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REALISATION OF A MASS FLOW MEASUREMENT DEVICE FOR A NEW REFERENCE GAS CALORIMETER

P. Ulbig[1], A. Benito[2], P. L. Cremonesi[3], J.-R. Filtz[4], R. Forster[5], F. Haloua[4], B. Hay[4], M. Jaeschke[5], S. Loubat[6], S. Sarge[1], and P. Wenz[1]

[1]*Physikalisch-Technische Bundesanstalt*
[2]*Enagas*
[3]*Snam Rete Gas*
[4]*Bureau National de Métrologie, Laboratoire National D'Essais*
[5]*Ruhrgas AG*
[6]*Gaz de France*

1. Introduction

As to fossil energy sources, gas consumption has still the strongest growth rate and has more than doubled world-wide since 1973. In 1999, the production and consumption of gas amounted globally to 2,2 billions of cubic metres. According to estimates of the World Gas Association, gas consumption will increase by an annual rate of 2,3 % until 2030 [1].

In view of the wide growing global demand for natural gas and the liberalisation of the gas market in Europe, the measurement accuracy is of decisive importance when determining the calorific value to ensure transparency on the European gas market. At the moment, however, only a few research institutes all over the world are able to determine the calorific value of gases with an expanded measurement uncertainty <0,2%. This applies not only to the determination of the calorific values of pure gases but also to the determination of the calorific value of synthetic and natural gas mixtures.

The reference values for the different components of natural gas as laid down in the standard ISO 6976 [2] are based on measurements which were taken more than 50 years ago. From today's view, for example for the measurements of methane, an uncertainty of 0,12 % has to be assumed.

Therefore, a study by the project name "Feasibility study for the design of a reference calorimeter" [3] was carried out by GERG (Groupe Européen de Recherches Gazières). Its purpose was to analyse from today's state of the art the possibility of determining the calorific value of gases with an expanded measurement uncertainty <0,05 %. In this study, different ways to determine the calorific value of gases by calorimetry were analysed. This meant in particular that different calorimeter systems were compared to one another by way of an uncertainty analysis. It could be shown that the aim to determine the calorific value with an expanded measurement uncertainty <0,05 % seems to be achieved best with the Rossini calorimeter [4]. The suggestion developed in the feasibility study also included a list of the different components needed for the periphery of the Rossini calorimeter as shown in Fig. 1. In this paper, details of the Rossini calorimeter, and the mass resp. mass flow determination system, will be described.

2. Purpose of the GERG project

A GERG (Groupe Européen de Recherches Gazières) project was set up to develop the new reference calorimeter for gas mixtures based on the principle of the Rossini-type calorimeter. An important objective of the project is to demonstrate that the new reference calorimeter allows determining the superior calorific value of pure gases and gas mixtures at 298,15 K with an uncertainty of less than 0,05 % at a 95% confidence level (two standard deviations). The working range of the calorimeter will be 39 kJ/g to 56 kJ/g on a mass basis or approximately 32 MJ/m^3 to 48 MJ/m^3 on a volumetric basis. The calorimeter will be designed for natural gases (mixtures of aliphatics, aromatics, olefins, inert gases, nitrogen (up to 15 %) and carbon dioxide (10 %), for synthetic natural gases (mixtures with up to 11 components) and for pure components (methane, ethane, propane and butane).

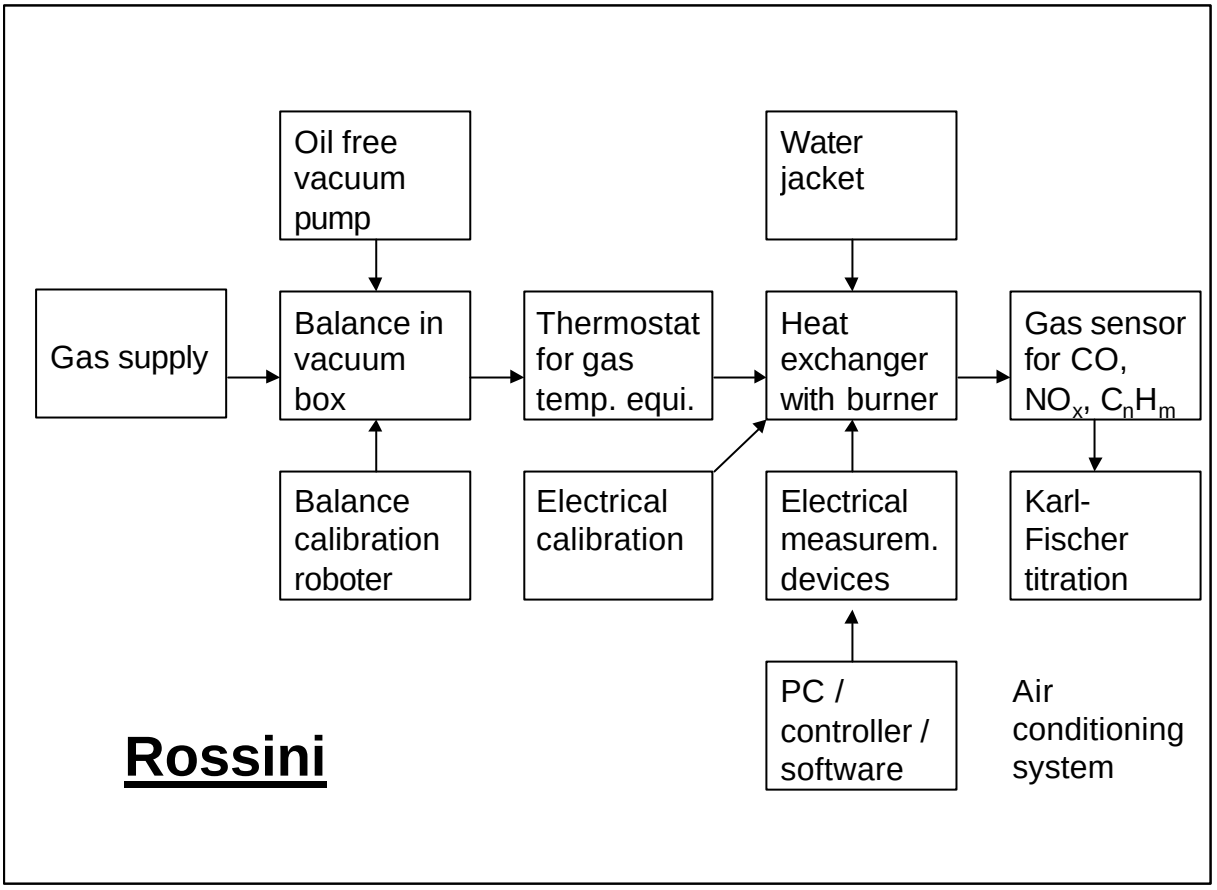

Fig. 1: Planned Rossini calorimeter including periphery

The project will provide the basis for measuring the calorific value of natural gases, C_2^+ components and pure gases in a comprehensible way. It will be the only instrument offering the possibility to verify calorific values by way of a traceability chain. The target uncertainty of 0,05 % is much smaller than the uncertainty of approximately 0,2% achieved today under optimal laboratory conditions (see Fig. 2).

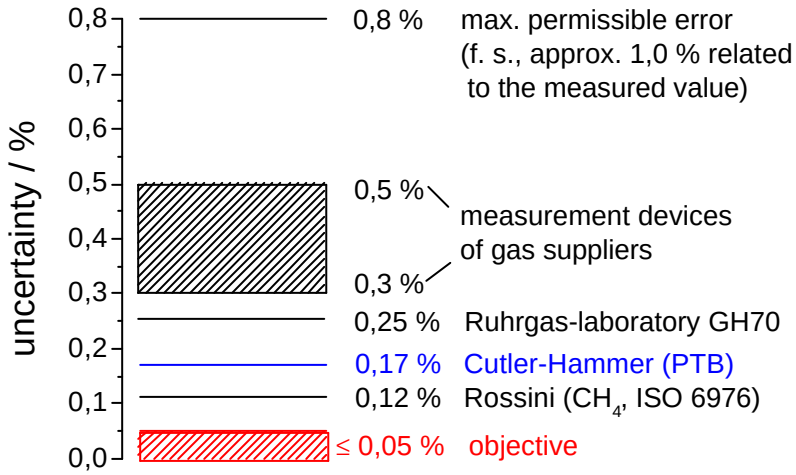

Fig. 2: Uncertainties of the calorific value for different measurement devices

This allows calibration of direct or indirect combustion calorimeters and inferential measuring methods such as process and laboratory gas chromatographs or other correlative methods for use in the laboratory or field. Therefore, an important benefit of this project is that it will reduce the uncertainty of these instruments quite significantly and optimise their use for gas billing.

In view of the great economic importance of natural gas, the availability of a reference calorimeter is long overdue. Particularly in cases of dispute, a calorimeter of this kind would allow determining the correct calorific value of a natural gas quality in custody transfer. This would help to avoid the lengthy discussions otherwise possible. With the liberalisation of the European gas market, calorific value measurement is set to play an increasingly important role because of a rising variety of gas qualities. It is expected that feeding biogas or landfill gas into pipeline systems will make the situation even more difficult.

From the metrological point of view a reference calorimeter is the only instrument that offers the possibility to verify calorific values by way of a traceability chain. An international comparison involving Office of Gas and Electricity Markets (OfGEM), UK, Physikalisch-Technische Bundesanstalt (PTB), D, Laboratoire National D'Essais (LNE), F, and Mendelejew All-Russian Research Institute for Metrology, RUS, is intended and will enhance and support the international acceptance and traceability of the new reference calorimeter.

The working group decided to develop the new reference calorimeter on the basis of the Rossini method, which has proven successful in the past. The project is parcelled in two steps: part 1 "Development of a reference calorimeter", and part 2 "Demonstration of measurement uncertainty". The reference calorimeter is being developed by PTB. Following completion of the project, Ruhrgas will apply for the reference calorimeter the accreditation by the Deutsche Kalibrierdienst (DKD, i.e. German Calibration Service). There is a multilateral agreement on the mutual recognition of their calibration certificates by sixteen national calibration services of the 25 European countries being member of EAL (European Co-operation for Accreditation of Laboratories). The calorimeter located in the DKD calibration laboratory will be operated jointly by all companies involved in the project. It is expected that the development of the calorimeter is completed by the end of 2003 and the uncertainty of the calorimeter has been proven through measurements on pure gas and gas mixtures by the end of 2005.

3. Concept of a new reference calorimeter

The Rossini-type calorimeter is a configuration in which the gas energy released during combustion raises the temperature of a water jacket around a burner. The calorific value of the gas is determined by analysing the temperature curve, the mass of the gas and the energetic equivalent determined by electrical calibration [5].

The gas is supplied to a balance where the amount of gas used for combustion is weighed. To avoid buoyancy corrections in the weighing result, this balance is placed in a vacuum chamber which can be evacuated to a pressure of 1 mbar. A calibration roboter allows the traceability of the determined weighing results to the national standard of mass. For the calculation of the calorific value, the determination of the mass of gas being burnt is of great importance, in addition, from the indication of mass versus time the mass flow can be calculated.

The gas is fed to the burner which is placed in a calorimeter. The heat of combustion is measured by a temperature increase in the calorimeter. For this purpose, the temperature-time curve recorded is divided in three parts (s. Fig. 3):

- The fore period, starting in the calorimeter as soon as the temperature changes linearly with time.
- The main period, starting at the time of heat release due to reaction or electric calibration.
- The after period, starting when heat development ends and the temperature is in equilibrium and linearly changes with time as in the fore period.

In order to determine the adiabatic temperature rise (ΔT_{ad}), the method of the fitting area which can be traced back to Regnault-Pfaundler [6], is used. The fore period is extrapolated forward and the after period backwards, until both triangle areas $A1$ and $A2$ are the same. The area conformity can be determined by numerical or graphic integration.

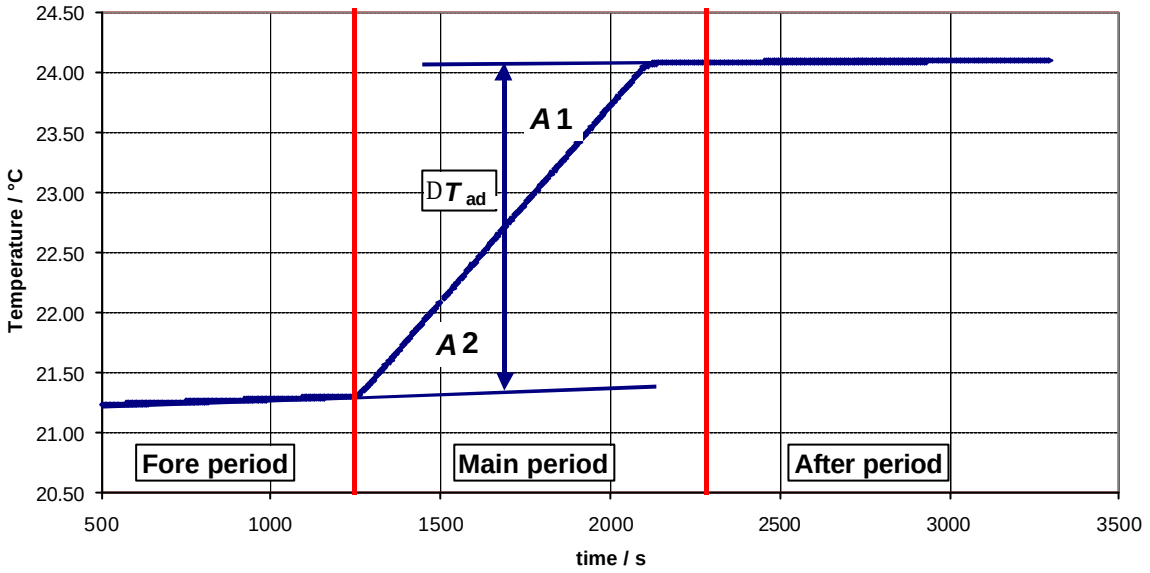

Fig. 3: Temperature-time curve in a calorimetric experiment

Multiplying this temperature rise by the energy equivalent of the calorimeter gives the amount of energy liberated in the reaction. The determination of the energy equivalent of the calorimeter calibration is done by a calibration heater, which causes the same temperature increase as in the calorimetric experiment. This allows the traceability of the measured calorific value of the burnt gas.

By means of the electric calibration of the reference gas calorimeter the energy supplied to the calorimeter can be calculated from the temperature increase measured during test. Here, by means of the measurement of the electric quantities current and voltage using traced back calibrated measuring assemblies the determined calorific value of the gas can be traced back to the unit of the energy, the Joule.

The superior calorific value H_s can be calculated according to the following formula:

$$H_S = \frac{C_{cal} \cdot \Delta T_{ad} + K}{m_{gas}} \qquad (1)$$

Here, ΔT_{ad} is the adiabatic temperature difference, K the energy correction factor (firing power, vapour discharge, water accumulation etc), m_{gas} the mass of combusted gas, and C_{cal} the caloric equivalent.

This caloric equivalent is determined by calibration, in which the same energy amount is transferred to the calorimeter as in the reaction. For this purpose a calibration heating is radially fastened around the burner with a resistance of 50 Ohm (see Fig. 4). Its arrangement in the immediate vicinity of the burner ensures that the dimensional arrangement of the source of energy supply is the same during calibration and test.

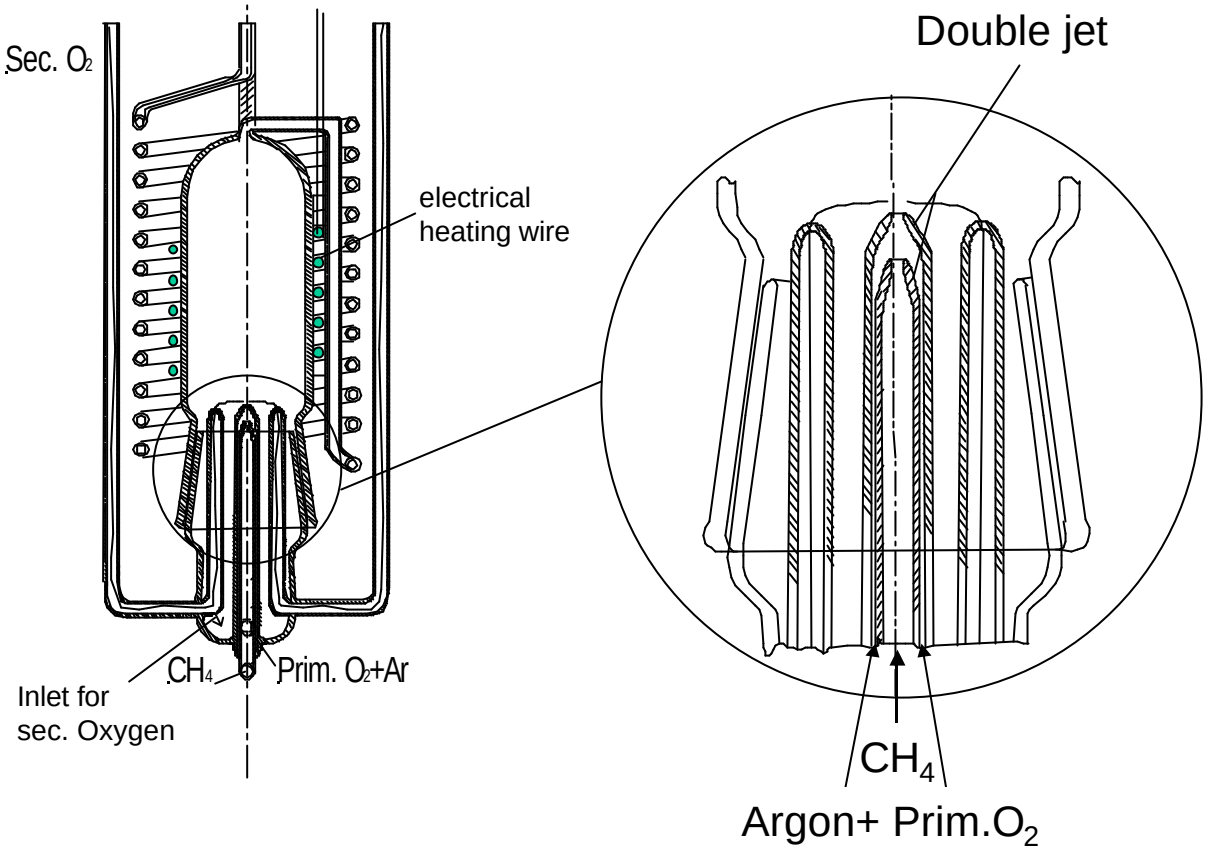

Fig. 4: Scheme of the burner and the electrical heating

Since the combustion of gases can be coupled with side reactions the efluent gases are analysed for the presence of residual hydrocarbons, carbon monoxide, water and nitrogen oxide.

4. Determination of the gas quantity and the mass flow

Already in the feasibility study, first thoughts were given to the development of a weighing device. Uncertainty calculations revealed that the influence of the air buoyancy leads to an increased uncertainty of the weighing results. When, on the other hand, the tests are carried out in an evacuated weighing chamber, the buoyancy of the air and the uncertainty of the weighing results can be minimised. On the basis of these findings, the following device was designed. The set-up (see Fig. 5) allows the comparison of measurements carried out under vacuum, in air or in another atmosphere, e. g. in nitrogen.

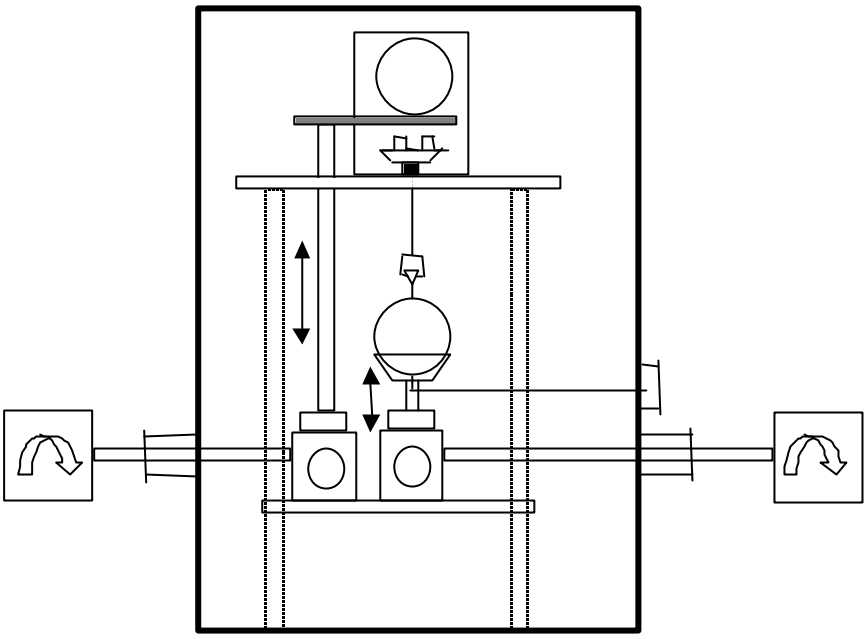

Fig. 5: Set-up of balance inside a vacuum chamber with motor driven coupling and calibration system

4.1 Flow chart of pipe systems and instruments

Figure 6 shows a scheme of the pipe system and the instruments of the apparatus. The fore-vacuum is generated by a rotary pump. Then, a fine vacuum (up to approx. 1 mbar) is generated by means of a turbomolecular pump.

The gas container is filled with the fuel gas via valve V102. Valve V101, with which the gas to the storage tank is shut off from the apparatus, has only a small dead volume. After the gas container has been filled, the pressure in the pipes through which the methane is flowing is approximately 30 bar. For the mass flow controller (FIC), it has to be reduced to a pressure range of 1,2 – 1,4 bar using a two-stage pressure reducer. The pressure of all other gases (argon, oxygen) is reduced to the necessary initial pressure by the pressure reducers of the gas bottle. Argon is used as rinsing gas and to stabilise the flame [7]. For this purpose, it is mixed with primary oxygen and supplied to the burner.

4.2 Balance

As weighing instrument, an analytical balance with a maximum loading capacity of 205 g, type Mettler AT 201, is used,. The resolution of the balance is 10 µg over the entire weighing range. It is modified for vacuum operation (Metrotec, Switzerland).

4.3 Gas container

The load of the balance is the limit value for the load which the gas container, including its necessary installations, is allowed to weigh. This requires that the size and the wall strength of the container be adapted to this maximum capacity. Furthermore, it must be possible to connect the container with the periphery of the device via a capillary. The working pressure in the gas container must overcome the pressure loss which builds up in the capillary so that the pressure necessary to keep the fuel gas streaming is guaranteed. For the capillary used (with an inside diameter of d=0,11 mm and a length of l=0,1m), this pressure loss is $p_{loss} \approx 4$ bar.

Bearing in mind the wall thickness which is necessary to resist the pressure, the ideal shape for the container is spherical, so the gas container was made of two shells welded together at the equator. The material is a high-strength special steel. The wall thickness is 0,5 mm. A sphere of that kind was subjected to pressure resistance testing. A bursting pressure of p=158 bar was determined and the maximum allowable working pressure therefore limited to p=60 bar.

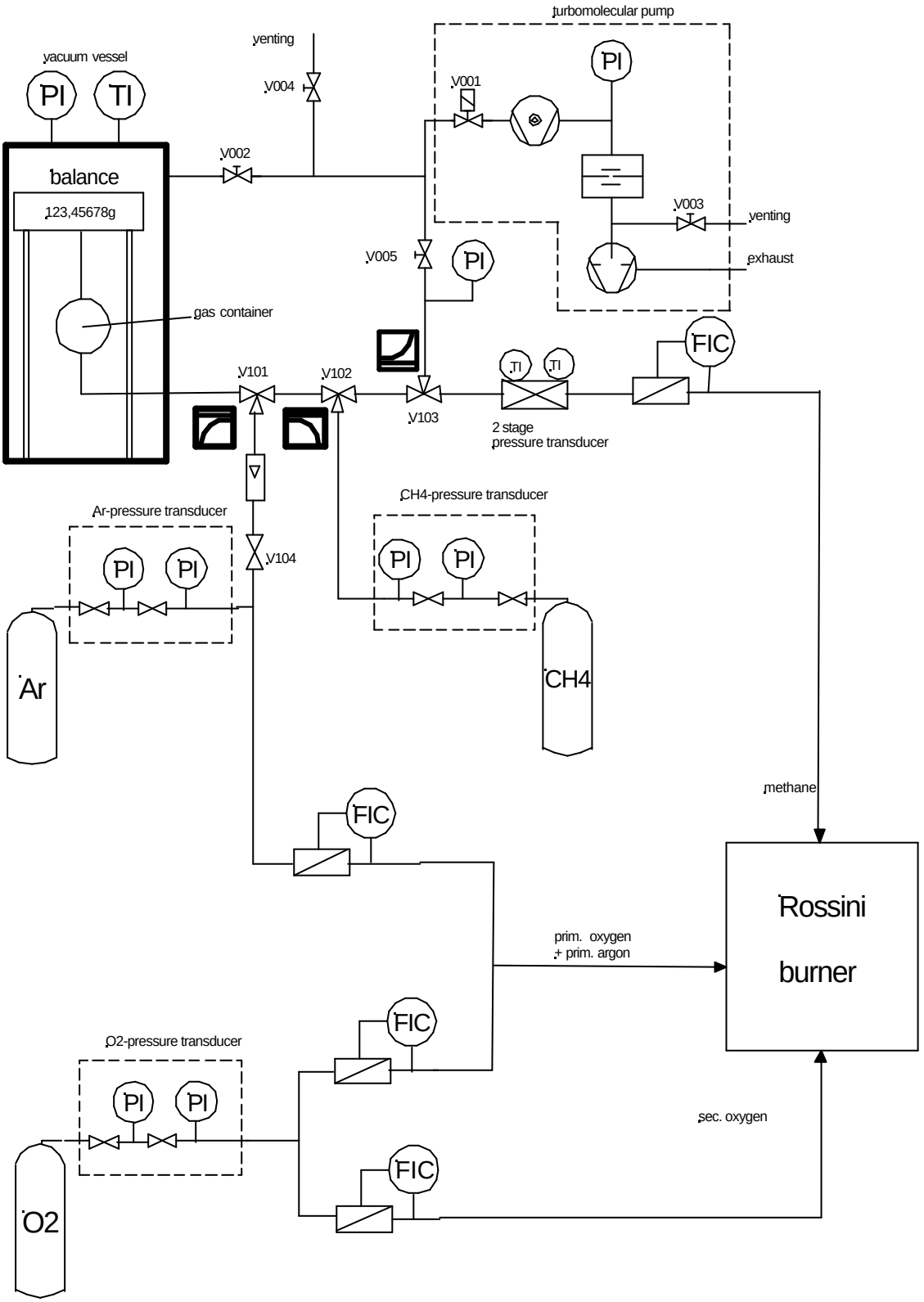

Fig. 6 : Piping concept of the Rossini calorimeter

4.4 Calibration robot and calibration mechanism

When determining a mass, calibrating the balance is the only way to trace the results back to the national mass standard. It is assumed that the correct value is realised by the weights which are

used for the calibration and whose mass is determined by comparison with the mass standards at the PTB Mass Laboratory.

The calibration unit consists of four calibration weights and one compensation weight, which may be a ring or a sphere. The masses and uncertainties of these weights were determined by comparison with the national standard. During the calibration process, these weights are sequentially placed on a ring which was specially developed for this purpose and is mounted on the load receptor of the balance. With such an arrangement, it is possible to carry out the experimental calibration of the apparatus described.

In detail, this arrangement allows different influence quantities to be determined in quantitative terms:

- determination of the standard deviation of a weighing result
- deviation of the measurement result from the characteristic curve of the balance
- determination of the resetting forces of the supply capillaries including hysteresis effects
- determination of the drift

The calibration weights consist of four weights whose masses are nominally identical and one weight with a greater mass which serves for dead load compensation. A coupling is provided for separating the load from the balance. To achieve separation, the container is lifted by an eccentric lifting device inside the vacuum container which is placed below the gas sphere. This lifting device is driven by a motor which is mounted outside the vacuum container and drives a shaft, so that the sphere holder is lifted until the coupling separates the load (gas container) from the balance.

For placing the weights, a second lifting device is provided which allows, by positioning with a step width of 0,1 mm, a step-by-step, millimetre-precise lowering of the guide fork. This is achieved by means of a second eccentric which is driven by a second motor to which the guide fork is mounted. In this way, sequential positioning of the weights is possible.

According to information from the balance manufacturer Mettler-Toledo, the position of the balance receptor changes in the micrometer range when a weight is placed on it, and the capillary is being deformed, i.e. an additional spring force acts on the balance. With the device here described it is possible to measure the resulting deviation of the weighing result by determining, with coupled-on container, a characteristic curve in the range of the weighing result to be determined. The deviation of the weighing result from the calibrated weights can thus be assigned to the systematic influence of the capillaries and corrected accordingly. The standard deviation can be determined by means of the calibration device both with coupled-on load and, for the balance alone, with decoupled load. Hysteresis effects caused by pressure-induced deflection of the capillaries, which itself acts as a force on the balance (spring-tube manometer effect), can be quantified by laying on the calibration weights several times, and included in the measurement result.

Before a test is carried out, the gas container is rinsed and evacuated several times by means of a turbomolecular pump. In pre-tests, the final pressure which can be reached in the gas container was determined. For a capillary with an inside diameter of d_i=0,11 mm, this is p=50 mbar. By alternately filling the container up to 60 bar (absolute) and evacuating it again, the mutual contamination of different gases in the gas container can be prevented. At the end of the filling procedure, the gas can be discharged and the mass flow can be obtained from the balance signal versus time.

After the gas has been discharged, the balance is loaded anew in a precisely defined range by placing on the substitution weights. This serves to substitute the gas mass which has been discharged. The drift of the balance can be determined by application of the compensation weight or at tare. Figure 7 shows the time sequence of the steps necessary for calibrating the balance and covering all influences. Here, the load which is composed by the mass of the gas container $m_{\text{gas-tank}}$, the mass of the gas m_{gas} and the additional mass of the fittings mounted to the balance $m_{\text{const.}}$ is denoted as G.

Example: $G = m_{\text{gas-tank}} + m_{\text{´gas}} + m_{\text{const.}} = 120\text{g}$

Tare Load: P = I+II+III=120g

Calibration weights: I=1g,II=1g III=118g,
IV=1g, V=1g

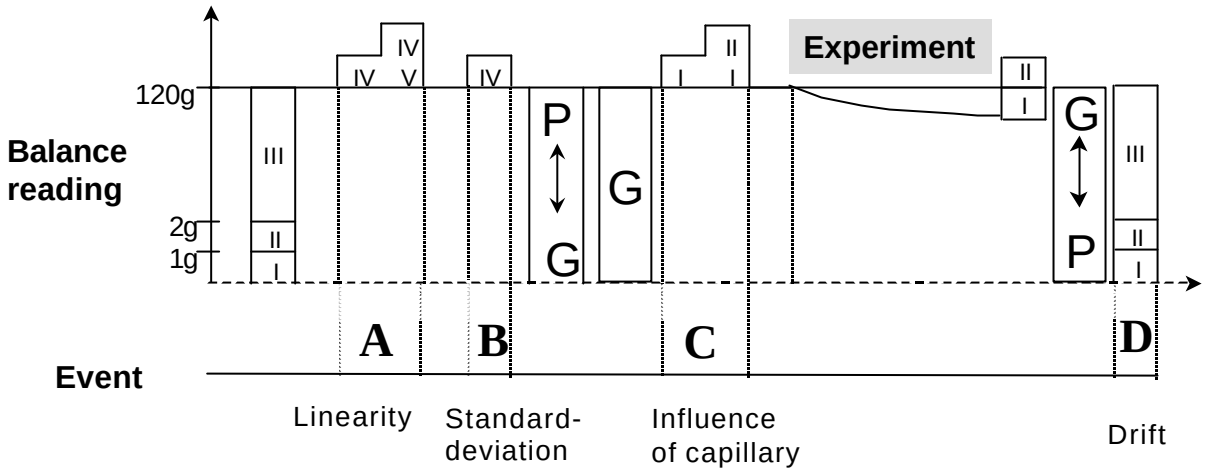

Fig. 7: Calibration scheme

It is the main advantage of dead weight compensation of the total mass of the weight attached to the balance that it offers the possibility of using the balance within a small dynamic range. This leads to a reduction of the standard deviation as the electromagnetic compensation system is permanently under strain. This could be shown by pre-tests with the balance described. The results of these tests are presented in Figures 8 and 9.

In the first test, a calibration weight with a conventional mass of 100 g was added several times. The weighing result is shown in Fig. 8. The standard deviation of this test series is 13 µg. In the second test (shown in Fig. 9), a dead weight of 100 g was placed on the load receptor of the balance, and a calibration weight with a conventional mass of 2 g added several times. Furthermore, the test was repeated without dead weight compensation.

It is obvious that in a small weighing range the weighing behaviour of the balance is better so that the standard deviation of the weighing results decreases. A strong change in the loading of the receptor induces a strong deflection of the weighing system. The higher the change in the load, the stronger the compensation the electromagnetic weighing system must bring about. When, however, care is taken for the balance to always work in loaded condition, a distinctly smaller standard deviation of 4,2 µg (at 100 g dead weight) and/or 5,2 µg without initial load is obtained. Furthermore, the drift is smaller, which can be seen from the fact that, when an initial load is applied, the measured values vary around the conventional mass of the calibration standard, whereas they show a strong drift when weighing 100 g in absolute terms.

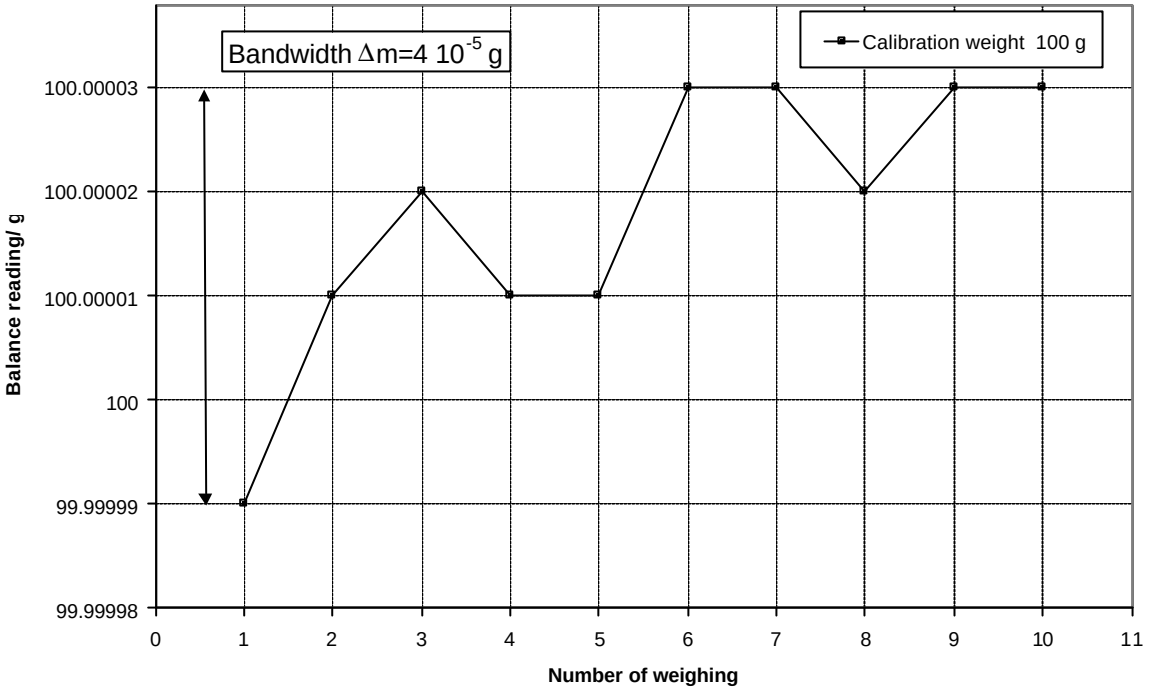

Fig. 8: Weighing of a calibration standard with a conventional mass of 100 g (Accuracy class E2)

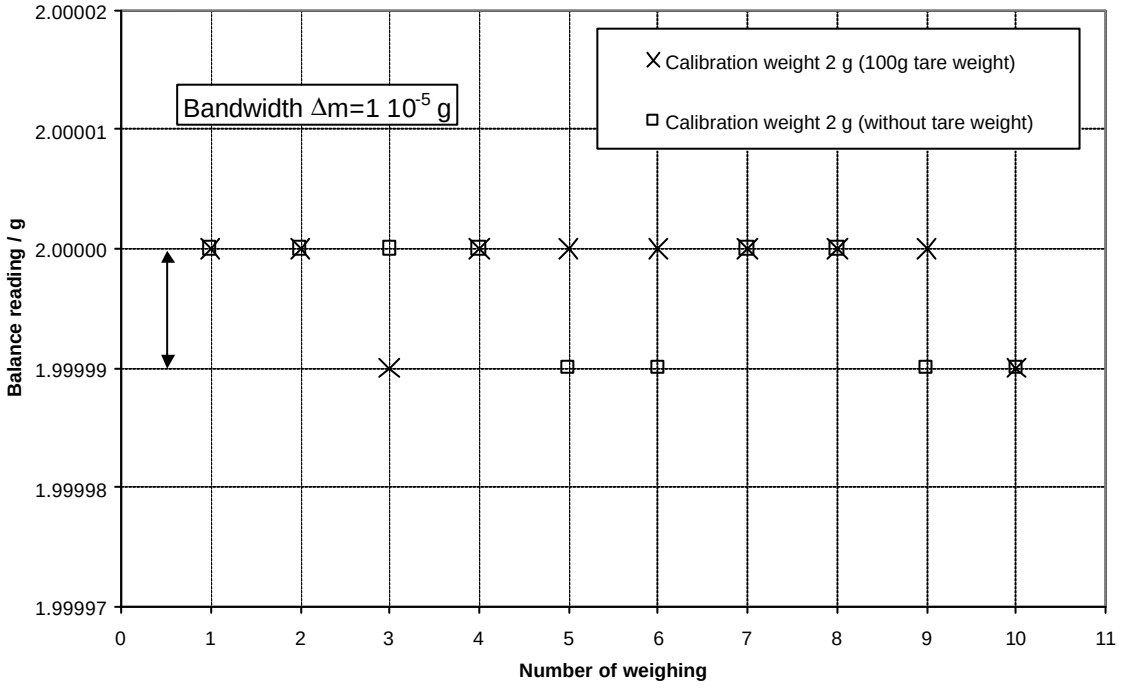

Fig. 9: Weighing of a calibration standard with a conventional mass of 2 g with and without dead weight (accuracy class E2)

It is another essential advantage of this procedure that the balance can be calibrated against calibration standards in the range of the gas mass to be discharged. The uncertainty of a weighing result is calculated according to [8].

$$u_{\mathrm{rel,w}} = 2 \cdot \sqrt{\frac{1}{m_{\mathrm{n}}^2} \cdot \left(s_{\mathrm{w}}^2 + \frac{d^2}{12} \right) + u_{m_{\mathrm{n}}}^2} \qquad (1)$$

So the relative uncertainty of a weighing result in the considered weighing range $u_{\mathrm{rel,w}}$ can be calculated from the standard deviation s_{w}, the variance of the rounding error of the digital indication with a division value of d for an assumed rectangular distribution, and the uncertainty of the mass standards $u_{\mathrm{m_n}}$.

When calculating the uncertainty for a calibration in the range of 2 g with a dead weight of 100 g, we obtain an absolute uncertainty of the weighing result of $u_{\mathrm{abs}}=2{,}6 \cdot 10^{-5}$ g. When, on the other hand, calibrating the balance in a weighing range of 100 g, we obtain the essentially higher value of $u_{\mathrm{abs}} = 1{,}04 \cdot 10^{-4}$ g for the absolute measurement uncertainty of the weighing result. In relation to the small absolute gas masses (in the range of 1 to 2 g only), these large weights entail a quadruplication of the uncertainty of a measurement result obtained by absolute weighing, therefore we have disregarded absolute weighing when developing the weighing procedure.

One of the questions arising when attempting to determine the gas mass by weighing is the impact the two load changes have on the calibration scheme. In this connection, [8] suggests to apply the dead weight in the weighing range one hour before calibration is carried out. For the calibration mechanism shown in Fig. 7 this means that the balance should be loaded with the dead weights (weights I+II+III) and/or the gas container long enough before the calibration weights are being placed.

4.5 Vacuum container

The weighing system is of modular design. It can be used under normal atmospheric conditions but it can also be mounted into a vacuum container so as to minimise the influence of air buoyancy.

In case of the latter solution, the stepping motors are mounted outside a vacuum bell via shafts, which ensures the heat development in the weighing space being reduced. The shafts are led through two vacuum ducts.

The vacuum bell can be thermostated by means of cooling spirals in the jacket so that working under precisely defined pressure and temperature conditions is also possible.

4.6 Uncertainty analysis of the weighing device and comparison with other measurement procedures based on weighing

In most cases, a physical value is not measured directly but is determined via a function of N different influence quantities. The uncertainty is calculated using a mathematical model for which the uncertainty contributions of the N different influence quantities have to be quantified. In accordance with the Gaussian error propagation law and with the *ISO Guide to the Expression of Uncertainty in Measurement* [9], the combined uncertainty of the physical value - here the mass of the gas m_{gas} having been discharged from the gas container during the calorimetric test - can be calculated according to the following equation.

$$u_{\mathrm{c}}^2(y) = \sum_{i=1}^{N} \left(\frac{\partial y}{\partial x_i} \right)^2 u^2(x_i) \qquad (2)$$

where y is the mass of the gas, calculated by way of the mathematical model via the input quantities x_i; $u_c(y)$ is the combined standard uncertainty of y; and $u(x_i)$ is the standard uncertainty of the input value x_i.

4.6.1 Uncertainty of the weighing system when operated in vacuum

The mathematical model for the determination of the gas mass m_{gas} is as follows:

$$m_{gas} = m_1 - (m_2 - m_{subst}) - m_r + m_{cap} + m_{drift} \quad (3)$$

In this equation, m_1 is the weight value at the beginning of the experiment, m_2 the weight value after gas discharge and substitution with m_{subst}, m_r the restoring force of the capillary, m_{cap} the gas mass which remains in the capillary and m_{drift} the zero point drift of the balance.

Due to the pressure difference in the capillary, part of the discharged gas mass is not accounted for by the balance, so a correction of the remaining gas mass is necessary. This part can be corrected for in the weighing result assuming ideal gas behaviour as an estimate.

$$m_{cap} = \frac{(p_1 - p_2) \cdot V_{cap} \cdot M}{R \cdot T} \quad (4)$$

In equation (4), p_1 and p_2 is the pressure in the capillary before and after the calorimetric experiment, V_{cap} the volume of the capillary, T the thermodynamic temperature, R the ideal gas constant and M the molecular mass of the gas. Under the usual test conditions, this correction is of the order of 30 µg.
The standard deviation of the balance was determined experimentally by means of an initial load of 100 g and a 2 g calibration weight with known uncertainty. The relative uncertainty of each weighing result in the calibrated weighing range could be determined by means of equation (1). The expanded measurement uncertainty (k=2) of 26 µg so obtained is assigned to the two weighings (m_1, m_2). The influence of the capillary was determined experimentally with a simplified set-up [3]. For a weight of 2 g, the systematic measurement deviation was m_r = 40 µg. The expanded measurement uncertainty was estimated at u_{m_r}=3,5·µg. The uncertainties of the other input quantities are listed in Table 1.

Table 1: Contribution of the different input quantities to uncertainty

Input quantity	Definition	Unit	Value	Expanded measurement uncertainty (k=2)
p_1	Pressure before calorimetric experiment	MPa	2,5	0,025
p_2	Pressure after calorimetric experiment	MPa	1,5	0,015
V_{cap}	Inner volume of capillary	m³	$1{,}4 \cdot 10^{-9}$	$1{,}4 \cdot 10^{-10}$
T	Thermodynamic temperature	K	298,15	2

The expanded relative measurement uncertainty (k=2) so obtained for 1 g of discharged gas is calculated at: $u_{rel,gas}$ = $5{,}8 \cdot 10^{-3}$ %. To illustrate the different uncertainty contributions, these are shown in Fig. 10.

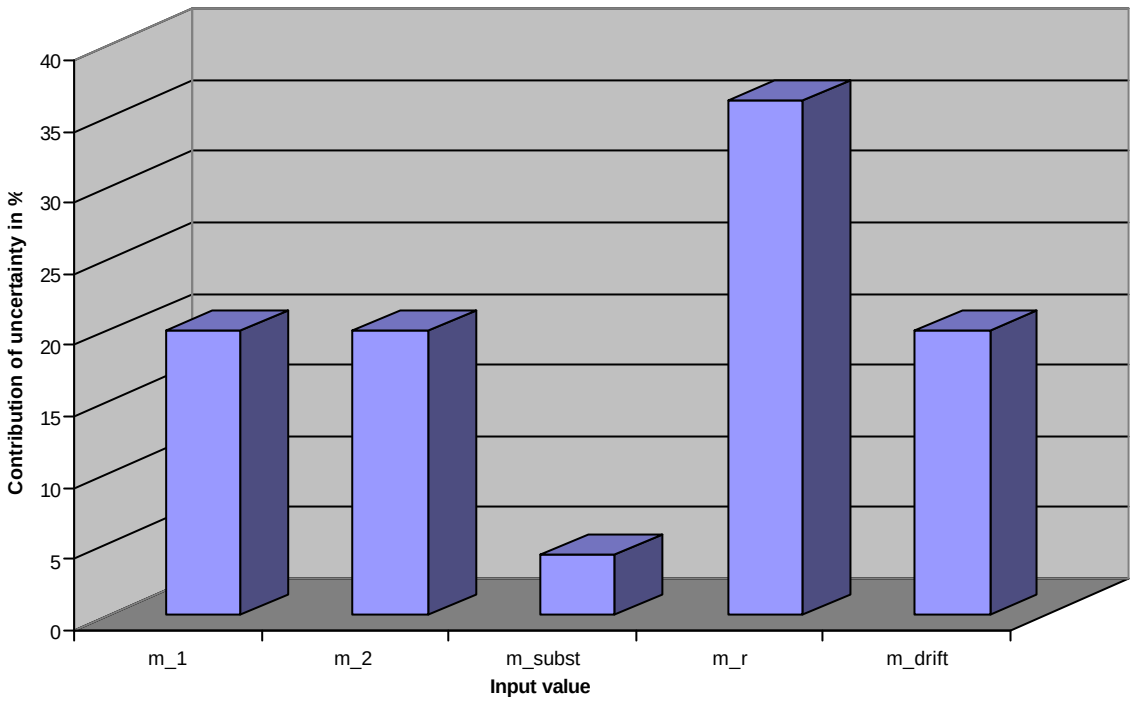

Fig. 10: Main quantities having an influence on the measurement uncertainty in the determination of the gas mass by weighing in vaccum

As can be clearly seen, the values measured by the balance (m_1, m_2, m_{Drift}) account for 60 % of the measurement uncertainty. As the uncertainty of the balance will not be any smaller in a test which is not carried out under calibration conditions, a reduction of this calculated measurement uncertainty seems improbable. Without carrying out precise experiments on the device examined it is difficult to assess the influence of the capillary. This value needs to be confirmed by experiments.

4.6.2 Uncertainty of the weighing device when operated in air

The measuring apparatus described also offers the possibility of weighing in air. The following model equation can be set up, neglecting the linear container expansion, i.e. with the volume of the container remaining constant:

$$m_{\text{gas}} = m_1 \cdot \left[1 + r_{air1} \cdot \frac{\left(\frac{1}{r_{c1}} - \frac{1}{r_n} \right)}{\left[1 - \left(\frac{r_{air1}}{r_{c1}} \right) \right]} \right] - m_2 \cdot \left[1 + r_{air\,2} \cdot \frac{\left(\frac{1}{r_{c2}} - \frac{1}{r_n} \right)}{\left[1 - \left(\frac{r_{air\,2}}{r_{c2}} \right) \right]} \right] - m_{\text{r}} + m_{\text{cap}} + m_{\text{drift}} \quad (5)$$

For the calculation of the vacuum masses, the weight values m_1 and m_2 are multiplied by the relevant air buoyancy correction factors [10]. Here, r_{n} is the density of the mass standard used for calibration, r_{c1} and r_{c2} the container density before and after the calorimetric experiment and r_{air1} and r_{air2} the air densities calculated by means of the physical measurands of temperature, pressure and humidity [11]. Table 2 shows, for an exemplary measurement, the input quantities temperature, density and humidity used to calculate the air density and the resulting measurement uncertainty for the air densities r_{air1}. and r_{air2}.

Table 2: Calculated air density at first weighing

Input quantity	Definition	Unit	Value	Expanded measurement uncertainty (k=2)
p_1	Atmospheric pressure at first weighing	MPa	0,101325	$3{,}00 \cdot 10^{-6}$
J_1	Temperature at first weighing	K	293,15	0,20
h_1	Relative humidity at first weighing	%	35,00	2
r_{air1}	Calculated air density 1	kg/m³	1,2008	0,00089

Table 3: Calculated air density at second weighing

Input quantity	Definition	Unit	Value	Expanded measurement uncertainty (k=2)
p_2	Atmospheric pressure at second weighing	MPa	0,103825	$3{,}00 \cdot 10^{-6}$
J_2	Temperature at second weighing	K	293,65	0,20
h_2	Relative humidity at second weighing	%	35,06	2
r_{air2}	Calculated air density 2	kg/m³	1,2283	0,00091

In Table 4, the other uncertainty contributions of the input quantities from equation (5) are listed.

Table 4: Density and uncertainty contributions of the different weights

Input quantity	Definition	Unit	Value	Expanded measurement uncertainty (k=2)
r_n	Density of mass standard	kg/m³	8000,00	150,00
r_{c1}	Container density before calorimetric experiment	kg/m³	559,70	0,0428
r_{c2}	Container density after calorimetric experiment	kg/m³	555,97	0,0426

As already described, the measurement uncertainty of the two weighing results (m_1, m_2) was determined at a value of 26 µg (k=2) from the calibration of the balance. For the calculations, the absolute amounts of m_r, m_{cap} with their uncertainty contributions were taken from 4.6.1. In this way, an expanded relative measurement uncertainty of $u_{rel,gas} = 32 \cdot 10^{-3}$ % results for 1 g of gas discharged from the container. Compared to the mass determination in the vacuum, this value is higher by the factor 5.

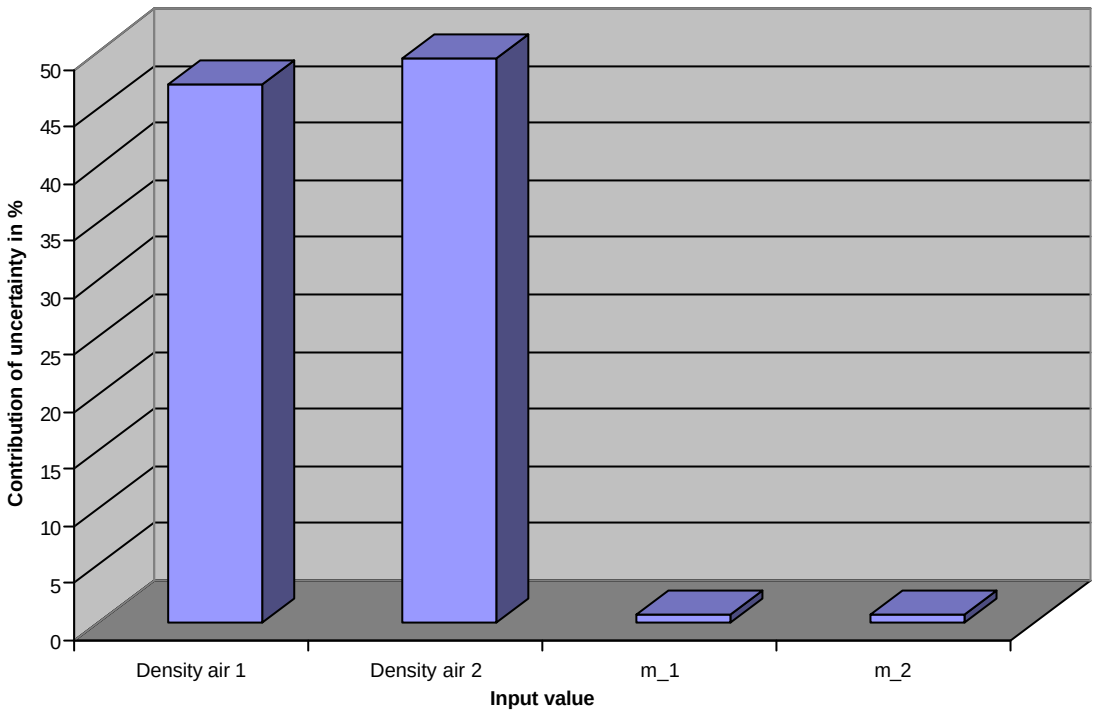

Fig. 11: Main quantities having an influence on the measurement uncertainty when determining the gas mass by weighing in air

Figure 11 shows the main quantities which have an influence on the measurement uncertainty of the gas mass determined. It is evident that weighing under atmospheric conditions with correction of the weighing results for air buoyancy is not helpful because the uncertainty in the calculation of the air density surpasses by far the uncertainty of the individual weighing results. The uncertainty in the calculation of the air density mainly derives from uncertainties in the measurement of the temperature and the air humidity.

4.6.3 Uncertainty analysis for difference weighing

Another possibility of determining the gas mass discharged from the container is the difference weighing of two containers of the same volume. The gas mass derives from the following equation:

$$m_{\text{gas}} = (m_{\text{g1}} - m_{\text{d1}}) - (m_{\text{g2}} - m_{\text{d2}}) - m_{\text{r}} + m_{\text{cap}} + m_{\text{drift}} \qquad (6)$$

In this equation, m_{g1} and m_{g2} are the masses of the gas container before and after the calorimetric experiment, whereas m_{d1} and m_{d2} are the masses of the reference container (dummy) before and after the experiment. In order to relate the measured weight values to the masses, the weighing results have to be corrected for air buoyancy as the container densities deviate from the densities of the mass standards used for calibration. For the discharged gas mass, it follows:

$$\begin{aligned} m_{\text{gas}} = &\left[\left(m_{\text{wg1}} + r_{air\,1}\cdot(V_{g1} - V_{ng1})\right) - \left(m_{\text{wd1}} + r_{air\,1}\cdot(V_{d1} - V_{nd1})\right)\right] - \\ &\left[\left(m_{\text{wg2}} + r_{air\,2}\cdot(V_{g2} - V_{ng2})\right) - \left(m_{\text{wd2}} + r_{air\,2}\cdot(V_{d2} - V_{nd2})\right)\right] - m_{\text{r}} + m_{\text{cap}} + m_{\text{drift}} \end{aligned} \qquad (7)$$

In this equation, m_{wg1} and m_{wg2} are the weight values of the gas container before and after the experiment, whereas m_{wd1} and m_{wd2} are the weight values of the substitution container before and after the experiment.

The buoyancy is allowed for in the calculation by means of the volume differences between the containers and the mass standards used for calibration ((V_{gi} – V_{ngi}) and/or (V_{di} - V_{ndi})). These volume differences are multiplied by the air density r_{airi} (i = 1 before the experiment; i = 2 after the experiment).

Difference weighing cannot, however, completely eliminate the deviations caused by the air buoyancy. As the balance has been calibrated with mass standards of 8000 kg/m³ density, each weight value m_W transmitted by the balance is allocated to a mass standard with the mass m_n.

For volume V_n of this mass standard, the following equation is valid:

$$V_n = \frac{m_n}{r_n} \tag{8}$$

As in equation (7) the weight value of the gas container changes and, accordingly, also the volume difference from the mass standard, it is not possible to mathematically eliminate the buoyancy component in the second weighing even if, in the first weighing, the masses and volumes of the two containers are identical. Therefore, with identical volumes and masses of the containers (in the first weighing), the result for the discharged gas mass is calculated according to the following formula:

$$m_{gas} = m_{wg1} - \left[m_{wg2} + r_{air2} \cdot (V_{nd2} - V_{ng2})\right] - m_r + m_{cap} + m_{drift} \tag{9}$$

With equation (8) and the weight values indicated, it follows:

$$m_{gas} = m_{wg1} - \left[m_{wg2} + r_{air2} \cdot \frac{(m_{wd2} - m_{wg2})}{r_n}\right] - m_r + m_{cap} + m_{drift} \tag{10}$$

Due to the identical masses of the container (in the first weighing) and of the dummy (in the second weighing) (m_{wd2}=m_{wg1}), it follows:

$$m_{gas} = (m_{wg1} - m_{wg2}) \cdot \left[1 - \frac{r_{air2}}{r_n}\right] - m_r + m_{cap} + m_{drift} \tag{11}$$

It is evident that for calculating the gas mass, the weight values have to be multiplied by a correction factor. To determine the uncertainty of a difference weighing, equation (7) was used as a mathematical model. The volumes of the mass standards were calculated by means of equation (8). As already described in 4.6.1, the measurement uncertainty of the four weighing results (m_{wg1}, m_{wg2}, m_{wd1}, m_{wd2}) was fixed at 26 µg, a value taken from the calibration of the balance. The measurement uncertainty of the air densities can be seen in Tables 2 and 3. The uncertainties of the other input quantities are summarised in Table 5.

Table 5: Uncertainty contributions of the different input quantities in difference weighing of two gas containers

Input quantity	Definition	Unit	Value	Expanded measurement uncertainty (k=2)
r_n	Density of mass standard	kg/m³	8000	150
V_{g1},V_{g2}	Volume of gas container before and after the experiment	m³	$268{,}00 \cdot 10^{-4}$	$1{,}0 \cdot 10^{-8}$
V_{d1},V_{d2}	Volume of dummy before and after the experiment	m³	$268{,}00 \cdot 10^{-4}$	$1{,}0 \cdot 10^{-8}$

An expanded measurement uncertainty of $u_{rel,gas}$ = 7,0·10^{-3} % is obtained. In this calculation, it was not however taken into account that due to the alternating placement, the weighing is equivalent to absolute weighing so that the standard deviation of the weighing results increases. When stating an uncertainty of 100 µg for the weighing results (m_{wg1}, m_{wg2}, m_{wd1}, m_{wd2}), a much greater uncertainty of $u_{rel,gas}$ =21·10^{-3} % derives.

4.6.4 Summary of the uncertainty analyses

The following conclusions can be drawn from the uncertainty analyses:

- The smallest measurement uncertainty for the determination of the gas mass discharged for the experiment: $u_{rel,gas}$ = 5,8·10^{-3} (k=2) is achieved by weighing in the vacuum (i.e. with air buoyancy corrections being eliminated).

- Absolute weighing with a computational correction for the air buoyancy leads only to insufficient results with regard to the measurement uncertainty: $u_{rel,gas}$=32·10^{-3}% (k=2). This possibility can therefore be ruled out for the determination of the gas mass.

- Comparison weighing, with a dummy of identical volume being weighed before and after the experiment, does not completely eliminate the air buoyancy but at least considerably reduces its influence. We have been able to show that, with an assumed small standard deviation of the balance, an uncertainty can be achieved which exceeds the value of the vacuum weighing by only 20 %: $u_{rel,gas}$ = 7·10^{-3} % (k=2). This method bears the advantage of reducing the experimental effort to a large extent.

4.7 Final uncertainty analysis

The experimental investigations have shown, that the experimental standard deviation of an attached gas container diverge from the values obtained by calibration experiments with mass standards under controlled conditions.

For the weighing of the gas container an experimental expanded measurement uncertainty (k=2) of 100 µg could be evaluated. This uncertainty includes the influence of the capillary. These results allow a reevaluation of the attainable expanded measurement uncertainty (k=2) for the described weighing device. Thus both weighing techniques, weighing under vacuum conditions and weighing with a difference gas container, can be finally compared as part of the relative uncertainty $u_{rel,gas}$ of the superior calorific value.

- For the determination of the burnt gas mass by weighing under vacuum conditions, the corresponding uncertainty of the weighing contributes with 0,014 % (k=2).

- For the determination of the burnt gas mass by weighing a difference gas container, the corresponding uncertainty of the weighing contributes with 0,021% (k=2).

It can be seen that the uncertainty of the gas mass determination under vaccum conditions has a smaller value, but finally it has to be seen by calculating the overall uncertainty of the reference calorimeter, if this uncertainty need to be obtained.

5. Conclusion

The detail planning of the reference gas calorimeter, supported by experimental investigations concerning the mass determination, was summarised with an extensive uncertainty analysis according to the “Guide to the Expression of Uncertainty in Measurement”. In contrast to the feasibility study carried out before starting this project, now the mass determination system is realised and the feasibility of this part was demonstrated. These results improve the basis of the

uncertainty calculations and make the results more reliable. In the very next future the influence of the gas capillary under working conditions has to be investigated

The scheduled system for the realisation of a mass flow resp. the very precise determination of the gas quantity gives chance to reach an overall uncertainty of the calorific value of <0,05 %.

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