



## Definitions

**Gas mixtures** are homogenous mixtures of different gases or vapors. The multitude of available substances gives rise to an almost unlimited number of possible combinations. However, the **producibility** of a gas mixture is limited by chemical, physical and safety restrictions. The **components** are the gases and vapors making up a mixture. The **carrier or balance gas** is the main component of a mixture.

The **concentration** can be expressed in different measurement units. The amount of substance (ppm) is often used, as this unit is pressure and temperature independent. Also widespread are volume content and mass concentration. These pressure and temperature dependent units are usually based on standard conditions of 0°C and 1013 mbar.

The actual value of a component can only be stated with a certain **accuracy**. In mathematical terms, the uncertainty is defined with the formula  $U = k \times s$ , where  $s$  is the standard deviation and  $k$  is the factor for the "expanded uncertainty". Messer uses the value  $k = 2$  for determining the expanded uncertainty. The necessary analytical process is chosen depending on the type and quantity of a component. The achievable accuracies range between 1-10% relative, depending on the process. With correspondingly elaborate production processes, accuracies below 1% relative (*Topline*) can be achieved.

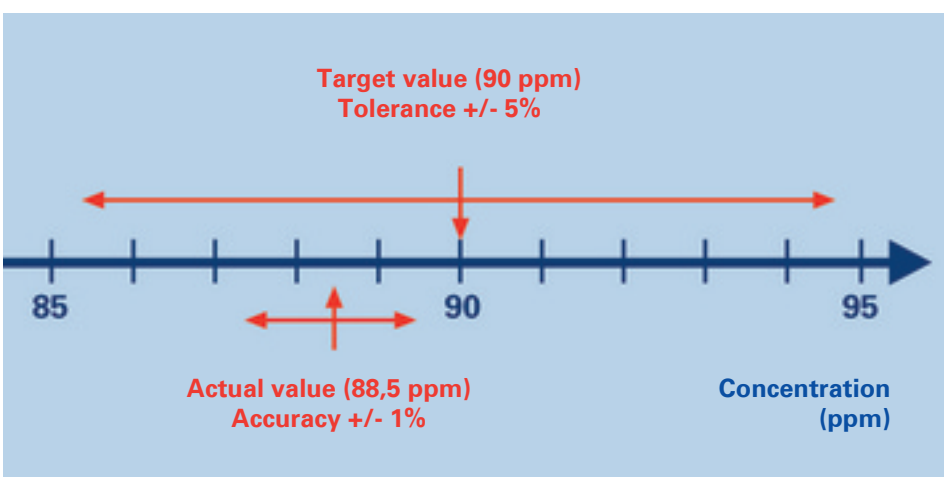
Test gases are used for calibrating measurement instruments. The content of a gas cylinder often lasts for many months. Therefore the **stability period** specifies the time from the date of manufacture, for which the actual value in the certificate applies. Usually this period is 12 months, although longer stability periods are, by all means, possible (*Longlife Option*).

Content expressed	Substance content	Volume content	Mass concentration	Mass content
SI-Unit	mol/mol	m <sup>3</sup> /m <sup>3</sup>	kg/m <sup>3</sup>	kg/kg
Usual measures	Mol%	Vol%	g/m <sup>3</sup>	Wt%
	ppm	vpm (ppmv)	mg/m <sup>3</sup>	g/kg
	μ mol/mol (ppb)	μ l/m <sup>3</sup> (ppbv)	μ g/m <sup>3</sup>	mg/kg (ppmw)
Formulas	$x_i = \frac{n_i}{n_G}$	$\varphi_i = \frac{V_i}{V_G}$	$\beta_i = \frac{m_i}{V_G}$	$w_i = \frac{m_i}{m_G}$

**with:**  $n_i, V_i, m_i$  = quantity of material, volume, mass of component  $i$   
 $n_G, V_G, m_G$  = quantity of material, volume, mass of mixture

The **tolerance** describes the permitted deviation of the actual concentration (actual value) of a component from the required concentration (target value). Depending on the process, the production tolerance is normally about 3%-10% relative, depending on the concentration range as well as type and number of components.

In this context, the internal treatment of the gas cylinders plays a crucial role. The production of stable test gases is only possible through thorough and consistent cylinder pre-treatment with extensive purging and evacuation cycles at high temperatures as well as appropriate conditioning procedures.



Tolerance and accuracy of gas mixtures based on example of 90 ppm NO Topline (tolerance +/-5%, accuracy +/-1%).

## Mixture categories

In accordance with the different gas mixture requirements, Messer offers the products in a variety of mixture categories which define the tolerance, accuracy and stability period:

Typ	Accuracy (% rel.)	Tolerance (% rel.)	Concentration	Stability (months)
<b>Tecline</b>	no certificate	2-10 %	1-100%	
<b>Traceline</b>	5 %	10 %	5-1000 ppb	< 12
<b>Labline</b>	2 %	5 %	1 ppm-100 %	12
<b>Topline</b>	<1 %	<5 %	10 ppm-100%	12

Longlife option 24/36/60: prolonged stability period (24/36/60 months)  
Accredited option: with calibration certificate from an ISO 17025 accredited laboratory

*Tecline* mixtures are supplied in accordance with a standard specification without a certificate. Typically, *Tecline* mixtures are used as operating or process gases. The *Labline* category consists of test gases with a certificate. The tolerance is 5% and the accuracy is usually 2%. For high precision measuring work, we recommend calibration with *Topline* mixtures with an accuracy of better than 1%. For trace and ultra-trace analysis, we offer the *Traceline* category with concentrations in the ppb range.

## Production of gas mixtures

**Dynamic processes** allow to carry out mass production and filling of standard gas mixtures. This involves controlling two or more volume flows of components and carrier gas via mass flow controllers, homogenizing them in a mixing chamber, if necessary analyzing the mixture after the mixing chamber and compressing it into the cylinders. The composition of the mixtures in a batch is identical within very low variances. Dynamic production is therefore the method of choice for standard mixtures (*Tecline*).

With the **manometric method** of filling gas cylinders, the partial pressures of the components are added together in accordance with Raoult's Law. This procedure involves measuring the pressure increase in the cylinder during and after the addition of each mixture component at a defined temperature.

The production tolerance mainly depends on the accuracy of the pressure gauges and temperature measurement. The advantage of this method is the high level of flexibility: all mixture types can be produced when the partial pressure reaches a measurable magnitude. The disadvantage of this method is the systematically lower process accuracy. A subsequent analysis of individual cylinders generally allows a much more accurate determination of the actual value of the component. That is why the analysis values and their uncertainty are certified.

With the **gravimetric method**, the individual components are weighed out. The mass contents are determined directly, which can then be converted into substance contents. The weighing process is one of the most accurate physical measuring processes that exist. That is why high precision gas mixtures can be produced by this method. Quantitative control analysis usually does not achieve these levels of accuracy. It is only used to confirm the process parameters. Certificates are issued for the value determined by gravimetric weighing and its uncertainty.



Manometric gas mixture production

If the required accuracy is not achievable by direct dosing of the component (e.g. because of low contents of light substances), then one or more gravimetrically produced pre-mixtures with higher contents of the required component are used in order to produce the final mixture.



*Gravimetric production*

### Homogenization

Immediately after gravimetric or manometric filling, it is possible that the individual components in the gas cylinder will form into layers. A homogenous mixing of the components is ensured by rolling the cylinders in an almost horizontal position.

### Analytical processes

The analytical tools for determining the composition of gas mixtures and test gases cover a broad spectrum of physical and chemical analytical methods. They range from monitor analysis and infrared and ultraviolet spectrometry to gas chromatography and mass spectrometry.

For multi-component mixtures **gas chromatography** is used. With its many different versions of separation columns and detectors this method offers suitable solutions even for very specific analyses. For chemically reactive gases conductivity measurement, potentiometry and the classical methods of titrimetry are used.

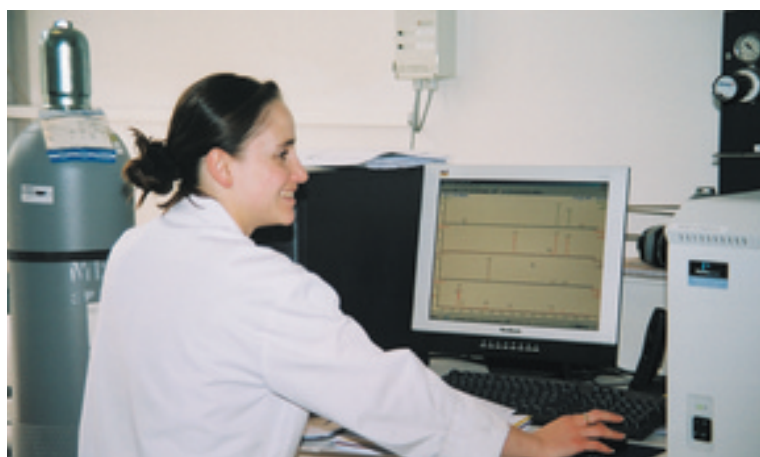
In general, the achievable analytical accuracy is in the range of  $\pm 2\%$  relative. Over and above this, special, highly developed calibration methods can be used to achieve measurement accuracies of  $\pm 1\%$ .

**Monitor analysis (non-dispersive IR or UV spectrometry, chemoluminescence, sum-FID)** makes it easy to measure certain components, for example IR-active ones, very quickly and accurately.

### Traceability

Most of the methods that are used for quantitative analysis are relative methods. Appropriate measures must be taken to ensure that the results achieved can be traced back to recognized standards. With gravimetric quantitative analyses, this is done by calibrating the scales used with certified weight standards. This means that the results obtained with these scales, i.e. the quantities of gravimetrically produced gas mixtures, can be traced back directly to the national mass standard of the relevant producer country.

Analytical quantitative analysis is based on the calibration gases used in our laboratories. Only high-precision, gravimetrically produced gas mixtures are used for this. If possible, these mixtures are confirmed through standard reference material (SRM) from third-party production, e.g. **NIST** (National Institute of Standards and Technology, USA), **VSL** (Van Swinden Laboratorium, Netherlands), **BAM** (Bundesanstalt für Materialforschung und -prüfung, Germany). If quantitative analysis is performed by means of a direct comparison with this standard reference material, the products are regarded as directly traceable to this standard.

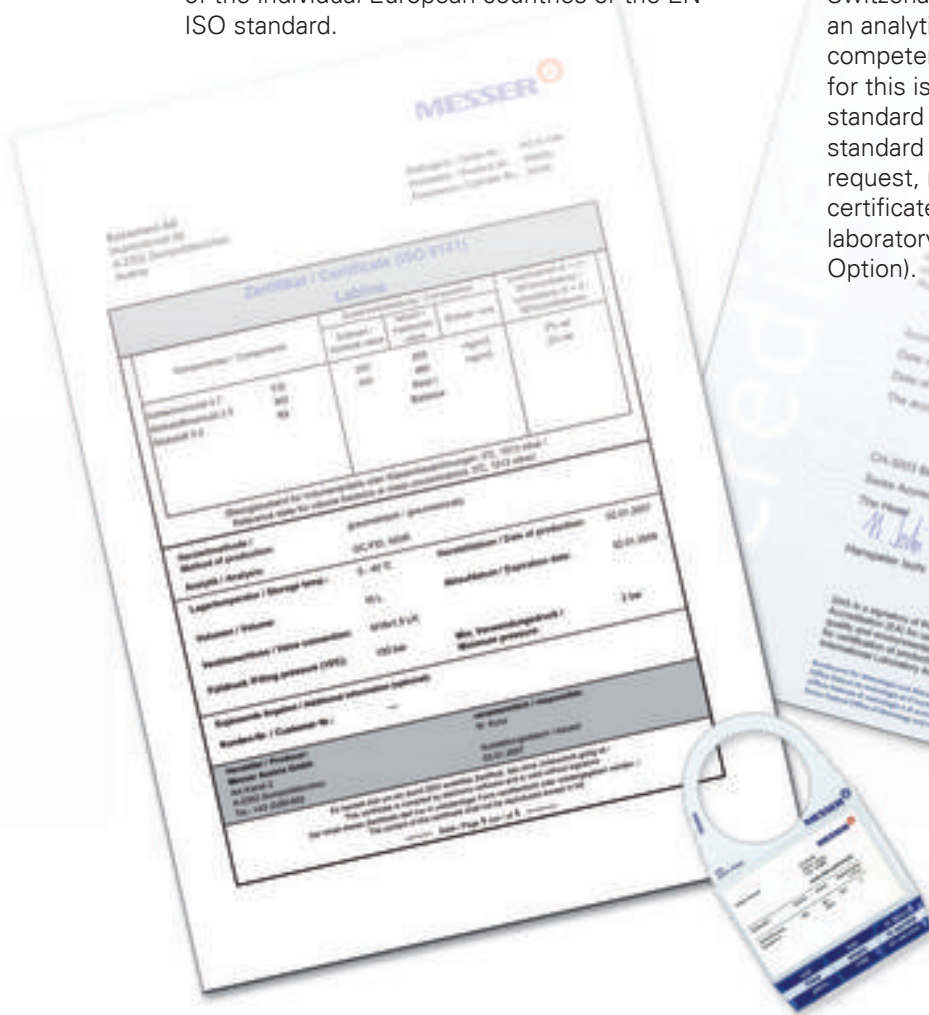


*Analysis of gas mixtures*

## Certificates

All individually produced gas mixtures are supplied with a certificate. This contains all the important information regarding the mixture components and the composition (content and uncertainty) as well as the cylinder. In reduced form, the certificate is attached as a label to each mixed gas cylinder.

The information on the certificate is in accordance with the relevant national regulations of the individual European countries or the EN ISO standard.



## Accreditation

The reliability of the content information provided on a certificate of a calibration gas is a crucial quality criterion. The fact that our customers can rely on our information has been confirmed by independent experts: Messer has several of its analytical laboratories accredited as test laboratories by the relevant state authorities. In Switzerland, for example, the relevant authority is METAS (Metrology and Accreditation Switzerland). An accreditation is a certification of an analytical laboratory's professional competence by independent experts. The basis for this is the internationally recognized quality standard EN ISO 17025. In addition to the standard certificate from Messer, users can, on request, receive a standard-compliant calibration certificate from the accredited calibration laboratory for many gas mixtures (Accredited Option).

## Service and Support

The range of applications is just as great as the range of possible gas mixtures. It is not always easy to choose the right mixtures for a given application. Technical feasibility and the potential costs are often a limiting factor.

Our customer consultants will be happy to help you choose the optimal solution for your specific requirements. We look forward to hearing from you!



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