

Rapid determination of the calorific value by means of a novel gas quality sensor

by **Achim Zajc, Thomas Ryll**

The gas quality in the German gas transmission and distribution network varies already considerably. The dynamics of the gas quality changes will increase for various reasons. One reason is the dry-up of traditional sources and the increased supply of gas from unconventional sources. The market space switching from L-gas to H-gas contributes to this, too. These trends require a fast and reliable determination of the calorific value. Here, the following article aims to provide a solution.

The European and thus also the German natural gas industry is in a state of upheaval. Traditional natural gas sources such as those from the Netherlands and domestic German natural gas subsidies are taken down annually [1]. The Dutch natural gas as well as the domestic production has the so-called L-gas quality. In order to ensure that millions of gas appliances continue to operate without interruption with decreasing production of L-gas, gas with H-gas quality must be adjusted to the L-gas quality by admixing nitrogen.

If new traditional natural gas sources are developed, this is usually done outside Europe. The introduction of LNG into the natural gas network as an alternative to Russian natural gas is also being discussed increasingly in Germany in order to counteract dependency on Russia. At the same time, the injection of renewable sources into the natural gas network is becoming increasingly important. In addition, the rapidly growing European and global natural gas trade has brought about changes.

For example, an E.ON project showed that in recent years, 30 % of households and 20 % of large customers are affected by strong fluctuations in the Wobbe Index. The fluctuations can be up to max. 1.5 kWh/m³ [2]. The variation of the natural gas quality in the gas industry hits the natural gas user. The effects on various industrial thermoprocesses (product quality, efficiency, pollutants, safety, lifetime, etc.) can be very different [3–4].

The dynamics of the natural gas quality presents the energy bill against new challenges and thus also the measurement of gas properties [5]. The classical natural gas

quality measurement uses process gas chromatography. Process gas chromatography is very accurate and verifiable. However, this technology is cost-effective and maintenance-intensive. In addition, the analysis time is 3–5 min (depending on the manufacturer) for control processes such as a natural gas blending system.

Measurement devices which determine the Wobbe Index offer the possibility, in combination with a density measurement, to measure the calorific value within seconds. However, similar to the process gas chromatographs, these systems are very costly and maintenance-intensive.

Precisely here the sensor technology starts. MEMS systems (microelectromechanical systems, also referred to as microsystem technology) are considerably cheaper to manufacture and miniaturization allows these systems to be installed much closer to the process (sampling point) in order to significantly reduce the sampling time, so that the analysis time including the sampling time is possible in less than 15 s (T_{90} time). The following article demonstrates the performance of a modern gas-sensing sensor from MEMS AG.

SET UP AND PRINCIPLE OF THE GAS QUALITY SENSOR

The only 3.5 x 2.1 mm² sensor chip, industrially produced in a complementary metal oxide semiconductor (CMOS) process, forms the heart of the microthermal sensor. As the name implies, this is a fully integrated hot wire anemometer with all analogue and digital circuits for signal amplification, AD conversion and digital communication. The chip allows

the measurement of the thermal conductivity κ as well as the heat capacity c_p of a gas mixture. The combination of the sensor chip with a critical nozzle additionally provides the density ρ . Now, even the link in the form of a correlation between these physical parameters of the mixture of gas and the gas composition of G is missing. **Fig. 1** shows the gas sensor gasQS of MEMS AG.

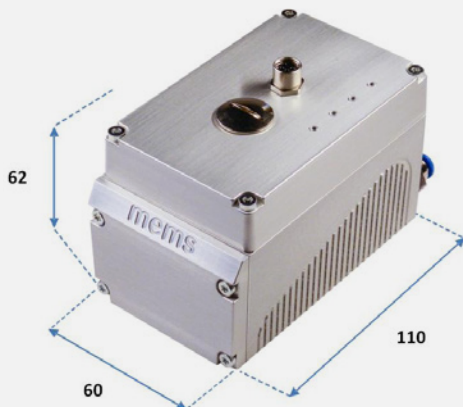


Fig. 1: Gas quality sensor gasQS of MEMS AG [6] (dimensions in mm)

MEASUREMENT OF PHYSICAL PARAMETERS

Fig. 2 shows the schematic set up of the sensor. When the valve is open, the gas to be analyzed flows out of the measuring line into the gas reservoir and flows in the direction of the critical nozzle.

If the gas flow in the feed line is greater than the flow through the nozzle, a pressure builds up in the gas reservoir. When the pressure reaches a value at which the nozzle changes into critical operation, the valve is closed shortly thereafter. The pressure in the reservoir drops again, the pressure drop is following an exponential decay law with a decay time:

$$\tau \propto \sqrt{M} \tag{1}$$

In most cases, the molecular weight M is directly proportional to the density ρ . If, therefore, the pressure in the

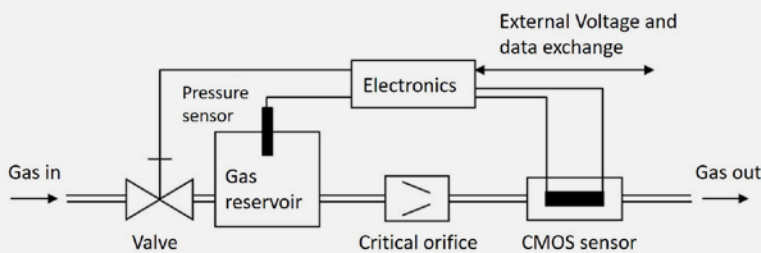


Fig. 2: Schematic set up of the sensor [6]

reservoir is measured as a function of time with a pressure sensor, the density of the gas mixture can be concluded. This simple relationship is valid only as long as the nozzle is operated critically, which means either an inlet pressure of approx. 5 bar (high pressure variant) or an outlet negative pressure of approx. 300 mbar (low pressure variant with pump).

The CMOS sensor element can be described with a one-dimensional heat conduction equation:

$$\frac{c_p}{\kappa} \cdot \rho v_x \cdot \frac{dT}{dx} = \nabla^2 T + \frac{1}{\kappa} \theta, \tag{2}$$

with $\rho \cdot v_x$ the mass flow over the CMOS sensor element, T the temperature, dT/dx the temperature gradient, $\nabla^2 T$ the Laplacian operator applied to the temperature, c_p the heat capacity, ρ the density and κ the thermal conductivity. The heat input of the hot wire is given by the θ -term. At the end of the pressure drop measurement, when the mass flow has come to a standstill, the left side of the equation (2) becomes zero. The measurement of the temperature distribution ($\nabla^2 T$) on the sensor chip by means of symmetrical thermocouples located upstream or downstream of the hot wire permits the determination of the thermal conductivity κ .

In addition to the measurement of the density, the critical nozzle has the function of generating a mass flow proportional to the (measured) pre-pressure $p v_x$. Since the latter flows through the sensor chip following the nozzle, the same mass flow also occurs in the pre-factor of the left-hand side of equation (2). This shows that the quantity $\frac{c_p}{\kappa}$ can be determined from the solution of equation (2) and, together with the already known thermal conductivity κ , the heat capacity c_p .

CORRELATION

If the desired gas quality (G) cannot be attributed directly to one of the sensory variables, one tries to establish a connection between the gas quality (G) and the measured physical gas parameters for a wide range of known gases as wide as possible. In other words to correlate the gas quality (G). This is all the more successful the more independent the physical gas parameters are, and the greater the physical relationship between gas quality (G) and these parameters. If a sufficiently accurate correlation has been found, the gas quality (G) can also be well correlated out of the measured physical gas parameters for an unknown gas mixture.

The true advantage of the correlation process lies in the fact that the number of variables for the correlation is not limited to the number of sensor measurement variables because the correlation process is not the solution of an equation system where the number of unknown variables is limited to the number of known variables.

The more parameters available, the better can be correlated. The more precisely the parameters can be measured and the more is known about the gas to be measured, the more accurate the result. The remaining error consists, on the one hand, of the pure correlation error and, on the other hand, of the effect of measurement errors on the physical gas parameters (Fig. 3). The former also occurs when the output variables can be measured without errors.

The correlative method of measurement can play out its advantages especially when it is a question of reacting quickly to a change in the gas composition, where one does not want to wait several minutes for the result of a measurement, as it is the case with practically all other methods.

In this case, the gas quality (G) is most simply plotted in a normalized manner with respect to a reference gas (here G20, i. e. methane). The selected reference gas is sensibly used at the same time to calibrate the sensor. Fig. 4 shows how the calibration of several gas-type gas sensors from the type gasQS of the company MEMS AG takes place at the same time. Since the calorific value and the sensor quantities ρ , κ and c_p are subject to similar physical laws, it can be assumed that a correlation to the calorific value can be found. This is actually the case (Fig. 5). The only requirement for the correlation function is that to each measured value triangle a dedicated calorific value is assigned. Otherwise, a function is selected in which the expected correlation error for the desired gas group is as small as possible.

The correlation method in the present case has the peculiarity that the output values of the correlation represent effective physical properties of the gas mixture, which are determined on the basis of a physical model (equation (2)) from the temperature distribution on the sensor chip. Thus, the behaviour of the sensor system or the measurement errors for any gas mixtures can be predicted if their values for ρ , κ and c_p are known from data tables. This has the advantage that a sensor can be specifically trimmed to specific gas groups (e. g. biogas) without the need to measure a large number of gases.

COMPARATIVE MEASUREMENTS WITH TEST GASES (BAM CERTIFIED SECONDARY TEST GASES)

BAM certified secondary calibration gases were used to test the performance in the determination of the calorific value by the gas quality sensor gasQS. The compositions of the measured gases are summarized in Table 1. This includes the calibration gases, which are necessary for a "complete measurement calibration" according to the PTB Technical Guideline G16 [9]. The calibration gases which are appropriate to the Technical Guideline G16 are also applicable to calibrate natural gas measurement devices according

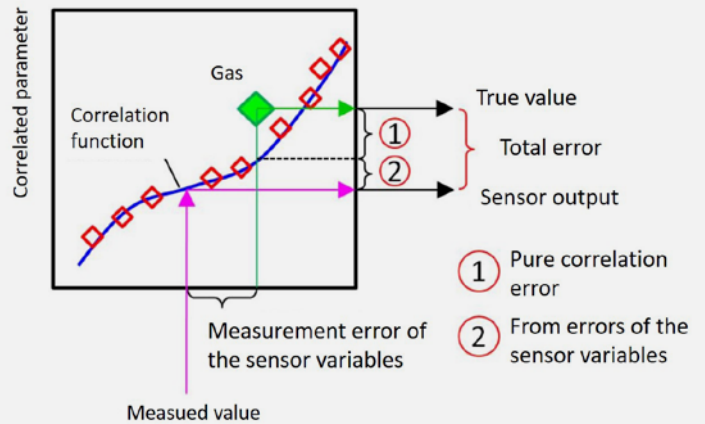


Fig. 3: Sources of errors for correlative measuring methods [7]



Fig. 4: Calibration of multiple gas quality sensors [6]

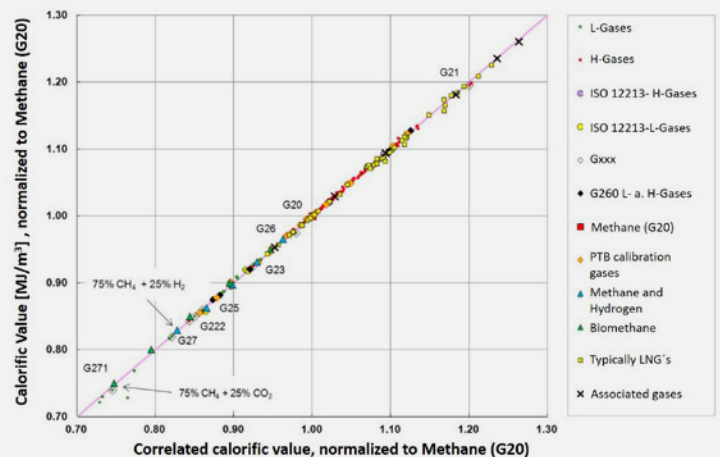


Fig. 5: Correlation of the calorific value [8]

Table 1: Composition of the test gases measured with the gas quality sensor gasQS

| Designation | P1-9K | 12M | L1-8K | H1-11K | 9M | 6H | 11D | 6L | 11M | L1-11K |
|----------------------|---------|--------|--------|---------|---------|--------|---------|--------|--------|---------|
| Details | Mol-% | | | | | | | | | |
| Hydrogen | 0.3001 | 1.0172 | | | 0.1984 | | | | | |
| Nitrogen | 2.944 | 4.0362 | 12.019 | 1.3398 | 4.0571 | 0.4344 | 4.0165 | 14.408 | 3.9761 | 11.0664 |
| Oxygen | 0.2957 | 0.5036 | | | 0.4183 | | | | 0.4988 | |
| Carbon Dioxide | 3.5266 | 1.5279 | 4.4997 | 0.3479 | 2.5076 | 1.8947 | 1.5029 | 0.9992 | 1.5197 | 1.5627 |
| Ethane | 0.3557 | 4.0994 | 0.748 | 0.394 | 2.5728 | 9.8515 | 4.0255 | 3.0053 | 4.0421 | 0.7463 |
| Propane | 4.6865 | 1.0306 | 0.3007 | 0.1941 | 1.0055 | 3.5502 | 1.0024 | 0.5032 | 0.9983 | 0.2993 |
| 2-Methyl-propane | 0.2977 | 0.2036 | 0.2006 | 0.0994 | 0.1996 | | 0.1929 | | 0.1983 | 0.0989 |
| n-Butane | 0.2939 | 0.2041 | 0.2 | 0.1004 | 0.1998 | 1.0677 | 0.1928 | 0.0997 | 0.1982 | 0.0981 |
| 2-Methyl-butane | | 0.0499 | 0.0491 | 0.0505 | | | 0.0498 | | 0.0501 | 0.0493 |
| 2,2-Dimethyl-propane | | | | 0.0505 | | | 0.0467 | | | 0,0515 |
| n-Pentane | | 0.05 | | 0.05 | | | 0.0497 | | 0.0491 | 0.05 |
| n-Hexane | | 0.0498 | | 0.0488 | | | 0.0495 | | 0.0482 | 0.0459 |
| Methane | 87.2998 | 87.228 | 81.983 | 97.3246 | 88.8409 | 83.202 | 88.8713 | 80.985 | 88.421 | 85.9316 |

to the PTB Technical Guideline G14 for biogas [10]. The so-called "12M" calibration gas is used for the performance test, which is suitable as a calibration gas with more than eleven components referred to PTB requirement 7.63 [11].

The measurements were carried out in the laboratory of BEGA.tec in Berlin. In this case, the test gases listed in Table 1 were measured by two different gas quality sensors of the type gasQS on the one hand with the serial number SN06 and on the other with the serial number SN15. The laboratory of BEGA.tec is approved as a state-approved laboratory for measuring instruments for natural gas under the code GBB 4. The GBB 4 calibration centre is particularly active in the field of gas-sensing devices and calorific value measuring devices. Furthermore, the GBB 4 is approved as

a calibration centre for the official certification of calibration gases of the third order (calibration gases for PGC).

The results obtained with the comparative measurements with the aid of BEGA.tec are shown for the density measurement in Fig. 6 and the results of the calorific values in Fig. 7.

Fig. 6a shows the results of the density measurements of the gas quality sensor gasQS against the reference values from NIST Standard Reference Database 23 [12]. The excellent correlation becomes clear from the graphical representation. Fig. 6b shows the scattering of the individual results for the density measurement over all test gases according to Table 1. It is clear that the results are within a band of $\leq \pm 0.4\%$.

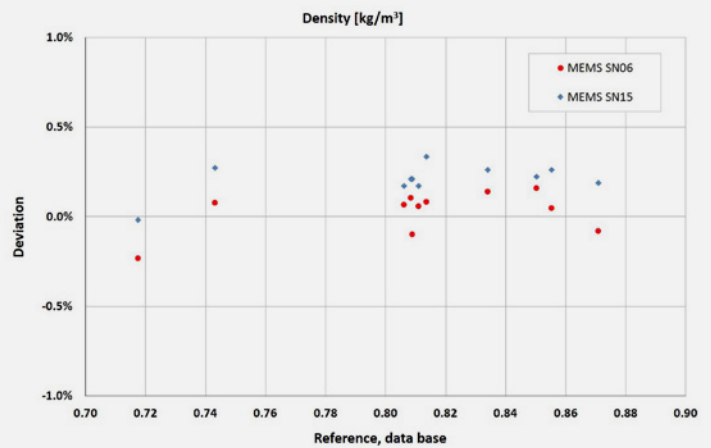
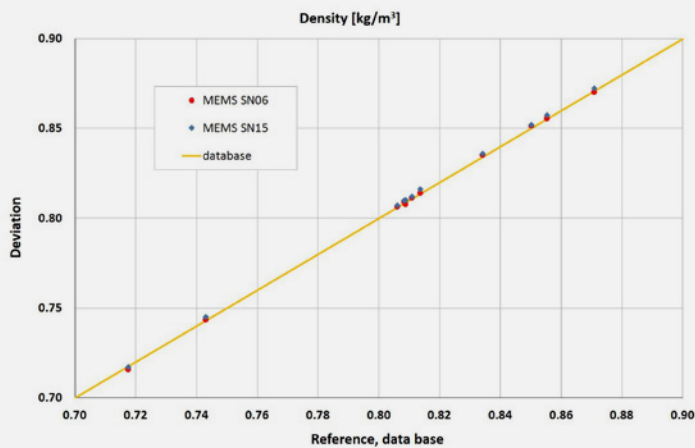
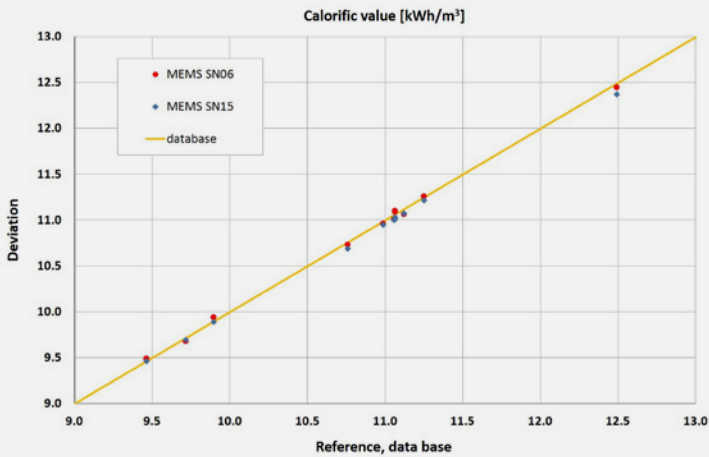
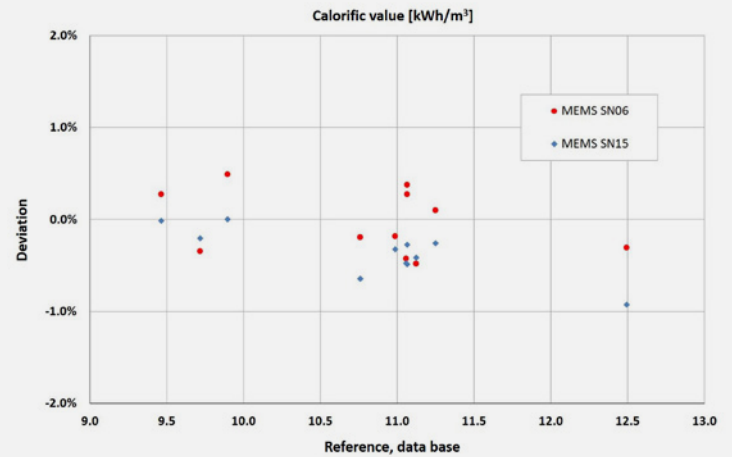


Fig. 6a: Correlation of the density

Fig. 6b: Deviation from the reference database


Fig. 7a: Correlation of the calorific value

Fig. 7b: Deviation from the reference database

Analogously to Fig. 6, the measured values for the calorific value for the two gas quality sensors gasQS with the serial numbers SN06 and SN15 are plotted against the NIST reference value in Fig. 7a. An excellent correlation is also found here. The graphical representation of

the deviations of the individual values from the NIST reference value shows that the results are affected by an error of $\pm 1\%$ (Fig. 7b).

Table 2 shows the typical natural gas compositions for H- and L-gases according to the DVGW guideline

Table 2: Typical natural gas compositions according to DVGW guideline G260 [13]

| Designation | Unit | Russ.-Natural gas H | North sea / Natural gas H | Denmark / Natural gas H | Netherlands / Natural gas L | Germany / Natural gas L | Biogas H | Biogas H + LPG |
|---------------------|--------------------|---------------------|---------------------------|-------------------------|-----------------------------|-------------------------|----------|----------------|
| Methane | Mol-% | 96.96 | 88.71 | 90.07 | 83.64 | 86.46 | 96.15 | 90.94 |
| Nitrogen | Mol-% | 0.86 | 0.82 | 0.28 | 10.21 | 10.24 | 0.75 | 0.69 |
| Carbon Dioxide | Mol-% | 0.18 | 1.94 | 0.60 | 1.68 | 2.08 | 2.90 | 2.68 |
| Ethane | Mol-% | 1.37 | 6.93 | 5.68 | 3.56 | 1.06 | | |
| Propane | Mol-% | 0.45 | 1.25 | 2.19 | 0.61 | 0.11 | | 5.00 |
| Butanes | Mol-% | 0.15 | 0.28 | 0.90 | 0.19 | 0.03 | | 0.50 |
| Pentanes | Mol-% | 0.02 | 0.05 | 0.22 | 0.04 | 0.01 | | |
| Hexanes + higher kW | Mol-% | 0.01 | 0.02 | 0.06 | 0.07 | 0.01 | | |
| Oxygen | Mol-% | < 0.001 | < 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.2 | 0.19 |
| Total Sulfur | mg/m ³ | < 3 | < 5 | < 3 | < 3 | < 3 | < 3 | < 3 |
| Calorific value | MJ/m ³ | 40.3 | 41.9 | 43.7 | 36.8 | 35.4 | 38.3 | 41.9 |
| Calorific value | kWh/m ³ | 11.2 | 11.6 | 12.1 | 10.2 | 9.8 | 10.6 | 11.6 |
| Density | kg/m ³ | 0.74 | 0.81 | 0.81 | 0.83 | 0.81 | 0.76 | 0.83 |
| Wobbe Index | MJ/m ³ | 53.1 | 52.9 | 55.0 | 46.0 | 44.7 | 50.0 | 52.3 |
| Wobbe Index | kWh/m ³ | 14.8 | 14.7 | 15.3 | 12.8 | 12.4 | 13.9 | 14.5 |
| Methane number | - | 90 | 79 | 72 | 88 | 97 | 102 | 76 |

G260 [13]. Comparing the values with Table 1, the calibration gas "12M" in the composition represents an H-gas and the calibration gas "L1-8K" is representing an L-gas. The measurement deviation for the calorific value of the "12M" calibration gas from the NIST reference value is -0.18 % (SN06) and -0.32 % (SN15). For the measurement deviation for the "L1-8K" calibration gas from the NIST reference value, 0.27 % (SN06) and -0.01 % (SN15) are obtained. In the case of a natural gas blending system in which H-gas is mixed with nitrogen at the L-gas level, the gas quality sensor gasQS can be used for process control.

CONCLUSION

The new gas quality sensor gasQS from MEMS AG provides the results of the calorific value and density measurement within a T_{90} time of < 15 s within an error range of $\leq \pm 1$ % over a very wide range of applications. If, e. g., the application area is restricted to the conditioning of H-gases with nitrogen to L-gases, the measurement deviation can be ≤ 0.5 %. A process gas chromatograph can provide a measurement deviation of ≤ 0.1 % for the calorific value measurement. In return, however, the process gas chromatograph also needs 3–5 min (depending on the manufacturer).

If, in addition to the measurement deviations, the speed and complexity of such a measuring system (device with peripherals such as pressure reduction, sample switching, calibration gas supply and sampling probe) is compared to that of a process gas chromatograph, the gasQS has the advantage of not using carrier gas or test gas for the calibration. This advantage is even more apparent when the investment costs are compared. A measuring system based on the gasQS can be implemented completely with peripherals for approx. € 60,000 without commissioning. A process gas chromatograph, on the other hand, comes at a system price with peripherals of approx. € 150,000 without commissioning.

In general, the gas quality sensor gasQS can be used in control processes for monitoring the calorific value of non-custody transfer measurements in a very short T_{90} time of 15 s. If the gas quality sensor is further developed and the approval for custody transfer measurements is obtained, this sensor could be used in distribution networks to determine the calorific value.

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