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A Two-Sinker Densimeter for Accurate Measurements of the Density of Natural Gases at Standard Conditions

Markus Richter · Reiner Kleinrahm ·
Stefan Glos · Wolfgang Wagner · Roland Span ·
Peter Schley · Martin Uhrig

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Abstract A special reference densimeter has been developed for accurate measurements of densities of natural gases and multicomponent gas mixtures at standard conditions of temperature and pressure ($T_s = 273.15\,\mathrm{K}$ and $p_s = 0.101325\,\mathrm{MPa}$). The densimeter covers the range from $0.7\,\mathrm{kg\cdot m^{-3}}$ to $1.3\,\mathrm{kg\cdot m^{-3}}$; the total measurement uncertainty in density is 0.020 % (95 % level of confidence). The measurement principle used is the two-sinker method, which is based on the Archimedes buoyancy principle. The certified calibration laboratory of E.ON Ruhrgas AG, Germany, uses this densimeter to verify the standard densities of certified calibration gases (binary and multicomponent gas mixtures). Moreover, the densimeter is used to determine the compositions of commercially available binary gas mixtures with a small uncertainty of (0.01–0.03) mol%.

Keywords Calibration gas · Gas composition · Natural gas · Standard density · Two-sinker densimeter

1 Introduction

Large quantities of natural gas are transported through pipelines from suppliers to customers. For the billing of the quantity delivered, its energy must be determined

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M. Richter · R. Kleinrahm (✉) · W. Wagner · R. Span
Ruhr-Universität Bochum, 44780 Bochum, Germany
e-mail: Kleinrahm@thermo.rub.de

S. Glos
Siemens Energy, 45478 Mülheim an der Ruhr, Germany

P. Schley · M. Uhrig
E.ON Ruhrgas AG, 45117 Essen, Germany

very accurately. The energy of natural gas is the product of the volume at standard conditions ($T_\mathrm{s} = 273.15\,\mathrm{K}$, $p_\mathrm{s} = 0.101325\,\mathrm{MPa}$) and the superior calorific value (upper heating value) at standard conditions. The superior calorific value has been calculated in recent times by means of the gas composition, measured with process gas chromatographs (PGCs). In order to determine the volume at standard conditions, the volume flow and the density of the natural gas are measured at flowing conditions in natural gas meter runs and then converted to standard conditions by means of the density at standard conditions. Both the density at flowing conditions and the density at standard conditions are nowadays calculated from reliable equations of state for natural gases, namely, from the AGA8-92DC equation of state [1] or the GERG-2004 wide-range reference equation of state [2]. For this calculation, the composition of the natural gas is also required in addition to the temperature and pressure. Consequently, the accuracy of the composition of the natural gas, determined with PGCs, is very important for an accurate calculation of the delivered energy. Therefore, PGCs used in large natural gas meter runs have to be calibrated at regular time intervals with certified binary gas mixtures and synthetic natural gases.

In Germany, gas quality measurements in measurement plants relevant to fiscal metering are subject to official verification. For this reason, the PGCs used must first be calibrated with officially certified calibration gases. Accurate calibration gas determination is even more important as gas quality is usually measured in only one measurement plant considered representative of a great number of volume flow measurement plants or of an entire supply area. Therefore, the certified calibration laboratory of E.ON Ruhrgas AG certifies approximately 400 calibration gases annually, mainly for PGCs. The calibration gases are used throughout Germany in fiscal gas metering. These “third-order calibration gases” (working standards) are derived from highly accurate reference standards, the so-called second-order calibration gases (secondary standards) that are tested and certified in Germany by the Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und -prüfung, BAM) in Berlin. The third-order calibration gases are determined by a chromatographic comparative PGC measurement against a secondary standard of the Federal Institute for Materials Research and Testing. In order to confirm the measurement result, a comparative analysis with a laboratory GC and another check with a “direct” measurement method are additionally performed. For this purpose, the density of the calibration gas at standard conditions is measured very accurately, and the standard density, calculated by means of the analyzed gas composition, is compared with this reference value. The gas will not be certified officially as a third-order calibration gas until the check measurement has confirmed the results obtained with the PGC being within the permissible specified deviations. (The deviation of the calculated standard density from the measured value should not be greater than 0.02 % to 0.05 %.)

With this background, a special reference densimeter has been developed for very accurate measurements of the densities of natural gases and multicomponent gas mixtures at standard conditions. For binary gas mixtures, it is also possible to determine the composition of the gases from the measurements with high accuracy. The densimeter was developed for E.ON Ruhrgas AG at the Chair of Thermodynamics of the Ruhr University Bochum, Germany in 2002 and 2003 [3,4], and it was improved and updated in 2008 and 2009. The measurement principle used is the two-sinker method, which is based on the Archimedes buoyancy principle. The article describes the reference densimeter and presents some typical measurement results.

2 Densimeter Design

Figure 1 shows a photo of the reference densimeter. It consists of the measuring device, a 48 cm (19 in) rack, an aluminum base frame (140 cm wide, 70 cm high), a pressure regulator, a small liquid circulation thermostat, and a diaphragm vacuum pump. The gas cylinder with the sample gas is located to the right of the apparatus; it is connected to the two-stage pressure regulator of the apparatus via a small stainless steel tube.

The measuring device is accommodated in a thin-walled cylinder made of PVC (polyvinyl chloride). The electronic balance used for the density measurement is installed above the cylinder in an aluminum case. The design of the measuring device and the density measurement method applied are described in the next section. Seven diaphragm valves and two flowmeters are installed on the front of the measuring device, which are used, for example, for admitting the sample gas and for controlled

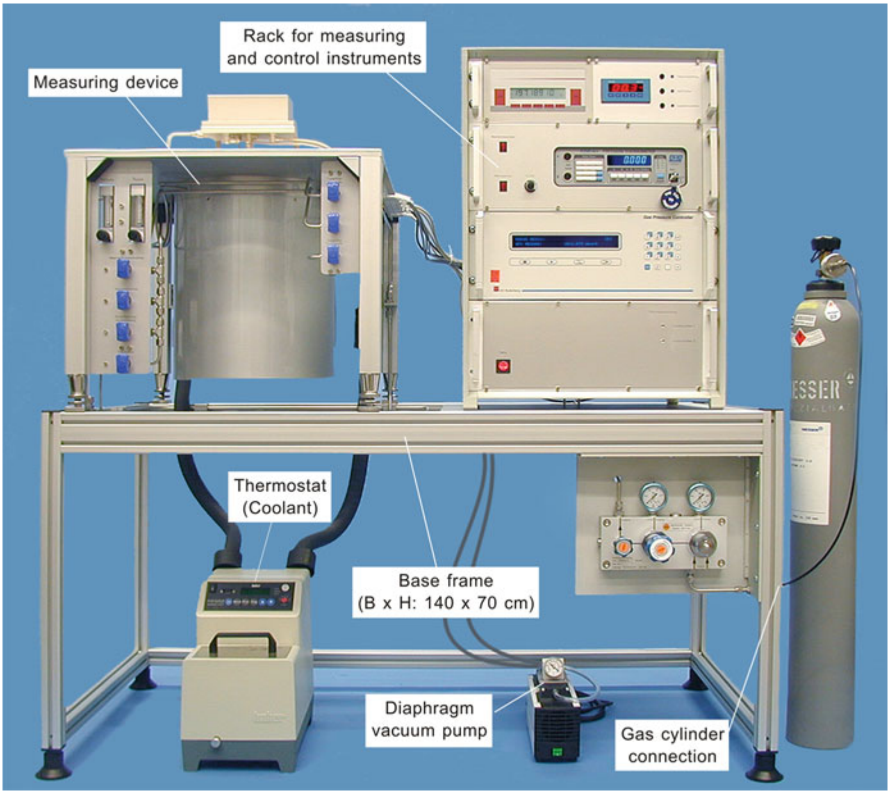

Fig. 1 Photo of the two-sinker reference densimeter

flushing of the device with sample gas. The diaphragm valves and flowmeters are connected to the pressure regulator and to the measuring device via small stainless steel tubes. A membrane-type filter is installed within the connection tube from the pressure reducer to the valves. In this way, the measuring device is protected if a gas sample is slightly contaminated with oil. On the right of the measuring device, the 48 cm (19 in) rack houses the required measuring instruments and control devices of the apparatus (temperature measurement unit, pressure measurement unit, pressure control unit, electronic balance display, power control unit for the electric heater of the measuring cell, control unit for stepper motor to change the two sinkers in the measuring cell, etc.). The liquid circulation thermostat is located below the measuring device and serves to control the temperature of the measuring cell (see Sect. 3.1). The measuring cell can be evacuated, if required, with the diaphragm vacuum pump on the right. The photo does not include the PC which serves to virtually fully automate the measurements (see Sect. 4).

3 Measuring Device

3.1 Design of the Measuring Device

The basic design of the measuring device is shown schematically in Fig. 2. The device consists of a measuring cell, the measuring-cell plate, a protection shield, a ring thermostat, an outer insulation cylinder (360 mm diameter, 420 mm height, made of PVC), and an electronic balance in an aluminum case above the base plate. The measuring cell, filled with the gas to be measured, includes two sinkers that serve to measure the density of the gas. The principle of the density measurement is explained in Sect. 3.2. The direction of gas flow to the measuring cell is indicated by arrows in the figure. This is explained in more detail in Sect. 4.

In order to control the temperature of the measuring cell, a cooling liquid (a mixture of ethylene glycol and water) flows through the copper ring thermostat, where the cooling liquid temperature is controlled with a small circulation thermostat (Huber Ministat, Germany). As soon as the desired measuring-cell set-point temperature of $t_\mathrm{s} = 0\,^\circ\mathrm{C}$ is obtained, the coolant is admitted to the ring thermostat with a temperature of approximately $t = -1\,^\circ\mathrm{C}$. The measuring-cell plate as well as the measuring cell, with the protection shield which is screwed firmly to the measuring-cell plate, can be adjusted quickly to the desired set-point temperature with an electric heater (50 W rating, approximately 7 W at steady-state conditions) attached to the copper ring. The space between the outer PVC cylinder and the protection shield, as well as between the base plate and the measuring-cell plate, is insulated with foamed plastic to reduce heat flow from the environment to the measuring cell. The aluminum protection shield conducts the major part of the remaining low heat flow of approximately 6 W directly into the copper measuring-cell plate. With this temperature control concept, the measuring cell and the measuring-cell plate are almost adiabatic and, in connection with the high thermal conductivity of the measuring cell material (copper, $\lambda > 350\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$), the temperature gradient along the measuring cell is very low (see below).

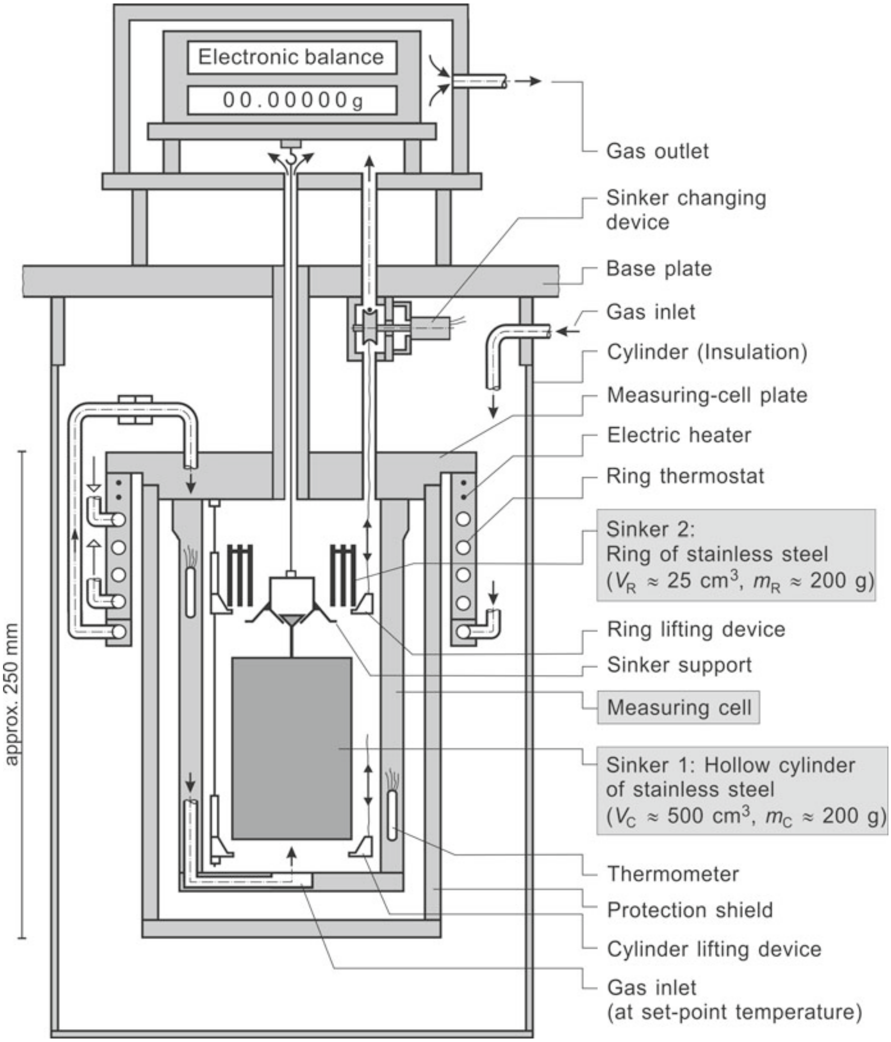

Fig. 2 Basic design of the measuring device. The gas flow through the densimeter is indicated by arrows (➞), and the cooling liquid flow through the ring thermostat is also indicated by arrows (⟶▷)

The temperature of the measuring cell is determined with two accurate Pt-100 Ω platinum resistance thermometers (main measurement and check measurement) in conjunction with a resistance-measuring bridge (ASL F250, UK). In order to control the temperature of the measuring cell, the voltage of the electric heater in the ring thermostat is controlled with an AC controller (0 V to 36 V). The input signal to the controller is calculated by means of the PC of the measuring device using a PI algorithm (proportional plus integral controller). The temperature variations of the measuring cell over time are ±2 mK in a steady-state condition. The total uncertainty in temperature at $t = 0$ °C is 15 mK (expanded uncertainty, $k = 2$), including variations over time and local gradients.

During a measurement, the pressure of the test gas in the measuring cell and in the entire measuring device is adjusted very quickly to the desired set-point value of $p_\mathrm{s} = 0.101325\,\mathrm{MPa}$ and then kept constant by means of a pneumatic pressure controller (DH-Instruments PPC3, USA). The pressure controller is connected to the measuring device via two tubes. The pressure variations over time are ±2 Pa. Two very accurate pressure sensors are used to measure the pressure. A Digiquartz sensor from Paroscientific is used for the main measurement, and it also serves for pressure control. A sensor from Mensor (Model 6100) is used for the check measurement. The uncertainty in the pressure measurement is 5 Pa ($k = 2$) at $p_\mathrm{s} = 0.101325\,\mathrm{MPa}$.

3.2 Density Measurement Principle

The density measurement principle applied is that of "two-sinker method." The method was developed by the Chair of Thermodynamics of Ruhr University Bochum, Germany, in the early 1980s [5,6]; the current status of development is described in two more recent articles [7,8]. This density measuring method also forms the basis of the certified precision gas densimeter [9] of E.ON Ruhrgas AG. The density measurement principle is explained in the following as shown in Fig. 2. (Annotation: In contrast to the earlier densimeters [5–9] of our group, we did not need a magnetic suspension coupling in the present case. Here, the measuring cell and the balance case could be directly connected via a tube, see Fig. 2, because the pressure is only about 0.1 MPa and the balance case is at ambient temperature. Moreover, the temperature of the gas in the measuring cell is always lower than the temperature of the same gas in the balance case. Hence, gas convection between the balance case and the measuring cell does not occur.)

The two-sinker method is based on the Archimedes buoyancy principle which is applied in a special way as a differential method [5–9]. Instead of the usual single sinker, two sinkers are used that are specially matched to each other. In the case of the densimeter described here, one sinker is a relatively large hollow cylinder made of stainless steel ($V_\mathrm{C} \approx 500\,\mathrm{cm}^3$; $\rho_\mathrm{C} \approx 0.40\,\mathrm{g \cdot cm^{-3}}$; $m_\mathrm{C} \approx 200\,\mathrm{g}$; gold-plated surface), and the other is a triple ring also made of stainless steel ($V_\mathrm{R} \approx 25\,\mathrm{cm}^3$; $\rho_\mathrm{R} \approx 8.00\,\mathrm{g \cdot cm^{-3}}$; $m_\mathrm{R} \approx 200\,\mathrm{g}$; gold-plated surface). Both sinkers have identical masses, virtually identical surface areas ($A \approx 360\,\mathrm{cm}^2$) and identical surface materials; however, their volumes differ considerably ($V_\mathrm{D} = V_\mathrm{C} - V_\mathrm{R} \approx 475\,\mathrm{cm}^3$). Each of the two sinkers can be placed on a sinker support or lifted from it (see Fig. 2). The sinker support is connected to an electronic balance via a small rod. A special sinker changing device is used to change the two sinkers. The device is fitted to the underside of the base plate of the measuring device. It consists of a small stepper motor connected to a pulley (20 mm diameter) that can be rotated through ±45°. A thin coated stainless steel wire is fitted to the pulley, and the two ends of the wire are introduced vertically into the measuring cell through two small tubes. There, the wire ends are connected to the two sinker lifting devices. The two sinker lifting devices basically consist of two suitably designed stainless steel rings guided vertically in the measuring cell by means of two rods. The lifting height of each ring is 16 mm.

The basic design of the sinker lifting devices is schematically shown in Fig. 3. The real construction is much more complex. Basically, the sinker lifting unit is designed

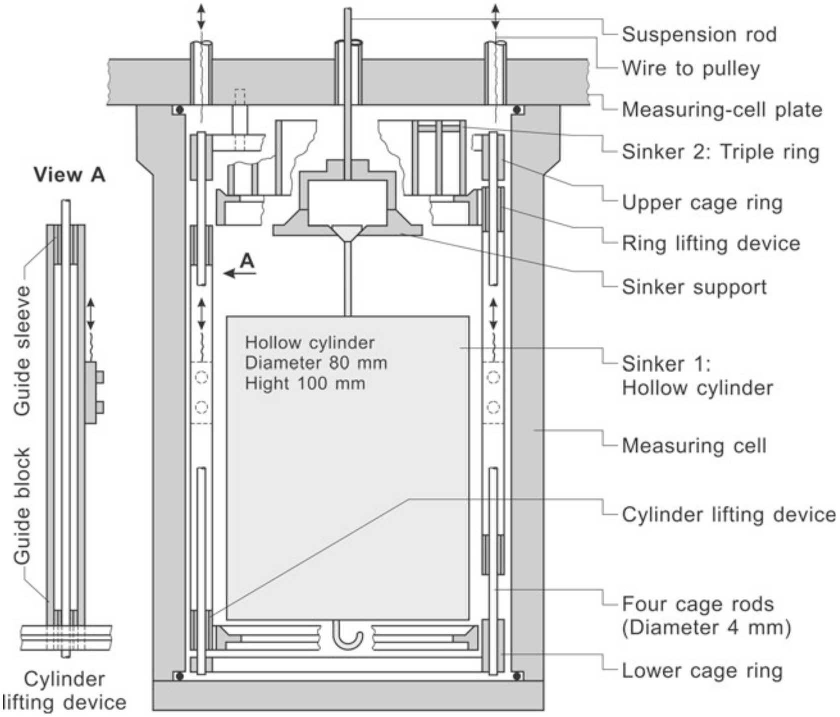

Fig. 3 Basic design of the sinker lifting devices in the measuring cell

like a cage. This cage consists of an upper and a lower cage ring which are connected by four rods, and the entire cage is attached to the measuring-cell plate. Each of the two sinker lifting devices consists of a horizontal ring that is connected with a vertical guide block about 135 mm in length. On the top and on the bottom of this guide block, two guide sleeves (10 mm high) are integrated. Each guide sleeve includes a small cylindrical tube (inner diameter 4.2 mm, outer diameter 5.0 mm). These thin tubes are made of PTFE (polytetrafluoroethylene, Teflon), because this material has a very small friction coefficient of only 0.04. In this way, the two lifting devices can smoothly glide up and down the cage rods. This design of sinker lifting devices have already been used for the earlier two-sinker densimeters [5–9] developed by our group.

It is very important that there is no magnetic interaction between the two sinkers and the sinker support, the cylinder lifting device, and the ring lifting device (see Fig. 3). Therefore, these components are made of suitable stainless steels that are as non-magnetic as possible. Otherwise, small magnetic forces between the sinkers and the sinker support or the sinker lifting devices can occur, and even small forces can cause elusive errors of several 0.01 mg in the weighing result of $m^{*}_{\mathrm{D,gas}}$ (see below). Moreover, these components were demagnetized before assembly by means of an alternating electrical field to eliminate any residual magnetism. It is important that the measuring device is also assembled with non-magnetic tools, because even slightly magnetic tools can again magnetize the stainless steel components of the measuring device.

In order to measure the density of a gas in the measuring cell, the two sinkers are alternately placed on and lifted from the sinker support. In this way, the difference in balance reading $m^*_{\mathrm{D,gas}}$ between the two sinkers, surrounded by the sample gas, can be measured very accurately by the electronic balance (Sartorius/Rubotherm, BP 211D model, 210 g weighing range, 0.01 mg resolution). The density of the gas in the measuring cell at standard conditions ($t_\mathrm{s} = 0\,°\mathrm{C}$, $p_\mathrm{s} = 0.101325\,\mathrm{MPa}$) can now be calculated by means of the simple equation:

$$\rho_\mathrm{s}(t_\mathrm{s}, p_\mathrm{s}) = \frac{m^*_{\mathrm{D,gas}} - m_\mathrm{D}}{V_\mathrm{D}(t_\mathrm{s}, p_\mathrm{s})}. \tag{1}$$

Here, $m_\mathrm{D} = (m_\mathrm{R} - m_\mathrm{C})$ is the difference in the masses of the two sinkers (subscripts: R = ring, C = cylinder, D = difference), $m^*_{\mathrm{D,gas}} = (m^*_{\mathrm{R,gas}} - m^*_{\mathrm{C,gas}})$ is the difference in the balance reading between the two sinkers when they are immersed in a sample gas, and $V_\mathrm{D}(t_\mathrm{s}, p_\mathrm{s}) = [V_\mathrm{C}(t_\mathrm{s}, p_\mathrm{s}) - V_\mathrm{R}(t_\mathrm{s}, p_\mathrm{s})]$ is the difference in the volumes of the two sinkers at standard conditions. The volumes of the two sinkers were calibrated[1] by the National Metrology Institute (PTB) in Braunschweig at $t = 4\,°\mathrm{C}$ and $t = 15\,°\mathrm{C}$; from this, the difference in volumes $V_\mathrm{D}(t_\mathrm{s}, p_\mathrm{s})$ can be calculated with an uncertainty of 0.003 % ($k = 2$). The difference in the masses of the two sinkers m_D, resulting from a minor production-inherent difference in masses of approximately −0.56 g, can be determined accurately and also simply checked (see Sect. 4), if required, by means of a reference measurement with methane.

In order to increase the accuracy of the measured value $m^*_{\mathrm{D,gas}}$, the two sinkers are exchanged and each sinker is connected to the balance 30 times during one measuring run (30 double changes, 60 measured values, over a period of about 24 min), and the statistical average is calculated. With a consistent application of the Archimedes principle as a differential method, all the interfering side effects that could affect measurement accuracy are compensated for automatically with this two-sinker density measurement method. Even the effect of gas adsorption on the sinker surfaces is approximately compensated for, because both sinkers have identical surface areas and identical surface materials (the surfaces were polished electrolytically and subsequently gold-plated) and, therefore, virtually the same mass of gas is adsorbed on both sinker surfaces. The uncertainty in the measured value $m^*_{\mathrm{D,gas}}$ is, therefore, relatively low and amounts to only 0.03 mg. For gas densities between $0.7\,\mathrm{kg \cdot m^{-3}}$ and $1.3\,\mathrm{kg \cdot m^{-3}}$, and a resulting measured value $(m^*_{\mathrm{D,gas}} - m_\mathrm{D})$ between 0.33 g and 0.62 g, this corresponds to a relative measurement uncertainty in density of between 0.005 % and 0.009 % ($k = 2$).

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[1] The volume calibration of the two sinkers were carried out by weighing them in air and in water using a hydrostatic balance. Since the density of the hollow cylinder ($\rho_\mathrm{C} \approx 0.40\,\mathrm{g \cdot cm^{-3}}$) is less than that of water, a small hook is integrated at the underside of this sinker (see Fig. 3). For the calibration of the cylinder in water, a specially produced calibration mass ($m_\mathrm{W} \approx 430\,\mathrm{g}$; $V_\mathrm{W} \approx 54\,\mathrm{cm^3}$; $\rho_\mathrm{W} \approx 7.96\,\mathrm{g \cdot cm^{-3}}$; diameter 60 mm; height 19 mm) with an integrated hook on its top side was suspended at the hook of the hollow cylinder. Hence, the combined density of the cylinder and the calibration mass was $\rho \approx 1.14\,\mathrm{g \cdot cm^{-3}}$ and larger than that of water.

4 Performance of Measurements

Depending on ambient temperature, approximately 1.5 h are required to put the reference densimeter into operation and reach the set-point temperature of $t_\mathrm{s} = 0\,^\circ\mathrm{C}$. In general, the device is operated in the stand-by mode with the measuring cell filled with methane at $p \approx 0.1$ MPa and controlled to maintain a temperature of $t_\mathrm{s} = 0\,^\circ\mathrm{C}$.

The balance must be calibrated before the measurements start. For this calibration, the balance case contains methane at a pressure of $p = 0.101325$ MPa and a temperature of $t \approx (21 \pm 3)\,^\circ\mathrm{C}$. The buoyancy effect of methane on the internal calibration masses of the balance is taken into account in an appropriate way. Next, the difference in the masses of the two sinkers is checked to ensure that it is within the permissible tolerance. For this check measurement, the density of methane at standard conditions ($t_\mathrm{s} = 0\,^\circ\mathrm{C}$, $p_\mathrm{s} = 0.101325$ MPa) is measured instead of the density of a sample gas (which will be explained in the following). The measurement result corresponds to the difference in the balance reading $m^*_{\mathrm{D,CH_4}} = (m^*_{\mathrm{R,CH_4}} - m^*_{\mathrm{C,CH_4}})$ of the sinkers in methane used as a reference gas. This value must agree within ± 0.02 mg with the calibrated and stored reference value $m^*_{\mathrm{D,CH_4}} = -0.215037$ g. If not, then it must be clarified why the deviation is greater (e.g., possible contamination of sinker surfaces). The difference in sinker masses $m_\mathrm{D} = (m_\mathrm{R} - m_\mathrm{C})$ can now be determined from the reference value $m^*_{\mathrm{D,CH_4}}$ and the standard density of methane $\rho_{\mathrm{s,CH_4}} = (0.71745 \pm 0.00006)\ \mathrm{kg \cdot m^{-3}}$ [10] (which is accurately known, see Sect. 5) by rearranging Eq. 1. As an alternative, Eq. 1 can also be rearranged as shown below to calculate the standard density of the sample gas:

$$\rho_\mathrm{s}(t_\mathrm{s}, p_\mathrm{s}) = \rho_{\mathrm{s,CH_4}} + \frac{m^*_{\mathrm{D,gas}} - m^*_{\mathrm{D,CH_4}}}{V_\mathrm{D}(t_\mathrm{s}, p_\mathrm{s})}. \tag{2}$$

With methane, the main component of natural gas, as the reference gas, the densimeter is intentionally calibrated at the standard density of pure methane as the “density reference point,” and this reference point can be checked quite easily.

In order to measure the standard density of a sample gas, the gas cylinder must be connected to the pressure regulator (approximately 0.25 bar gauge outlet pressure; see Fig. 1). Then, in a first step, the inlet tubes are flushed with the test gas via a bypass (for approximately 1 min at an approximately $2\ \mathrm{dm^3 \cdot min^{-1}}$ standard volume flow rate). It is not necessary to evacuate the measuring system for filling the measuring cell with the sample gas. Rather, it is sufficient to purge the measuring system adequately with the new sample gas at $p \approx 0.1$ MPa. For the first flushing cycle, the measuring cell (approximately $1.1\ \mathrm{dm^3}$ volume) is flushed at a standard volume flow rate of approximately $2\ \mathrm{dm^3 \cdot min^{-1}}$ over a period of approximately 4 min. For this purpose, the sample gas is passed into the measuring device via an inlet valve and a small stainless steel tube. Then, the sample gas is thermostated in the ring thermostat to a temperature of within approximately ± 1 K and, subsequently, in special inlet channels in the measuring-cell cylinder to a temperature of within approximately ± 5 mK from the measuring-cell set-point temperature of $t_\mathrm{s} = 0\,^\circ\mathrm{C}$. In Fig. 2, arrows are used to indicate gas flow. Once it has passed through the measuring cell, the sample gas is channeled to the balance case via the connecting tube which also accommodates the small rod connecting the sinker support in the measuring cell to the balance. From there, the gas is discharged to the waste gas line via a flowmeter. Approximately 15 min after the first purge cycle, the measuring cell must again be purged in the same way as described for the first flushing cycle. This is necessary to preclude any measurement errors resulting from desorption of the gas last measured from the inner surfaces of the measuring cell, as well as from diffusion of the gas from gaps or dead spaces in the measuring cell. Any desorption or diffusion effects could significantly distort gas composition and thus also the density measured for the new sample gas.

After the second purging cycle, pressure control can be started immediately. The density measurement can be started after a waiting period of approximately 15 min to allow for establishing thermal equilibrium in the measuring cell. Approximately 24 min are required for one measuring run. During this time, the two sinkers are alternated, and each sinker is connected to the electronic balance via the sinker support 30 times (30 double changes of the sinkers). The measured values are displayed continuously on the PC screen. Figure 4 shows, as an example, the online screen recorded for a natural gas standard density measurement. The upper chart plots the density values measured and a comparison density while the chart below plots the deviations from temperature and pressure set points. Both charts are plotted over a measurement period of approximately 24 min (abscissa). The density in $\mathrm{kg \cdot m^{-3}}$ is plotted along the upper left ordinate. The scaling is calculated once the first density values are available. It is automatically divided into six fields with the height of each field corresponding to a 0.01 % change in density. The chart also plots a calculated standard density value for comparison (displayed as a solid line). This value is usually calculated from the GERG-2004 equation of state for natural gases [2]. (It can be seen in Fig. 4 that the calculated value agrees well with the measured values. The reason is that the composition of the measured certified multicomponent gas mixture is very accurately known; see also Sect. 6). The deviations of the measured temperature values from the set-point temperature of $t_\mathrm{s} = 0\,^\circ\mathrm{C}$ within the limits of ±20 mK are plotted along the lower ordinate on the left, and the deviations of the measured pressure values from the set-point pressure of $p_\mathrm{s} = 0.101325\,\mathrm{MPa}$ within the limits of ±10 Pa are plotted along the lower ordinate on the right. The example also shows the small scatter over time of the temperature and the pressure during one measuring run. The two windows in the lower part of the online screen display further information which is not explained in more detail at this point.

The measurements are performed automatically using a PC. The densimeter is operated via a screen menu. The PC is connected to all electronic devices via a serial-to-ethernet device server, and controls the temperature of the measuring cell and the density measurement, collects all measured data, and displays the online charts. Once a measuring run has been completed, all required measured values are stored and a detailed measurement record is printed, if required.

When the measurements of a gas have been completed, other gas cylinders can be connected successively to the reference densimeter for testing. Testing of a gas requires approximately 1.5 h in total. Up to four gases can be tested daily, including verification of the density reference point with methane prior to and after completion of the measurements.

Prüfpunkt Nr.: DKD - 11D - DP9813

Δ ρ/ρ = 0.010%

MP: 58 von 60

Waagenanzeige= -0,00001g

Dichte ρ 0,80874 kg/m³

Abweichung Δ ρ -0,004 %

Temperatur t 0,001 °C

Druck PPC3 p 1013,25 mbar

$t_{\mathrm{Haupt}} - t_{\mathrm{Vgl}}$ -0,001 K

$p_{\mathrm{Haupt}} - p_{\mathrm{Vgl}}$ -0,03 mbar

Mensor p 1013,28 mbar

Sollwert (w): 0,000 °C

Istwert (x): 0,001 °C

Δ T (x-w): 0,001 K

Sollwert Ministat: -1,1 °C

Istwert Ministat: -1,2 °C

Heizleistung = 10,18 W

U_{St} = 3,37 V

Abtastzeit: 5 s

Fig. 4 Online screen for a standard density measurement displayed on the PC. The diagram plots measured density values as well as the deviations of measured temperatures and pressures from set-point values over the measuring time

The total uncertainty in the standard density measured can be calculated in accordance with an ISO guide [11] from the uncertainties of the individual influencing factors. These individual uncertainties are the uncertainty in temperature of 15 mK (both for testing a gas and for calibration of the densimeter with methane), the uncertainty of 5 Pa in pressure (for testing and calibration), the uncertainty in weighing of 0.03 mg or 0.02 mg (for testing and calibration, respectively), the uncertainty of 0.008 % in the standard density of the reference gas methane (see Sect. 5), and the uncertainty of 0.003 % in the difference of sinker volumes. The resulting total uncertainty is 0.020 % (95 % level of confidence, $k = 2$) for standard densities of $\rho_s = (0.7 - 1.3)\ \mathrm{kg \cdot m^{-3}}$. The typical repeatability of the measured values is ±0.005 %. The densimeter operating manual [10] explains in detail how the total uncertainty is calculated.

5 Verification of Measurement Uncertainty

In order to verify the measurement uncertainty of 0.020 % calculated for the reference densimeter, the standard densities of nine selected pure gases were measured after the density reference point was calibrated with methane. The test gases are listed in Table 1. With the exception of propane and isobutane, the standard densities of the gases are known very accurately; their uncertainties are between 0.002 % (nitrogen)

Table 1 Standard densities[a] ρ_s of selected pure gases used for test measurements

Test gas	Standard density
Methane (reference gas)	$\rho_{s,CH_4} = (0.71745 \pm 0.00006)\ kg \cdot m^{-3}$
Neon	$\rho_{s,Ne} = (0.89988 \pm 0.00004)\ kg \cdot m^{-3}$
Nitrogen (check gas)	$\rho_{s,N_2} = (1.25039 \pm 0.00003)\ kg \cdot m^{-3}$
Ethylene	$\rho_{s,C_2H_4} = (1.26109 \pm 0.00010)\ kg \cdot m^{-3}$
Ethane	$\rho_{s,C_2H_6} = (1.35500 \pm 0.00013)\ kg \cdot m^{-3}$
Argon	$\rho_{s,Ar} = (1.78396 \pm 0.00005)\ kg \cdot m^{-3}$
Carbon dioxide	$\rho_{s,CO_2} = (1.97681 \pm 0.00010)\ kg \cdot m^{-3}$
Propane	$\rho_{s,C_3H_8} = (2.0103 \pm 0.0005)\ kg \cdot m^{-3}$
Isobutane	$\rho_{s,C_4H_{10}} = (2.6886 \pm 0.0008)\ kg \cdot m^{-3}$
Sulphur hexafluoride	$\rho_{s,SF_6} = (6.6163 \pm 0.0005)\ kg \cdot m^{-3}$

[a] These standard densities were calculated from accurate equations of state; see Footnote 2 and Ref. [10]

and 0.010 % (ethane) [10].[2] While the density measurement range of the densimeter is specified to range from $\rho_s = (0.7 \text{ to } 1.3)\ kg \cdot m^{-3}$, thus covering the standard densities of all natural gases, higher densities can also be measured without any problem, such as the density of SF_6 with $\rho_s \approx 6.6\ kg \cdot m^{-3}$.

The results of the test measurements are shown graphically in Fig. 5. The figure shows, for each gas, the percentage deviation of the measured density value from the density reference value (zero line) specified in Table 1. It is obvious that the measurement results agree very well with the density reference values. The deviations are less than ±0.005 % in most cases.

Following prior verification of the density reference point with methane $\{\rho_s = (0.71745 \pm 0.00006)\ kg \cdot m^{-3}$ [10]$\}$, such a test measurement is also suitable for easily and quickly verifying the measurement uncertainty of the device. Apart from being a main component of natural gas, nitrogen is best suited as a check gas with its standard density of $\rho_s = 1.25039\ kg \cdot m^{-3}$ and a small uncertainty of only 0.002 %. The deviation of the measuring result from the density reference value should be less than ±0.01 %. Greater deviations, if any, have to be investigated and clarified.

6 Presentation of Typical Measurement Results

Figure 6 shows the results of typical measurements on four certified gas mixtures (two binary gas mixtures and two synthetic natural gases) to illustrate the results obtained

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[2] The values given in Table 1 for the standard densities ρ_s (as well as the values given in Table 2 for the compression factors Z_s) of the 10 gases were calculated from the currently most accurate equations of state in most cases, for example, for methane [12] and nitrogen [13] (see Ref. [10]). The uncertainties given for the standard densities (95 % level of confidence) were calculated from the uncertainties of the individual quantities using the following equation: $\rho_s = (p_s M)/(T_s R_m Z_s)$; with $p_s = 0.101325\,MPa$, $T_s = 273.15\,K$, the molar gas constant $R_m = (8.314472 \pm 0.000030)\ J \cdot mol^{-1} \cdot K^{-1}$ [14], the molar mass M, for example $M_{CH_4} = (16.04246 \pm 0.00108)\ g \cdot mol^{-1}$ for methane [15] and $M_{N_2} = (28.0134 \pm 0.0004)\ g \cdot mol^{-1}$ for nitrogen [15], and the compression factors at standard conditions, for example, $Z_{s,CH_4} = (0.997613 \pm 0.000015)$ for methane [12] and $Z_{s,N_2} = (0.999543 \pm 0.000010)$ for nitrogen [13]. The uncertainty of the compression factor at standard conditions is derived from the uncertainty of the equation of state as well as from the uncertainty of the basic experimental data.

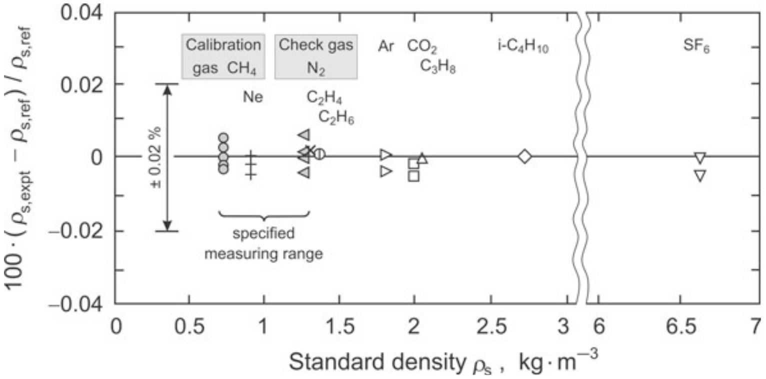

Fig. 5 Verification of the 0.020 % measurement uncertainty of the reference densimeter by measurement of the standard density of nine selected pure gases. The diagram shows, for each gas, the percentage deviation of the measured density $\rho_{s,\mathrm{expt}}$ from the reference density $\rho_{s,\mathrm{ref}}$ [10] (zero line) listed in Table 1. The uncertainties of the reference values are 0.002 % to 0.010 % for seven of the nine gases

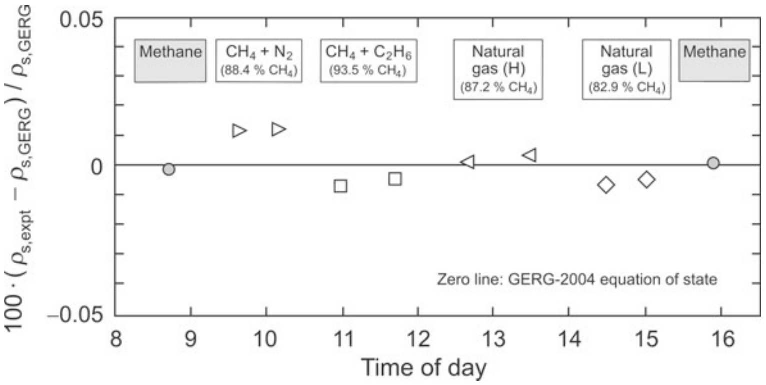

Fig. 6 Typical measurement results for four gas mixtures (two binary gas mixtures and two synthetic natural gases). The diagram plots the percentage deviations over time of day of the standard densities measured $\rho_{s,\mathrm{expt}}$ from the values calculated $\rho_{s,\mathrm{GERG}}$ from the GERG-2004 equation of state for natural gases [2]. For checking purposes, the standard density of methane was measured at the beginning and at the end of the measurements

with the reference densimeter. In order to check repeatability, the measurements were performed twice and a check measurement with methane was performed before and after the measurements. The abscissa of the diagram plots the time of day, and the ordinate plots the deviations of the measured values from the calculated values (zero line). The standard density values for comparison were calculated with the GERG-2004 wide-range reference equation of state for natural gases [2]. The uncertainty in the standard densities calculated with this equation was estimated to be 0.01 % for typical natural gases. To this, the uncertainty in gas composition determined with a laboratory gas chromatograph must be added. Since the gas composition is required as input to the equation of state, the uncertainty in the calculated standard densities is approximately several ±0.01 % depending on the test gas and gas analysis accuracy.

It is obvious from Fig. 6 that the two values measured for each gas agree very well and that, as a consequence, the repeatability of gas mixture density measurements is also very good. It is further obvious that the calculated standard densities (zero line) agree very well with the measured values (measurement uncertainty of 0.020 %). The good agreement in this case is due to the highly accurate production of each of the four measured gas mixtures so that their compositions are very well known (compositions of the gas mixtures in mole fraction x, rounded: gas 1: $x_{\mathrm{CH_4}} = 0.884$, $x_{\mathrm{N_2}} = 0.116$, $\rho_{\mathrm{s}} \approx 0.78\,\mathrm{kg \cdot m^{-3}}$; gas 2: $x_{\mathrm{CH_4}} = 0.935$, $x_{\mathrm{C_2H_6}} = 0.065$, $\rho_{\mathrm{s}} \approx 0.76\,\mathrm{kg \cdot m^{-3}}$; gas 3: natural gas (H), $x_{\mathrm{CH_4}} = 0.873$, $x_{\mathrm{N_2}} = 0.010$, $x_{\mathrm{CO_2}} = 0.015$, $x_{\mathrm{C_2H_6}} = 0.078$, $x_{\mathrm{C_3H_8}} = 0.019$, $x_{\mathrm{C_4H_{10}\,to\,C6H14}} = 0.005$, $\rho_{\mathrm{s}} \approx 0.83\,\mathrm{kg \cdot m^{-3}}$; gas 4: natural gas (L), $x_{\mathrm{CH_4}} = 0.829$, $x_{\mathrm{N_2}} = 0.133$, $x_{\mathrm{CO_2}} = 0.009$, $x_{\mathrm{C_2H_6}} = 0.024$, $x_{\mathrm{C_3H_8}} = 0.003$, $x_{\mathrm{C_4H_{10}\,to\,C6H14}} = 0.002$, $\rho_{\mathrm{s}} \approx 0.82\,\mathrm{kg \cdot m^{-3}}$).

7 Determination of the Composition of Binary Gas Mixtures

Binary gas mixtures are often used for calibration and checking of PGCs and laboratory GCs. Moreover, they are used for calibration and checking of gas calorimeters and gas densimeters. Many such binary gas mixtures are commercially available in several quality grades for many various applications. The uncertainty of the composition is usually not better than 1 % with respect to the mole fraction of the minor component. Even in the best quality, which is expensive and the delivery time is quite long, the uncertainty is usually not better than 0.1 % for mole fractions between 0.05 and 0.5, and not better than 0.5 % for mole fractions between 0.001 and 0.05. With this background, it is important to realize that the composition of binary gas mixtures, consisting of natural gas components, can usually be determined from the measured standard density with an uncertainty of (0.01–0.03) mol%, which is, in many cases, far superior to that obtained from the manufacturer.

The molar mass M_{mix} of a binary gas mixture is defined by the following equation:

$$M_{\mathrm{mix}} = x_1 M_1 + x_2 M_2, \tag{3}$$

where M_1 is the molar mass of the main component methane ($\mathrm{CH_4}$), M_2 is the molar mass of a further major component in natural gases, i.e., nitrogen ($\mathrm{N_2}$), carbon dioxide ($\mathrm{CO_2}$), ethane ($\mathrm{C_2H_6}$), propane ($\mathrm{C_3H_8}$), *n*-butane, or isobutane ($\mathrm{C_4H_{10}}$), and x is the mole fraction of a component. In typical natural gases and in binary gas mixtures used for calibration purposes, the mole fraction of methane is $x_{\mathrm{CH_4}} \geq 0.80$ and the mole fraction of the second component usually is $x_2 \leq 0.20$, e.g., $x_{\mathrm{N_2}} \leq 0.20$, $x_{\mathrm{CO_2}} \leq 0.10$, $x_{\mathrm{C_2H_6}} \leq 0.20$, and $x_{\mathrm{others}} \leq 0.05$. The rearrangement of Eq. 3 with $x_1 = (1 - x_2)$ yields the mole fraction x_2 of the second component:

$$x_2 = \frac{M_{\mathrm{mix}} - M_1}{M_2 - M_1}. \tag{4}$$

The equation of state for real gas mixtures at standard conditions can be written as

$$\frac{p_{\mathrm{s}} M_{\mathrm{mix}}}{\rho_{\mathrm{s,mix}} T_{\mathrm{s}} R_{\mathrm{m}}} = Z_{\mathrm{s,mix}}, \tag{5}$$

where $R_{\mathrm{m}} = (8.314472 \pm 0.000030)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ [14] is the molar gas constant and $Z_{\mathrm{s,mix}}$ is the compression factor of the gas mixture. Equation 5 can be rearranged to obtain the molar mass,

$$M_{\mathrm{mix}} = \rho_{\mathrm{s,mix}} Z_{\mathrm{s,mix}} \frac{T_{\mathrm{s}} R_{\mathrm{m}}}{p_{\mathrm{s}}}, \tag{6}$$

and the combination with Eq. 4 yields the mole fraction[3] x_2:

$$x_2 = \left(\rho_{\mathrm{s,mix}} Z_{\mathrm{s,mix}} \frac{R_{\mathrm{m}} T_{\mathrm{s}}}{p_{\mathrm{s}}} - M_1 \right) / (M_2 - M_1). \tag{7}$$

Here, $\rho_{\mathrm{s,mix}}$ is the value of the measured standard density, and $Z_{\mathrm{s,mix}}$ is a calculated value from the GERG-2004 equation of state [2].

The uncertainty Δx_2 of the mole fraction x_2 can be calculated in accordance with an ISO guide [11] with the result:

$$\Delta x_2 = \left[\left(\frac{\Delta \rho_{\mathrm{s,mix}}}{\rho_{\mathrm{s,mix}}} \frac{M_{\mathrm{mix}}}{M_2 - M_1} \right)^2 + \left(\frac{\Delta Z_{\mathrm{s,mix}}}{Z_{\mathrm{s,mix}}} \frac{M_{\mathrm{mix}}}{M_2 - M_1} \right)^2 + \left(x_1 \frac{M_1}{M_2 - M_1} \frac{\Delta M_1}{M_1} \right)^2 + \left(x_2 \frac{M_2}{M_2 - M_1} \frac{\Delta M_2}{M_2} \right)^2 \right]^{0.5}. \tag{8}$$

Hence, the uncertainty Δx_2 of the mole fraction x_2 depends on the uncertainty $(\Delta \rho_{\mathrm{s,mix}} / \rho_{\mathrm{s,mix}})$ of the measured standard density, which is 0.020 %, the uncertainty $(\Delta Z_{\mathrm{s,mix}} / Z_{\mathrm{s,mix}})$ of the compression factor, and the uncertainty $(\Delta M_1 / M_1)$ and $(\Delta M_2 / M_2)$ of the molar masses of the main component methane and the second component N_2, CO_2, C_2H_6, C_3H_8, or C_4H_{10}. The compression factor and the molar mass of these pure gases are listed in Table 2 along with their particular uncertainty. The value $M_{\mathrm{mix}} / (M_2 - M_1)$ in Eq. 8 characterizes the difference in the molar masses of the two components, and this ratio significantly influences the accuracy of the calculated mole fraction x_2.

The molar mass of each gas listed in Table 2 and its uncertainty can be calculated from the molar mass of the elements and its uncertainty (Wieser [15]).

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[3] The mole fraction x_2 should be determined from Eq. 7 with two iteration steps. In the first step, the required compression factor $Z_{\mathrm{s,mix}}$ should be calculated from the GERG-2004 equation of state [2] with the gas composition, which is approximately known from the gas analysis. In the second step, the compression factor can usually be calculated with sufficient accuracy with the mole fraction x_2 determined in the first iteration step. This iteration is appropriate because an uncertainty of, e.g., 0.1 mol% in the gas composition can cause an uncertainty of up to 0.002 % in the calculated compression factor, and this uncertainty can cause a subsequent uncertainty of up to 0.003 mol% in the gas composition to be determined.

Table 2 Compression factor[a] Z_s at standard conditions ($T_s = 273.15\,\mathrm{K}$, $p_s = 0.101325\,\mathrm{MPa}$) and molar mass M of several selected pure gases along with their particular uncertainty

Gas	Molar mass $M(\mathrm{g{\cdot}mol^{-1}})$	Uncertainty $(\Delta M/M)10^6$	Compression factor Z_s	Uncertainty $(\Delta Z_s/Z_s)10^6$
Methane	16.04246	68	0.997613	15
Nitrogen	28.0134	14	0.999543	10
Carbon dioxide	44.0095	32	0.993259	20
Ethane	30.06904	67	0.990052	50
Propane	44.09562	67	0.97860	200
n-Butane	58.12220	67	0.9591	800
Isobutane	58.12220	67	0.9645	300

[a] The compression factors Z_s were calculated from accurate equations of state; see Footnote 2 and Ref. [10]

The compression factor at standard conditions of the listed gases and its uncertainty were determined by Glos et al. [3] and Richter et al. [10]. They were determined specifically for each gas on the basis of the currently most reliable equations of state, as well as from the uncertainty in the basic experimental data. For example, the equation of state of Wagner and de Reuck [12] was used for methane, and the equation of state of Span et al. [13] was used for nitrogen (see Footnote 2). The compression factor $Z_{s,\mathrm{mix}}$ for a binary gas mixture can currently be calculated with the best possible accuracy from the GERG-2004 reference equation of state [2]. At present, this equation is in the process of being adopted as the international standard ISO 20765-2 [16]. Based on our experience, the uncertainty of $Z_{s,\mathrm{mix}}$ can be conservatively estimated by means of the following equation:

$$\frac{\Delta Z_{s,\mathrm{mix}}}{Z_{s,\mathrm{mix}}} = \sqrt{x_1}\frac{\Delta Z_{s,1}}{Z_{s,1}} + \sqrt{x_2}\frac{\Delta Z_{s,2}}{Z_{s,2}}. \tag{9}$$

As an example, the uncertainty Δx_2 of the mole fraction x_2 of the second component was calculated with Eq. 8 for six binary gas mixtures for the case $x_1 = 0.90$ methane and $x_2 = 0.10$ nitrogen, carbon dioxide, ethane, propane, *n*-butane, or isobutane. The calculated uncertainties Δx_2 are 0.030 mol%, 0.014 mol%, 0.030 mol%, 0.015 mol%, 0.016 mol%, and 0.011 mol%, respectively. Hence, the composition of selected binary gas mixtures, with a concentration of the second component between 1 mol% and 20 mol%, can be determined from the measured standard density with a small uncertainty of only (0.01 to 0.03) mol%. In order to illustrate these explanations, the measurements of the standard density of the two binary gas mixtures plotted in Fig. 6 can be considered. The four measured values correspond with the calculated densities (zero line) within 0.012 %. Hence, the calculation of the concentration of the second component in both gas mixtures (about 11.6 mol% nitrogen and 6.5 mol% ethane, respectively) agrees with the analyzed concentration within 0.018 mol%.

The densimeter operating manual [10] (147 pages) contains a detailed description of the reference densimeter design, measurement performance, measurement uncertainty calculation, as well as other information. General information concerning the two-sinker density measuring method used here, along with accurate gas and liquid density measurements and reference equations of state for fluids, are given on the homepage of the Chair of Thermodynamics (http://www.ruhr-uni-bochum.de/thermo/).

8 Conclusions

A special two-sinker densimeter was developed for the gas industry. It is used to measure the density ρ_s of natural gases and multi-component gas mixtures at standard conditions ($T_s = 273.15\,\mathrm{K}$, $p_s = 0.101325\,\mathrm{MPa}$). This density ρ_s is an important value for the calculation of energy of natural gases and the billing of quantities delivered. In spite of the low gas densities, which are usually between $0.7\,\mathrm{kg \cdot m^{-3}}$ and $0.9\,\mathrm{kg \cdot m^{-3}}$, the total uncertainty of the density measurements is very small, namely $0.020\,\%$ ($k = 2$). Moreover, the new densimeter can be used to determine the compositon of commercially available binary gas mixtures with a small uncertainty of only (0.01 to 0.03) mol%. Such binary gas mixtures are often used by the gas industry for the calibration of process gas chromatographs.

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