Process gases for analytical applications

Analysis is the art of separating a substance into its constituents and making qualitative and quantitative determinations about it

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.

Analytical methods - the right gas for the right purpose

The methods employed and their uses are just as diverse as their fields of application. The specialized field of gas analysis in inorganic and organic analytical chemistry has undergone phenomenal development during the last thirty years: in the early 1970s, classic absorption/volumetric and titrimetric methods were common industrial practice and gas chromatography was still a rarity; nowadays, preference is given to analytical methods involving instrumentation. Depending on the application, various methods have become established. For example, gas chromatography and analysis using NDIR methods are now preferred in environmental monitoring or process control, whereas spark erosion spectrometry has become popular in the metal industry. Many of these methods require high purity gases or gas mixtures to work as well as high-precision reference gases for calibration purposes. The detection limits, attainable analytical accuracy and the reliability of the results often depend on the quality of the gases used. Messer offers a wide range of high-purity gases, standard mixtures and customized gas mixtures that fulfill all the required performance criteria. For the high-purity gases, the levels of typical undesirable impurities (usually H_2O, O_2 and/or N_2, hydrocarbons and CO + CO_2) are specified. The grade of purity is summarized by means of the commonly used point notation, e.g. Helium "6.0" if the sum of the specified impurities is less than 1 vpm (please refer to the separate information on "High-purity Gases"). When choosing a suitable gas, the "correct" gas quality as well as the necessary gas supply system all requirements concerning the particular application have to be taken in account.

The most widely used analytical methods and their specific requirements with respect to their process gases are described below.

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. Due to the relatively short analysis times, helium is often used as the carrier gas; nitrogen or hydrogen are also used. The needed purity of the carrier gas depends on the nature and concentration of the substance being detected.

Downstream of the column, the individual constituents of the sample are indicated by a suitable detector. Which kind 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, its limits of detection are in the ppm to % range. There is no need of any other process gases 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 generally is 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 sub-ppb range. For this detector, we offer special gases of "ECD quality" with a specified level of halogenated hydrocarbon impurities of less than 1 vpb. 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 of the detector any contaminants that could stick to its cathode. A mixture of 5% or 10% methane in argon (ECD) as well as ECD grade nitrogen has proven to be suitable for this.

Gas chromatography				**Gas purities / measuring range**		
Detector	**Carrier gases**	**Operating gases**	**Undesirable impurities**	< 100 ppb	< 10 ppm	> 10 ppm
TCD	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		
ECD	H_2, He, N_2	N_2, Ar/CH_4	hal. HC, SF_6	ECD grade		
FPD	H_2, He, N_2	H_2	HC, CO	6.0	5.5	5.0
		synth. air		HC free		
HID	He		H_2, O_2	7.0 - 6.0	6.0	
DID	He		H_2O, O_2, HC CO, CO_2, hal. HC	7.0 - 6.0	6.0	6.0
ED	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	

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 discharge ionization detector **(DID)**. The table gives a summary of the requirements for the carrier and process gases required by various detectors depending on the concentration range.

Atomic emission spectrometry

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 re-emit the absorbed energy with a wavelength that is characteristic for each metal. The intensity of this emission is directly related to the concentration. The various methods are differentiated according to the type of excitation.

If excitation takes place in a flame, this is termed **flame photometry**. This is frequently used for alkali metals and alkaline earth metals. Propane 2.5 or acetylene 2.6 is used as the 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 the argon used for this is critical, because oxygen and moisture at a concentration of a few ppm in the plasma may lead to undesirable secondary reactions. The individual constituents of the sample may then be in the form of oxides or hydroxides instead of their reduced form. Therefore, we recommend the use of Argon 4.8 or, even better, "Argon for spectrometry".

Elements in metal alloys can also be determined by **spark erosion spectrometry**, an analytical procedure 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 a direct measure of the concentration. As in the ICP method, the presence of oxygen and moisture perturbs the sensitive measurements. Therefore, we have developed a special grade, "Argon for spectrometry" that has reduced levels of oxygen and moisture impurities. The detection limits can be improved further if Oxisorb and Hydrosorb purification cartridges are used (see the chapter "Gas purification"). An argon/hydrogen mixture can also be used that acts as a reducing agent, allowing detection of any oxides which are present.

Spark erosion spectrometry: Spots on metallic samples

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.

Mass spectrometer for purity analysis of gases

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. 2,400 °C) is generally sufficient for the analysis of most metals. For metals that form very stable oxides, such as chromium or vanadium, nitrous oxide (laughing gas) is often used as the oxidation gas. This produces a very hot flame (approx. 2,800 °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. 2,100 °C) produced from Hydrogen 5.0 and air.

In a **graphite tube furnace**, the required energy (up to approx. 3,000 °C) is produced electrically. Argon (purity 4.8 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 is sometimes used to analyze gas mixtures. NDIR monitors are especially popular for the analysis of carbon monoxide or carbon dioxide in automobile exhaust gases. In general, for **infrared spectroscopy**, the FT-IR 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.

FT-IR spectrometer with long-path cell

Important specialized cases include the **chemo-luminescence** method to determine nitrogen oxides NO/NOx and emission spectroscopy in the UV/visible range with plasma excitation to analyze the purity of reactive gases.

The use of **mass spectrometry** to analyze gases is now routine, even in standard operations to monitor e.g. tank farms and air separation units or even for filling of high-purity gases. The most commonly used ionization method is electron impact ionization; examples for special cases are ionization at atmospheric pressure (atmospheric pressure ionization mass spectrometry – APIMS) to measure ultra fine traces in high-purity gases as well as ionization with inductively coupled plasmas, which, like emission spectrometry, can be used for sensitive analysis of metals in reactive gases.

Method	Use of gas	Gas
Atomic emission spectrometry (AES)		
Flame photometry	Fuel gas	Propane 2.5, Acetylene 2.6
	Oxidation gas	Synth. air
ICP spectromety	Plasma gas/ carrier gas	Ar 4.8, Ar for spectrometry
Spark erosion spectroscopy	Plasma gas	Ar 4.8, Ar for spectrometry, Ar/H_2mixtures
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 higher than 4.8, Ar/H_2 mixtures
Ionisation Chamber	Filling gas	5 / 10 Vol.% CH_4 in Ar (P5 or P10 gas)

Measurement of radioactivity

Special gas mixtures for filling Geiger-Müller counters allow nuclear radiation to be measured. Gas mixtures with 5 or 10 Vol% of methane in argon are generally used and are known 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 in various degrees by undesirable impurities, such as oxygen or water. Also, other secondary constituents can raise the zero line or the noise and thus shift the detection limit. 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 means of suitable purification processes (see the separate information on "Gas purification systems").

Additionally required gases

In addition to the pure gases and gas mixtures needed for direct operation of the equipment or the analyzers, a range of other gases are used in analytical applications that are not discussed in detail here. 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. Messer offers not only competent advice but also all the required gases in the required purity. For example, we have a special grade for extraction with supercritical carbon dioxide (SFC), namely CO_2 SFC, optionally also pressurised by gaseous helium.

Calibration gases

Most of the methods of analysis currently used in practice are, in principle, 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. We also produce the high-precision gas mixtures used for this, customized according to the particular requirements of the analytical task with the desired tolerance and accuracy in our special gas facilities (see the separate information on "Gas mixtures").

Central gas supply - gases on tap

Use of gases

Handling gases requires the user to exercise great care for reasons of safety and quality. Only the use of suitable gas supply systems and pipelines can ensure that the quality of the gas is not affected during its passage from the storage container to the point-of-use. Wherever possible, we recommend the installation of a central gas supply system that allows the required pressurized gas bottles to be set up outside the laboratory. The gases can then be fed through suitable pipelines into the laboratory so that they are available "on tap". Our customer advisory service is available for help and advice (see the separate information on "gas supply systems and components for special gases").

Analysis controls quality

Today, analytical procedures 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. The quality of the operating and calibration gases often plays a decisive role. Messer offers a comprehensive range of high-purity gases, standard and individual gas mixtures as well as the required gas supply systems.

Talk to us!

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