For many applications besides pure gases also defined gas mixtures are required. For many routine applications, from operating gases for analytical equipment, banana ripening and laser applications to the operation of ionisation 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.

In some applications for instance in order to check or calibrate measuring instruments every intended use determines the exact composition of the mixtures.

These individual gas mixtures are produced on customer’s request provided by the physical and chemical feasibility as well as by the compliance with the relevant safety regulations.

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

The composition of a gas mixture is defined by the amount of the various components in a carrier gas. Different units may be used for specifying concentrations. The amount of substance (% or 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. For the conversion from one unit into another Messer uses software based on the standard ISO 14912 (Gas analysis – Conversion of gas mixture composition data).

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

The producibility of a gas mixture is defined 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 has to be produced for the first time and defines in detail all relevant process parameters. For the mixture’s calculation a specially developed thermodynamic software package is used.

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 tolerance is normally about 5% to 10% relative, depending on the concentration range as well as type and number of components.

The actual value of a component can only be stated with a certain uncertainty. On the certificates Messer states always the expanded uncertainty with the coverage factor k=2 meaning that the true value lies with a probability of 95% in the specified interval.

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. Usually this period is 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

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

<table>
<thead>
<tr>
<th>Type</th>
<th>Uncertainty</th>
<th>Tolerance</th>
<th>Concentration</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% rel.</td>
<td>% rel.</td>
<td>Months</td>
<td></td>
</tr>
<tr>
<td>Tecline</td>
<td>no certificate</td>
<td>2-10 %</td>
<td>1-100 %</td>
<td></td>
</tr>
<tr>
<td>Traceline</td>
<td>5 %</td>
<td>10 %</td>
<td>5-1000 ppb</td>
<td>&lt;12</td>
</tr>
<tr>
<td>Labline</td>
<td>2 %</td>
<td>5 %</td>
<td>1 ppm-100 %</td>
<td>12</td>
</tr>
<tr>
<td>Topline</td>
<td>&lt;1 %</td>
<td>&lt;5 %</td>
<td>10 ppm-100 %</td>
<td>12</td>
</tr>
</tbody>
</table>

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 individual gas mixtures with a certificate. The tolerance is 5 % and the uncertainty of the actual value is usually 2 %. For high precision measuring work, we recommend calibration with Topline mixtures with an uncertainty of better than 1 %. For trace analysis, we offer the Traceline category with concentrations in the ppb range.

Production of individual gas mixtures

Messer uses different processes for manufacturing gas mixtures. Usually the components of a mixture are successively filled in the pressurized 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 increase 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 lower process accuracy. A subsequent analysis of gas mixtures, e. g. for accredited gas mixtures according to ISO 6143 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures) 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 according to ISO 6142 (Gas analysis - Preparation of calibration gas mixtures - Gravimetric method), the individual components are weighed out. 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.

According to request Messer offers gas mixtures in different pressurized gas cylinders. Choice of cylinder and valve material is determined by the requirements of the mixture. For instance 10- or 50-liter aluminium cylinders with valves made of stainless steel and filling pressures of 150 bar are often used. Mixtures are classified according to CLP regulation by means of expert software which includes drawing up a complete safety data sheet and labelling the cylinder. The safety data sheet contains all relevant safety instructions for the usage of the gas mixture.
Laboratory accreditation according to ISO/IEC 17025 and ISO Guide 34

ISO 17025 specifies the requirements for the competence of testing and calibration laboratories. The main provisions concern the operation and the scope of a quality management system as well as the evidence of the necessary technical competence for performing calibration.

The “accreditation” of a laboratory describes the formal confirmation by a national accreditation body formally stating that an accredited laboratory has the competence to perform certain conformity evaluation tasks according to ISO/IEC 17025. These tasks may include manufacturing as well as analysing the gas mixtures.

Accreditation means the formal recognition of the technical and organisational competence of a laboratory to execute the calibration work. In the course of accreditation the laboratory competence for a defined spectrum of gas mixtures – the scope of accreditation – is described and formally documented in the list of calibration and measurement capabilities.

The essential quality features of gas mixtures with a calibration certificate are traceability of gas mixtures’ composition to national standards and determination of uncertainty in accordance with a recognized method.

To ensure the quality of the calibration data the accredited laboratories are obliged to participate regularly in comparison programmes between laboratories (round robin tests) or in suitability tests.

Messer has received accreditation as calibration laboratory for five laboratories all over Europe.

**Traceability**

Ensuring the traceability of gas mixtures’ composition to standards from national metrological institutes or to the International System of Units (SI) is an essential requirement for the accuracy of certified values and for the determination of uncertainty. Gravimetrically produced gas mixtures can be traced back to the SI unit “mass” by calibrating the scales used with certified weight standards. The results obtained with these scales, i.e. the quantities of gravimetrically produced gas mixtures with calibration certificate
produced gas mixtures, can be traced back directly to the national mass standard of the relevant producer country. When the composition of a manometrically produced gas mixture is determined the results are based on the calibration gases used in our laboratories. Only high-precision, gravimetrically produced gas mixtures are used for this, so the results can be traced back to the mass standard again. Alternatively, the composition’s traceability of these mixtures can be ensured by comparing with standard reference materials (SRM). Standard reference materials are gas mixtures of the highest metrological quality which are manufactured by national metrological institutes. Reference materials as such are deemed equivalent to the standards of physical variables. Instead of comparing traceability directly it can also be performed in several stages but leading to a higher uncertainty with every single step.

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

**Manometric production and analytical certification of the composition:**
- uncertainties of calibration gases and / or reference materials used
- uncertainty of analytical comparison measurement

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

The uncertainty of the gas mixture’s composition is determined from all relevant influencing factors following the BIPM/ISO “Guide to the Expression of Uncertainties in Measurement”.

For calibration gases it is common to state the “expanded uncertainty” \( U=k*s \) with the coverage factor \( k=2 \). By choosing this coverage factor it is possible to achieve statistically a confidence interval of 95% for the composition as declared.

**Reference materials**
The accreditation according ISO Guide 34 confirms the competence of our laboratory in Switzerland to manufacture certified reference materials.

Certified reference materials (CRM) play an important role in analytical chemistry as they satisfy highest metrological standards. They are primarily used in laboratories which are subject to GMP or ISO/IEC 17025 regulations. ISO Guide 34 defines the competencies and activities which a manufacturer of reference materials at least has to satisfy. Particular importance is attached to:

- production planning
- testing and processing of raw materials
- production process as well as production and quality controls
- performing tests to confirm homogeneity and stability of reference materials
- characterization of reference material / determination of characteristic data
- assignment of characteristic data and of statement on uncertainty to the reference materials
- release of characteristic data and issuance of certificates
- handling and storage of reference materials as well as transport/distribution and customer service.

In the accreditation procedure conducted by the Swiss Accreditation Service Messer Schweiz AG could demonstrate that all activities concerning quality of reference materials consistently comply with regulation ISO Guide 34 as well as the production of gas mixtures.

Based on the laboratories with accreditation Messer is able to ensure and continuously improve quality of accredited and non-accredited calibration gas mixtures as well as reference materials. External and inter-company round robin tests help to ensure that the compositions and uncertainties of gas mixtures produced at any Messer location are comparable and traceable according to the requirements of our customers throughout Europe.
Every individually produced gas mixture is supplied with a certificate. This contains all the important information regarding the gas mixture. In reduced form, the certificate is attached as a label to each gas cylinder.

The information on the certificate is in accordance with ISO 6141 (Gas analysis - Requirements for certificates for calibration gases and gas mixtures).

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. Not only production and analysis of the calibration gas mixtures influence the quality of these mixtures: storage and handling can also have significant effects.

The right choice of the gas supply system is as crucial as the careful withdrawal of the calibration gas mixture. Our customer consultants will be happy to help you choosing the optimal solution for your specific requirements.