Gases for Life

Process Gases for Analytical Applications

High purity gases for analytical applications

The field of analytical application is extremely diverse. Whether they are used to monitor the quality of foodstuffs, to test engines in the automotive industry, to control processes in the chemical or pharmaceutical industries, in medicine, metallurgy or environmental monitoring: analytical methods are used everywhere for process control, quality assurance or even to prove compliance with statutory regulations. The methods employed and their uses are just as diverse as their fields of application. Nowadays gas chromatography or monitoring is used in environmental or process control, food products or drinking water is checked by ICP and metal alloys are analyzed by spark erosion spectrometry. Many of these methods require high purity gases or gas mixtures for operation as well as high precision reference gases for calibration purposes. The detection limits, achievable analytical accuracy and the reliability of the results often depend on the quality of the gases used. Messer offers a broad range of high purity gases, standard mixtures and customized gas mixtures that fulfil all the required performance criteria.

Gas chromatography

Gas chromatography is used to analyze mixtures of gaseous or volatile liquid substances. The prepared sample is applied to a so-called chromatography column by means of an injector or a sample loop. The individual substances interact with the material in the column in a characteristic manner. A carrier gas transports the individual substances through the column at different speeds depending on the intensity of this interaction. Helium is often used as the carrier gas due to the relatively short analysis times. Alternatively, nitrogen and hydrogen are also often used as carrier gas. The required purity of the carrier gas depends on the type and concentration of the substance being detected.

The detector of a gas chromatograph is installed downstream of the column. A measuring signal is created due to the compounds registered by the detector. This measuring signal serves for qualitative and quantitative analysis. The choice of the optimal detector depends on the type and concentration range of the molecules to be analyzed. Which kinds of operating gases are required in addition to the carrier gas directly depends on the type of detector. In principle, a thermal conductivity detector (TCD) can detect all substances. However, the detection limit is in the % to ppm range. There is no need for any process gas other than a carrier gas of purity level 5.0 or higher. A flame ionization detector (FID) can detect all combustible substances except hydrogen. It requires a hydrogen purity of 5.0 to 6.0 and hydrocarbon-free air to feed the flame. In the automotive industry, a mixture of helium and hydrogen (60:40) is often used instead of pure hydrogen. The detection limit for hydrocarbons is generally in the upper ppb-range. An electron capture detector (ECD) is particularly sensitive for the specific detection of halogenated compounds with a detection limit in the low ppb-range. For this detector, we offer special gases of „ECD quality" with a specified level of halogenated hydrocarbon impurities of less than 1 ppbv. In addition to the carrier gas, usually helium „ECD" or nitrogen „ECD", a „make-up gas" is required to operate this detector. This gas is used to flush out any contaminants that could stick to the cathode. A mixture of 5% or 10% methane in argon (ECD) as well as ECD grade nitrogen has proven to be suitable for this. Certain detectors can be used for the specific detection of individual substances, e.g. a flame photometric detector (FPD), a photo-ionization detector (PID), an atomic emission detector (AED) or a helium ionization detector (HID). The table below summarizes the requirements of the carrier and process gases of various detectors and the appropriated gas qualities.

Gas chromatography

Detector	Carrier gases	Operating gases	Undesirable impurities	Gas purities/measuring ranges		
				< 100 ppb	*< 10 ppm*	*> 100 ppm*
TCD	H_2, He, Ar, N_2	H_2, He, Ar, N_2	H_2, O_2	-	5.5	5.0
FID	H_2, He, N_2	H_2	HC, CO	6.0	5.5	5.0
		synth. air		HC-free	HC-free	HC-free
ECD	H_2, He, N_2	N_2, Ar/CH_4	hal. HC, SF6	ECD-quality	ECD-quality	ECD-quality
FPD	H_2, He, N_2	H_2	HC, CO	6.0	5.5	5.0
		synth. air		HC-free	HC-free	HC-free
HID	He	He	H_2, O_2	7.0 - 6.0	6.0	-
DID	He	He	H_2O, O_2, HC CO, CO_2, hal. HC	7.0 - 6.0	6.0	6.0
AED	He	He	-	6.0	6.0	-
	-	N_2	-	6.0	5.5	-
	-	H_2, O_2	-	5.0	5.0	-
	-	CH_4	-	4.5	4.5	-
MS	-	He	H_2O, O_2	7.0 - 6.0	6.0	-

Atomic emission spectroscopy

Atomic emission spectrometry (AES) can be used to analyze samples containing metals. The absorbed energy ionizes and excites the metallic constituents of the sample. The excited ions reemit the absorbed energy with a wavelength that is characteristic for each metal. The intensity of this emission is proportional to the concentration. The various methods are differentiated according to the type of excitation.

If excitation takes place in a flame, it is called flame photometry. This is frequently used for alkaline metals and alkaline earth metals. Propane 2.5 or acetylene 2.6 is used as fuel gas.

ICP spectroscopy (inductively coupled plasma) is based on a similar principle. However, it is an essentially all-purpose method that can be used to detect nearly all substances. High frequency induction is used to generate an argon plasma that transfers the energy to the constituents in the sample.

The emissions are characteristic of the substance and are directly proportional to the concentration. The purity of argon applied to this method is crucial as only a few ppm of oxygen and moisture can induce undesirable secondary reaction in the plasma. The individual constituents of the sample may then be converted to oxides or hydroxides. These reactions change the emission properties of the sample, thus falsify the analysis result. In order to prevent this disturbing effect, we recommend the use of Argon 5.0.

Elements in metal alloys can also be determined by spark erosion spectrometry, an analytical method used in steel production and casting processes. Similar to ICP spectroscopy, an electrical gas discharge is used to generate an argon plasma that ionizes the constituent atoms on the surface of the metal sample. This produces a spark as the substance vaporizes. The emitted radiation is characteristic for the individual elements and its intensity is also proportional to the concentration. As in the ICP method, the presence of oxygen and moisture perturbs the sensitive measurements. For this purpose, we recommend the use of Ar 5.0 or even better. The detection limits can be further improved if Oxisorb and Hydrosorb purification cartridges are used. An argon/hydrogen
mixture can also be used that acts as a reducing agent, allowing detection of any present oxides.

Atomic absorption spectroscopy

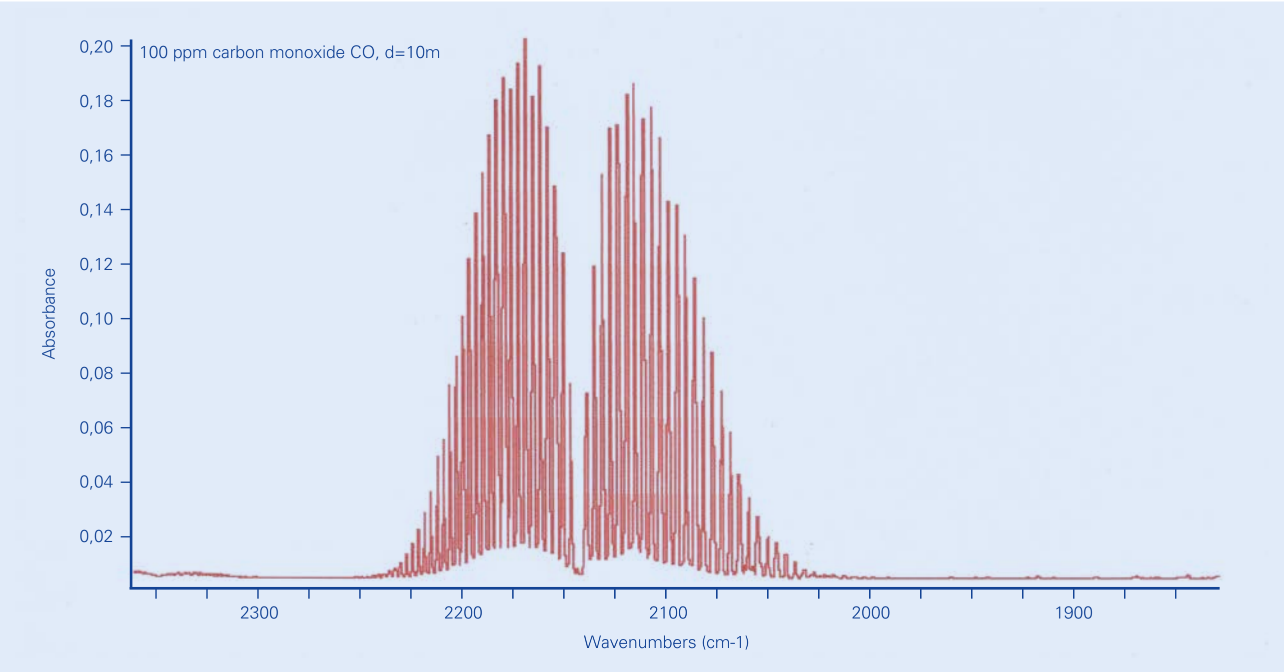
Atomic absorption spectroscopy (AAS) is a modified form of flame photometry. Radiation from an element-specific spectral light source is passed through a sample that has been thermally dissociated into atoms and the attenuation of the radiation intensity due to absorption is measured. The attenuation of the intensity is a measure of the concentration of the respective metal in the sample. Again, various methods are differentiated according to the type of excitation.

In flame AAS, the sample is atomized by a flame. This requires additional fuel and oxidation gases. A flame produced from acetylene (purity 2.6) and air (at approx. 2400 °C) is generally sufficient for the analysis of most metals. Nitrous oxide (laughing gas) is often used as the oxidation gas for metals that form very stable oxides, such as chromium or vanadium. This produces a very hot flame (approx. 2800 °C) that can decompose these metal oxides. In the case of the lighter alkaline metals or alkaline earth metals, the best source of energy is often a „cooler" flame (approx. 2100 °C) produced from Hydrogen 5.0 and air.

In a graphite tube furnace, the required energy (up to approx. 3000 °C) is produced electrically. Argon (purity 5.0 or higher) or argon/hydrogen mixtures are used as an inert gas to prevent oxidation of the graphite tube.

FTIR and NDIR spectroscopy

Spectroscopy from the UV to the IR range can be applied for gas mixtures analysis. NDIR monitors are popular especially for the analysis of carbon monoxide or carbon dioxide in automobile exhaust gases. In general, for infrared spectroscopy, the FTIR method has become established using long-path gas cells with variable path lengths, if necessary. New spectrometry techniques that use tunable lasers are becoming increasingly popular.



IR-Spectrum of carbon monoxide

Other analytical methods

Mass spectrometry is a standard method for gas analysis. It finds application in various fields, for instance, research and development, the monitoring of tank farms, in air separation units, or the filling of high purity gases. A mass spectrometer ionizes the compounds of the sample to realize qualitative and quantitative detection. The most common technique is the electron impact ionization. Apart from that, there are examples of specialized ionization techniques. For instance, atmospheric pressure ionization mass spectrometry (APIMS) is used to measure ultra-traces in high purity gases, and ionization with inductively coupled plasma is applied for sensitive analysis of metals in reactive gases.

Further specialized analytical methods are the chemoluminescence to determine nitrogen oxides NO/NO_X and emission spectroscopy in the UV/visible range using plasma excitation to analyze the purity of reactive gases.

Measurement of radioactivity

Special gas mixtures for filling Geiger-Müller counters allow to measure nuclear radiation. Usually gas mixtures of 5 or 10 Vol% methane in argon are used. They are designated as P5 and P10 gas, respectively. The purity of the gas is also important for reliable operation of the measurement systems. In particular the content of electro-negative impurities (e.g. halogenated hydrocarbons) has to be very low.

Zero gases

All analytical methods are affected differently by undesirable impurities, such as oxygen or humidity. These disturbing impurities and other secondary constituents can create noise or raise the baseline. As a consequence, the detection limit is downgraded.

Therefore, the gases have to have a minimum purity of 5.0 or even better. If necessary, certain impurities can be removed at the „point-of-use" by suitable purification processes.

Calibration gases

All methods of analysis currently used in practice are comparative methods. This means that the analyzer must be calibrated before quantitative measurements are possible. In the case of gas analysis, this is generally carried out by measuring a zero gas as well as one or more calibration gases with a defined composition. For this purpose, Messer also offers high-precision gas mixtures, customized according to the particular requirements of the analytical task, including the desired tolerance and uncertainty. For more information, we recommend the separate information "Gas mixtures - Individual solutions specific to your application".

Other required gases

In addition to the pure gases and gas mixtures needed for direct operation of the analytical equipment, a range of other gases is used. For example, specific detectors require cooling with liquid nitrogen or even liquid helium (nuclear magnetic resonance, NMR), optical systems are often purged with pure nitrogen and some gases are also used in sample preparation. Apart from high quality products, we also offer competent advice to choose a suitable product for the individual analytical task.

Method	**Use of gas**	**Gas**
Atomic emission spectrometry (AES)		
Flame photometry	Fuel gas	Propane 2.5, Acetylene 2.6
	Oxidation gas	Synth. air
ICP spectrometry	Plasma gas/carrier gas	Ar 5.0
Spark erosion spectroscopy	Plasma gas	Ar 5.0, Ar/H_2 mixtures
Atomic absorption spectrometry (AAS)		
Flame AAS	Fuel gas	Acetylene 2.6, H_2 5.0
	Oxidation gas	Ambient air, synth. air, O_2, N_2O 2.5
Graphite tube AAS	Inert gas	Ar 5.0 or higher, Ar/H_2 mixtures
Ionisation Chamber	Filling gas	5 / 10 Vol.% CH_4 in Ar (P5 or P10 gas)

Specialty gas equipment

Operating and calibration gases are usually stored compressed or liquified in suitable cylinders. For the withdrawal from their containers the use of appropriate equipment plays a crucial role to ensure safety and preserve the quality. Only the use of suitable gas supply systems and pipelines can ensure that the quality of gas is not affected during its transfer from storage to the point-of-use. Wherever possible, we recommend the installation of a central gas supply system that allows the required pressurized gas cylinders to be placed outside the laboratory.

The gases can then be fed through suitable pipelines into the laboratory to be available „on tap“. Our customer advisory service is available for support and advice (see the separate information on „Specialty gas equipment – Cylinder pressure regulators and gas supply systems for specialty gases“).

Service and support

Today, analytical methods are an essential component of daily practice in very different areas of business. The reliability and accuracy of the attainable results depend on many limiting conditions. Thereby the quality of operating and calibration gases plays a decisive role. We will be glad to support you in choosing high purity gases, standard and individual gas mixtures as well as the required gas supply systems.

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