

Accuracy of gas measuring devices



The accuracy of measurement results that can be expected for gas sensors or gas measuring devices is of great importance for both users and manufacturers of these measuring devices. The user (customer) expects a precisely specified accuracy from the manufacturer, which must be verifiable for all. In the standards, which are mostly adapted to the different fields of application, these specifications are described in detail.

This application report is intended to present these relationships in a practical and generally applicable manner to facilitate the evaluation of specifications. For the special requirements arising from the various areas of application, reference is made to the relevant standards and regulations.

“When you can measure what you are speaking about, and express it in numbers,
you know something about it, when you cannot express it in numbers,
your knowledge is of a meager and unsatisfactory kind; it may be the beginning of knowledge,
but you have scarcely, in your thoughts advanced to the stage of science.”

William Thomson, Lord Kelvin



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The term accuracy is generally used as a technical term for the quality of measuring equipment. In this context, all possible influencing factors and errors are usually subsumed to quantify the accuracy. In gas measurement technology, this often leads to misunderstandings, since there are many influencing factors and sources of error that can affect the measurement result. One must therefore consider these influencing factors and error influences separately.

According to DIN 55350-13, **accuracy** is the approximation or deviation e from the measurement result or displayed value x_a to a reference value x_w . This reference value represents the true or correct value. It therefore applies:

$$e = x_w - x_a$$

To be able to determine the accuracy, the reference quantity x_w is therefore of decisive importance. Compared to the definitions of the SI units (1m, 1kg, 1s, ...), there are no defined reference values for gas analysis.

The reference to the SI system is only via the amount of substance (mol). The amount of substance n is a measure for the number of atoms or molecules. The mole is the SI unit for the amount of substance. One mole contains exactly $6.02214076 \cdot 10^{23}$ atoms or molecules.

This number is the fixed numerical value for the **Avogadro constant N_A** of $6.02214076 \cdot 10^{23}$ per mole and is referred to as the **Avogadro number**.

Example:

If there are $6.02214076 \cdot 10^{22}$ He atoms and $5.419926684 \cdot 10^{23}$ N₂ molecules in a binary gas mixture, a gas mixture of $c = 10$ mol.-% He in N₂ is obtained for ideal gases (10mol.-% = 10Vol.-%). For real gases, however, this relation may show slight deviations (DIN EN ISO 14912).

For practical use, however, this approach is difficult to implement, so that test gases are mostly used as the known gas concentration c (= true value). The suppliers of these test gases specify a manufacturing tolerance of $\pm 5\%$. The exact composition is determined by certified analysis methods (Anders, Häßelbarth 2014). These gas mixtures are specified with a relative analytical tolerance of $\pm 2\%$. A requested gas mixture of e.g., 200ppm that has a true value of 205ppm after analysis can thus be between 201ppm and 209ppm. The "true value" thus has a tolerance band of $\Delta c = 8$ ppm.

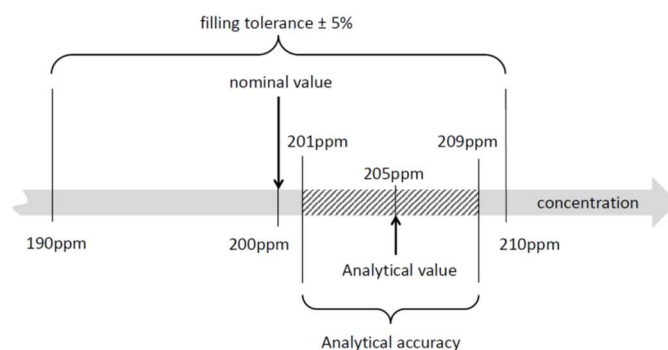


Figure 1: Manufacturing tolerances for commercial test gases

Alternatively, such test gases can also be produced with appropriate mixing equipment (Nelson 1992, Wiegler 2016). For this purpose, 100% gases (e.g., 100Vol.-% CO₂ and 100Vol.-% N₂) are mixed in a defined manner. The accuracy of these mixing devices is 1-2%, depending on the design. Thus, more accurate gas mixtures cannot be generated with this method either.

To be able to check the calibration function of a gas measurement, different gas mixtures must be used which are distributed as evenly as possible over the measuring range (e.g., in 10% increments).

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With an ideal calibration function ($y=x$ and $R^2=1$), the measuring device would indicate an error range of $\pm 2\%$ with certified test gases or directly produced gas mixtures. This error influence is not given by the accuracy of the gas measuring device.

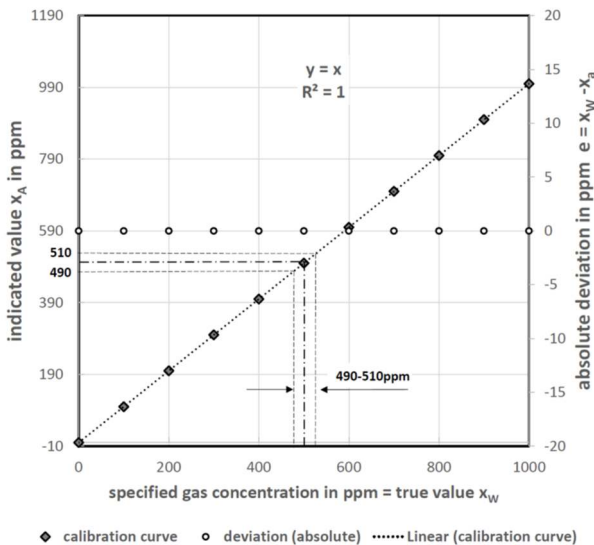


Figure 2: Ideal calibration function without deviations

To check a real calibration function, the gas measuring instrument must first be adjusted in the zero point and end point. The deviations are then "0" in both points. If the end point is adjusted with a certified test gas, this value can already deviate by max. $\pm 2\%$. This error is therefore accepted. If this test gas is then diluted with a gas mixing device (e.g., N_2 addition), an additional error of the mixing device of max. 1-2% is added.

Figure 3 shows such a check. The deviations are all below ± 10 ppm. For a measuring range of 0-1000 ppm the relative error, related to the measuring range, is smaller than $\pm 1\%$. This error is mostly also called linearity error F_{lin} .

This consideration ignores the fact that the end point may deviate by ± 20 ppm due to the test gas tolerance.

With an ideal gas mixing device, the 500 ppm value would thus be between 490 and 510 ppm.

If the calibration function is determined and checked at the factory with the same test gas and gas mixing device, these errors do not occur.

In extreme cases, deviations of up to $\pm 4\%$ are possible when the customer checks with a different test gas.

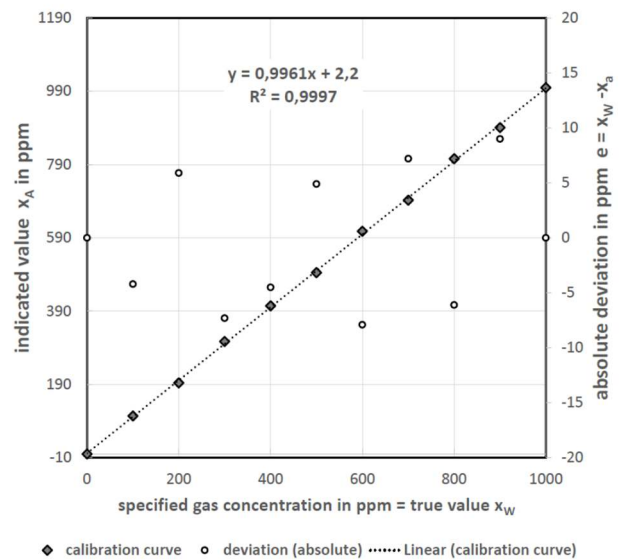


Figure 3: Real calibration function with the corresponding deviations

In addition to these uncertainties in the provision of test gas, there are additional error influences that can significantly affect the accuracy of the measurement result. These are mainly the following influences:

- F_{zero} = Temperature influence at zero point (< 1% F.S. / 10K)
- F_{span} = temperature influence in deflection (< 2% of F.S./10K)
- F_p = pressure influence in deflection (1-2%/10hPa)
- F_{ZD} = drift at zero point (< 2% at maintenance interval)
- F_{SD} = drift in the end point (< 2% in the maintenance interval)



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These influencing factors can be stabilized during the recording of the calibration function by carrying out the measurement in a climatic chamber ($\pm 0.5\text{K}$). The temperature influences are then negligible. Furthermore, the warm-up phase of the gas measuring instrument must be completed.

The drift is also eliminated by the previous zero and end point adjustments. The air pressure will change insignificantly during the measurement (1-2 hours), so that this influence can then also be eliminated.

Statistical signal changes (noise) lead to an additional measurement uncertainty, which essentially influences the detection limit F_{DL} . This noise variable is mostly in the range $<1\%$ of F.S. The detection limit can be reduced by averaging.

Further errors can be caused by random deviations, which are determined by repeated flowing with zero gas (zero point) and test gas (reference point). The repeatability standard deviation F_r is determined by $n=20$ consecutive measurements and then evaluated as follows:

$$F_r = \sqrt{\frac{\sum(x_a - \bar{x})^2}{n - 1}}$$

with \bar{x} as the mean value of the measuring signals x_a

The repeatability error F_r is mostly $<1\%$ of full scale. The maximum total error F_G can be determined by the sum of the squares of the individual errors as follows:

$$F_G = \sqrt{F_{lin}^2 + F_{zero}^2 + F_{span}^2 + F_p^2 + F_r^2 + F_{ZD}^2 + F_{SD}^2 + F_{DL}^2}$$

The total error F_G can thus have a maximum value of 4-5%. The minimum error F_G is then for:

$$F_{zero} = F_{span} = F_p = F_{ZD} = F_{SD} = 0 \quad \text{at } F_G < 1.5\%.$$

Conclusion:

The accuracy of a gas measuring device depends on many external influencing factors, which can only be compensated for to a certain extent. The individual error influences are therefore quantified separately. Since the adjustment is carried out using appropriate test gases as secondary standards, these test gases have the greatest influence on the absolute accuracy. A further influence is given by the gas mixing device used. An indication of the accuracy can therefore only be given under constant operating conditions ($p=\text{const.}$, $T=\text{const.}$), which is then typically $<2\%$ of the full-scale value (F.S.).

References:

- Nelson, G., O.: Gas Mixtures, Preparation and Control. Lewis Publishers, Boca Raton 1992
- Wiegleb, G.: Gas measurement technology in theory and practice. Springer Vieweg Wiesbaden 2016
- Anders, B., Hässelbarth, W.: Analytical verification of calibration gas mixtures according to DIN ISO 6143. Beuth Verlag Berlin 2014.
- DIN EN ISO 14912. Gas analysis - conversion of composition data for gas mixtures. November 2006
- DIN 51989-1. Gas analysis - Absolute volumetric method for the dynamic production of calibration gases. May 2014
- DIN EN 15267-3 Air quality certification of automatic measuring equipment. March 2008



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Appendix:

1. Example for an certificate of analysis (test gas) based on DIN ISO 6141



Gase / Energie / Tankstellen

Westfalen AG
48136 Münster
USt.-ID-Nr. DE 126 117 135

UN 1956 VERDICHETES GAS, N.A.G., (STICKSTOFF,
SCHWEFELDIOXID), 2.2, (E)

Bitte Lagertemperatur beachten !
(Please note storage temperature!)

U/T: 79

Kompetenzzentrum Sondergase
Competence-Center Specialty Gases
Dr. Wolfgang Miethe
Tel +49 5459 806 740
Fax +49 5459 806 749
e-mail w.miethe@westfalen.com

Analysenzertifikat

(certificate of analysis) order **3989201**
Dieses Zertifikat stimmt überein mit den Empfehlungen
der DIN ISO 6141 (This certificate is in accordance with
the recommendations of DIN ISO 6141)

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(page)

Kundenmaterial: (material no.)	Behälternummer: (cylinder no.)	27600504268740	Gemischnummer: (gasmixture no.)	GG0007077
Bestandteil (component)	Sollwert (nominal value)	Istwert (analytical value)	Einheit ¹⁾ (unit)	Analysentoleranz ²⁾ (analytical accuracy)
Schwefeldioxid 3.0 [SO ₂]	500,00	504,00	ppm	± 2,00 % relativ
Stickstoff 5.0 [N ₂]	Rest	Rest		

¹⁾ Konzentrationsangaben sind, falls nicht anders vermerkt, als Stoffmengenanteile (= Molanteile) zu verstehen. (Concentration data are, unless otherwise noted, to be understood as mole fraction of the component (=parts per mole)).
²⁾ Die Analysentoleranz gibt, falls nicht anders vermerkt, die Unsicherheit des Gehaltes einer Komponente als Produkt der Standardunsicherheit mit dem Erweiterungsfaktor an. (The analytical tolerance, unless otherwise noted, indicates the uncertainty of the content of a specified compound as a product of standard uncertainty with the extension factor.)

Fülldruck ideal bei 15° C: (filling pressure at 15°C)	200,00 bar	Behältervolumen: (cylinder volume)	20,00 l	Fülldatum: (date of filling)	07.2020
Min. Verwendungsdruck: (min. pressure of utilization)	5,00 bar	Herstellgenauigkeit: (filling tolerance)	± 10,00 % relativ	Lagertemperatur: (storage temperature)	-10 °C bis +40 °C
Ventilanschluss: (valve outlet)	M 19 x 1,5 links	Haltbarkeit ab Fülldatum: (stability since date of filling)	12 MON		
Produkt: (product)	GG0007077	Prüfgas/Gasgemisch	T20 MFI		

Datum: 02.07.2020
(date)

Prüfer/Ersteller:
(tester/author)

D. Bergschneider
SGZ Hörstel

Qualitätsmanagementsystem
DIN EN ISO 9001 Reg.-Nr. 1709
Technische Gase/Westfalengas
QM-Beleg: F-TG-49.4/01; IMS 2.4



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2. Example of a data sheet/specification

ULTRA.sens® AK100

NO ₂ / SO ₂ / O ₃	
General features	
Measurement principle	Non-dispersive ultraviolet (NDUV); dual beam
Measurement range	see list of measurement ranges
Gas flow	0.1 – 1.5 l/min
Dimensions	225mm x 120mm x 82mm
Weight	approx. 580g
Tube connector	4/6mm tube
Lifetime of UV radiation source	> 40 000h
Measuring response¹	
Warm-up time	1 min (initial), <15 min ²
Response time(t ₉₀)	1.5s – 15s ³
Detection limit (3·σ)	< 0,5ppm ⁴
Linearity error	< ± 1% F.S.
Repeatability	± 0.5% F.S.
Long term stability (zero)	< ± 2% F.S./24h
Long term stability (span)	< ± 2% F.S./month
Temp. Influence zero	< 1% F.S./10K
Temp. Influence span	< 2% F.S./10K ⁵
Cross sensitivity	< 2% F.S. ⁶
Pressure influence	< 1.5%/10hPa of reading ⁷
Electrical inputs and outputs	
Supply voltage	24 (15 – 30) VDC
Supply current (peak)	< 0.1A
Average power consumption	< 1W
Digital output signal	RS 232 (ASCII) or CAN bus
Climatic conditions	
Operating temperature	5 – 45 °C ⁸
Storage temperature	-20 – 60 °C
Air pressure	600 – 1200 hPa (mbar)
Ambient humidity	0 – 95% rel. humidity (not condensing)

F.S. full scale ¹ related to P_a = 1020hPa; T_a = 25°C; flow = 1l/min ² full specification, demands to environmental conditions ³ depends on digital filter settings ⁴ at zero point ⁵ with span temperature compensation ⁶ to each calibrated gas channel, other gases on request ⁷ without pressure compensation ⁸ stable climatic conditions recommended



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