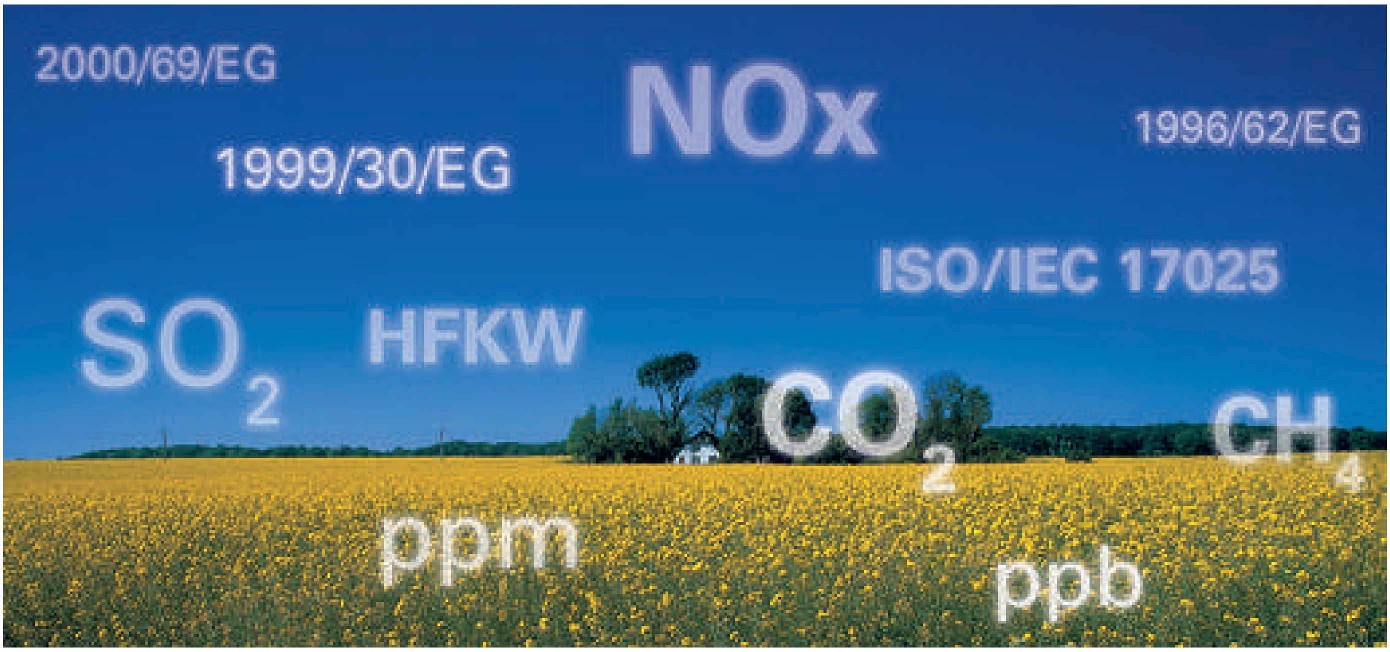


Promoting environmental protection by environmental monitoring

The Earth's ecosystem is both extremely complex and far less stable than we once imagined. Since the beginning of the industrial age, mankind influences more and more the own environment. Over the pas few decades, the general public has become increasingly aware of the dramatic consequences this has been having on our living space. The hole in the ozone layer, forest decline and the global greenhouse effect are only a few examples. Worldwide sustainable handling of the Earth is just in the early states. Intensive monitoring, understanding of interactions within the overall system and the compilation of regulations, as well as their rigorous implementation and control, constitute the fundament of environmental protection. Reliable high-precision gas analysis – sometimes at extremely low concentration ranges – is an indispensable tool in this context.

By the mid-1970s, attention was already drawn to the possible negative effects of chlorofluorocarbons (CFCs) on the Earth's ozone layer. Nevertheless, their use in aerosol cans, for example, or as refrigerant in air conditioners, initially continued to have ever stronger growth. It was only after the discovery of the so-called "ozone holes" and their continuous enlargement the Montreal protocol was signed in 1987, ultimately leading to the complete ban on CFC emissions in 1990. Since the mid-1990s, the ozone holes have begun to close again. However, due to the long lifetime of CFC-compounds in the atmosphere this process will last several more decades.

Air quality monitoring high in the mountains

Although science is still far from comprehending all atmospheric processes in detail, several substances other than CFCs have been identified as the cause of a variety of negative effects. There is now little doubt of the harmful effects that so-called 'greenhouse gases' are having on the climate – gases such as CO_2, SF_6, methane and perfluorinated hydrocarbons. We also have conclusive proof that the 'acid rain' generated by high sulphur dioxide or nitrogen oxides emissions is the root cause of forest decline. The use of lowsulphur fuels for vehicles and the installation of flue gas purification units for combined heating and power plants have already yielded significant benefits in environmental terms.

Emission monitoring of industrial plants

Accordingly numerous treaties, laws and directives have been (and continue to be) established at global, European and national levels. Their provisions ban, or at least limit, the emission of these substances and set requirements for their reduction. These laws and directives also regulate the monitoring of emissions. This can extend right through to the continuous monitoring of emissions in power plants, refineries, waste incineration plants or in the chemical industry. Depending on the process, this typically requires the monitoring of CO, CO_2, NOx, SO_2 and possibly other organic compounds.

Chemistry contributes to our well-being; unfortunately emissions are inevitable.

Road traffic

Along with industrial plants, road traffic is a major source of air pollution. There are special regulations governing this area. For every vehicle type there are European emission standards that must be adhered to gain official design approval. Moreover, statutory regulations for registered vehicles require periodic proof of compliance with emission limits (exhaust emission test).

"Environmental analysis" – Imission measurements

The ability to determine the concentration of pollutants in the surrounding air as precisely as possible is an essential prerequisite for understanding atmospheric processes and tracking the effects of any measures implemented. According to corresponding European directives European countries have to operate measurement networks. The relevant measurements are carried out and evaluated on an quasi-continous basis – not only wherever high pollutant concentrations have to be expected, but also in 'clean air zones'.

Analytical procedures

EU directive 1996/62/EC stipulates that ambient air quality must be monitored. For this, national measurement networks have been installed in all countries of the European Union.

EU directive 1999/30/EC sets limit values for sulphur dioxide, nitrogen oxides, particulate matter and lead, and EU directive 2000/69/EC sets limit values for carbon monoxide and benzene. These directives also stipulate measurement procedures and measurement intervals (see table).

Component	Meas. procedure	Meas. Interval
Sulphur dioxide	UV-fluorescence	every half hour
Sulphur dioxide	Impregn. Filter, Ion	daily
Nitrogen oxides: NO, NO_2,	Chemoluminescence	every half hour
Nitrogen dioxide	Impregnated filters	daily
Ozone	UV-absorption	every half hour
Carbon dioxide	IR-absorption	every half hour
Carbon dioxide	Gas chromatography	every half hour
Carbon monoxide	IR-absorption	every half hour
Methane	Gas chromatography	every half hour
Nitrous oxide (N_2O)	Gas chromatography	every half hour
Sulphur hexafluoride (SF_6)	Gas chromatography	every half hour
Peroxyacetylnitrate (PAN)	Gas chromatography	every half hour
Mercury	Atomic fluorescence	every half hour
Hydrocarbons (VOC)	Gas chromatography	twice a week, sample
Hal. Hydrocarbons	Gas chromatography	daily

Component	Meas. procedure	Meas. interval
Ions in rainfall	Ion chromatography	daily (bulk)
Ions in rainfall	Atomic abs. + Ion chr.	weekly (wet only, bulk)
Heavy metals in rainfall	ICP/MS; Atomic	weekly
Sulphates in dust	Impregnated filters, Ion chr.	daily
Σ NH_3 + NH_4^+ in dust	Impregnated filters, Ion chr.	monthly
Σ HNO_3 + NO_3^- in dust	Impregnated filters, Ion chr.	monthly
Heavy metals in dust	ICP/MS	monthly

Sulphur dioxide fluoresces after irradiation with UV light. The intensity of these fluorescent radiation is directly proportional to the sulphur dioxide concentration.

Nitrogen oxides are detected by means of chemoluminescence. Here nitrogen monoxide is oxidised with ozone to form nitrogen dioxide in an excited state. The excitation energy is released as light. In order to measure nitrogen dioxide, it must first be reduced to nitrogen monoxide in the presence of a catalyst. Thus chemoluminescence can be used to measure either nitrogen monoxide or both nitrogen oxides simultaneously. The nitrogen dioxide concentration is determined by subtracting the nitrogen monoxide value from the total.

Calibration of instruments in the laboratory

Carbon monoxide and carbon dioxide can be measured very precisely using infrared methods. Both substances absorb infrared light at different characteristic wavelengths. These substances can also be detected using gas chromatography. Such measurements are usually carried out together with the determination of many other air pollutants such as methane, sulphur hexafluoride, benzene, and other hydrocarbons and halogenated hydrocarbons (CFCs, HFCs). The use of detectors such as flame ionisation detectors (FIDs) or electron capture detectors (ECDs) permits extremely accurate measurement of these pollutants.

Calibration

All measured values are first generated as signals with signal strength being proportional to the concentration of the corresponding substance. In order to determine the actual value of the concentration, the instrument has to be calibrated. A sample, whose precise concentration value is known, is measured and the signal strength determined. The same procedure is carried out with a so-called 'zero gas', which does not contain the component to be measured. This is used to determine the zero point on the calibration curve. In the ideal case, the calibration graph is a straight line drawn through the zero point and the measured point of the reference.

Connecting calibration gases at the measurement station

Calibration gases

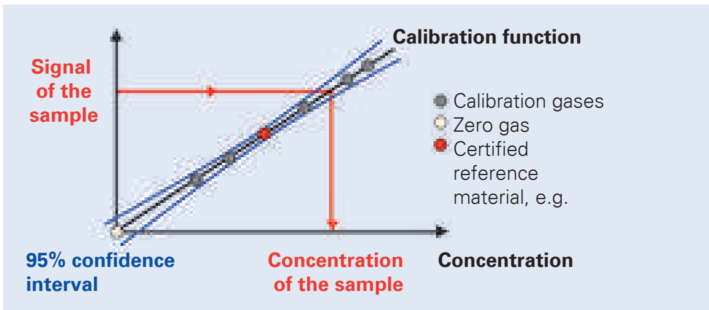
Highly accurate measurements can be obtained only with calibrated instruments. Quality assurance measures are specified in the relevant EU directives (e.g. EU directive 1996/62/EC). Every environmental measurement relies on international comparability and the possibility to trace back the calibration materials used to primary reference standards.

Specially manufactured calibration gas mixtures are often used as reference standards for gaseous air pollutants. In the case of less volatile components, with corresponding vapour pressure, permeation systems can also be used. Here the vapour of the respective component is added to a carrier gas stream. A specified concentration can be obtained by maintaining flow, pressure and temperature at very constant and precise levels.

The advantage of ready-made calibration gas mixtures in comparison to permeation systems is their general independence to fluctuations in pressure and temperature. They can be supplied directly from the pressurised gas cylinder to the instrument. So they are considerably easier in use when conducting field measurements. Fully automated measurement stations are exposed to wind and weather. Temperature and barometric pressure fluctuations are inevitable; they can be held to a reasonable minimum at best only with sophisticated air conditioning systems.

High-precision calibration gases

Calibration gases for emission measurements are normally produced in the ppm-range. With linear calibration functions the magnitude of the concentration required should be approximately 80 % of the maximum value of the instrument's measurement range. Production methods have already been described elsewhere (see 'Gas Mixtures' brochure).



For imission measurements, the measured values are generally lower by a factor of 1000; here measurements must be carried out in the ppb range. This places high demands on the calibration of the instruments. Supply of the required reference standards is particularly challenging. High-precision calibration gas mixtures in the ppb range can be produced only through so-called 'cascade' filling methods. Here high-precision gas mixtures are first produced with higher concentrations of the desired components. Those mixtures then serve as the basic gases for the production of calibration gases with lower concentrations.

In principle, this is also possible for on-site measurements, where higher concentrated calibration gas mixtures can be diluted using mass flow controllers or critical orifices. The advantage of this method is that it offers some flexibility regarding concentrations. The accuracy of these dilution methods depends both on the accuracy of the higher concentrated calibration gas mixtures as well as on flow calibration accuracy and on temperature and pressure variations.

The accuracy of standard calibration gas mixtures in the ppb range produced using gravimetric methods largely depends on the accuracy of the scales. The concentration values of these mixtures are also directly traceable back to the mass standard of the standard kilogram, as the scales are calibrated with certified weights. Moreover, these mixtures are also compared with international standard mixtures of the metrological institutes (e.g. NIST, VSL, Metas, NPL, BAM, etc).

Particular care must be taken when using ppb mixtures. Gas supply systems should use only chemically inert materials such as stainless steel. Thorough purging with dry carrier gas is absolutely essential, as even the slightest traces of moisture strip the few molecules of an active substance such as sulphur dioxide or nitrogen oxides and remove them from the gas flow. This makes it difficult or impossible to reach the calibration value. Plastic piping should be tested for material compatibility. Not all plastics are equally suited to all gases; some plastics can even be vulnerable to corrosive components. Moreover, many plastics also show high permeation rates for moisture or other substances. Consequently, the use of these materials should be avoided wherever possible.

Accreditation

In order to ensure the highest possible quality of manufactured calibration gases on a continuous basis, a rigorous quality management system is absolutely essential. Along with the general quality management system according to ISO/EN 9001 et seq, the more comprehensive system according to ISO/IEC 17025 (General requirements for the competence of testing and calibration laboratories) should be applied. The latter standard also includes the requirements specific on laboratories.

Analytical instruments automatically record all required measurement data around the clock.

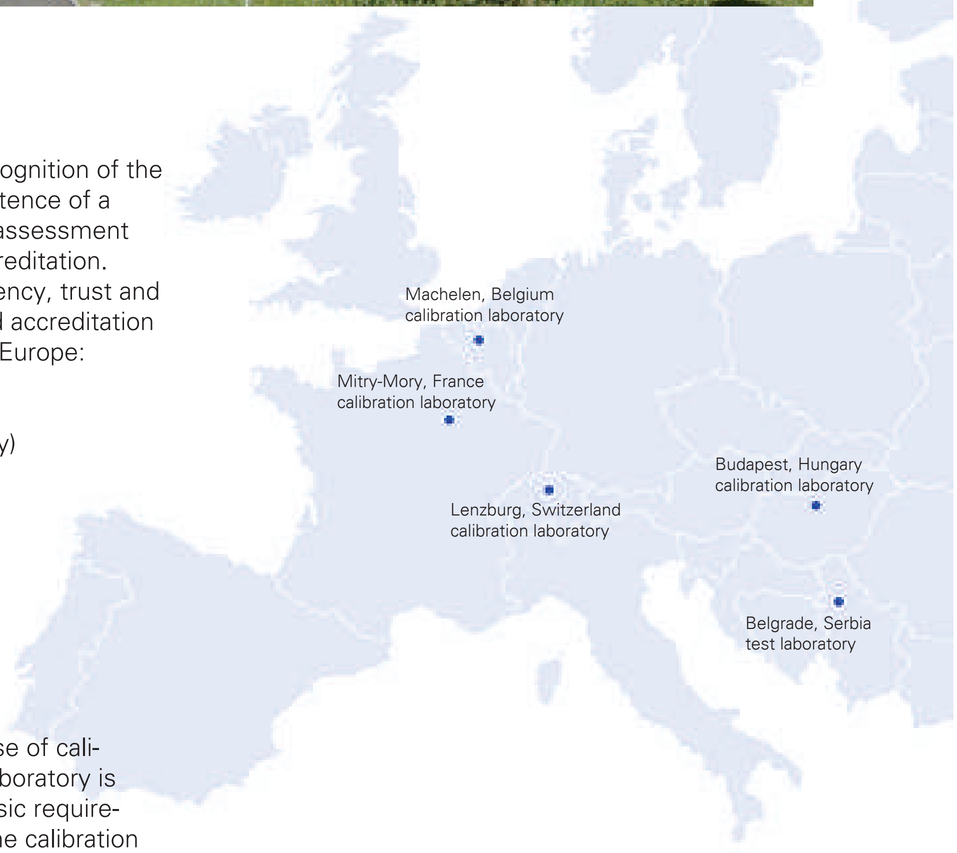
The "accreditation" of a laboratory is defined as the confirmation by a third party formally stating that an accredited laboratory has the competence to perform certain conformity evaluation tasks according to ISO/IEC 17025. Such conformance assessments can be carried out according to testing or calibration. The difference is that a test laboratory is authorised to test only measurement installations and materials, whereas a calibration laboratory is also authorised to produce and certify internationally recognised calibration gases which can be traced back to international standards.

Accreditation means the formal recognition of the technical and organisational competence of a body to carry out the competence assessment tasks listed in the object of the accreditation. Competence is the key to transparency, trust and comparability. Messer has obtained accreditation for several laboratories throughout Europe:

- Messer Schweiz AG, Lenzburg, Switzerland (calibration laboratory)
- Messer France, Mitry-Mory, France (calibration laboratory)
- Messer Hungarogáz, Budapest, Hungary (calibration laboratory)
- Messer Benelux, Machelen, Belgium (calibration laboratory)
- Messer Tehnogas, Belgrade, Serbia (test laboratory)

In some European countries, the use of calibration gases from an accredited laboratory is mandatory. This arises from the basic requirements for test materials used for the calibration of instruments according to the relevant EU directives. With accredited laboratories located all over Europe, Messer is always in a position to meet your needs rapidly and reliably.

We're glad to help!



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