Testo
Whitepaper

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Use of electrochemical sensors in portable exhaust gas analyzers for emission measurements in industrial applications.

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Introduction: Reasons for using gas analysis for industrial flue gases

Gas analysis (i.e. measurement technology for determining the composition of gases) is an indispensable tool for ensuring economical and safe process management in virtually all areas of industry. The focus is on combustion processes, although this is a generic term that encompasses a large number of different processes. In figure 1, the progression of a combustion process is presented in sections, beginning (left) with the input of fuel and combustion air into a combustion chamber, via the actual combustion and the different processes driven by it, to the exhaust gas cleaning and finally the emission testing.

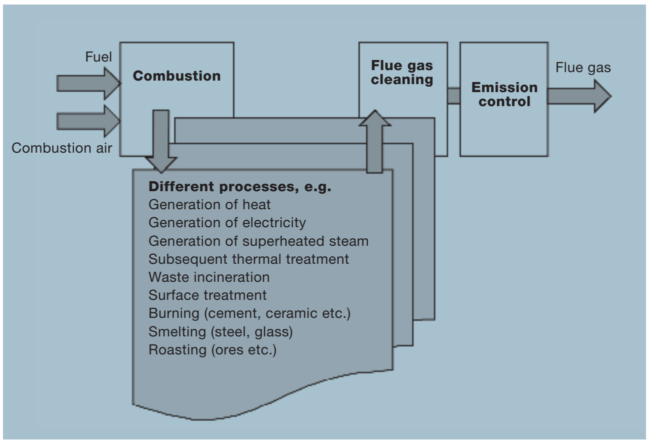

Fig. 1: Variety and procedural stages of combustion processes

Gas analysis provides information in all levels of this procedural chain on the composition of the combustion and exhaust gases, allowing the economic, safe operation of the plant, in compliance with the legal stipulations, and is thus also crucial to the quality and efficiency of production.

Gas analysis instruments are used in the analysis of combustion gases in industry in a variety of applications which are absolutely not limited to the partial area of emission monitoring alone. With a certain degree of overlapping, the following areas of application can be differentiated:

1. Setting and service work for general checking, for example after plant maintenance, for error detection in the event of unstable processes, in preparation for official measurements, following repairs etc.
2. Process measurements for the optimization of consumption, at the fuel, combustion air and burner stages, as well as in the combustion chamber, with the objective of saving fuel, improving efficiency and extending the working lifetime of the plant.
3. Process measurements for monitoring a defined gas atmosphere in the combustion chamber or in special combustion chambers or furnaces during processes such as burning, roasting, surface treatment etc.
4. Process and emissions measurements for monitoring the correct functioning of flue gas cleaning equipment.
5. Emissions measurements for monitoring compliance with limit values for pollutants in the flue gas upstream or in the chimney.

Fig. 2: testo 350 exhaust gas measurement at the engine

Fig. 3: testo 350 exhaust gas measuring instrument with flue gas probe

Use of combustion heat

In general, combustion plants are systems which exploit the heat arising from the combustion of solid, liquid or gaseous fuels for a certain purpose. In households, combustion plants are used mainly for producing heat. The possibilities for use in industrial operations are various.

Typically, combustion plants are used in industrial applications for

- Heating purposes (heating plants and building heating systems)
- Generating electrical energy
- Generating steam or hot water (e.g. use in process plants)
- Production of various materials (e.g. use in the cement, glass or ceramics industry)
- Thermal surface treatment of metallic workpieces
- Burning waste and salvaged materials (waste, used tyres etc.).

Exhaust gas/flue gas and its composition

The transformation of the primary chemical energy in the fuel into secondary thermal energy by the process of oxidation is described as combustion, during which combustion temperatures up to over 1000 °C are reached. The necessary oxygen is supplied as part of the combustion air. In combustion, a considerable volume of exhaust gas is produced as a by-product, in addition to the main product, heat. The exhaust gas is also referred to as flue gas, and contains reactive substances from the fuel and the combustion air as well as residual substances – above all dust, sulphur oxides, nitrogen oxides and carbon monoxide. In the combustion of coal, HCl and HF can be contained in the exhaust gas, and in the combustion of salvaged materials, their component substances (such as HCl and HF, but also various hydrocarbons, heavy metals etc.) are also contained in the exhaust gas.

For this reason, industrial combustion plants are equipped with extensive and often very complex exhaust gas cleaning systems such as dust filters and various flue gas scrubbers. These remmove the pollutants to a large extent from the raw gas. Raw gas is the term used to describe the flue gas in its original composition after combustion; pure gas is the exhaust gas which is emitted into the atmosphere after passing through the cleaning stages. For pure gas, the strict permitted limit values stipulated in the framework of environmental protection apply for the air pollutants such as dust, sulphur oxides, nitrogen oxides and carbon monoxide.

In Germany, the requirements are laid down individually in the 13th and 17th German Federal Immission Directive (BImSchV) and the Technical Instructions on Air Quality Control (TA Luft).

The most important flue gas components are explained next.

Exhaust gas/flue gas and its composition

Nitrogen (N_2)

With 79 vol.% nitrogen is the main component of the air. This colourless, odourless and tasteless gas is supplied through the combustion air, but does not take part in the actual combustion process; it just passes through as ballast and waste heat carrier and is returned to the atmosphere. However, parts of the nitrogen, in combination with the nitrogen contained in the fuel, contribute to the formation of the hazardous nitrogen oxides (see below).

Carbon dioxide (CO_2)

Carbon dioxide is a colourless and odourless gas with a slightly sour taste, which is generated in all combustion processes and by breathing. With its filtering properties for heat radiation it essentially contributes to the greenhouse effect. It is contained in natural air at a content of 0.03 %. The maximum permitted workplace concentration is 0.5 % in Germany. Loss of consciousness occurs in humans as soon as the concentration in the inhaled air exceeds 15 vol.%.

Water vapour (humidity)

The hydrogen contained in the fuel combines with oxygen to form water (H_2O). Together with the water from the fuel and the combustion air, depending on the flue gas temperature (FT) this is discharged as flue gas moisture (at high FT) or as condensate (at low FT).

Oxygen (O_2)

Oxygen that has not been used in combustion due to an air surplus is discharged as a gaseous flue gas component and is a measure of combustion efficiency. It is used for the determination of combustion parameters and as reference value.

Carbon monoxide (CO)

Carbon monoxide is a colourless and odourless toxic gas. It is mainly generated by incomplete combustion of fossil fuels (furnaces) and automotive fuels (motor vehicles) and other carbonaceous materials. Overall CO is no great danger to humans, because with the oxygen in the air it rapidly combines to CO_2. Locally, however, CO is very dangerous, because a concentration of only 700 ppm in the air inhaled by humans will cause death within a few hours. The maximum permitted workplace concentration in Germany is 50 ppm.

Nitrogen oxides (NO and NO_2, molecular formula NO_X)

In combustion processes, the nitrogen from the fuel, and at high temperatures also the nitrogen contained in the combustion air, combine to a certain extent with the combustion air oxygen, initially to nitrogen monoxide NO (fuel NO and thermal NO), which in the presence of oxygen in the exhaust gas flue, and subsequently also in the atmosphere, oxidizes in a further step to the dangerous nitrogen dioxide (NO_2). Both oxides are toxic; NO_2 in particular is a dangerous respiratory poison and in combination with sunlight contributes to the formation of ozone. Complex technology is used for cleaning NO_X exhaust gas, e.g the selective catalytic reduction (SCR) process. Special combustive measures such as graduated air supply are used to already reduce nitrogen oxides in the combustion.

Sulphur dioxide (SO_2)

Sulphur dioxide is a colourless, toxic gas with a pungent smell. It is produced as a result of the oxidation of the larger or smaller volume of sulphur contained in the fuel. The maximum workplace concentration value is 5 ppm. In combination with water or condensate, sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4) are produced, both of which are linked to various different types of environmental damage to vegetation and building fabrics. Flue gas desulphurization (FGD) systems are used to reduce suphur oxides.

Hydrogen sulphide (H_2S)

Hydrogen sulphide is a toxic gas with a pungent smell in the even smallest concentrations (approx. 2,5 µg/m^3). It is a naturally occurring constituent of natural gas and petroleum and is therefore present in refineries and natural gas processing plants, but also in tanneries, agricultural businesses and last but not least following incomplete combustion in vehicle catalytic converters. Methods for eliminating H_2S from exhaust gases include combustion to SO_2, certain absorption processes or, for larger proportions, transformation into elementary sulphur in a Claus plant.

Form and composition of fuels

Solid fuels (coal, peat, wood, straw) contain mainly carbon (C), hydrogen (H_2), oxygen (O_2) and in lower quantities sulphur (S), nitrogen (N_2) and water (H_2O), and are combusted either in packed bed, a fluidized bed or in a dust particle cloud.

Liquid fuels originate on the one hand from crude oil and its processing, with a differentiation between extra light (EL), light (L), medium (M) and heavy (H) heating oil, and on the other hand from biological fuels (vegetable oil, biodiesel, bioethanol), which are also used primarily as biological fuels in vehicles. Liquid fuels are introduced to the combustion chamber together with the combustion air via a burner as a mist.

Gaseous fuels are a mixture of combustible (CO, H_2 and hydrocarbons) and non-combustible gases. Today, natural gas is often used, whose main component is the hydrocarbon methane (CH_4). Gaseous fuels are already mixed with the combustion air in the burner.

Gas analyzers and measurement principles

Gas analyzers are provided by many manufacturers in different designs and based on different measurement principles. The heart of every analyzer are the substance-specific sensors or sensor systems. Their function is based on physical, chemical or electrical principles such as absorption, adsorption, transmission, ionization, heat tone or paramagnetic or electrochemical properties.

The sensors react to a change in the measurement parameter “gas concentration” with a corresponding change in their property (e.g. increased light absorption or reduction of conductivity), from which a measurement signal can be formed.

In terms of design, a distinction is made between:

- Mobile, lightweight and portable analyzers for quick measurements in a range of locations and
- Stationary analyzers permanently installed in the plant for continuous long-term measurements over months and years

and between

- Analyzers that measure directly in the process stream (“in situ” devices) and
- Analyzers to which a sample extracted from the process stream and prepared is added for measurement (“extractive” instruments).

Newer developments allow the combination of mobile measuring instruments which are also suitable for permanent, stationary measurements: An example of this is the testo 350 analyzer, which is light and easily transportable yet suitable and approved for long-term measurements over several weeks.

Use of electrochemical sensors in Testo gas measuring instruments

Testo is the world market leader for exhaust gas measuring instruments and portable measurement technology. Thanks to its worldwide sales and customer service network, Testo receives various customer requirements and wishes, which lead to an improvement of the sensors used.

Electrochemical sensor technology combines many advantages. To mention a few examples:
- A small design; a common sensor design is cylindrical with a diameter of 29 mm and a height of 25 mm, this results in a volume requirement of 16.5 cm^3
- A minimum input for the necessary electrical switching of typically 0.3 mW (3 V * 100 µA)
- Stable zero point of typically 1 to 2 ppm
- Very good linearity allowing one-point calibration and adjustment
- And very good measurement accuracy.

For this reason, many gas measuring instrument manufacturers use this sensor technology in their measuring instruments.

Testo gas measuring instruments also use electrochemical gas sensors for most parameters, such as O_2, NO, NO_2 or CO. The gas sensors used in the Testo instruments stand out thanks to several special properties which will be explained in more detail in the following.

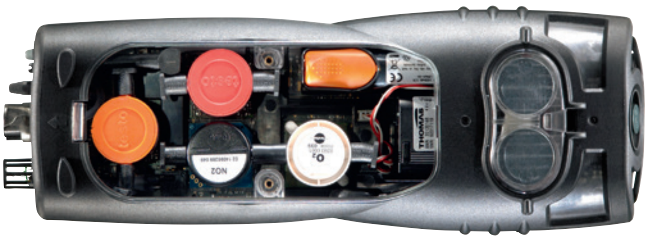

Fig. 5: testo 340 with electrochemical sensors

Functional principle of electrochemical gas sensors

The functional principle of the electrochemical gas sensors will be explained using the typical example of a three-electrode sensor for the measurement parameter carbon monoxide. Fig. 6 shows the sensor components and the processes.

The carbon monoxide molecules (CO) permeate through the gas-permeable membrane to the working electrode, where H+ ions are formed as a result of a chemical reaction. These migrate in the aqueous electrolyte to the counter-electrode, where a current flow is generated in the external circuit by means of a further chemical reaction triggered by the oxygen (O_2) from the fresh air also supplied. The third electrode (reference electrode) serves to stabilize the sensor signal. The operating life of this type of sensor is about 2 years.

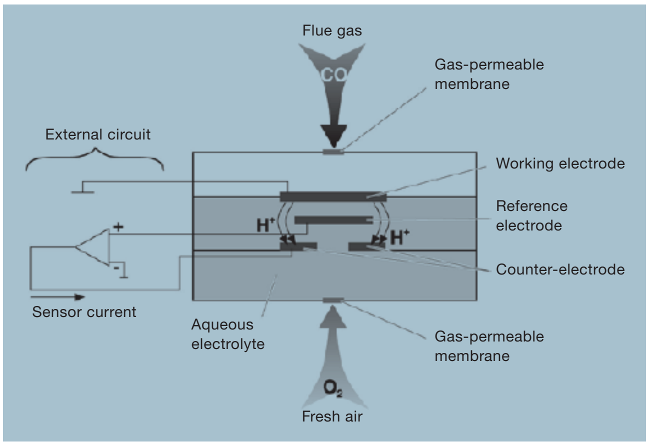

Fig. 6: Functional diagram of electrochemical three-electrode sensor

Properties of the exclusive Testo design

The exclusive Testo design is based on a proven electrochemical sensor technology which has been further developed and improved in several crucial points to the benefit of Testo's customers.

In contrast to all other available electrochemical gas sensors, the exclusive Testo design has connection ports which allow an easy integration into the gas path in the instrument. The gas path in Testo instruments is formed by hose components which are plugged on to the sensor ports. This enables the customer to change the sensors very easily, even at the measurement site. The result of this is reduced downtimes which would be caused by the back and forth transport of the measuring instruments to the manufacturer or to service centres.

Since the gas path leads through, and not past the sensors, their height including the gas path is lower than in other commercially available sensors with comparable specifications, which has a positive effect on the dimensions of the measuring instruments.

Every exclusive Testo sensor has a sensor circuit board permanently attached to it. The circuit board has a standardized plug-in connection which forms the electromechanical interface to the instrument. Independently of the details of the sensor set-up, e.g. the number and position of the measurement lines, this interface remains always the same over the entire series, simplifying the handling of the sensors. The sensor circuit board contains a storage component, a so-called EEPROM. In the EEPROM, all sensor-specific information is stored, e.g. sensor identifiers, compensation, adjustment and calibration data, but also ancillary parameters for the calculation of the measurement value display. In addition to this the maximum permitted gas concentration values are stored, with whose help the sensor is protected from overload. Any error notifications which may occur during operation are also saved in the EEPROM. Directly during the installation of a sensor into a Testo measuring instrument, all information is available which is needed for an immediate, smooth start. A parameterization of the sensor, e.g. the input of compensation coefficients, is thus unnecessary. Replacement and retrofit sensors can be installed by the user without any problems and without the need for tools. The Testo gas measuring instruments do not need to be sent in to customer service for a sensor to be replaced.

Exclusive Testo sensors with standardized digitalized output signals

Thanks to the integration into the sensor circuit board of the switching, which varies from sensor to sensor, and thanks also to the standardization of the digitalized output signal passed on from the sensor to the measuring instrument, any sensor type can be operated at any slot in the instrument. This means for example, that in instruments with a fresh air dilution slot such as the testo 350, depending on the measurement application and the gas concentrations occurring, a different sensor type can be used on this special slot and correspondingly protected from damaging gas concentrations. Refitting is easy to carry out, and the instrument recognizes the altered order of the sensors when it is switched on and starts up.

From the operating hours and the accumulated load, an interval for recalibration and a for filter check by the customer or Testo customer service is calculated, and preented in the form of a clear traffic light system.

A further property is the temperature sensor on the circuit board which measures the exact temperature for each sensor and compensates the temperature influence on the sensor.

A further advantage of the exclusive Testo series in comparison to commercially available gas sensors is the care taken with gases which cause cross-sensitivities in the sensor. Cross-sensitivity is the term used to describe the sensitivity of a sensor or a measuring instrument to other parameters than the one to be measured. Like most gas sensor technologies, electrochemical gas sensors are also not free from cross-sensitivities. The state of technology for some sensor types is the use of integrated filters which hold back the cross-gases. If this is not possible a calculated cross-gas compensation is carried out, i.e. a compensation of the signal produced by the cross-gas. With regard to the built-in filters, the exclusive Testo sensors have excellent lifetimes, and some have the possibility of exchanging just the filter instead of the entire sensor. There is no need to replace a valuable, complete sensor in which only the low-cost filter is used up.

Fig. 7: Electrochemical gas sensor with cross-gas filter

In order to obtain as accurate a measurement result of the exclusive Testo sensors as possible, a great effort is put into a subsequently necessary calculation in cases of cross-sensitivities. This affects on the one hand the works compensation in which the compensation coefficients are adjusted accurately and individually with test gases. And on the other hand, Testo uses proprietary calculation algorithms which take into account and compensate gas concentration and temperature dependencies.

Special solutions adapted to special applications

The applications in which Testo gas measuring instruments are used differ widely. The trick was to develop gas sensors which are suitable for all applications.

These often deal with the adjustment and monitoring of combustion plants. The gases to be measured here, mainly O_2, CO and NO, and the concentrations to be expected, are clearly defined. However, they are also very different depending on the application. In order to cover the entire bandwidth of gas concentrations with a high level of accuracy, special NOlow and COlow sensors were developed which, with regard to their measuring range, are adapted to the various applications with especially low concentrations. Thanks to the available measuring range extension using controlled dilution, the low-range sensors can also perform well in emission peaks.

The selection of the exclusive Testo sensors is thus adapted to the applications and the measurement parameters.

The gas measuring instrument testo 350 is often used for monitoring the most diverse processes in which other gas measurement parameters than those of combustion systems are relevant, or in which significantly different concentration values are to be expected. The exclusive Testo sensor series alos covers special solutions for such applications at an attractive price. There are sensors for the more rarely needed measurement parameters H_2S and HC, the latter, which records hydrocarbons as a sum parameter, being based on the heat tone principle, i.e. it does not measure electrochemically.

The broad range of emission sensors in uniform design is complemented by a CO_2 sensor with NDIR (non-dispersive infrared) technology. With its measuring range up to 50 vol%, it is adapted to combustion processes and to processes in which CO_2 is present as a process gas, e.g. cement production.

The sensors' colour coding allows the specification of the gas sensors to be identified at a glance.

Fig. 8: testo 350 with electrochemical sensors

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Conclusion

With the exclusive Testo sensor range, Testo offers its customers a large selection of robust gas sensors optimized for application in emission and process measurement technology. Their uncomplicated handling during installation and commissioning; their reliability; the highly accurate measurement of gas concentrations, which has been repeatedly confirmed by independent institutes; as well as the easy calibration due to their linearity – these are the outstanding properties of this sensor series.

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