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Measurements of the Calorific Value of Methane with the New GERG Reference Calorimeter

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Abstract A new reference calorimeter has been developed under a European research project and set-up by Physikalisch-Technische Bundesanstalt (PTB) in Germany. The objective of the project is to measure the superior calorific value (SCV) of methane and other pure gases with a measurement uncertainty of less than 0.05 %. This paper presents the measurement results obtained for methane. Nine repeatability measurements were made. The molar SCV obtained when the measurements were averaged is 890.578 kJ·mol^{-1}. This value agrees very accurately with the value of 890.63 kJ·mol^{-1} specified by ISO 6976 [*Natural Gas—Calculation of Calorific Values, Density, Relative Density and Wobbe Index from Composition*. International Standard ISO 6976, corrected and reprinted 1996-02-01]. Twice the standard deviation determined for the measurements is 0.023 % and is thus clearly lower than in previous

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experiments. Two independent uncertainty analyses confirm that the envisaged total uncertainty of 0.05 % is achieved (95 % confidence level).

Keywords GERG · Methane · Natural gas · Reference calorimeter · Superior calorific value

1 Introduction

For billing natural gas deliveries, it is commercially very important to determine energy quantities and thus superior calorific values (SCVs) accurately. Currently, SCVs are usually calculated on the basis of gas chromatography in accordance with International Standard ISO 6976 [1]. The SCVs specified in ISO 6976 for pure gases are based on measurements made in the 1930s and 1970s. The uncertainties involved in the ISO values can only be roughly estimated today. For methane, the uncertainty is specified to amount to 0.12 % (two times the standard deviation).

1.1 SCV of Methane

The SCV of methane as the main constituent of natural gas is of particular importance, all the more since methane is often used in gas calorimetry as a reference material for calibration. The SCV of methane was first determined experimentally in 1848. While several scientific papers have been published since then, only two are considered adequate in ISO 6976 in terms of accuracy to be included in the determination of the SCV of methane.

One of the two publications is a paper by Rossini [2,3] at the National Bureau of Standards, USA; the other is a paper by Pittam and Pilcher [4] at Manchester University, UK. Rossini's work is particularly important. First, the measurement setup described by Rossini is still the basis for several reference calorimeters developed later, including, for example, the GERG reference calorimeter described in this paper. Second, Rossini's measured values (aside from methane, also hydrogen and carbon monoxide) were used for calibration in papers published later. Pittam and Pilcher, for example, calibrated their calorimeter against Rossini's measurements on hydrogen [5].

Two other measurement series for the SCV of methane were published by Dale et al. [6] and Alexandrov [7] in 2002. The work of Dale et al. at the Office of Gas and Electricity Markets (OFGEM), Leicester, UK is based on the type of calorimeter used by Pittam and Pilcher. Alexandrov at the Mendeleev Institute of Metrology, St. Petersburg, Russia used a heat flow calorimeter for his measurements which has a completely different mode of operation than the calorimeters mentioned above. It is planned to take these more recent measurement series into consideration in the current revision of ISO 6976. The measurement results obtained for methane with the new GERG reference calorimeter and contained in this paper are published for the first time. The results are compared with the results presented by the authors mentioned previously in Sect. 5.

1.2 GERG Project: Development of a New Reference Calorimeter

A Groupe Européen de Recherches Gazières (GERG) project was initiated in 2002 to develop a new reference calorimeter for determining the SCVs of pure gases and gas mixtures. The objective of the project is to determine SCVs with a measurement uncertainty of less than 0.05 % (95 % confidence level) and ensure traceability of the values measured to national standards. Two previous studies thoroughly examined the feasibility of this objective [8,9]. Both feasibility studies found that a 0.05 % uncertainty based on the Rossini measurement principle [2,3] could be achieved. The studies proposed major improvements to the measurement technology and the experimental procedure.

On this basis, six partners decided to develop and set up the calorimeter in accordance with the procedure described above. The project partners are Enagas (Spain), E.ON Ruhrgas AG (Germany), GDF Suez (France), Laboratoire national de métrologie et d'essais (LNE, France), Physikalisch-Technische Bundesanstalt (PTB, Germany), and Snam Rete Gas (Italy). PTB in Braunschweig developed and set up the calorimeter (first project phase). In the second project phase, which is supported by DVGW (German Gas and Water Association), measurements are performed on pure gases and the measurement uncertainty of 0.05 % is validated. The project is to be completed by the end of 2009.

2 Concept of GERG Reference Calorimeter

The objective of a reference calorimeter is to measure the quantity of energy involved in the complete combustion of a specific amount of a hydrocarbon fuel gas. For a Rossini-type calorimeter, this is achieved by allowing the energy liberated in the reaction to be transferred to a well-stirred water bath and measure its temperature rise (see Fig. 1).

An ideal calorimeter would be thermally isolated from its environment so that the temperature change observed is solely due to the reaction. Complete isolation from the environment is not possible in practice, so a calorimeter is usually surrounded by a thermostatically controlled jacket and allowance is made for the various sources and sinks of energy. In calorimetry, this is usually called an isoperibolic principle.

The energy released is the product of the adiabatic temperature rise during combustion $\Delta T_{\text{ad,comb}}$ and the heat capacity of the calorimeter C_{comb}. For the purpose of simplification, parameter K covers several energy corrections discussed in more detail in Sect. 4.

Accordingly, referred to the mass of combusted gas m_{gas}, the SCV H_{s} is:

$$H_{\text{s}} = \frac{C_{\text{comb}} \Delta T_{\text{ad,comb}} + K}{m_{\text{gas}}}. \tag{1}$$

The heat capacity of the calorimeter is determined by electrical calibration. In the calibration experiment, about the same energy quantity as generated during combustion is

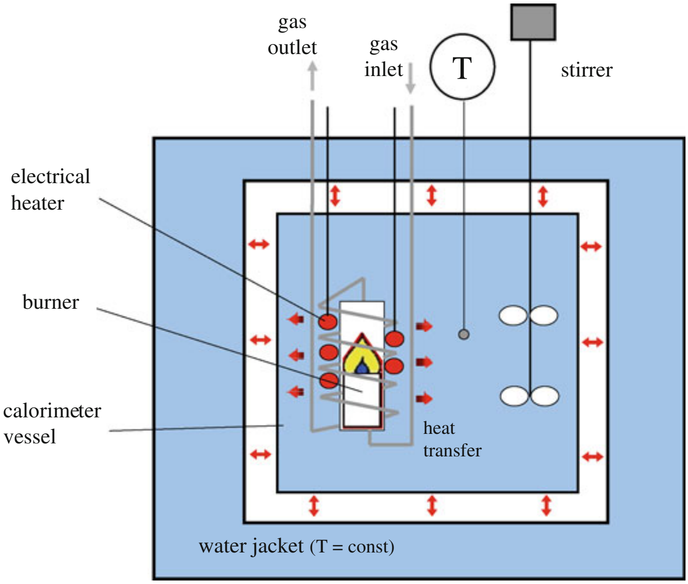

Fig. 1 Principle of an isoperibolic calorimeter

released by an electrical heating wire. This principle of comparison ensures traceability of the SCV to SI units.

Finally, the mass of the combusted gas must be determined. In this respect, there is a major difference to Rossini's experiment [2,3]. While Rossini determined the mass of the gas based on the water produced during the combustion process, which is directly related to the methane burnt, the GERG calorimeter determines the mass by direct weighing. Small quantities of uncombusted gas are measured by an infrared analyzer. This approach was one of the experimental improvements developed during the prestudy [9].

In the work by Dale et al. [6], the mass was also determined by weighing. But other than in this paper, correction for uncombusted gas was made by way of additional short combustion experiments of approx. 80 s. The mass of gas which is lost at ignition and extinction should be the same for long and short runs. So, if the energy liberated and the mass of gas burnt in the short run are subtracted from the energy and mass for the long run, the resultant values should then be due to just the gas burnt.

Table 1 lists more differences in the experimental procedure between various isoperibolic calorimeters.

3 Design and Experimental Procedure

The experimental setup of the GERG calorimeter was explained in detail in the final report on the first project phase [10]. Improvements to the experimental setup were also presented in [11].

Table 1 Comparison of isoperibolic calorimeters

Method	Rossini [2,3] (NIST, 1931)	Pittam and Pilcher [4] (Man. Univ. 1972)	Dale et al. [6] (OFGEM, 2002)	GERG reference calorimeter (this paper)
Mass determination	Determined from mass of water produced (absorption tubes)	Determined from mass of carbon dioxide produced (absorption tubes)	Direct weighing; correction for unburnt gas from short runs (0.16 g)	Direct weighing (online); correction for unburnt gas from IR analysis
Amount of burnt gas	0.8 g	0.8 g	1 g	1 g
Calibration	Electrical (heating tubes)	Combustion of hydrogen and oxygen, based on Rossini values [5]	Electrical (heating tubes)	Electrical (heating wire wound around the burner)
Temperature readings	Every minute	Every 30 s	Every 3 s	Every 2 s

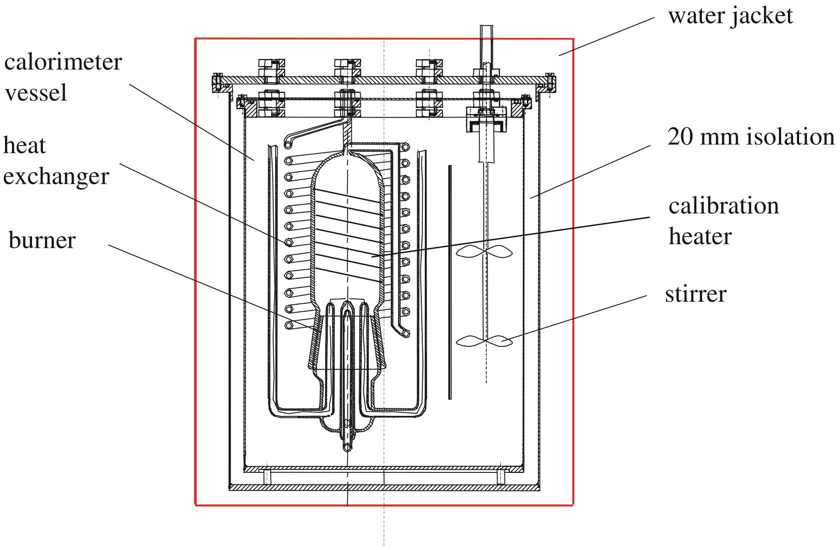

Fig. 2 Cross section of calorimeter

3.1 Calorimeter and Burner

The main components of the calorimeter are shown in Fig. 2. The burner made of Duran glass with a heat exchanger is installed in a calorimeter vessel consisting of two bodies. A stirrer ensures homogeneous mixtures. The calorimeter vessel also includes

Fig. 3 Constant-temperature chamber with thermostat (*left*) and weighing chamber (*right*) and electronic control unit and data acquisition system outside the chamber

temperature measurement points (a Pt25 thermometer and a thermistor) and a cooling finger.

The calorimeter vessel is enclosed in a high-precision thermostat which is controlled to maintain a constant temperature (water jacket). To minimize heat transfer, the calorimeter vessel consists of an inner body and an outer body, the 20 mm gap between the two bodies being insulated with polystyrene foam.

3.2 Constant-Temperature Chamber

To minimize the influence of varying ambient temperatures on the calorimeter, the entire experimental setup consisting of the thermostat with the calorimeter vessel and the weighing unit is enclosed in a constant-temperature chamber (see Fig. 3). The chamber ensures constant temperatures within ±30 mK. As a result, the temperature variation in the thermostat for the surroundings of the calorimeter vessel is less than ±0.1 mK under equilibrium conditions.

3.3 Temperature Measurement

The temperature measurement must be sensitive and ensure fast response to temperature changes. In the past [2–4], resistance thermometers have often been used in isoperibolic gas calorimetry following the Rossini principle. However, in view of their sluggish response, especially when used in combination with commercial AC bridges as in [6], platinum resistance thermometers can be used effectively only in the initial and final periods. In this work, the fast temperature rise during the main period is measured with a fast response thermistor. The sensor (semiconductor) is a YSI 46046 thermistor (Yellow Springs Instruments, Yellow Springs, OH, USA). In

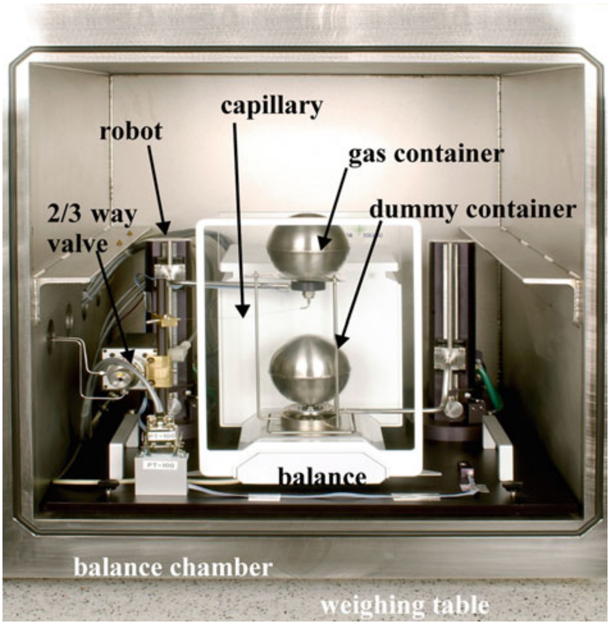

Fig. 4 Weighing setup inside balance chamber

our arrangement, the thermistor is calibrated before the experiment against a traceable Pt25 resistance thermometer (ISOTECH, Fulda, Germany) in combination with an ASL F18 thermometry bridge (Automatic Systems Laboratories, Redhill, Surrey, England).

3.4 Determination of Mass of Fuel Gas

A fully automatic weighing unit accommodated in a weighing chamber is used to determine the combusted gas quantity (approx. 1 g). The weighing unit is shown in Fig. 4. Prior to the experiment, a gas container (stainless-steel sphere) is filled with fuel gas, for example, methane, until a pressure of approximately 10 bar is reached. The mass of the gas container is determined with a Mettler Toledo AT 201 precision balance (Mettler Toledo Schweiz AG, Greifensee, Switzerland) which achieves a resolution of 10 μg. Pure gas is withdrawn from the sphere via a thin capillary and supplied to the burner. The weighing results are recorded prior to and after combustion. The balance is calibrated during each experiment. The pressure, temperature and humidity are measured in the weighing chamber to correct the weighing results for buoyancy effects. To eliminate any residual influence of ambient conditions as well as drift of the balance, the mass is determined by differential measurement. For this purpose, the gas sphere is replaced with a dummy sphere which has approximately the same volume and the same mass as the sphere filled with fuel gas. In addition, the gas withdrawn is substituted by additional weights.

The fuel gas released is not completely burnt during the combustion experiment. Of a total gas mass of 1 g, approximately 3 mg sent through the burner during ignition and at the end of combustion are not burnt. The concentration of the unburnt fuel gas leaving the calorimeter in an oxygen/argon mixture is measured with an infrared analyzer (Ultramat 6, Siemens AG, München, Germany). Maximum concentrations of approximately 1600 ppm occur in the case of methane. The Ultramat device is calibrated using calibration gases with various concentrations of methane in nitrogen in the relevant range. The integrated infrared signal together with the volume flow measured with mass flow controllers is then used to determine the total mass of unburnt fuel gas.

3.5 Determination of Mass of Water

Water is the main constituent of the reaction products formed during the combustion experiment. Approximately 2.2 g of H_2O are formed when 1 g of methane is burnt. The largest part of the water condenses in the heat exchanger and collects as a liquid inside the burner vessel. Only approximately 8.5 % of the water leaves the calorimeter in the form of vapor. The quantity of the condensed water and/or of the noncondensed water vapor influences both the heat capacity of the calorimeter and the enthalpy balance and must, therefore, be determined accurately.

To accurately determine the quantity of the water vapor, the waste gas is sent through an absorption column consisting of three absorption tubes filled with magnesium perchlorate. The mass of water absorbed is determined by weighing the absorption tubes prior to and after the experiment.

Once the final period has ended, the absorption tubes are again connected to the waste gas duct of the calorimeter and the condensed water remaining in the calorimeter is displaced from the calorimeter using a purging gas (argon). The absorption tubes are again weighed once purging has ended (approximately 4 h). The increase in mass corresponds to the mass of the condensed water.

3.6 Electrical Calibration

Electrical calibration has become an established method in gas calorimetry because of direct traceability of the electrical measured values to SI units. Approximately the same energy quantity is released during electrical calibration as is released during a combustion experiment. The heat in the calibration experiment is released by a Thermocoax two-wire heating resistance ($R = 52.7\,\Omega$, THERMOCOAX SAS, Suresnes, France). The wire is wound around the dome of the burner, thus ensuring similar temperature profiles of calibration and combustion.

The heat capacity of the calorimeter is a function of electrical energy and adiabatic temperature increase:

$$C_{\mathrm{cal,elec}} = \frac{E_{\mathrm{elec}}}{\Delta T_{\mathrm{ad,elec}}}. \tag{2}$$

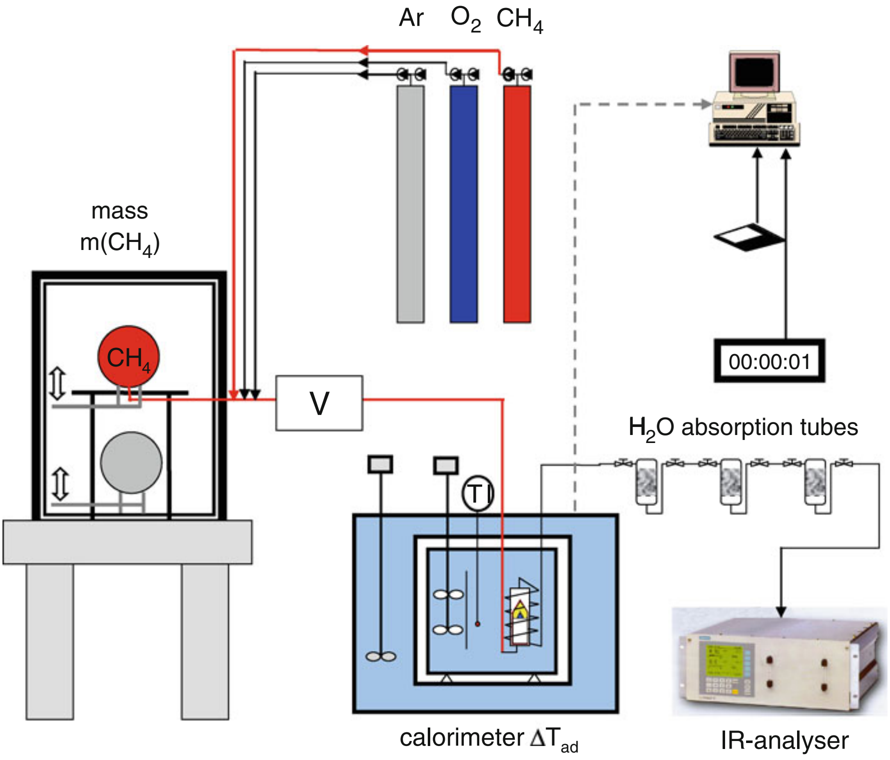

Fig. 5 Schematic presentation of calorimeter setup and gas flows

The electrical energy is determined as the sum of i time intervals Δt_i

$$E_{\text{elec}} = \sum_i \frac{U_{\text{heat},i}\,U_{\text{ref},i}}{R_{\text{ref},i}} \Delta t_i, \tag{3}$$

where U_{heat} is the voltage drop at the electrical heater and U_{ref} is the voltage drop at the reference resistance R_{ref}. The voltages are measured with an Agilent 3458A multimeter (Agilent Technologies, Santa Clara, CA, USA).

3.7 Experimental Procedure

The entire experimental procedure is automatic and controlled with Labview-based software (National Instruments, Austin, TX, USA). Figure 5 shows a schematic presentation of the setup and gas flows.

An oxygen/argon mixture is added to the fuel gas and fed to the burner through a nozzle. Argon does not participate in the reaction, but serves to stabilize the flame.

Before the experimental run starts, the calorimeter is cooled to 22 °C and the temperature in the water jacket is set to 26.85 °C (300 K). After an equilibration interval of about 4 h, the initial period starts. During the initial period, which lasts approximately

60 min, no gas flows through the calorimeter. Once the calorimeter temperature has reached 23.5 °C, gas flow and ignition are started simultaneously. Combustion continues for about 20 min. The start time of the main period t_{mi} corresponds to the start time of gas flow. Immediately after the extinction of the flame during the main period, gas flow through the calorimeter is stopped.

4 Evaluation of Measurements

The basic equation for determining SCVs was already described by Eq. 1.

$$H_{\mathrm{s}} = \frac{C_{\mathrm{comb}}\Delta T_{\mathrm{ad,comb}} + K}{m_{\mathrm{gas}}} \tag{1}$$

The heat capacity of the calorimeter determined by electrical calibration must be corrected for the influence of the water condensed during combustion ($C_{\mathrm{comb}} = C_{\mathrm{cal}} + C_{\mathrm{H_2O,liq}}$). Parameter K reflects further energy corrections such as the contribution of the vaporization enthalpy resulting from the condensed water, the energy contribution of the fuel and auxiliary gases, and the ignition energy which are only factors in the combustion experiment. The mass m_{gas} is determined using the method described in Sect. 3.4.

4.1 Determination of Adiabatic Temperature Rise ΔT_{ad}

The experiment starts at a temperature of 23.1 °C inside the calorimeter. Due to the heat transfer between the calorimeter vessel and the water jacket prior to ignition, the temperature of the calorimeter increases slowly. This period is called the *initial period*. After some minutes the combustion starts and this leads to a high rate of temperature increase during the so-called *main period*. After the burner is switched off, the temperature of the calorimeter increases further slightly due to heat transfer. After the heat is completely released and distributed, the *final period* starts. A schematic temperature–time curve of a combustion experiment is shown in Fig. 6.

Compared to an adiabatic calorimeter an additional temperature correction term, ΔT_{ex}, describing the heat exchange with the surroundings is added in order to determine the adiabatic temperature rise in an isoperibolic calorimeter (see Eq. 4);

$$\Delta T_{\mathrm{ad}} = T_{\mathrm{mf}} - T_{\mathrm{mi}} - \Delta T_{\mathrm{ex}}. \tag{4}$$

The rate of change of temperature of the calorimeter during the initial and final periods is given by the following equation:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = u(t) + k\left(T_0 - T(t)\right), \tag{5}$$

where T is the volume-averaged temperature of the calorimeter, T_0 is the temperature in the water jacket, $u(t)$ is the temperature rate due to heat production in the calorimeter,

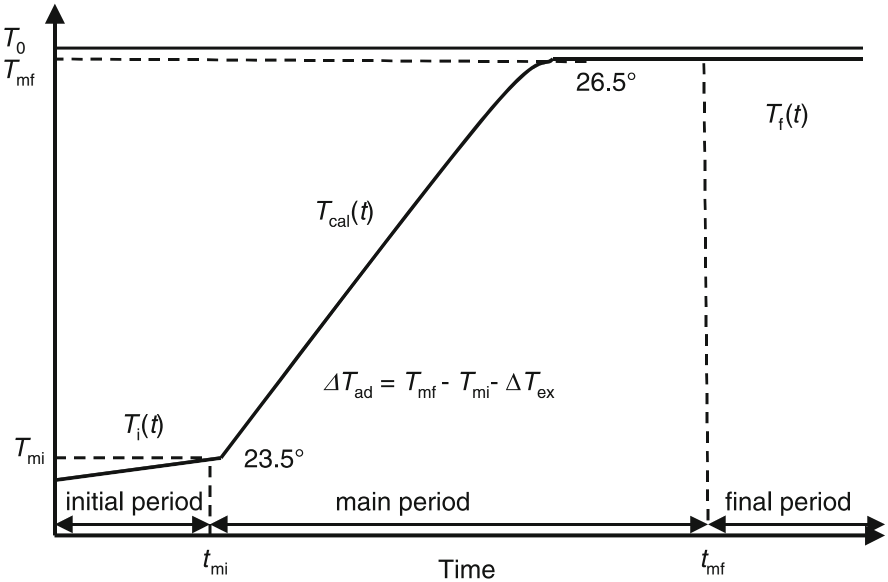

Fig. 6 Determination of the adiabatic temperature rise

and k is the cooling constant which governs the heat transfer between the calorimeter and the surroundings, derived from Newton's law of cooling.

If left for a long time, the calorimeter will reach an equilibrium temperature T_∞, slightly above the jacket temperature. At this point, $\mathrm{d}T/\mathrm{d}t = 0$ and from Eq. 5 it follows that $u(t) = -k(T_0 - T_\infty)$. Substituting for $u(t)$ leads to

$$\frac{\mathrm{d}T}{\mathrm{d}t} = +k\,(T_\infty - T)\,. \tag{6}$$

With Eq. 6 an exponential analytical expression for the initial and final periods may be obtained. For the initial period (subscript i) follows that

$$T_\mathrm{i}\,(t) = T_\infty - (T_\infty - T_\mathrm{mi}) \cdot \exp\left(-k\,(t - t_\mathrm{mi})\right), \tag{7}$$

where T_mi is the temperature at the beginning of the main period (end of initial period) and t_mi is the time at the beginning of the main period.

In a new analytical approach, the constants k and T_∞ are determined by a simultaneous exponential regression of the temperature–time data in the initial and final periods. The temperature correction term, ΔT_ex, for the main period can now be calculated assuming constant values for k and T_∞ during the whole experiment:

$$\Delta T_\mathrm{ex} = k \int_{t_\mathrm{mi}}^{t_\mathrm{mf}} (T_\infty - T\,(t))\,\mathrm{d}t. \tag{8}$$

Thus, all information is available to determine the adiabatic temperature rise. The measured temperature–time curve is analyzed through Eqs. 7 and 8 using the Simpson rule for numerical integration during the main period.

5 Measurement Results for Methane

A measurement series comprising a total of nine calibration and nine combustion experiments was made with the GERG reference calorimeter. Table 2 lists the results together with the data of previous authors. The last column of the table contains the measurement results of this work.

The results of this paper were calculated from the mass-related measured values with a value of 16.04246 kg·kmol^{-1} [12] for the molar mass. The data of Alexandrov were treated in the same way. The original data of Rossini [2,3] were revised in the paper of Armstrong and Jobe [13] with respect to the current values for molar mass and electrical units. Two data sets are specified in the paper of Dale et al. [6], shown under Lythall and Dale in Table 2, which were measured with the same experimental setup but at different times.

Figure 7 compares relative deviations from the current value to ISO 6976 (890.63 kJ·mol^{-1}) [1].

The average value of the measurement series presented in this paper agrees very well with the value of ISO 6976 and thus also with the previous work of Rossini [2,3]. The deviation from the ISO value is only −0.006 %. Twice the standard deviation determined on the basis of the nine measurements corresponds to 0.023 %. This is the lowest value compared to all other authors. With 0.149 % and 0.092 %, respectively,

Table 2 Experimental data for the superior calorific value of methane (in kJ · mol^{-1})

Run ID	Rossini [2,3,13]	Pittam and Pilcher [4]	Lythall [6]	Dale [6]	Alexandrov [7]	This work
1	891.823	890.36	890.60	890.34	889.63	890.639
2	890.633	891.23	890.69	890.11	890.47	890.459
3	890.013	890.62	890.87	890.49	890.85	890.443
4	890.503	890.24	890.62	891.34	890.37	890.780
5	890.340	890.61	890.81	890.36	890.44	890.568
6	890.061	891.17	890.94	890.44	890.79	890.530
7			890.71	890.47	890.66	890.597
8			890.59	890.87	890.02	890.628
9			890.64	890.31		890.562
10				890.33		
Mean value (kJ · mol^{-1})	**890.562**	**890.705**	**890.719**	**890.506**	**890.405**	**890.578**
2 std. dev. (kJ · mol^{-1})	1.327	0.821	0.253	0.702	0.815	0.203
2 std. dev. (%)	0.149	0.092	0.028	0.079	0.092	0.023

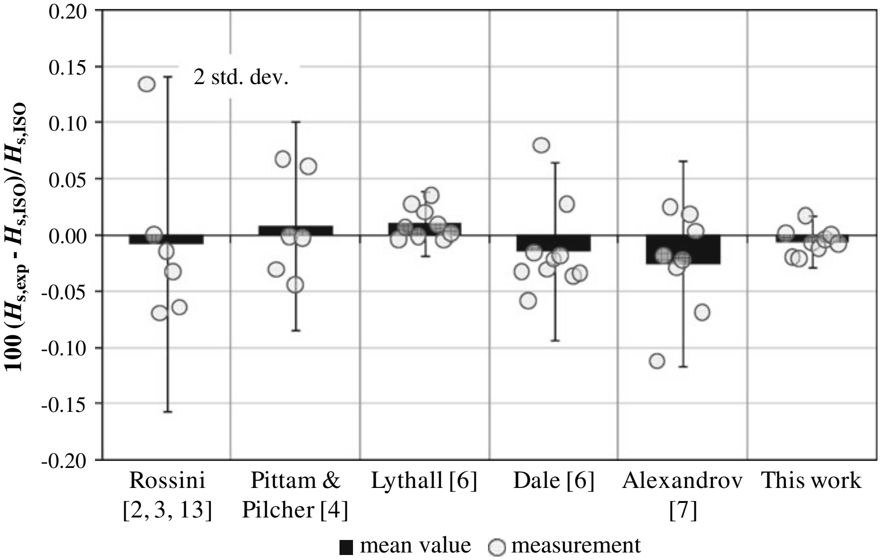

Fig. 7 Percentage deviations of measurements from ISO 6976 [1]

twice the standard deviation of the early measurements of Rossini [2,3] and Pittam and Pilcher [4] is significantly greater.

As described in Sect. 2, the above-mentioned authors use different methods for determining the mass of combusted gas (see Table 1). Under the GERG project, weighing is applied in combination with an analytical method for determining the uncombusted gas quantity (IR analysis) as this is considered the most accurate method. For verification, small amounts of methane were released from the gas container in several offline experiments and the mass was determined both by direct weighing and by IR analysis as described in Sect. 3.4. The results of these experiments indicate some minor, but systematic differences which will be investigated in further tests. However, the differences are within the total uncertainty.

The GERG calorimeter design can basically also be used to determine the mass using the methods of the other authors, for example, of Rossini (water/methane mass balance) or Dale (long run/short run). For this project, these approaches were mainly intended to serve as an additional consistency check for validating the results obtained.

For an evaluation based on the method of Dale, additional short measurements were made in which an amount of approx. 0.1 g of methane was burnt. The evaluation of three measurement pairs (long run/short run) produced an average SCV which was approx. 0.04 % lower than the average value listed in column 7 of Table 2 and thus confirmed the value within the expected measurement uncertainty.

An evaluation using the Rossini method has not produced satisfactory results so far. The evaluation of the nine measurements made resulted in a standard deviation which is an order of magnitude greater than expected. It was assumed that very small quantities of water possibly diffuse from the thermostat to the fuel gas through a small leak in the calorimeter, thus influencing the quantity of water determined by weighing. However, this effect is negligible with respect to the water determination for the enthalpy correction (see Sect. 3.5).

6 Measurement Uncertainty

Two independent uncertainty analyses were made under the GERG project, one by PTB and one by LNE. Considering the complexity of the uncertainty consideration, the detailed calculation is to be published in a separate article. The uncertainty consideration by PTB was made with the GUM workbench [14]. LNE developed its own software for the uncertainty consideration and uses the raw data made available by PTB for its calculation. Both calculations confirm that the total uncertainty of a measurement is approximately 0.05 %.

As confirmed by the uncertainty analyses, determination of temperature ΔT_{ad} and, in particular, assumed correlations between ΔT_{ad} of the calibration run and the combustion run have a decisive influence on the total uncertainty. Another study is to investigate in more detail the correlation coefficient of $\Delta T_{\mathrm{ad,cal}}$ and $\Delta T_{\mathrm{ad,comb}}$. This might lead to a changed value for the total uncertainty.

The calculated measurement uncertainty of 0.05 % refers, for the time being, to a single measurement consisting of a calibration run and a combustion run. The uncertainty involved in the average value is reduced when several repeatability measurements are made, such as nine measurements in this case. This finding is also to be quantified more precisely in the study under way.

Acknowledgments The authors are grateful to all who have contributed to this work, especially to D. Hansen of PTB for his contribution to the experimental work and to M. Hartmann of PTB for his support in the setup of the calorimeter.

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