

Gas Mixtures

Individual and standard gas mixture for your specific application



Besides pure gases, defined gas mixtures are also required for many applications. For many routine applications, from operating gases for analytical equipment, banana ripening and laser applications to the operation of ionization chambers, Messer provides an extensive range of standard mixtures. Thanks to their standard specification, these mixtures can be produced in batches and delivered from stock. Details of the different standard mixtures can be found in the relevant data sheets.

The highest demands apply to gas mixtures when they are used for the operation of sensitive analytical instruments in quality assurance, safety technology,

emission or environmental monitoring. Messer offers individual calibration gas mixtures to realize appropriate and reliable calibration of analytical equipment. Messer follows a strict quality management system in order to ensure manufacturing with the highest quality standards.

Our main European plants for specialty gases and gas mixtures are in Zwijndrecht (Belgium), Mitry-Mory (France), Lenzburg (Switzerland), Gumpoldskirchen (Austria), Budapest (Hungary) and Pancevo (Serbia). Messer's many years of experience and the high-level expertise of our employees in development, production and analysis, ensure that we always offer our customers the high standards of quality they expect.

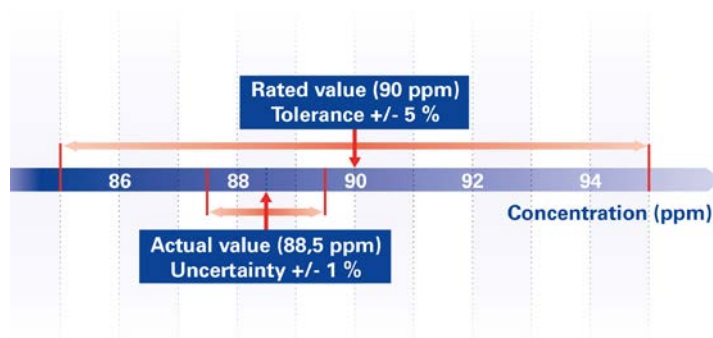
Characterization of individual gas mixtures

The composition of a gas mixture is defined by the amount of the various components in the mixture. Different units may be used for specifying composition. Mole fraction is often used, as this unit is pressure and temperature independent. Volume fraction and mass concentration are also widespread. These pressure and temperature dependent units are usually referred to standard conditions (0°C and 1013 mbar). For the conversion from one unit into another Messer uses software based on the standard EN ISO 14912 (Gas analysis – Conversion of gas mixture composition data).

The feasibility of a gas mixture is limited by chemical, physical and safety restrictions. For instance, gas mixtures containing both oxidizing and flammable components can only be produced under limited conditions. A team of Messer's experienced experts checks every single gas mixture which is produced for the first time and defines all relevant process parameters in detail. A specially developed thermodynamic software package is used for the calculation of the mixture.

The (production) tolerance defines the permitted deviation of the actual content (actual value) of a component from the required content (rated value) in the mixture. The tolerance is normally about 5% to 10% (relative) depending on the production process, the concentration range, and the type and number of components.

The actual content of a component can only be stated with a certain degree of uncertainty. Messer's certificates always state the expanded uncertainty with the coverage factor $k=2$, meaning that the true content lies with a probability of 95% in the specified interval.



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

When gas mixtures are used for calibrating measurement instruments, the content of a gas cylinder often lasts for many months. The stability period specifies the time from the date of manufacture for which the actual value in the certificate applies. This period is usually 12 months, although longer stability periods for many gas mixtures are possible (Longlife Option). In this context, the internal treatment of the gas cylinders plays a crucial role. The production of stable gas mixtures 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.

Mixture categories

The required specification of a gas mixture clearly depends on its application. In order to meet the various demands optimally, Messer offers a variety of mixture categories. These categories define the tolerance, uncertainty and stability period:

Type	Uncertainty	Tolerance	Concentration	Stability
	% rel.	% rel.		Months
Tecline	no certificate	2-10 %	1-100 %	
Traceline	5 %	10 %	5-1000 ppb	<12
Labline	2 %	5 %	1 ppm-100 %	12
Topline	<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



Gravimetric production of gas mixtures

method according to ISO 6142 (Gas analysis – Preparation of calibration gas mixtures – Gravimetric method). This method is based on weighing the masses of the particular components. Weighing is one of the most accurate physical measuring methods, which is why the gravimetric preparation is employed to manufacture high precision calibration gas mixtures.

Homogenization is implemented to establish a uniform distribution of all components of the gas mixture throughout the volume of the gas cylinder.

Finally, the gas mixtures are analyzed according to ISO 12963 (Gas analysis - Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration) or ISO 6143 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures). In case of mixtures manufactured by the manometric method, the result of the analysis serves for certification of the composition and the respective uncertainties. The determined composition and the corresponding uncertainties of the gravimetric filling method are more accurate than those of the analysis. For this reason, the gravimetric data and uncertainties are certified.

Every individually produced gas mixture is supplied with a certificate. This contains all the important information regarding the gas mixture. The information of the certificate is in accordance with ISO 6141 (Gas analysis - Requirements for certificates for calibration gases and gas mixtures). In reduced form, the certificate is attached as a label to each gas cylinder.

Tecline mixtures are delivered with a standard specification without a certificate. Typically, Tecline mixtures are used as operating or process gases. The Labline category consists of individual gas mixtures with a certificate. The tolerance is 5 % (rel.) and the uncertainty of the actual value is usually 2 % (rel.). For high precision measuring work, we recommend calibration with Topline mixtures with an uncertainty of better than 1% (rel.). For trace analysis, we offer the Traceline category with concentrations in the ppb range.

Manufacturing of individual gas mixtures

Messer uses different processes for manufacturing gas mixtures. The components of a mixture are usually successively filled into the compressed gas cylinder. If direct dosing of the component is not possible (e.g. because of low contents), then one or more pre-mixtures with higher contents of the required component are used in order to produce the final mixture.

With the manometric method, the pressure increases in the cylinder during and after the addition of each mixture component is measured. The advantage of this method is the high level of flexibility; the disadvantage is the systematically low process accuracy.

The most common procedure for manufacturing of high precision calibration gas mixtures is the gravimetric



Calibration of the used balances

Laboratory accreditation according to ISO 17025 and ISO 17034



Besides the composition, the essential quality features of gas mixtures with a certificate is the determination of uncertainty according to a recognized method and the traceability of the composition to national standards.

Traceability

Metrological traceability is defined as the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty. The chain of traceability allows any measurement to be referenced to the original definition of the unit. Traceability permits the comparison of measurement results independent of when and where the measurements were performed.

The composition of gravimetrically produced gas mixtures can be traced back to the unit of mass, namely the SI unit "kg" by calibrating the scales with certified weight standards. Therefore, the compositions of gravimetrically manufactured gas mixtures are traceable to the national mass standard.

The analytically determined composition of a gas mixture can also be traced back to the national mass standard, as only gravimetrically produced reference materials are utilized for calibration of the analysis method. Alternatively, primary reference materials (PRM) manufactured by the national meteorological institutes can be used to trace back to the SI unit amount of substance (mol).

Uncertainty

Uncertainty is a parameter, associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand. The parameter may be, for instance, a standard deviation (or a given multiple of it), or the half-width of an interval having a stated level of confidence. In case of gas mixtures the expanded uncertainty with the coverage factor $k=2$ is usually applied, meaning that the true value lies with a probability of 95% in the specified confidence interval.

The main factors influencing the uncertainty of a given gas mixture composition are listed below:

Gravimetric manufacturing:

- uncertainty of weighing masses of the individual components
- components purity of the gas mixture
- changes in air density and, therefore, in buoyancy of the cylinder during the weighing process due to changes in temperature, air pressure or air humidity
- mass increase or loss of cylinders due to handling during the weighing process

Analytical determination of the composition:

- uncertainty of analytical comparison measurement
- uncertainties of calibration gases and / or reference materials used

Accreditation according to ISO 17025 and ISO 17034

The ISO 17025 specifies the general requirements for the competence of testing and calibration laboratories. For example, a laboratory accredited according to ISO 17025 has proven its competence to carry out calibration as well as to manufacture and analyze gas mixtures. A laboratory accreditation according to ISO 17025 specifies the method of testing or calibration. It can be based on ISO 6142 (Gas analysis – Preparation of calibration gas mixtures – Gravimetric method) or ISO 6143 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures).

The ISO 17034 describes the general requirements for the competence of reference material producers. A manufacturer accredited according to ISO 17034 is competent to produce certified reference materials (CRMs).

The certificate from a laboratory accredited according to ISO 17025 describes the composition at the time of determination. The stability period of the gas mixture is separately certified on the certificate according to ISO 6141, which is supplied in addition. The composition of a gas mixture from a reference material producer accredited according to ISO 17034 is certified for a defined period of time.

In general, calibration gases certified by an accredited laboratory play an important role in analytical chemistry as they satisfy the highest metrological standards. They are primarily used in laboratories, which are subjected to GMP or ISO 17025 regulations.

Both standards set the guidelines for the organization of operation, the requirements for human resources, facilities and environment, the applied processes and the management system. A national accreditation body evaluates the competence based on the guidelines stated in ISO 17025 and ISO 17034. The certified scope of laboratory accreditation designates the components and the corresponding concentration ranges for which the competence is verified by the national body.

In Europe, Messer operates four laboratories with an accreditation according to ISO 17025. Our long-term experience in manufacturing and analyzing individual gas mixtures and the skills of our teams enable us to offer highly accurate and traceable products.

Our plant in Switzerland is accredited according to ISO 17034, thus we have the competence for manufacturing CRMs. As a manufacturer of CRMs, we proved the reliability of our processes, validated our technical expertise and showed our commitment to quality.

Proficiency Tests

Accredited calibration and testing laboratories are obliged to participate in proficiency tests such as interlaboratory comparisons to validate the high level of quality and to continuously improve the production processes. In addition to external proficiency tests, all Messer specialty gases plants in Europe take part in in-house proficiency tests. The in-house proficiency test of Messer is a unique approach, tailored to the scope of production. On the basis of the six laboratories of Messer, it is possible to perform statistical evaluation of the analytical data. Accredited non-Messer laboratories are also participating to the scheme occasionally. This assures that the results of all laboratories are traceable and comparable within the metrological hierarchy.

Messer offers gas mixtures in various cylinder sizes and filling pressures on demand. The cylinder and valve materials are determined by the chemical and physical properties of the mixture. For instance, 10- or 50-liter aluminum cylinders with valves made of stainless steel and a filling pressures of 150 bar are frequently used.

The safety data sheet is of significant importance as it contains all relevant safety instructions for safe handling of gas mixtures. Every classification of a gas mixture is performed in a software-based approach according to the CLP regulation. This proceeding supports the efficient and reliable establishment of safety data sheets and labelling of cylinders.



Specialty gas equipment

For reliable calibration of analytical equipment, especially in the low concentration range, it is essential to eliminate any influence changing the composition of the gas mixture. This also involves the use of suitable withdrawal equipment. Messer offers appropriate withdrawal equipment and gas supply systems to preserve the quality of the gas mixture and to ensure safety.

Service and support

Messer's many years of experience in development, production and analysis ensures that we are always able to offer our customers the high-quality standard they expect. We will be glad to support you in choosing the optimal solution for your specific requirements.



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