care of the correction, there are two procedures as follows:

- (a) The correction of the temperature values according to the mean drift rate is noted, and performed jointly with the corrections resulting from the treatment of other systematic effects at the end. The evaluation of the corrected measurement series then gives the best estimate of the adiabatic temperature rise.
- (b) The respective bias of the adiabatic temperature rise is noted,

$$b(\Delta T_{\text{ad}}|\text{Drift}) = \Delta T_{\text{ad}}(\{T_i\}) - \Delta T_{\text{ad}}(\{T_{i,\text{corr}}\}) \quad (24)$$

and at the end the adiabatic temperature rise obtained from the original measurement series is corrected by subtracting the bias sum.

Procedure (b) is preferred here, see “[Combined uncertainty](#)” section.

Departure of sampled temperatures from bath averages Relevant departures of the temperature at the measurement site from the bath average are restricted to the main period. The uncertainty evaluation is based upon a simple model as follows: a constant difference Δ throughout the “activity” period, followed by a transition period of monotonic decrease to zero difference throughout the rest of

the main period. Letting $[t_{\text{on}} \leq t \leq t_{\text{off}}]$ and $[t_{\text{off}} \leq t \leq t_{\text{equ}}]$ denote the activity period and the transition period, respectively, and using a linear decrease in the transition period, the model is defined by a ramp function as follows: $\vartheta_{\text{SB}}(t) = 0$ for $t < t_{\text{on}}$, $\vartheta_{\text{SB}}(t) = \Delta$ for $t_{\text{on}} \leq t \leq t_{\text{off}}$, $\vartheta_{\text{SB}}(t) = \Delta[(t_{\text{equ}} - t)/(t_{\text{equ}} - t_{\text{off}})]$ for $t_{\text{off}} \leq t \leq t_{\text{equ}}$ and $\vartheta_{\text{SB}}(t) = 0$ for $t > t_{\text{equ}}$.

Note: By default the transition period of the departures from the bath average is taken to be the same as the transition period of the random fluctuations in the main period. However, in specific cases, a different choice may be appropriate.

As in the treatment of drift, case A, we take positive and negative departures to occur equally probably, with no preference in a specified range $[-\Delta_{\max} \leq \Delta \leq \Delta_{\max}]$. Accordingly the control parameter Δ is treated as a random variable with a rectangular probability distribution between specified limits $-\Delta_{\max}$ and Δ_{\max} . This distribution has a mean value of zero and a standard deviation of $u(\Delta) = \Delta_{\max}/\sqrt{3}$.

Due to the mean value of zero, there is no correction to make. But the uncertainty of the control parameter gives rise to an uncertainty of the adiabatic temperature rise calculated from a measurement series. The associated variance contribution could be calculated by the same procedure as the one used for the variance contributions of drift and jacket temperature. However, in this case the difference between values of the adiabatic temperature rise calculated from the modified series and the original series may be calculated directly by integrating the ramp function $\vartheta_{\text{SB}}(t)$ with Δ put to $u(\Delta) = \Delta_{\max}/\sqrt{3}$.

$$D_{\text{SB}}(\Delta T_{\text{ad}}(\{T_i\})) = k \int_{t_{\text{ini,e}}}^{t_{\text{fin,s}}} \vartheta_{\text{SB}}(t) dt = k \frac{\Delta_{\max}}{\sqrt{3}} \left(L_{\text{act}} + \frac{L_{\text{trans}}}{2} \right), \quad (25)$$

where $L_{\text{act}} = t_{\text{off}} - t_{\text{on}}$ and $L_{\text{trans}} = t_{\text{equ}} - t_{\text{off}}$ denote the length of the activity period and the transition period, respectively.

The difference squared gives the variance contribution of this effect:

$$u^2(\Delta T_{\text{ad}}|\text{Sampling}) = [D_{\text{SB}}(\Delta T_{\text{ad}}(\{T_i\}))]^2 \quad (26)$$

Due to the mean value zero of the control parameter, the respective bias of the adiabatic temperature rise is zero.

Model error: change of cooling constant and convergence temperature

The model assumes that the cooling constant and the convergence temperature are the same throughout all periods. However, separate regression of the data in the initial and final periods yields significantly different values

of $k[\text{ini}] \neq k[\text{fin}]$ and $T_\infty[\text{ini}] \neq T_\infty[\text{fin}]$. Simultaneous regression typically yields values of $k[\text{sim}]$ and $T_\infty[\text{sim}]$ between those from separate regression. Apparently the large temperature rise in the main period effects an appreciable change of k and T_∞ . If this change were known, the exchange term would be obtained by (alternative evaluation):

$$\Delta T_{\text{ex}}[\text{alt}] = \int_{t_{\text{ini,e}}}^{t_{\text{fin,s}}} k(t)[T(t) - T_\infty(t)]dt. \quad (27)$$

In the current approach (dedicated evaluation), the exchange term is calculated according to:

$$\Delta T_{\text{ex}}[\text{ded}] = k[\text{sim}] \int_{t_{\text{ini,e}}}^{t_{\text{fin,s}}} [T(t) - T_\infty[\text{sim}]]dt. \quad (27a)$$

In order to investigate the error due to this approximation, we assume a linear change of k and T_∞ from the initial-period values $k[\text{ini}]$ and $T_\infty[\text{ini}]$ to the final-period values $k[\text{fin}]$ and $T_\infty[\text{fin}]$. More specifically, we assume that this change happens in the active part of the main period (combustion or electrical heating). The associated variance contribution is given by the mean square of the differences obtained from (n) replicate measurements:

$$u^2(\Delta T_{\text{ex}}[\text{ded}]|\text{Model}) = \frac{1}{n} \sum_{i=1}^n (\Delta T_{\text{ex},i}[\text{ded}] - \Delta T_{\text{ex},i}[\text{alt}])^2. \quad (28)$$

However, there are also differences between (i) the values $T_{\text{ini,e}}[\text{sep}]$ and $T_{\text{ini,e}}[\text{sim}]$ and (ii) the values $T_{\text{fin,s}}[\text{sep}]$ and $T_{\text{fin,s}}[\text{sim}]$ from separate and simultaneous regression. Considering this, the adiabatic temperature rise would be calculated according to:

$$\Delta T_{\text{ad}}[\text{alt}] = T_{\text{fin,s}}[\text{sep}] - T_{\text{ini,e}}[\text{sep}] - \int_{t_{\text{ini,e}}}^{t_{\text{fin,s}}} k(t)[T(t) - T_\infty(t)]dt, \quad (29)$$

while in the dedicated approach

$$\Delta T_{\text{ad}}[\text{ded}] = T_{\text{fin,s}}[\text{sim}] - T_{\text{ini,e}}[\text{sim}] - k[\text{sim}] \int_{t_1}^{t_F} [T(t) - T_\infty[\text{sim}]]dt. \quad (29a)$$

Thus, the variance contribution of the model error in the present approach is estimated by:

$$u^2(\Delta T_{\text{ad}}[\text{ded}]|\text{Model}) = \frac{1}{n} \sum_{i=1}^n (\Delta T_{\text{ad},i}[\text{ded}] - \Delta T_{\text{ad},i}[\text{alt}])^2. \quad (30)$$

Evaluation error

Uncertainty on the limits of the main period As already stated previously, for the upper limit, the standard deviation of the values on the plateau of candidate values (see “[Model of isoperibol temperature rise](#)” section) is used directly as a contribution of the uncertainty on the upper limit to the uncertainty of the adiabatic temperature rise. This number could be expressed as a product of a rather large standard uncertainty $u(t_{\text{fin,s}})$ and a small sensitivity coefficient, but this is hardly worthwhile. The contribution of the uncertainty on the lower limit is neglected.

Integration error According to Bronstein and Semendjajew [14] the approximation error for the Simpson rule can be estimated as follows:

$$\Delta \Theta_{\text{Simpson}} \approx \frac{\Theta_{\text{Simpson}} - \Theta_{\text{Simpson}}^{[2]}}{15}. \quad (31)$$

In this equation $\Theta_{\text{Simpson}}^{[2]}$ is the result obtained using the even sampling points $t_0, t_2, t_4, t_6, \dots$ exclusively. For this purpose, the number m has to be a multiple of 4. Taking the absolute value of this estimate as a standard uncertainty, the variance contribution of the integration error is:

$$u^2(\Delta T_{\text{ad}}|\text{Simpson}) = k^2 \left(\frac{\Theta_{\text{Simpson}} - \Theta_{\text{Simpson}}^{[2]}}{15} \right)^2. \quad (32)$$

Combined uncertainty

Note: In the case presented, there is at most one bias contribution: from determinate drift (case B), if applicable. However, since the methodology should be applicable to other cases too, a general description was chosen.

In the uncertainty evaluation we have accounted for various error sources and the associated uncertainty contributions by way of random and systematic effects on the series of temperature-rise data, estimates of the effect of model error, and estimates of errors made in the evaluation of a given data series. Since these effects/errors are all mutually independent, the combined standard uncertainty of the adiabatic temperature rise, *corrected for bias (if any)*, is obtained by adding the variance contributions of the effects/errors and taking the square root of the sum:

$$u^2(\Delta T_{\text{ad,corr}}|\Sigma E) = \sum_E u^2(\Delta T_{\text{ad}}|E). \quad (33)$$

In this equation, the sum is taken over all contributing effects/errors. The combined bias (if applicable) of the adiabatic temperature rise is obtained by adding the biases (if any) determined in the evaluation of the systematic effects:

$$b(\Delta T_{ad}|\Sigma E) = \sum_E b(\Delta T_{ad}|E). \tag{34}$$

In this equation, the sum is again taken over all effects/errors, but there will only be few (if any) non-zero contributions. The result for the adiabatic temperature rise is corrected by subtracting the combined bias:

$$\Delta T_{ad} \rightarrow \Delta T_{ad,corr} = \Delta T_{ad} - b(\Delta T_{ad}|\Sigma E). \tag{35}$$

Although not recommended by the GUM, there may be cases where the correction is doubtful. Then, as an alternative, no correction is carried out, and the bias is added in quadrature to the variance sum obtained for the corrected result:

$$u^2(\Delta T_{ad}|\Sigma E) = u^2(\Delta T_{ad,corr}|\Sigma E) + b^2(\Delta T_{ad}|\Sigma E). \tag{36}$$

This procedure was first proposed in [15] and is meanwhile widely used, see e.g. [16]. Basically, it amounts to replacing the variance as a measure of uncertainty for unbiased estimates by the mean squared error as a measure of uncertainty for biased estimates.

Estimation of correlation coefficients

As mentioned before, the evaluation of the standard uncertainty of single results for the adiabatic temperature rise is not the only task. In addition an estimate of the correlation coefficient between the results of a combustion run and the associated calibration run is required, because these data are jointly used in the determination of the calorific value of the respective gas sample. Another issue requiring correlation coefficients would be the uncertainty of mean values calculated from the results of replicate measurements.

Due to the fact that there are no correlations between the effects/errors within a run, between-run correlation could only occur between same effects. Examining the list of candidate pairs, correlation between random fluctuations can be excluded. The same applies to correlation between integration errors and correlation between effects related to the location of main period limits. This leaves us with three candidate correlated pairs as follows:

- Thermistor drift in run 1–thermistor drift in run 2
- Change of k and T_∞ in run 1–change of k and T_∞ in run 2
- Departure from bath average in run 1–departure from bath average in run 2.

This is the moment requiring specification, how the assignment of a random variable to the control parameter of a systematic effect is to be understood. If the control parameter is taken to be a random variable with a specified probability distribution, this can mean that:

- the parameter value is the same from run to run, but this value is not exactly known (fixed effect), or
- the parameter value varies from run to run in accord with the specified distribution (independent random effect).

In addition to these two “pure” cases, there is also an intermediate case as follows:

- the parameter value varies from run to run in accord with the specified distribution, but there is correlation between these variations (correlated random effect).

As a consequence of between-run correlation, the level of change between consecutive runs is lower than expected from the standard deviation of the probability distribution. The limiting cases of no correlation ($r = 0$) and complete correlation ($r = 1$) between runs correspond to the pure cases above.

Thermistor drift Between-run correlation of drift rates is rather probable, in particular with the indefinite specification (case A). This could be investigated experimentally. In the present case, however, the uncertainty contribution of thermistor drift is comparatively small. Therefore, drift would only contribute marginally to the prospective correlation coefficient.

Change of k and T_∞ Between-run correlation is certainly to be expected. Given that the temperature rise in the main period is the driver of the change, and considering that combustion and calibration are carefully designed to generate the same temperature rise, one could even expect complete correlation. This assumption would be appropriate for correlation between successive combustion runs or successive calibration runs. However, there is reason to believe that the change of system parameters behind k and T_∞ is somewhat different for calibration and combustion (e.g. no water is produced in calibration). Therefore, a correlation coefficient between 0.5 and 1 could be expected.

Departure from bath average Transient gradients effecting between-run correlation of the departures at the measurement from the bath average are certainly not beyond imagination, but currently we have no data supporting such an assumption.

Given defensible estimates of the between-run correlation coefficients for the errors from each of the three effects above, the correlation coefficient for the (corrected) adiabatic temperature rise from two runs could be calculated as follows:

$$\begin{aligned} & r(\Delta T_{ad,corr-1}, \Delta T_{ad,corr-2}) \\ &= \sum_E r(\Delta T_{ad,corr-1}, \Delta T_{ad,corr-2}|E) \\ & \quad \times \frac{u(\Delta T_{ad,corr-1}|E)}{u(\Delta T_{ad,corr-1})} \frac{u(\Delta T_{ad,corr-2}|E)}{u(\Delta T_{ad,corr-2})}, \end{aligned} \tag{37}$$

where the sum is over the contributions of the three effects under consideration.

Considering the discussion above, the contribution of thermistor drift can be neglected. Since there is no basis for an estimation of the correlation coefficient of departures from bath averages, the default estimate is zero. The correlation coefficient of model errors could be estimated as 1 for two calibrations, the same for two combustions, and 0.8 for a calibration and the associated combustion. With these raw estimates, the correlation coefficient for two calibrations or two combustions is given by

$$r(\Delta T_{\text{ad,corr-1}}, \Delta T_{\text{ad,corr-2}}) \approx \frac{u(\Delta T_{\text{ad,corr-1}}|\text{Model})}{u(\Delta T_{\text{ad,corr-1}})} \frac{u(\Delta T_{\text{ad,corr-2}}|\text{Model})}{u(\Delta T_{\text{ad,corr-2}})}, \quad (38)$$

while the “mixed” correlation coefficient, i.e. for a calibration and the associated combustion is

$$r(\Delta T_{\text{ad,corr-1}}, \Delta T_{\text{ad,corr-2}}) \approx 0.8 \frac{u(\Delta T_{\text{ad,corr-1}}|\text{Model})}{u(\Delta T_{\text{ad,corr-1}})} \frac{u(\Delta T_{\text{ad,corr-2}}|\text{Model})}{u(\Delta T_{\text{ad,corr-2}})} \quad (39)$$

In the calculation of the calorific value of a gas, the values of the adiabatic temperature rise from combustion

be specified with more than two digits. However, for comparison purposes, in the example the decimal presentation is given with a higher number of digits.

Combustion run

Basic data

Measurement series G567, initial period 0–4,000 s, main period 4,000–8,000 s, final period 8,000–12,000 s. Evaluation of the data in the initial and final periods gives $k = 1.97121 \times 10^{-5} \text{ s}^{-1}$, $T_{\infty} = 27.082220 \text{ K}$, $T_{\text{ini,e}} = 23.480469 \text{ K}$ and $T_{\text{fin,s}} = 26.615263 \text{ K}$. Evaluation of the data in the main period gives $\Theta = 103162.763 \text{ K s}$. With these data an adiabatic temperature rise of $\Delta T_{\text{ad}} = 3.032963 \text{ K}$ is obtained.

Random fluctuation of temperature data—initial and final periods

The regression program returns a variance/covariance matrix as follows:

$$\begin{bmatrix} u^2(T_{\infty}) & u(T_{\infty}, k) & u(T_{\infty}, T_{\text{ini,e}}) & u(T_{\infty}, T_{\text{fin,s}}) \\ \cdot & u^2(k) & u(k, T_{\text{ini,e}}) & u(k, T_{\text{fin,s}}) \\ \cdot & \cdot & u^2(T_{\text{ini,e}}) & u(T_{\text{ini,e}}, T_{\text{fin,s}}) \\ \cdot & \cdot & \cdot & u^2(T_{\text{fin,s}}) \end{bmatrix} = \begin{bmatrix} 6.93932 \times 10^{-10} & -4.02958 \times 10^{-15} & -2.44630 \times 10^{-12} & -2.36790 \times 10^{-10} \\ \cdot & 3.78593 \times 10^{-20} & 1.21108 \times 10^{-16} & 1.24350 \times 10^{-16} \\ \cdot & \cdot & 1.05259 \times 10^{-12} & -1.37380 \times 10^{-14} \\ \cdot & \cdot & \cdot & 1.11690 \times 10^{-12} \end{bmatrix}$$

and from calibration enter as a quotient. Correlation will reduce the standard uncertainty of such a quotient. Therefore, putting the correlation coefficient to zero will give a worst-case uncertainty estimate. On the other hand, correlation will increase the standard uncertainty of a sum. Therefore, if the target is to generate a worst-case estimate of the uncertainty of a mean value, the correlation coefficient should be put to unity.

Examples

Uncertainty data can hardly be estimated with a relative precision better than 10%. Therefore, such data should not

Since this matrix is symmetric, $u(a, b) = u(b, a)$, the entries below the main diagonal were omitted. The units are those for the respective squares or products inherited from the units of the parameters.

From these variances/covariances and the basic data above, the variance contribution is calculated according to Eqs. 13–13b. In addition, the associated standard uncertainty is calculated as the square root of the variance contribution.

Variance contribution: $7.55361 \times 10^{-12} \text{ K}^2$

Standard uncertainty: $2.75 \mu\text{K}$

Note: Throughout the examples section, standard uncertainties relating to adiabatic temperature rise are expressed in micro-Kelvin.

Random fluctuation of temperature data—main period

High-level period: 1,498 s, $m_H = 749$ points; transition period: 80 s, $m_T = 40$ points, low-level period: the remaining 2,422 s, $m_L = 1,211$ points (including 276 s, 138 points in the beginning of the main period), see Fig. 3. The high-level standard deviation was determined by fitting a quadratic polynomial to the data of the high-level period and calculating the standard deviation of the residuals. The low-level standard deviation was determined in the same way from the data of the low-level period. The results are $s_{MH} = 440 \times 10^{-6}$ K, $s_{ML} = 19 \times 10^{-6}$ K. With $\Delta t = 2$ s and k from the basic data, the variance contribution is calculated according to Eq. 16a.

Variance contribution: 2.5787×10^{-13} K²

Standard uncertainty: 0.51 μ K

Drift in temperature measurement

For the thermistor in use, positive and negative drift have been observed, so the case A evaluation is used. The maximum drift rate is $R_{max} = 3.45 \times 10^{-9}$ K s⁻¹. The data series was subjected to simulated drift at the rate given by the standard uncertainty $u(R)$ derived from R_{max} , and the adiabatic temperature rise was calculated from the modified data series. Then the difference of the results obtained from the modified data and the original data was calculated. The squared difference gives the variance contribution, while the absolute value of the difference itself gives the associated standard uncertainty.

Variance contribution: 3.0795×10^{-12} K²

Standard uncertainty: 1.75 μ K

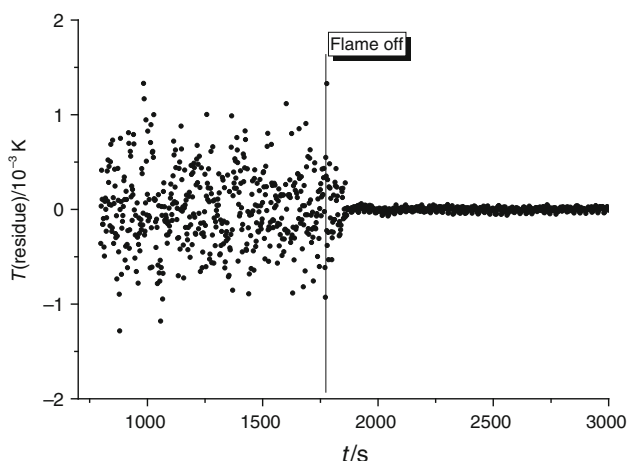


Fig. 3 Fluctuation of main period temperature data (residuals) for a combustion run

Table 4 Combustion run—comparison with alternative procedure

Combustion run	$\Delta T_{ad}[ded]/K$	$\Delta T_{ad}[alt]/K$	Difference/ μ K
G538	3.041972	3.041286	686
G540	3.041349	3.041170	179
G541	3.042021	3.041716	306
G543	3.042357	3.043117	-760
G550	3.042424	3.042694	-270
G557	3.034083	3.033534	549
G564	3.034838	3.034673	165
G567	3.032958	3.032869	89
G576	3.033940	3.033967	-27

Change of cooling constant and convergence temperature

Data from nine combustion runs including the current one were evaluated using the dedicated procedure and the alternative procedure. Table 4 presents the results.

The mean squared difference gives the variance contribution.

Variance contribution: 1.75990×10^{-7} K²

Standard uncertainty: 419.51 μ K

Departure of sampled temperatures from bath averages

Based upon measurements carried out at the Laboratoire national de métrologie d'essais, France (LNE) [17] and the Physikalisch-Technische Bundesanstalt, Germany (PTB) and upon a simulation study by E.ON Ruhrgas AG, Germany, the maximum difference between the temperature at the measurement site and the bath average was estimated as 14 mK. Therefore, a rectangular distribution between limits $\Delta_{min} = -14$ mK and $\Delta_{max} = 14$ mK was used. The time parameters for the error model are the same as used in the model for the level of random fluctuations in the main period.

As done for drift, the data series could be subjected to a change of the main period data, at the level given by the standard uncertainty $u(\Delta)$ derived from Δ_{max} , in order to calculate the adiabatic temperature rise from the modified data series and determine the difference to the result obtained from the original data series. However, in this case a shortcut is available. The target difference was calculated according to Eq. 25, with $\Delta_{max} = 14$ mK, $L_{act} = 1,498$ s and $L_{trans} = 80$ s. The squared difference gives the variance contribution, while the absolute value of the difference itself gives the associated standard uncertainty.

Variance contribution: 6.00500×10^{-8} K²

Standard uncertainty: 245.05 μ K

Uncertainty on the limits of the main period

For the upper limit, the standard deviation of the values on the plateau of candidate values was calculated. The squared standard deviation gives the variance contribution. The contribution of the uncertainty on the lower limit is neglected.

Variance contribution: $4.38903 \times 10^{-12} \text{ K}^2$

Standard uncertainty: $2.10 \text{ } \mu\text{K}$

Integration error

Using only the even sampling points $t_0, t_2, t_4, t_6, \dots$ of the main period, an integral value of $\Theta_{\text{Simpson}}^{[2]} = 103162.747 \text{ K s}$ was obtained. Using this value and that of the original integral, the integration error is calculated according to Eq. 32. The squared error, multiplied by k^2 , gives the variance contribution, while the absolute value of the error, multiplied by k , gives the associated standard uncertainty.

Variance contribution: $4.435 \times 10^{-16} \text{ K}^2$

Standard uncertainty: $0.02 \text{ } \mu\text{K}$

Table 5 gives a summary of the uncertainty evaluation. As there is no bias, there is no need to consider a bias correction and different uncertainty estimates for corrected and non-corrected values of the adiabatic temperature rise.

Calibration run

Basic data

Measurement series G571, initial period 0–4,000 s, main period 4,000–8,000 s, final period 8,000–12,000 s. Evaluation of the data in the initial and final periods gives $k = 1.97068 \times 10^{-5} \text{ s}^{-1}$, $T_\infty = 27.084013 \text{ K}$, $T_{\text{ini,e}} = 23.480251 \text{ K}$ and $T_{\text{fin,s}} = 26.617018 \text{ K}$. Evaluation of the data in the main period gives $\Theta = 103194.399 \text{ K s}$. With these data an adiabatic temperature rise of $\Delta T_{\text{ad}} = 3.035441 \text{ K}$ is obtained.

Random fluctuation of temperature data—initial and final periods

The regression program returns a variance/covariance matrix as follows:

$$\begin{bmatrix}
 u^2(T_\infty) & u(T_\infty, k) & u(T_\infty, T_{\text{ini,e}}) & u(T_\infty, T_{\text{fin,s}}) \\
 \cdot & u^2(k) & u(k, T_{\text{ini,e}}) & u(k, T_{\text{fin,s}}) \\
 \cdot & \cdot & u^2(T_{\text{ini,e}}) & u(T_{\text{ini,e}}, T_{\text{fin,s}}) \\
 \cdot & \cdot & \cdot & u^2(T_{\text{fin,s}})
 \end{bmatrix}
 =
 \begin{bmatrix}
 6.50457 \times 10^{-10} & -3.72110 \times 10^{-15} & -1.90094 \times 10^{-12} & -2.10459 \times 10^{-11} \\
 \cdot & 3.28072 \times 10^{-20} & 9.60863 \times 10^{-17} & 1.10468 \times 10^{-16} \\
 \cdot & \cdot & 8.37731 \times 10^{-13} & -1.19484 \times 10^{-14} \\
 \cdot & \cdot & \cdot & 9.38175 \times 10^{-13}
 \end{bmatrix}$$

Table 5 Combustion run—contributions of the uncertainty sources

Uncertainty source	Bias in μK	Variance in K^2	Standard uncertainty in μK	Variance fraction in %
Random fluctuation of temperature data—initial and final periods	–	7.554×10^{-12}	2.75	0.0032
Random fluctuation of temperature data—main period	–	2.579×10^{-13}	0.51	0.0001
Drift in temperature measurement	–	3.080×10^{-12}	1.75	0.0013
Change of cooling constant and convergence temperature	–	1.760×10^{-7}	419.51	74.5546
Departure of sampled temperatures from bath averages	–	6.005×10^{-8}	245.05	25.4390
Uncertainty on the limits of the main period	–	4.389×10^{-12}	2.10	0.0019
Integration error	–	4.435×10^{-16}	0.02	0.0000
Summation/combination	–	2.361×10^{-7}	485.86	100.0

Final result: $\Delta T_{\text{ad}} = \Delta T_{\text{ad,corr}} = 3.032963 \text{ K}$; $u(\Delta T_{\text{ad}}) = u(\Delta T_{\text{ad,corr}}) = 485.9 \text{ } \mu\text{K}$; $b(\Delta T_{\text{ad}}) = 0$

Since this matrix is symmetric, $u(a, b) = u(b, a)$, the entries below the main diagonal were omitted. The units are those for the respective squares or products inherited from the units of the parameters.

From these variances/covariances and the basic data above, the variance contribution is calculated according to Eqs. 13–13b. In addition, the associated standard uncertainty is calculated as the square root of the variance contribution.

Variance contribution: $6.56294 \times 10^{-12} \text{ K}^2$
 Standard uncertainty: 2.56 μK

Random fluctuation of temperature data—main period

High-level period: 1,508 s, $m_H = 754$ points; transition period: 80 s, $m_T = 40$ points, low-level period: the remaining 2,412 s, $m_L = 1,206$ points. The high-level and low-level standard deviations were determined in the same manner as in the combustion run: $s_{MH} = 400 \times 10^{-6} \text{ K}$, $s_{ML} = 19 \times 10^{-6} \text{ K}$. Further calculation gives the following.

Variance contribution: $2.1450 \times 10^{-13} \text{ K}^2$
 Standard uncertainty: 0.46 μK

Drift in temperature measurement

Input data and evaluation procedure are the same as in the combustion run.

Variance contribution: $3.0795 \times 10^{-12} \text{ K}^2$
 Standard uncertainty: 1.75 μK

Change of cooling constant and convergence temperature

Data from eight calibration runs including the current one were evaluated using the dedicated procedure and the alternative procedure. Table 6 presents the results.

The mean squared difference gives the variance contribution.

Table 6 Calibration run—comparison with alternative procedure

Calibration run	$\Delta T_{ad}[\text{ded}]/\text{K}$	$\Delta T_{ad}[\text{alt}]/\text{K}$	Difference/ μK
G524	3.014606	3.014426	180
G539	3.014027	3.013922	105
G542	3.015845	3.015558	286
G545	3.013877	3.014403	−526
G558	3.034117	3.033783	334
G563	3.033680	3.033679	1
G568	3.034440	3.034868	−427
G571	3.035441	3.035115	325

Variance contribution: $1.00259 \times 10^{-7} \text{ K}^2$
 Standard uncertainty: 316.64 μK

Departure of sampled temperatures from bath averages

The evaluation procedure is the same as in the combustion run. Again $\Delta_{max} = 14 \text{ mK}$ and $L_{trans} = 80 \text{ s}$, while $L_{act} = 1,504 \text{ s}$.

Variance contribution: $6.04869 \times 10^{-8} \text{ K}^2$
 Standard uncertainty: 245.94 μK

Uncertainty on the limits of the main period

The evaluation procedure is the same as in the combustion run.

Variance contribution: $1.21522 \times 10^{-11} \text{ K}^2$
 Standard uncertainty: 3.49 μK

Integration error

The evaluation procedure is the same as in the combustion run.

Variance contribution: $8.7599 \times 10^{-16} \text{ K}^2$
 Standard uncertainty: 0.03 μK

Table 7 gives a summary of the uncertainty evaluation.

Correlation coefficients

Based upon the considerations in “[Estimation of correlation coefficients](#)” section, preliminary estimates of correlation coefficients are obtained as follows.

- Combustion—combustion: $r \approx 0.7$
- Calibration—calibration: $r \approx 0.6$
- Combustion—calibration: $r \approx 0.5$

However, these estimates currently lack a sound basis. Therefore, if safeguarding against the underestimation of uncertainty is mandatory, $r = 0$ provides worst-case estimates of the uncertainty of differences and quotients of adiabatic temperature values from different runs, while $r = 1$ does the same in the case of sums, mean values and products.

Discussion

The uncertainty budget is almost completely dominated by two uncertainty sources: the change of cooling constant and convergence temperature and the departure of sampled temperatures from bath averages. Somewhat unfortunately, the uncertainty contributions for these two sources (and for

Table 7 Calibration run—contributions of the uncertainty sources

Uncertainty source	Bias in μK	Variance in K^2	Standard uncertainty in μK	Variance fraction in %
Random fluctuation of temperature data—initial and final periods	–	6.563×10^{-12}	2.56	0.0041
Random fluctuation of temperature data—main period	–	2.145×10^{-13}	0.46	0.0001
Drift in temperature measurement	–	3.080×10^{-12}	1.75	0.0019
Change of cooling constant and convergence temperature	–	1.003×10^{-7}	316.64	62.3626
Departure of sampled temperatures from bath averages	–	6.049×10^{-8}	245.94	37.6237
Uncertainty on the limits of the main period	–	1.215×10^{-11}	3.49	0.0076
Integration error	–	8.760×10^{-16}	0.03	0.0000
Summation/combination	–	1.611×10^{-7}	400.96	100.0

Final result: $\Delta T_{\text{ad}} = \Delta T_{\text{ad,corr}} = 3.035441 \text{ K}$; $u(\Delta T_{\text{ad}}) = u(\Delta T_{\text{ad,corr}}) = 401.0 \mu\text{K}$; $b(\Delta T_{\text{ad}}) = 0$

the drift in temperature measurement as well) are based upon rather rough estimates. Therefore, efforts will be taken to improve the uncertainty analysis for these two sources.

As far as possible, calculated standard uncertainties should be compared with experimental standard deviations. If the latter are considerably larger than the former, something is definitely wrong with the uncertainty evaluation: the uncertainty budget is incomplete, or uncertainty components have been underestimated. If the calculated standard uncertainties are larger than the experimental standard deviations, this may be due to an overestimation of uncertainty contributions. However, there are also other possibilities: systematic effects dominating the uncertainty budget or between-run correlation of errors from random effects (see note below).

Repeatability conditions are best achieved for calibration runs, and the standard deviation of the heat capacity obtained from 12 replicate runs is 4.2×10^{-5} relative, while the standard uncertainty calculated in “[Calibration run](#)” section is 13.2×10^{-5} relative. This amounts to a factor of 3, by which the calculated standard uncertainty exceeds the experimental standard deviation. There are two possible sources for that: (i) overestimation of dominating uncertainty contributions, and (ii) between-run correlation of the errors resulting from dominating effects. In the present case there is reason to believe that both sources are operative. As explained in “[Estimation of correlation coefficients](#)” section there is certainly a strong between-run correlation of the effects of change of k and T_{∞} and possibly also some correlation of the effects of sampling error. On the other hand, the uncertainty contributions for these two sources are based upon rather rough and conservative estimates. Future investigations will hopefully provide a basis for improved estimates of the relevant uncertainty contributions and correlation coefficients.

Note: In the presence of between-run correlation, the experimental standard deviation s from replicate runs will (on average) underestimate the “true” standard deviation σ . The expectation of s^2 is given by $E[s^2] = (1 - r)\sigma^2$, where r is the average correlation coefficient. Thus, a ratio of $s/\sigma = 3$ corresponds to an average correlation coefficient of $r \approx 0.9$. However, considering that the dominating uncertainty contributions are only rough and conservative estimates, this calculation merely supports the idea that there may be strong between-run correlation.

Conclusions

A practical approach for evaluating the uncertainty of results for determinations of the adiabatic (corrected) temperature rise in isoperibol calorimetry was presented. The uncertainty sources considered are fairly comprehensive, including deviations from common model assumptions. The methodology is firmly based on the recommendations of the GUM [11]. For this purpose, the standard approach based upon a measurement equation, where the target quantity is expressed as a function of the relevant input quantities which then take the part of the uncertainty sources, was complemented by a cause/effects approach. With the latter the uncertainty contributions of systematic effects on temperature-rise data, model error and evaluation error are determined directly from the effect on the results for the adiabatic temperature rise. The standard approach was used for propagating the parameter variances and covariances due to random variability of the temperature data. Computational implementation of the uncertainty calculation is straightforward. Although developed for a specific modification of the Regnault–Pfaundler method, the approach is sufficiently general to make it applicable to virtually any other scheme for the evaluation of temperature–time curves in temperature-rise calorimetry.

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References

1. Rossini FD. The heat of formation of water. *Bur Stand J Res.* 1931;6:1–35.
2. Rossini FD. The heats of combustion of methane and carbon monoxide. *Bur Stand J Res.* 1931;6:37–49.
3. Rossini FD. The heat of formation of water and the heats of combustion of methane and carbon monoxide. A Correction. *Bur Stand J Res.* 1931;7:329–30.
4. Schley P, Beck M, Uhrig M, Sarge SM, Rauch J, Haloua F, Filtz J-R, Hay B, Yakoubi M, Excande J, Benito A, Cremonesi PL. Measurement of the calorific value of methane with the new GERG reference calorimeter. *Int J Thermophys.* 2010;31:665–79.
5. ISO 6976. Natural gas—calculation of calorific value, density, relative density and Wobbe index from composition (2nd ed. 1995-12, corrected and reprinted 1996-01; currently under revision); 1995.
6. Alexandrov YI. Estimation of the uncertainty for an isothermal precision gas calorimeter. *Thermochim Acta.* 2002;382(1–2): 55–64.
7. Dale A, Lythall C, Aucott J, Sayer C. High-precision calorimetry to determine the enthalpy of combustion of methane. *Thermochim Acta.* 2002;382(1–2):47–54.
8. Santos LMNBF, Silva MT, Schröder B, Gomes L. Labtermo: methodologies for the calculation of the corrected temperature rise in isoperibol calorimetry. *J Therm Anal Calorim.* 2007;89: 175–80.
9. Borrell P. The application of computer curve fitting techniques to Regnault-Pfaundler calculations of calorimetric data. *Thermochim Acta.* 1974;9:89–93.
10. West ED, Churney KL. A two-body model for calorimeters with constant-temperature environment. *J Appl Phys.* 1968;39(9): 4206–15.
11. ISO. Guide to the expression of uncertainty in measurement (1st ed., corrected and reprinted 1995); 1993. Also published on the BIPM website (www.bipm.org/en/publications/guides/gum.html) as BIPM/JCGM 100 Evaluation of measurement data—guide to the expression of uncertainty in measurement; 2008.
12. BIPM/JCGM 104. Evaluation of measurement data—an introduction to the “Guide to the expression of uncertainty in measurement” and related documents. 2009. www.bipm.org/en/publications/guides/gum.html.
13. BIPM/JCGM 101. Evaluation of measurement data—supplement 1 to the “Guide to the expression of uncertainty in measurement”—propagation of distributions using a Monte Carlo method. 2008. www.bipm.org/en/publications/guides/gum.html.
14. Bronstein IN, Semendjajew KA. *Taschenbuch der Mathematik.* 18th ed. Frankfurt/Main: Verlag Harri Deutsch; 1979. p. 336.
15. Lira IH, Woeger W. Evaluation of the uncertainty associated with a measurement result not corrected for systematic effects. *Meas Sci Technol.* 1998;9:1010–1.
16. ISO 15796. Gas analysis—investigation and treatment of analytical bias. 1st ed. International Organization for Standardization; 2005.
17. Haloua F, Villermaux C, Filtz J-R, Zarea M, Hay B. Thermal characterisation of an isoperibolic calorimeter bath. In: *Proceedings of the 9th TEMPMEKO conference, vol. 2.* ISBN 953-6313-71-5; 2004. p. 1223–30.