Be sure. **testo**

Practical Guide
Industrial Flue Gas Analysis

Emissions and process measurement guidelines

3rd, revised edition

Foreword

Dear Reader

Determining flue gas concentrations allows legally required emission limit values to be monitored, thus enabling protection of the environment. On the other hand, gas concentrations or gas matrices generated during the process often provide a very good indication of the existing process quality, which ultimately has a considerable influence on the product quality.

This Practical Guide contains the basic principles of common combustion processes, with a specific focus on their use in industrial applications. The available measurement methods, the characteristics associated with the measuring tasks, the expected gas measurement parameters, concentrations and their significance with regard to the process are also described. This is a useful reference guide for using portable gas analyzers in industry, based on the experiences of global users of Testo measuring instruments.

Additional ideas and suggestions for improvement are always welcome.

Happy reading!

Prof. Burkart Knospe,
Chairman of the Board of Directors

Contents

1. The combustion process

1. The combustion process

1.1 Energy and combustion

Energy
(from the Greek) means "acting force" and is defined as the ability of a substance, body or system to carry out work. Energy can be assigned to certain energy types depending on their form.

Energy can be classified into six categories:
- Mechanical energy (flowing water, driving car, helical spring)
- Thermal energy (boiling water, gas flame)
- Chemical energy (chemical reactions, combustion, explosion)
- Electrical energy (car battery, electric current)
- Electromagnetic energy (light, thermal radiation)
- Nuclear energy (nuclear fission)

The various forms of energy can be converted from one form into other, whereby, within an ideally closed system, the sum of all energies remains constant (conservation of energy). This actually applies in respect of the universe as a system. In practice, however, energy is lost to a greater or lesser extent when energy is converted, and this loss affects the efficiency of the conversion process. The natural energy carriers (coal, natural gas, petroleum, solar radiation, hydropower, etc.) are described as primary energies, while the forms generated through energy conversions (electricity, heat, etc.) are called secondary energies. These energy carriers differ not only in their appearance, but also in their energy content. For the purposes of comparison, the quantity of energy that could be released if a given quantity of the energy source were fully burned is generally specified. Table 1 gives a few examples to illustrate this.

The measuring unit for energy is the joule (J).

1. The combustion process

Energy source	Energy content [MJ]
1 kg lignite	9.0
1 kg wood	14.7
1 kg hard coal	29.3
1 m^3 natural gas	31.7
1 kg crude oil	42.6
1 kg light fuel oil	42.7
1 kg gasoline	43.5
For comparison 1 kWh	3.6

Tab. 1: Energy content of various fuels

Conversion of energy units:
1 erg   10-7 J
1 cal   4.184 J
1 Btu   1055.06 J
Btu: British thermal unit

Combustion

is the conversion of primary chemical energy contained in fuels such as coal, oil or wood into secondary thermal energy through the process of oxidation. Combustion is therefore the technical term for the reaction of oxygen with the combustible components of fuels, during which energy is released.

Combustions take place at high temperatures (up to 1000 °C and higher) and whilst emitting heat. The necessary oxygen is supplied as part of the combustion air. At the same time, a considerable volume of flue gas and, depending on the type of fuel, a certain quantity of residual materials (ash, slag) are formed.

Oxidation

Term for all chemical reactions during which a substance combines with oxygen. During oxidation, energy is released. Oxidation is of great significance when it comes to technology (combustion) and biology (respiration).

Greenhouse effect

In principle, the greenhouse effect is a natural phenomenon and a prerequisite for life on earth. Without this effect, the average global temperature near the Earth's surface would be -18 °C instead of +15 °C today; the earth would be uninhabitable! The cause of this natural effect is primarily the water vapour content of the atmosphere near the Earth's surface, which allows solar radiation to pass through, but prevents the long-wave thermal radiation that develops on the ground from escaping; this is reflected back to the Earth's surface. The heat management of greenhouses is also based on this principle. However, excessive burning of fossil fuels (carbon dioxide emissions) and the release of substances from chemicals and agriculture (CFCs, methane, etc.) considerably intensify this natural effect, which leads to a slow increase in the Earth's temperature and affects climatic conditions, etc.

More details on the topic of combustion can be found in Section 1.4.

1. The combustion process

1.2 Combustion plants

Combustion plants are facilities for generating heat by burning solid, liquid or gaseous fuels. They are needed for many different purposes, for example
- For heating purposes (heating plants and building heating systems)
- For generating electricity
- For generating steam or hot water (used in processing plants, for example)
- For manufacturing certain materials (for use in the cement, glass or ceramics industry, for example)
- For thermal surface treatment of metallic workpieces
- For burning waste and scrap materials (waste, used tyres etc.)

Please refer to the detailed application examples in Section 4.

The combustion takes place in a furnace; other parts of the plant supply and distribute the fuel, supply the combustion air, transfer the heat and carry away the combustion gases and combustion residues (ash and slag).

Solid fuels are burnt either in a fixed bed, a fluidized bed or in an entrained dust cloud. Via a burner, liquid fuels are fed to the combustion chamber together with the combustion air in the form of mist; gaseous fuels are already mixed with the combustion air in the burner.

Flue gas from combustion plants contains the reaction products of fuel and combustion air as well as residual substances, generating primarily dust, sulphur and nitrogen oxides and also carbon monoxide. During the combustion of coal, HCl and HF, and during the combustion of scrap material, their constituents (HCl and HF, but also various hydrocarbons, heavy metals, etc.) may also be present in the flue gas.

Within the context of environmental protection, the flue gas from combustion plants is subject to strict regulations with regard to the limit values of pollutants such as dust, sulphur and nitrogen oxides and also carbon monoxide which are permissible in the clean gas (when released into the atmosphere). To comply with these limit values, combustion plants are equipped with extensive facilities for cleaning flue gas, such as dust filters and various flue gas scrubbers. In Germany, the specific requirements are laid down in the 13th and 17th Federal Immission Control Ordinance (BImSchV) and in TI Air. Further information about this can be found in Section 2.3.

1.3 Fuels

Fuels are available in various forms and compositions:
- Solid fuels (coal, peat, wood, straw) primarily contain carbon (C), hydrogen (H_2), oxygen (O_2) and small quantities of sulphur (S), nitrogen (N_2) and water (H_2O).
- Liquid fuels derive from petroleum or the processing of it, whereby a distinction is made between extra-light (EL), light (L), medium (M) and heavy (S) fuel oils.
- Gaseous fuels are a mixture of combustible (CO, H_2 and hydrocarbons) and non-combustible gases. These days, natural gas is very often used, the main component of which is the hydrocarbon gas methane (CH_4).

Knowledge of the composition of the fuel is essential to managing combustion as efficiently, and therefore as economically, as possible. An increasing portion of non-flammable (inert) substances reduces the gross/ net calorific value and increases the level of dirt that collects on the heating surfaces. An increasing water content pushes up the water vapour dew point and consumes fuel energy to evaporate the water in the flue gas. The sulphur contained in the fuel is combusted to SO_2 and SO_3, which can generate aggressive sulphurous acid or sulphuric acid when the gas cools down to below the dew point. Please also refer to Section 1.7

The composition of some solid fuels is shown in the following table.

Fuel	Content (mass content in %)			
	Carbon in dry matter	Sulphur	Ash	Water
Hard coal	80-90	1	5	3-10
Ortho-lignite	60-70	2	5	30-60
Meta-lignite	70-80			10-30
Wood (air-dry)	50	1	1	15
Peat	50-60	1	5	15-30

Tab. 2: Composition of fuels

Please refer to Section 1.6 for explanations relating to the calorific value of fuels.

1.4 Combustion air, air ratio

The combustion air provides the oxygen required for combustion. It consists of nitrogen (N_2), oxygen (O_2), a small proportion of noble gases and a variable proportion of water vapour (Tab. 3). In some cases, even pure oxygen or an oxygen/air mixture is used for combustion.

Essential combustion air constituents (except the oxygen used in the combustion process) can all be found in the flue gas.

Component	Volume content [%]
Nitrogen	78.07
Oxygen	20.95
Carbon dioxide	0.03
Hydrogen	0.01
Argon	0.93
Neon	0.0018

Tab. 3: Composition of pure and dry air on the Earth's surface

1.4.1 Ideal combustion, fuel-air ratio, material balance

The minimum oxygen requirement for complete (ideal) combustion of the combustible constituents depends on the fuel composition: For example, the combustion of 1 kg of carbon requires 2.67 kg of oxygen, but 1 kg of hydrogen requires 8 kg and 1 kg of sulphur only 1 kg of oxygen. This case of exact quantity ratios is considered an ideal combustion or combustion under stoichiometric conditions.

The corresponding chemical equations are as follows:

Carbon: $C + O_2 \rightarrow CO_2$
Hydrogen: $2H_2 + O_2 \rightarrow 2H_2O$
Sulphur: $S + O_2 \rightarrow SO_2$
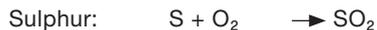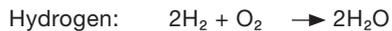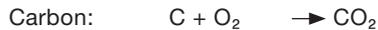
The ideal combustion can be based on the model shown in Figure 1:
The amount of oxygen supplied is just enough to fully burn the fuel present; there is no surplus oxygen or fuel.
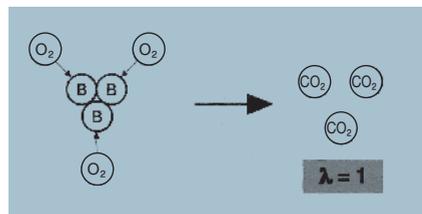
Figure 1: Model for an ideal combustion

In practice, however, this ideal (minimum) amount of oxygen is not sufficient for complete combustion due to the imperfect mixing of fuel and oxygen, so the system needs to be supplied with more oxygen, and therefore combustion air, than is required stoichiometrically. This additional air is referred to as "excess air" and the ratio of the actual air volume to the air volume required stoichiometrically is referred to as the air ratio (λ).

Fig. 2 shows this excess air combustion model; here, due to the excess air, λ is >1.

Maximum combustion efficiency is therefore established with marginal excess air or oxygen, i.e. at $\lambda>1$ (oxidizing atmosphere). The air ratio and knowing what it is are extremely important factors for ensuring optimum combustion and economic efficiency of the plant operation:

• Unnecessarily high excess air reduces the combustion temperature and increases the amount of unused energy dissipated via the larger volume of flue gas.

• With too little excess air, apart from poor fuel utilization this will also increase the harmful environmental impact due to unburned residues in the flue gas.
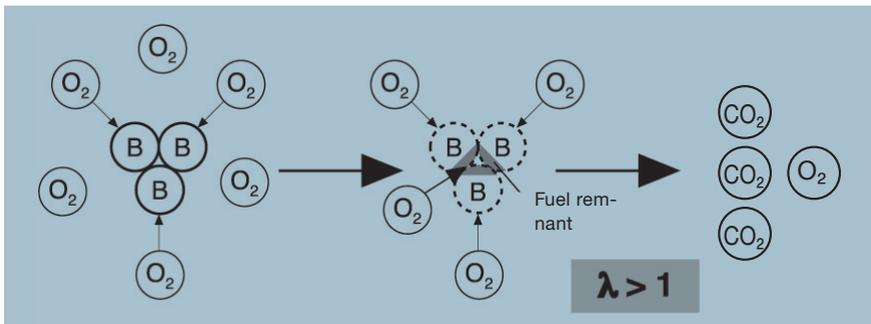
Figure 2: Model for combustion with excess air

Table 4 shows the typical air ratio ranges for various combustion plants. As a matter of principle, the following applies: the smaller the reaction surface for the fuel in relation to the unit of mass (coarse-grained fuel), the higher the amount of excess air that must be chosen to ensure complete combustion. The reverse is also true, which is why solid fuels are ground finely and liquid fuels are atomized. However, special processes, e.g. thermal surface treatment, are deliberately operated with insufficient air at $\lambda<1$, as this is necessary to ensure the required refinement process.

Oxidizing atmosphere

Here, more oxygen is available than is necessary for the oxidation of oxidizable substances in the fuel. Complete oxidation (combustion) is therefore possible.
Simply put: Oxidation = addition of oxygen (CO is oxidized to CO_2).

Reducing atmosphere

Here, there is too little oxygen to oxidize all oxidizable substances. The opposite of oxidation occurs, i.e. a reduction.
Simply put: Reduction = removal of oxygen (SO_2 is reduced to S).

Combustion plant	Range for λ
Combustion engines	0.8-1.2
Pressure jet gas-fired installation	1.1-1.3
Oil burner	1.2-1.5
Coal dust burner	1.1-1.3
Grate furnace for brown coal	1.3-1.7
Neon	0.001

Tab. 4: Typical ranges for air ratio λ

1.4.2 Determining the air ratio

The air ratio can be determined from the concentrations of the flue gas components CO, CO_2 and O_2, the correlations are shown in the so-called combustion chart, Fig. 3. When there is ideal mixing of fuel and air, any CO_2 content is related to a specific CO content (in the range $\lambda<1$) or to a specific O_2 content (in the range $\lambda>1$). The CO_2 value on its own is not definite due to the curve profile beyond a maximum, which means that an additional test is required to establish whether the gas also contains CO or O_2 in addition to the CO_2. When operating with excess air (i.e. normal scenario), a definitive measurement of O_2 is now generally preferred. The curve progressions are fuel-specific, i.e. each fuel has its own diagram and a specific value for $CO_{2\,max}$, see Table 7. In practice, the correlations of these numerous diagrams are often summarized in the form of an easily manageable nomogram ("fire triangle", not illustrated here). This can be applied to any type of fuel.

The following two formulae may be applied to the theoretical calculation of the air ratio from the CO_2 or O_2 readings:

$$\lambda = \frac{CO_{2max}}{CO_2} \qquad \lambda = 1 + \frac{O_2}{21 - O_2}$$

with

$CO_{2\,max}$: Fuel-specific maximum CO_2 value (see Tab. 7). If required, this value can be determined by Testo as a service.

CO_2 and O_2: Measured (or calculated) values in the flue gas
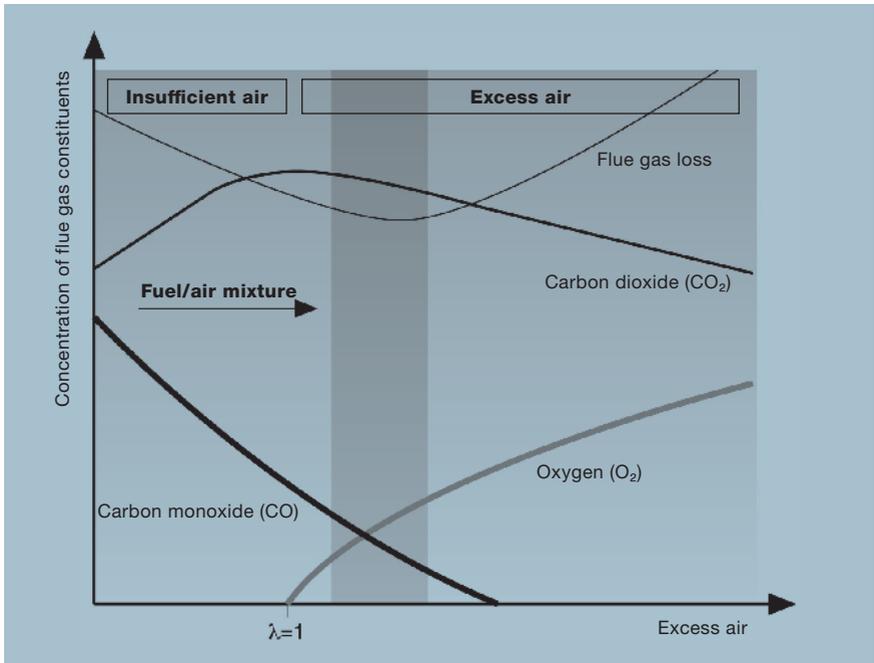
Figure 3: Combustion chart

Please refer to Section 2.1 (combustion optimization) for a detailed depiction of the correlations in the combustion chart.

1.4.3 Combustion air requirement

The actual air requirement is calculated
• From the minimum oxygen required for ideal combustion (this depends on the fuel)
• The required excess oxygen and
• The relative oxygen content in the air. For dry air under atmospheric pressure, this is 20.95 %. In practice, however, the ambient air used as combustion air is never completely dry, which means that the humidity also has to be factored into the calculation of the air volume to ensure an exact process.

1.4.4 Gas volume, diluting effect, reference value

Combustion air and humidity (water vapour) increase the absolute gas volume.

Figure 4 illustrates this phenomenon for the combustion of 1 kg fuel. In stoichiometric conditions, i.e. without excess air, approx. 10 m^3 of flue gas is produced in dry conditions and 11.2 m^3 in humid conditions, while the same amount of fuel on combustion with 25% excess air results in a flue gas volume of 13.9 m^3 in humid conditions. This has the same effect as a dilution, which reduces the relative portions of the constituents of the flue gas! For example, the absolutely constant SO_2 content is reduced in relative terms from 0.2 (stoichiometric, dry) to 0.18 (stoichiometric, humid) or 0.14 (25% excess air, humid) and the oxygen from 4.4 to 4. Please refer to Table 5.

	Nitrogen	CO_2	SO_2	Water	Oxygen
Stoich./dry	82.6	16	0.20	0	0
Stoich./humid	74.7	14.4	0.18	10.7	0
25 % EA/dry	82.8	12.7	0.16	0	4.4
25 % EA/humid	75.6	11.6	0.14	8.7	4

Tab. 5: Relative composition of flue gas in % in different conditions
(EA = excess air)
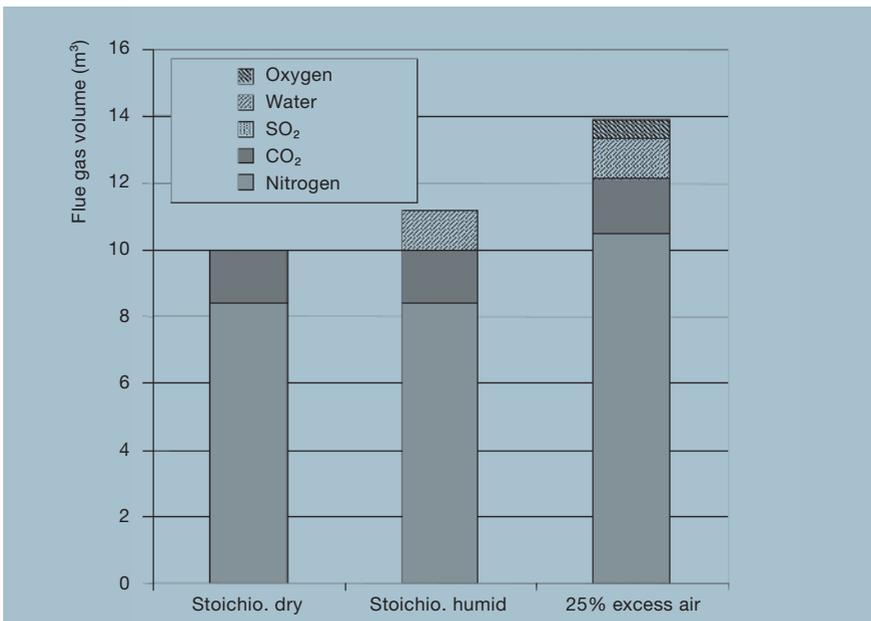
Figure 4: Diluting effect of humidity content and excess air

Reference values

From the depicted correlations, it is clear that concentration observations can usually only be made in conjunction with reference values. It is only then that the readings have any meaning and can be compared with other measurement results, and in particular with statutory requirements! In practice, the following are used:

• Reference to a specific dilution due to excess air; a measure of this is the oxygen content, the reference is expressed by e.g."Reference value 8% oxygen".
  This reference to the oxygen value is generally applied in the specifications of the TI Air; however, it is also used outside of the TI Air: for a plant, the reference point is defined close to the oxygen content when the plant is started up.

• Reference to a specific dilution due to the humidity content of the gas; a measure of this is the temperature of the gas, the reference is expressed, for example, by "based on dry flue gas" or "at dew point 4 °C".

• Reference to the normal state of a gas. This pertains to the dependence of a gas volume on the actual values of pressure and temperature, please refer to Section 3.1.1

1.5 Flue gas (exhaust gas) and its composition

The flue gas generated in combustion processes is also referred to as exhaust gas. Its composition depends on the fuel and the combustion conditions, e.g. the air ratio. Many of the constituents of flue gas are classified as air pollutants, and must therefore be removed from the flue gas before it is released into the atmosphere via cleaning processes, which are extremely time-consuming and costly in some cases, in conformity with statutory regulations (please refer to Section 2.3). Flue gas in its original composition after combustion is also referred to as crude gas, and once it has passed through the cleaning stages it is called clean gas.

The most important flue gas components are explained below.

Nitrogen (N_2)
At 79 vol.%, nitrogen is the main component of the air. This colourless, odourless and tasteless gas is supplied via the combustion air, but does not play a direct role in the actual combustion process; it is carried as a ballast and a 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. Due to its property of filtering radiated heat, it is a major contributor to the greenhouse effect. Natural air only contains 0.03 %; the permissible MAC (maximum allowable concentration) is 0.5 %; concentrations of more than 15 % in the air inhaled by humans cause unconsciousness.

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 humidity (at high FT) or as condensate (at low FT).

Oxygen (O_2)

Oxygen that has not been used in combustion in the event of excess air 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 a reference value.

Carbon monoxide (CO)

Carbon monoxide is a colourless and odourless toxic gas. It is mainly generated during the incomplete combustion of fossil fuels (furnaces) and automotive fuels (motor vehicles) and other materials containing carbon. CO is generally innocuous to humans, since it soon bonds with the oxygen in the air to form CO_2. However, within enclosed spaces 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 MAC value is 50 ppm.

Nitrogen oxides (NO and NO_2, total formula NOX)

In combustion processes, the nitrogen from the fuel and, at high temperatures, also from the combustion air, is combined to a certain extent with the combustion air/oxygen, initially forming nitrogen monoxide NO (fuel NO and thermal NO), which in the presence of oxygen is oxidized in a further step to form the hazardous nitrogen dioxide (NO_2) in the flue gas duct and later in the atmosphere. Both oxides are toxic; NO_2 in particular is a dangerous respiratory poison and, in combination with sunlight, contributes to the formation of ozone. Sophisticated technologies such as the SCR process are used to clean flue gases containing NO_X. Special combustion measures, e.g. staged air supply, are used to reduce nitrogen oxides during 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 sulphur contained in the fuel. The MAC 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 numerous types of environmental damage to vegetation and building fabrics. Flue gas desulphurization plants (FGD) are used to reduce sulphur oxides.

Hydrogen sulphide (H_2S)

Hydrogen sulphide is a toxic and extremely malodorous gas, even in very low 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. Combustion to SO_2, certain absorption processes or, in the case of larger quantities, conversion to elemental sulphur in a Claus plant are some of the processes used to eliminate H_2S from flue gases.

Hydrocarbons (HC or C_XH_Y)

Hydrocarbons are an extensive group of chemical compounds composed exclusively of carbon and hydrogen. HCs are the most important substances in organic chemistry; they occur naturally in petroleum, natural gas or carbon. HCs can be emitted both when HC products are manufactured (e.g. in refineries) but also when they are used and disposed of (solvents, plastics, paints, fuels, waste etc.). Incomplete combustions are a particular source of HC emissions. This also includes forest and bush fires as well as cigarettes, for example. HCs contribute to the greenhouse effect.

Examples of HCs include methane (CH_4), butane (C_4H_{10}) and benzene (C_6H_6), but also the carcinogenic substance benzo[a]pyrene. The whole potential of a flue gas for volatile organic compounds is often referred to as the total C or Ctotal. This total is usually determined in the flue gas.

Hydrogen cyanide (HCN)

Hydrogen cyanide (also known as hydrocyanic acid) is a very toxic liquid with a boiling point of 25.6 °C; it exists in flue gases, if present, in gaseous form. HCN may exist in waste incineration plants.

Ammonia (NH$_3$)

Ammonia plays a role in flue gases in conjunction with the SCR process for flue gas denitrification. In the denitrification reactors, it is added to the flue gas in precisely metered quantities and causes the conversion of the nitrogen oxides into nitrogen and water. The unused residue (NH$_3$ slip) is greatly reduced via downstream cleaning stages, and in the clean gas is usually at or below 2 mg/m^3.

Halogen halides (HCl, HF)

During the combustion of coal and/or waste materials, the hydrogen halides HCl and HF may form, and these form aggressive acids in combination with humid atmospheres. These substances are largely washed out of the flue gas by the flue gas cleaning plants (scrubbers).

Solids (dust, soot)

Solid pollutants in the flue gas come from the incombustible components of solid and liquid fuels. These include, for example, the oxides of silicon, aluminium, calcium etc. in the case of coal and the sulphates of various substances in the case of heavy fuel oil. The harmful effect of dust on humans is mainly due to the accumulation of toxic and carcinogenic substances in the dust particles.

1.6 Gross calorific value, net calorific value, efficiency, flue gas loss

Gross calorific value, net calorific value

The gross calorific value (formerly referred to as the upper net calorific value) is a characteristic value for fuel and refers to the energy released during full combustion in relation to the quantity of fuel used. The net calorific value (formerly referred to as the lower net calorific value), on the other hand, is the released energy minus the evaporation heat of the water vapour generated during combustion at 25 °C, again in relation to the quantity of fuel used.

Basically, the net calorific value is less than the gross calorific value.

Condensing boiler

Condensing boilers are boilers which, in addition to the combustion heat, also make use of the condensation heat of the flue gas by means of heat exchangers. In terms of the net calorific value, these boilers can achieve combustion efficiencies of 107%. However, the condensate that is generated and contaminated with

pollutants must be disposed of in an environmentally friendly manner.

Efficiency of a combustion

The efficiency is a variable determined from performance values while the plant is in stationary operation. The efficiency (this is always less than 100%) is the ratio of the energy supplied to the combustion chamber overall to the energy required or used to carry out the process (heating, melting, sintering, etc.). Efficiency is made up of several components:

• The combustion efficiency describes the proportion of the total input power (energy per time unit) that is available in the combustion chamber after combustion. This makes it an important factor for the quality of the combustion.

• The furnace efficiency, which largely depends on its design, describes the quality of the furnace and the operation via the relationship between the supplied energy and the energy available in the furnace.

• The total efficiency is obtained by multiplying the combustion and furnace efficiencies.

Energy balance of a combustion plant

In stationary operating mode, the sum of all the energies supplied to the plant must be equal to the sum of the energies delivered by the plant; please refer to Table 6.

Supplied energies	Discharged energies
Net calorific value and tangible fuel energy	Tangible heat and chemically bound energy of flue gases (flue gas loss)
Tangible heat of combustion air	Tangible heat and net calorific value of fuel residues in ash and slag
Thermal equivalent of the mechanical energy converted in the plant	Surface losses as a result of heat conduction
Heat brought in through the product	Heat dissipated with the product
	Convection losses as a result of furnace leaks

Tab. 6: Contributions to maintaining the energy balance

The main contribution to the loss is the flue gas loss. It depends on the difference between the flue gas temperature and combustion air temperature, the O_2 or CO_2 concentration in the flue gas and on fuel-specific factors (Table 7). In condensing boilers, this flue gas loss is reduced in two ways – via utilization of the condensation heat and via the resultant lower flue gas temperature.
The flue gas loss can be calculated using the following formulae:

$$qA = \left[(FT-AT) \times \left[\frac{A2}{(21-O_2) + B} \right] \right] - KK$$

FT: Flue gas temperature
AT: Combustion air temperature
A2, B: Fuel-specific factors (see table)
21: Oxygen content in the air
O_2: Measured O_2 concentration
KK: Variable which shows the variable qA as a minus value if the dew point is undershot. Required for measurement on condensing systems.

For solid fuels, factors A2 and B equal zero. In that case, using the factor f, the formula is simplified to create the so-called Siegert formula.

$$qA = f \times \frac{FT - AT}{CO_2}$$

The fuel-specific factors used in the formulae are set out below.

Fuel	A2	B	f	$CO_{2\,max}$
Fuel oil	0.68	0.007	-	15.4
Natural gas	0.65	0.009	-	11.9
LPG	0.63	0.008	-	13.9
Coke, wood	0	0	0.74	20.0
Briquettes	0	0	0.75	19.3
Lignite	0	0	0.90	19.2
Hard coal	0	0	0.60	18.5
Coke oven gas	0.60	0.011	-	-
Town gas	0.63	0.011	-	11.6
Test gas	0	0	-	13.0
Peat	50-60	1	5	15-30

Tab. 7: Fuel-specific factors

Note

If required, the fuel-specific factor $CO_{2\,max}$ can be determined by Testo as a service.

1.7 Dew point, condensate

Dew point

The dew point or dew point temperature of a gas is the temperature at which the water vapour contained in the gas changes from the gaseous to the liquid state of aggregation, see Fig. 5. This transition is known as condensation, the liquid it produces is called condensate. Below the dew point, the water vapour is in liquid state and above the dew point it is in gaseous state; an example of this is the formation and evaporation of mist or dew as the temperature changes. The humidity content determines the dew point temperature. The dew point of air with a humidity content of 30% is approx. 70 °C, while the dew point of dryer air with only 5% humidity content is approx. 35 °C.

Note:

If measurement is carried out using an instrument without gas conditioning, the dew point temperature of the gas is approximately equal to the ambient temperature, .e.g. 25 °C. If these measurements are then compared with values measured with a gas conditioning unit, i.e. dew point temperature of 5 °C, for example, the resultant difference in the readings due to the different humidity content is approximately 3 %!
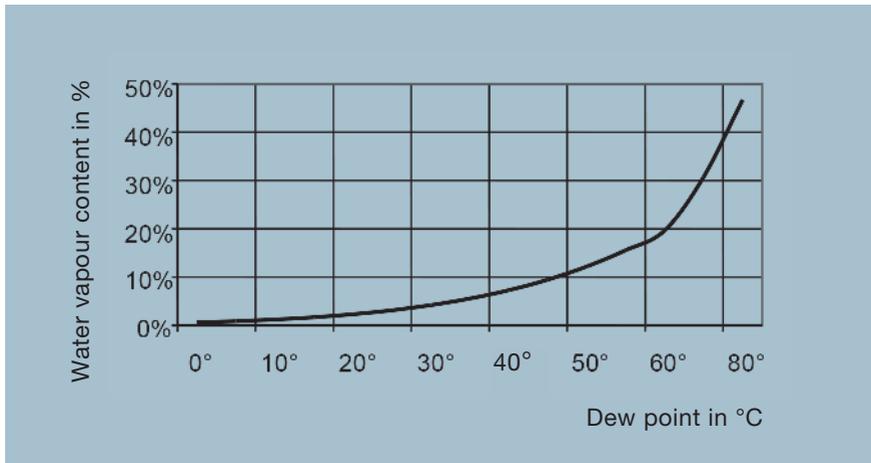

Figure 5:   Water vapour content as a function of the dew point (air pressure 1013 mbar)

Heated lines, measuring gas coolers

Flue gases with 8% humidity, for example, have a dew point of about 40°C, which means that condensate forms below this temperature. This has two important consequences for the plant as a whole as well as for the measuring equipment:

• If the flue gas contains sulphur dioxides, for instance, then at temperatures below 40 °C (e.g. in unheated pipes) these combine with the condensing water vapour to form sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4), both of which are extremely corrosive and can cause considerable damage to the system components that come into contact with them. For this reason, the temperature of the flue gas in the plant is kept above the dew point (i.e. above 40 °C in the case of the above example) until the flue gas reaches the scrubber.

The same applies to those components of measuring instruments through which the flue gas flows and above all to the components of the sampling device, such as probes and hoses. For this reason, heated probes and measurement gas lines are used and their temperature is kept above the dew point of the gas. Failure to observe this measure will result in damage to the measuring instruments and incorrect measurements!

• Testo's newly developed and patented method of particularly high gas flow velocity combined with a specially coated surface of the measurement gas lines offers a further alternative for preventing the formation of condensation. As a result, it is no longer necessary to heat the lines, which is extremely important for mobile devices in view of the resulting reduction in power consumption. Water vapour is absent from the cooled flue gas to a greater or lesser extent depending on the temperature to which the gas is cooled, with the result that the other components of the gas, such as CO, which have not changed quantitatively form a higher relative portion of the flue gas; the corresponding readings are then higher than in the moist flue gas! For comparable readings, the respective measurement gas must therefore have the same temperatures and therefore the same humidity content.

As a consequence, measuring gas coolers (they could also be called measuring gas dryers) are used in the gas analysis upstream of the analyzer; these bring the gas to a defined temperature and therefore a defined level of drying and keep it there.

Note
- Cooling gas means drying gas.
- In dry gas, the readings for gas components are comparatively higher than those in humid gas.

Testo instruments use what is known as a Peltier cooler for measurement gas cooling, its function is based on the fact that the interface between two different types of metals heats up or cools down depending on the direction of current flow. This cooler can cool the measurement gas in the testo 350 to +3 °C and keep it constant.

Permeation coolers, which are also common on the market, have the disadvantage of not being able to maintain a defined dew point; moreover, they are susceptible to clogging by dust particles, which leads to increased spare parts costs.

2. Reasons for using gas analysis for industrial flue gases

Gas analysis (measuring technology for analyzing the composition of gases) is an indispensable tool for economical and safe process control in practically all industrial sectors. The focus is on combustion processes, although this is a generic term that encompasses a large number of different processes. Figure 6 shows the sequence of a combustion process in segments, beginning (left) with fuel and combustion air being supplied to a combustion chamber, the combustion itself and the different processes involved in it, through to the flue gas cleaning and the final emission control.
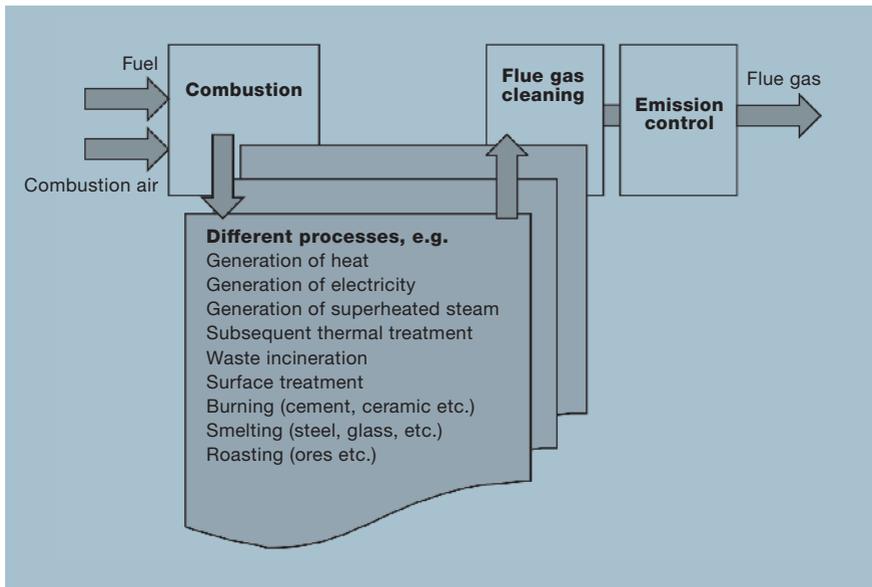
Figure 6: Variety and process stages of combustion processes

2. Reasons for using gas analysis for industrial flue gases

Gas analysis provides information about the composition of combustion and flue gases at all stages of this process chain. This makes it an indispensable tool for economical, safe plant operation that complies with the official regulations and, at the same time, for guaranteeing production quality and efficiency.

Gas analyzers are offered by many manufacturers in different designs and based on a variety of measuring principles; more details can be found in Section 3 of this Guide.

Testo's gas analyzers are widely used in industry for analyzing combustion gases, and they are by no means limited to emissions monitoring. The following areas of application are well established, with a certain degree of overlap:

1. Adjustment and servicing work for general monitoring, for example following plant maintenance, for troubleshooting in the event of unstable processes, in preparation for official measurements, following repairs etc.

2. Process measurements for combustion optimization of fuel, combustion air, burner and within the combustion chamber, with the aim of saving fuel, improving efficiency and extending the service life of the plant. These applications are also related to the emission measurements (hereinafter referred to as points 4 and 5), since optimized combustion usually also leads to a reduction in emission levels.

3. Process measurements for monitoring a defined gas atmosphere in boiler rooms or in special combustion chambers or furnaces during processes such as burning, roasting, surface treatment etc.

4. Process and emissions measurements for monitoring flue gas cleaning equipment to make sure that it is functioning properly.

5. Emissions measurements for monitoring compliance with limit values for pollutants in the flue gas upstream of or at the stack.

2.1 Gas analysis for combustion optimization

Major contributions to combustion optimization are made by
• The composition of fuel and combustion air (gas analysis field of application)
• The ignition behaviour and the combustion temperature
• The design of the burner and combustion chamber, as well as
• The fuel/combustion air ratio (gas analysis field of application).

The optimum ratio of fuel to combustion air (air quantity λ) for a given plant and a given fuel can be determined from gas analysis readings using the combustion chart (see Fig. 7). Here, the concentration progressions of the gas components CO, CO_2 and O_2 are shown in relation to the air ratio. The line representing ideal combustion with 0 excess air (λ =1) is in the middle of the diagram, to the right of this, the volume of excess air increases and to the left is the increasing air deficiency range (insufficient air also means insufficient oxygen!).
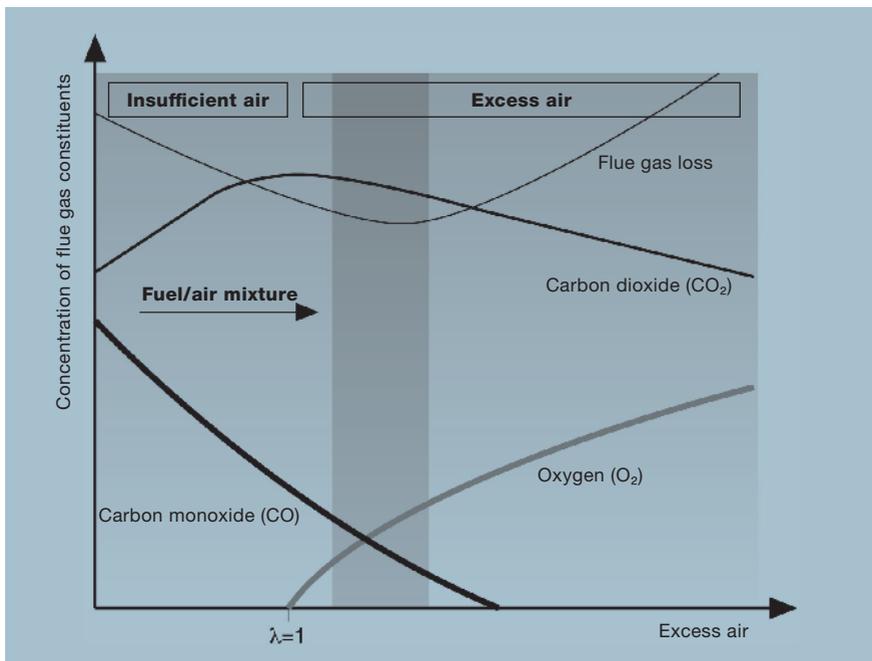
Figure 7: Combustion chart

(Insufficient air)

- When there is insufficient air, CO is present because there is not enough oxygen available to oxidize all CO to CO_2. Due to its toxicity, CO that is present in the event of insufficient air is extremely dangerous when it leaks out of the plant!
- As the insufficient air decreases, i.e. the O_2 concentration increases, the CO concentration decreases through oxidation to CO_2 and the CO_2 concentration increases accordingly. This process is completed at or a little above $\lambda=1$, CO approaches zero and CO_2 reaches its maximum.
- Oxygen is not present in this range or is not measurable, as any oxygen added is immediately used to oxidize the CO.

Right-hand area at $\lambda>1$
(Excess air)

- In the range $\lambda>1$, O_2 increases because the oxygen supplied as the excess air increases is no longer consumed through oxidation due to a lack of CO. In practice, however, a certain amount of excess air is always required to ensure complete combustion, as the distribution of oxygen across the combustion chamber is not uniform. The particle size of the fuel is also significant: the smaller the particle, the more intensive the contact with oxygen is and the less excess air is required.
- CO_2, on the other hand, decreases again relative to its maximum value at $\lambda=1$, however not due to a chemical reaction, but as a diluting effect due to the increasing amount of combustion air, which brings in virtually no CO_2 itself.

Conclusion

Optimum combustion is achieved if there is sufficient excess air and therefore oxygen to burn all the CO (λ range = 1.0 to approx. 1.3), but at the same time there is a low ceiling on the amount of excess air, so that as little hot flue gas and therefore thermal energy as possible is lost to the atmosphere as a result of unnecessarily high amounts of excess air.

The energy-optimized λ range for a combustion plant (this also depends on plant-specific data) can be determined by measuring the two components CO_2 and CO (CO_2 on its own is ambiguous due to the curve progression over a maximum!) or by measuring O_2 alone. The latter option of measuring O_2 is now widely used.

Depending on the plant and its operator, the measuring or gas sampling points can be located at various points in the combustion chamber.

The correlations between air ratio, excess air and typical oxygen content in dry flue gas shown in the diagram are given in figures in Tab. 8 for the combustion of hard coal.

Air ratio λ	Excess air as %	Oxygen content as %
0.9	Insufficient air	Insufficient oxygen
1.0	0	0
1.1	10%	2
1.2	20%	3.5
1.3	30%	4.8
1.4	40%	6.2

Tab. 8: Correlation between excess air and oxygen content in dry flue gas from a hard-coal-fired facility

Economic relevance

Apart from reducing emissions, the main aim of optimizing combustion by operating a plant with the optimum, i.e. generally the minimum possible, amount of excess air is to reduce costs by saving fuel.

A rule of thumb, which is common in practice and documented in the literature, states that by lowering the excess oxygen by one percentage point (not by 1% relative!), i.e. from 4.5 to 3.5%, for example, the efficiency of a combustion plant can be increased by 1% and the fuel costs can be reduced accordingly.

For example, with monthly fuel costs of $15 million for a medium-sized power plant, this results in monthly savings of $30,000 if, by means of gas analysis, regular plant operation can be implemented at only 0.2% points closer to the optimum excess air value than before! Similar savings are possible if short-term deviations from the optimum operating conditions can be detected and remedied at an early stage through the use of gas analysis.

2.2 Gas analysis
for process control

2.2.1 Process heater
for combustion processes

In contrast to conventional combustion plants (boiler firing systems), process heaters feature direct contact between the furnace or hot combustion gases and a material undergoing thermal treatment, thereby initiating a series of process steps. The production of cement clinker illustrates this, as an example for other similar processes (see Section 4.3.1 for details):

• The moist raw material is crushed and dried with hot flue gases.

• The separated raw meal is heated to approximately 800 °C by hot gas as it moves downwards in the counter-current.

• In the calciner, the CO_2 is expelled from the raw meal at approximately 950 °C via a multi-stage combustion process (the material is deacidified).

• The raw meal together with additives is burned (sintered) in the furnace at around 1400 °C.

Gas analysis makes it possible to assess these process steps with regard to excess air, to calculate false air flows and to balance the individual plant components separately. This is important for the calciner performance (measurement of CO_2 and O_2), for example, since insufficient calcination can cause significant malfunctions in the furnace operation.

In processes of this kind, substances can pass from the product being processed into the flue gas, increasing the usual emissions produced by the combustion plant. In certain cases, however, pollutants can conversely be passed from the gas into the product being processed or into specially designated substances (slag). An example of this is the cement or lime industry, where the sulphur in the fuel becomes a constituent of the product as sulphur oxide in the combustion process. Conversely, during the production of glass or bricks, sulphur oxides are released from the product being burned, increasing the flue gas concentration

considerably. The same applies to increased CO emissions in processes operated counter-currently to input material and flue gas (e.g. in rotary kilns). In remote zones away from the furnace, there may be insufficient oxygen, resulting in incomplete combustion with increased CO concentration. Heavy metals may be integrated into the incinerator charge (cement, lime) or released from this into the flue gas (metal industry, glass production).

Through process-related measures such as furnace chamber design, flame conduction, incinerator charge and furnace chamber temperature, combustion air supply, etc., process-related emissions can be greatly reduced. Gas analysis provides the necessary information to achieve this.

2.2.2 Industrial combustion plants

The term "industrial combustion plant" refers to combustion plants that are used in industry for generating steam and hot water or heating up other heat transfer media. This also includes combustion plants for converting materials, in refineries or coking plants, for example. The heat output of industrial combustion plants is generally in the megawatt range. As a result, they are predominantly covered by the TI Air emissions regulations, and in rare cases (capacity > 50 MW or > 100 MW for gas-fired installations) the Large Combustion Plant Ordinance (13th BImSchV) applies.

Here, the gas analysis tasks relate to optimizing combustion, controlling the flue gas cleaning and monitoring the limit values.

2.2.3 Thermochemical surface treatment

This is a heat treatment process, which changes the chemical composition of a workpiece or its surface through the diffusion in or out of certain elements from the surrounding gas atmosphere. This is used primarily to harden steel, but also to bake glazing and paints in the ceramics industry. These processes almost exclusively use gas as a treatment medium (in rare cases powder as well), and they are characterized by the nature and concentration of the elements diffused in (e.g. nitrogen for nitration, chromium for chrome plating) and process temperatures (approximately 400 - 1100 °C). Continuous flow and batch furnaces come in a wide range of different designs.

In all cases, gas analysis is required both for optimum plant operation (reduced costs and safety) and for monitoring the process-specific gas atmosphere (product quality, including documentation in accordance with ISO 9000 ff.). The most important components for analysis are O_2, CO, CO_2 and SO_2. Please refer to the application example in Section 4.4.6.

2.2.4 Safety measurements

Process applications of gas analysis can also include measurements which are used to protect personnel and plants. This concerns toxic, but primarily flammable and explosive gases, especially carbon monoxide CO. In coal dust silos and coal pulverizing plants, for example, monitoring CO enables smouldering hazards to be detected at an early stage, and the build-up of explosive gas mixtures in electrostatic precipitators can be prevented. The same applies to the monitoring of plants with regard to hazardous methane concentrations or other explosive gases, particularly in chemical plants.

Explosion limits

Mixtures of combustible substances with air or oxygen are flammable in certain concentration ratios. There is a lower and upper flammable limit for every mixture. These values are pressure- and temperature-dependent; they indicate the portion of the flammable component for both limits at a certain temperature and a certain pressure (generally 20°C and 1 bar) in vol.% or g/m3. The ignition or explosive range is the range between the two limits, see Table 9.

Flammable substances	Formula	Flammable limits in air in vol.% for T=20 °C and p=1 bar	
		lower	upper
Ammonia	NH_3	15.0	28.0
Carbon monoxide	CO	12.5	74
Hydrogen	H_2	4.0	75.6
Methane	CH_4	5.0	15.0
Propane	C_3H_8	2.1	9.5
Butane	C_4H_{10}	1.5	8.5
Acetylene	C_2H_2	1.5	82.5

Tab. 9: Flammable limits (explosive range) of flammable gases

The heat effect measuring principle (see Section 3.2.2) is used to analyze gas mixtures for combustibles. This determines the sum of all combustibles. When monitoring a mixture for its lower explosive limit (LEL), the measuring range of the instrument should therefore be based on the component with the lowest LEL.

2.3 Gas analysis for emission control

In most countries, many types of industrial plants (major power stations, steelworks, cement works, glass works, chemical plants and lots more) and local authority facilities, right through to small production sites, are subject to strict regulations governing flue gas emissions into the atmosphere. Suitable measures must be taken to ensure and regularly verify that the components defined as pollutants do not exceed certain limit values in the flue gas. Individual countries have passed laws and regulations in this area, extensive regulations in some cases; in Germany there is the Federal Immission Control Act, while its counterpart in the USA is the Clean Air Act. There are no standard regulations governing Europe as a whole or the Asian region. Many countries therefore base their national regulations on the provisions of the BImSchG or the Clean Air Act.

Gas analysis plays a key role in implementing and monitoring the measures required to limit emissions.

Emission

The air pollutions, noises, vibrations, heat etc. coming out of a plant (source)

Immission

The air pollutions, noises, vibrations etc. acting on people, animals, plants, soil, buildings etc.

2.3.1 Legal framework for emissions/immissions in the Federal Republic of Germany

The legal framework for all environmental protection regulations in Germany comprises:

• The German Federal Immission Control Act (BImschG) for the protection of the environment in its version dated 2017; and based on this

• Numerous legal regulations (German Federal Immission Control Ordinance (BImSchV)) to implement this law, and finally

• TI Air which contains special technical instructions for the authorities with specific requirements in terms of the approval and monitoring of plants in accordance with the 4th German Federal Immission Control Ordinance (BImSchV).

The Federal Immission Control Act is broken down into the following sections, among others:

1. General Provisions §§ 1 - 3
2. Establishment and Operation of Installations §§ 4 – 31
3. Nature of Installations, Substances, Products, Fuels and Lubricants; Greenhouse Gas Reduction in Fuels §§ 32 – 37g
4. Nature and Operation of Vehicles, Construction of and Alterations to Roads and Railtracks §§ 38 – 43
5. Monitoring of Air Pollution and Improvement of Air Quality, Clean Air Plans and Noise Abatement Plans §§ 44 – 47
6. Noise Abatement Plans §§ 47a – 47f
7. General regulations §§ 48 – 62
8. Final provisions §§ 66 - 73

2. Reasons for using gas analysis for industrial flue gases

To date, a total of 42 legal regulations have been enacted. Table 10 gives a selection of these, with the five sets of regulations particularly relevant to combustion systems highlighted. Fig. 8 shows the assignment of certain ordinances to plant types (fuel used and plant capacity).

1st BImSchV	Small-scale combustion plants
3rd BImSchV	Sulphur content of light fuel oil
4th BImSchV	Plants requiring a license
9th BImSchV	Basic principles of the licensing process
11th BImSchV	Emissions declaration
13th BImSchV	Large-scale combustion plants
17th BImSchV	Waste incineration installations
27th BImSchV	Crematoria

Tab. 10: Legal regulations concerning the German Federal Immission Control Act (selection)

Figure 8: Classification of plant types and regulations

Emission values and emission limit values

- Emission values are standards with a liability ranging below emission limit values; emission values for air pollution control are specified in TI Air. These are defined as values, "the exceeding of which can be avoided by applying state of the art technology".
- Emission limit values are legislative emission standards and are therefore directly binding for those affected. These values are set out, for example, in the 1st German Federal Immission Control Ordinance (BImSchV), 4th BImSchV/TI Air, and the 13th, 17th and 27. BImSchV

2.3.2 Specifications from the German Federal Immission Control Act (BImschG) for Germany (selection)

Ordinance on small-scale combustion plants (1st German Federal Immission Control Ordinance (BImSchV))

This regulation applies to all combustion plants that do not require licenses, with an output of up to 1, 5 or 10 MW (depending on the fuel, see Fig. 8). The chimney sweep is the officer in charge of monitoring these plants. He or she must establish once a year whether the requirements for heating plants in respect of emissions limits are being met.

In the case of solid fuel plants, dust-like emissions and, in certain cases, carbon monoxide (CO) are determined. In the case of oil-fired and gas-fired installations, the flue gas loss is determined as a parameter from the measurement of the oxygen or carbon dioxide content in the flue gas and the difference between the flue gas temperature and room temperature (the temperature of the combustion air corresponds largely to room temperature). The smoke number is also determined for oil-fired installations.

**Ordinance on plants requiring a li-
cense (4th German Federal Immis-
sion Control Ordinance (BImSchV))**

This ordinance includes a list of ap-
prox. 150 types of plants with rated
heat outputs in the lower megawatt
range that require a license to operate.
The plant types are grouped together,
see Table 11. The regulation for imple-
menting the 4th German Federal Im-
mission Control Ordinance (BImSchV)
is the "Technical Instructions on Air
Quality Control", or "TI Air" for short.
Please refer to the following section.

Group	Bulk chemical industries
1	Heat generation, mining, energy
2	Non-metallic minerals, glass, ceramic, construction materials
3	Steel, iron and other metals including processing
4	Chemical products, pharmaceuti- cals, mineral oil refining and further processing
5	Processing plastics and other materials
6	Wood, cellulose
7	Food, beverages, tobacco and animal feed, agricultural products
8	Recovery and disposal of wastes and other materials
9	Storage, loading and unloading of substances and preparations
10	Other plants

Tab. 11: Group classification of plant types
in the 4th German Federal Immission Control
Ordinance (BImSchV)

**TI air
(Technical Instructions on Air
Quality Control)**

TI air is an administrative regulation re-
lated to the BImSchG. It contains reg-
ulations that a plant must comply with,
from the building application through
to monitoring ongoing operation. The
scope of application extends only to
those plants requiring a license, which
are listed in the 4th German Federal
Immission Control Ordinance (BIm-
SchV).

TI Air is broken down into four parts:

Part 1: Regulations for applicability

Part 2: General regulations on air pollution control

Part 3: Requirements for limiting and setting emissions

Part 4: Redevelopment of old plants

Part 3 of TI Air is particularly relevant to gas analysis technology. This contains the main requirements for limiting emissions in plants requiring a license.

Section 2.1 sets out the general rules, with substances classified into four classes according to their harmful effects: the limit value for the most hazardous substances (Class I, e.g. arsine or phosgene) is 1 mg/m3, whereas the limit value for sulphur oxides or nitrogen oxides (Class IV), for example, is 500 mg/m³. These requirements are generally applicable. However, in specific cases described in more detail in Section 2.3, they are replaced by more stringent special requirements.

Section 2.2 deals specifically with the procedure for measuring and monitoring emissions and specifies, among other things, that

• When approving plants, appropriate sampling points and measuring stations are to be designated, which will facilitate representative and metrologically flawless measurement of emissions;

• Emissions of air pollutants for which limits have been defined in the approval notice, are to be established via initial and recurrent individual measurements;

• In the event of particularly high mass flows of substances subject to emissions limits, these are to be monitored via continuous measurements, and

• Individual readings must be taken on a regular basis for particularly hazardous substances for which continuous measurement would be desirable but technically unviable.

Individual measurements according to TI Air (measurement in accordance with § 26, 28 BImSchG)

Prior to the individual measurement, an initial measurement is carried out by an approved test centre following new installation or substantial modification of a plant. This initial measurement can be regarded as an acceptance of the plant and is performed within 3-12 months of commissioning. The individual measurements are then carried out every 3 years after this. The concentrations of the noxious gases subject to measurement are determined as a mean value over a half-hour measuring period and checked

for compliance with the limit values. A minimum of 3 measurements must be taken for plants under constant operating conditions, otherwise the minimum number of measurements is 6. Before the measurement, the plant operator should adjust the combustion system to optimum operation.

Continuous measurement in accordance with TI Air

During the daily operating duration of the plant, the "half-hourly average" is calculated from the measurement data acquired every half hour. From these values,"daily averages" are then calculated, stored and statistically evaluated, whereby the limit values specified for the plant must not be exceeded.

- Official individual measurements in accordance with TI Air may only be carried out using measuring instruments that have passed the qualification test set down in TI Air.
- Only stationary measuring equipment that has passed the qualification test in accordance with TI Air may be used for continuous measurement.
- Testo analyzers are suitable both for individual measurements and for continuous measurements.

Finally, Section 2.3 contains particular regulations for certain types of plants, affecting large areas of the industry. 12.

Section in TI Air	Type of plant being dealt with
3.3.1	Heat generation, mining and energy
3.3.2	Non-metallic minerals, glass, ceramic, construction materials
3.3.3	Steel, iron and other metals
3.3.4	Chemical products, drugs, refineries
3.3.5	Surface treatment with organic substances, production of films, processing of plastics
3.3.6	Wood, cellulose
3.3.7	Food, beverages, tobacco and animal feed, agricultural products
3.3.8	Waste incineration (recently governed by the 17th German Federal Immission Control Ordinance (BImSchV)), composting plants
3.3.9	Storage, loading and unloading materials
3.3.10	Other
Special case	Power stations, CHP plants and heating plants > 50 MW (> 100 MW in the case of gas combustion plants) are covered by the 13th German Federal Immission Control Ordinance (BImSchV) rather than TI Air

Tab. 12: Classification by plant type in TI Air (Section 3.3)

Note:

The pollutant limit values applicable to certain types of plants are stated in Section 4 of this Guide, for the corresponding application examples.

Ordinance on large-scale combustion plants (13th German Federal Immission Control Ordinance (BImSchV))

These include combustion systems with a heat output of > 50 MW using solid and liquid fuels and > 100 MW using gaseous fuels. These plants are not dealt with in the 4th German Federal Immission Control Ordinance (BImSchV) or TI Air. Emissions limits are established for dust, dust constituents, sulphur dioxide, nitrogen oxides, carbon monoxide and gaseous chlorine and fluorine compounds depending on heat output and the type of plant. Some of these values are subject to a dynamic sampling principle, which means the values may be lowered as soon as the state-of-the-art allows it.

Pollutant	Pollutant limit value in mg/m^3 according to the 13th German Federal Immission Control Ordinance (BImSchV)			
	Fuel			
	Solid	Biofuels	Liquid	Gaseous
Dust	10	10	10	5 - 10
CO	150 - 200	150 - 250	80	50 - 250
NO, NO$_2$	150 - 400	150 - 250	100 - 250	50 - 200
SO$_2$, SO$_3$	150 - 400	150 - 200	150 - 350	5 - 350
Mercury	0.03	0.03	-	-

Tab. 13: Limit values for pollutants according to the 13th German Federal Immission Control Ordinance (BImSchV (excerpt)

Ordinance on waste incineration plants (17th BImSchV)

Waste incineration plants are used for the thermal treatment of solid, liquid, or paste-type waste (domestic and hospital waste, sludge, used tyres, and also paints, varnishes and solvents) with the aim of reducing the amount of waste and its potential pollution levels. In terms of the permissible pollutant limit values, the flue gases produced during this combustion must comply with the valid specific provision governing waste incineration (17th BImSchV); a selection of the values specified therein is shown in Table 14.

	Pollutant limit values in mg/m^3 according to the 17th BImSchV	
Pollutant	Max. daily average	Max. half-hourly average
Total dust	5	20
Total carbon	10	20
Hydrogen chloride	10	60
Hydrogen fluoride	1	4
SO_2 and SO_3	50	200
NO, NO_2	150	400
Mercury	0.03	0.05
Carbon monoxide CO	50	100
NH_3	10	15

Tab. 14: Pollutant limit values according to the 17th BImSchV (selection)

Ordinance on crematoria (27th German Federal Immission Control Ordinance (BImSchV))

These define measures to be taken in terms of monitoring emissions from crematoria. (Please also refer to Section 4.6.1)

Analyzers for monitoring emissions in accordance with the German Federal Immission Control Act (BImschG)

The analytical methods used for emissions monitoring in accordance with the German Federal Immission Control Act (BImschG) work according to the same physical or chemical principles that are used in other areas of gas analysis. However, the requirements for the instruments are specified here and the instruments must prove that they meet the specifications in a qualification test.

The large number of components in the flue gas require sufficient selectivity from the methods and instruments, as well as low and known degrees of cross-sensitivity. The measuring methods must be reliable and reproducible and allow calibration. High availability must also be ensured, along with virtually maintenance-free operation.

Due to high flue gas temperatures, high humidity and dust contents and also aggressive flue gas components, the measuring tasks also place particular requirements on the sampling process. Moreover, when carrying out sampling, it is important to bear in mind that the sampling is representative of the plant, which, in the case of plants with high temporal and/or spatial variability of the pollutants, requires grid measurements or distributed individual measuring points, for example.

Qualification test for measuring instruments

Only measuring instruments that have successfully demonstrated their qualification for this purpose may be used to monitor air pollution control in line with the requirements of the German Federal Immission Control Act (BImschG).

According to this principle, sufficient quality and comparability of measurements must be ensured, as well as uniform practice for plant monitoring. The qualification test is conducted according to prescribed guidelines (minimum requirements); it is completed by means of laboratory tests and a

field test by a few specially approved test institutions. Proof of a successfully completed qualification test is supplied in the form of a certificate or public announcement of the results by the responsible Ministry in the relevant Ministerial Gazette.

The testo 350 analyzer has passed the qualification test for O_2, CO, NO, NO_2 and SO_2 for measuring tasks defined in the 13th and 17th German Federal Immission Control Ordinance (BImSchV) and in TI Air.

2.3.3 Emissions monitoring in the USA

1. Emissions monitoring in the USA is based on the Clean Air Act and its amendments (Clean Air Act Amendments, CAAA) from 1991. CAAA is a federal law. With reference to this law, the EPA (Environmental Protection Agency) passed framework regulations designed to reduce and monitor emissions. In particular, there was a shift from monitoring very large emitters to smaller sources (titles 5 and 7, see below).

2. CAAA divides emitters into 7 sections (titles) according to their size, three of which are particularly relevant to the use of Testo instruments:
   Title 4: Power plants
   Title 5: Industrial sources
   Title 7: Smaller sources

   The assessment of an emitter is carried out according to various criteria, e.g. the thermal output or its potential to emit a certain quantity of specified pollutants, e.g. 100 t NO_X/year. Further subdivisions focus on the permissible limit values (parts) and standards/guidelines for measuring instruments (methods) for certain types of plant.

3. The shift towards smaller plants also has consequences for measuring technology. Continuous emission monitoring systems (CEMs) are still prescribed for monitoring large emitters. These entail an initial investment of several $100,000 with annual maintenance costs of $30,000 and up. There is no way that smaller emitters can justify this expense, and the EPA has now cleared the way for other, smaller metrological solutions (see point 7).

4. Within the USA, there is a division of responsibilities between the federal authorities and those of the individual states. Title 4 generally comes under the jurisdiction of the Federal Government, while title 7 comes under the jurisdiction of the States; in the case of title 5, the States have jurisdiction, provided that they demonstrate relevant implementation activities. To exercise their responsibility, there are authorities (Departments of Environmental Quality, DEQ) in the individual states that are empowered to introduce the standard set down by the EPA or impose more stringent regulations. The DEQ in California (known as the South cost air quality management district, SCAQMD) employs 2,400 people and has introduced a variety of specific regulations and measurement methods, including those for the use of mobile devices to determine NO_X.

5. A special procedure has been established for small emitters in accordance with title 7. The approximately 34,000 plants affected are to be assessed on the basis of relatively relaxed regulations (compliance assurance monitoring, CAM) by the authorities of the individual states, at their discretion, to establish any need for measures. Measuring methods are neither specified nor expressly prohibited here! This paves the way for new processes and instruments.

6. The EPA does not carry out equipment testing or certification, but it defines test methods which describe the application of a particular instrument technology for specific measurement tasks. An example of this is the method for measuring certain gas components with electrochemical sensors: This method is generally approved for O_2, for NO_X approval has been granted by SCAQMD, it is not disqualified from being used for SO_2 and efforts are currently under way to approve it for CO.

7. The testo 350 complies with test methods 1 (for gas flow), 3 (for CO_2 and O_2), 6c (for SO_2) and 7e in combination with what is referred to as the conditional test method 022 (for NO_X).

2.3.4 Methods for purifying flue gas

Air pollutant emissions from flue gas can be considerably reduced by taking appropriate measures or installing the necessary components in the plant:

• The emission of particulate matter is reduced or virtually eliminated by using a dust separator.

• The emission of gaseous pollutants can be reduced to a certain extent by using low-emission fuels. However, crucial reduction is achieved by optimizing combustion and purifying the flue gas produced through absorption or adsorption reactions or via afterburning. In these procedures, gas analysis plays a decisive role in monitoring and optimizing the measures taken!

Dedusting methods

Plants for dedusting gas flows (dust separators) work on the basis of a variety of principles:

- **Separation via centrifugal force or gravity**

  Here, the particles are channelled via their gravity or via centrifugal forces into such separator zones which are outside the flue gas flow. Particularly well-known examples of this type of separation are the separators based on centrifugal force known as cyclones, in which the particles gain a moment of momentum from a specially designed gas inlet aperture which transports the particles into a separating chamber. From there they are fed to a dust collector.

- **Separation via electrical forces in electrostatic precipitators**

  Electrostatic precipitators utilize the force effect on charged particles in an electric field for dust separation. The dust particles are first charged by adding negative ions and are then, as a result of this charge, conducted to a collecting electrode in the electrical field. There the dust is deposited as a layer; the layer is loosened (cleaned) by knocking against the electrode and the dust is transported into a bunker. Electrostatic precipitators are primar-

ily used to clean extremely large volumes of gas in power stations, ironworks, metallurgical works or cement works, for example.

In principle, electrostatic precipitators may explode due to the formation of an explosive gas mixture within the electrical field. For effective protection, the CO concentration upstream of the filter should be monitored.

- **Separation via adhesive forces in e.g. fabric filters**

  In this form, the particles are separated in or on the surface of certain filter media (membrane, fabric, grains) which the gas passes through. The most common are bag or pocket filters made from fibres. Depth filters include primarily packed bed filters, where separation is carried out on the surface of grains, as a layer that the gas flows through.

- **Separation via droplet formation in e.g. spray scrubbers**

  Here, the particles are bound to a scrubbing liquid introduced to the gas flow and are separated together with it. The disadvantage of this process is the generation of a contaminated scrubbing liquid.

Denitrification methods

Primary and/or secondary measures are used for denitrifying flue gases (or to be more exact, the removal of nitrogen oxides NO and NO_2).

- Primary measures include the staged air supply method, fluidized-bed combustion and the use of special burners. All of these measures will considerably reduce the formation of nitrogen oxides during combustion.
- One secondary measure (these impact on the flue gas after it leaves the combustion chamber) which has become widely accepted is the Selective Catalytic Reduction (SCR) process. In this process, the flue gas is enriched with a mixture of ammonia (NH_3) and air, after which the nitrogen oxides are converted into nitrogen and water in a chemical reaction. The abbreviation DENOX is also used for these types of plants.

Fluidized-bed combustion

In fluidized-bed combustion systems, the pulverized fuel is supplied to the combustion chamber, above a base that is equipped with nozzles. The combustion air flows through the nozzles from underneath, causing the fuel particles to form a fluidized bed. The particles not burned or not fully burned are conducted back into the combustion chamber from the flue gas

flow via appropriate measures, and this creates a circulating fluidized bed. The fluidized-bed process offers significant advantages: the fuel particles come into particularly close contact with the oxygen in the combustion air and the combustion is therefore near complete. The combustion temperature is around 900 °C, which prevents the formation of thermal nitrogen oxides in nearly all cases; adding lime to the fuel also enables desulphurization during combustion.

Staged air supply

Staged air supply is also a very effective primary measure, since it suppresses the formation of both fuel NO and thermal NO. This reduces the air supply at the burner (primary air), the air ratio is therefore <1, CO formation increases, the NO_X content remains low and is further reduced by the formation of stable N_2 molecules. More combustion air (burnt-out air) is then added above the burner in a further stage and ensures that combustion continues. As a result, the CO is greatly reduced, but hardly any NO is formed as the nitrogen is already present as stable N_2 molecules.

Low NO$_x$ burners

Similar to the staged air supply in the combustion chamber, these burners operate with an air supply that is distributed over several different spots within the burner and include internal air recirculation. This results in complete combustion with reduced formation of nitrogen oxides.

Desulphurization process

Among the many methods of flue gas desulphurization, wet scrubbing with lime/limestone (secondary measure) is the most common. In a wash tower, the flue gas is sprayed with a washing suspension (finely ground limestone in water), as a result of which most of the sulphur dioxide (SO$_2$) is bonded via a chemical reaction. The gaseous SO$_2$ is initially turned into a solution before it is bonded as calcium sulphate dihydrate (gypsum). The gypsum generated in large quantities is at least partly reused as a construction material. The abbreviation FGD (flue gas desulphurization plant) is also used for these plants.

Thermal afterburning

3. Gas analysis technology

3.1 Terminology used in analysis technology (selection)

3.1.1 Concentration specifications

The term "concentration" describes the portion of a substance in a total solid, gaseous or liquid mixture, e.g. alcohol in beer or oxygen in air. Various measurements are used to specify a concentration, such as:

• Mass concentration (reference to the mass of the substance) with the dimension [g substance/m^3 gas volume]
• Volume concentration (reference to the volume of the substance) with the dimension [cm^3 substance/m^3 gas volume]
• Particle concentration (reference to the number of particles of the substance) with the dimension [number of particles of substance/total number of particles]

In emissions and immissions technology, the units of mass concentration and particle concentration are juxtaposed. The unit of mass used in this case is the gram, or its subdivisions, while the term ppm (part per million)

is common for particle concentration. Subdivisions of these units are used depending on the concentration, please refer to the following Tables 15 and 16.

A quantity of pollutants is thus specified

• Either in g (or mg or μg etc.) with reference to a given gas volume, generally a cubic metre (m^3), e.g. 200 mg/m^3
• Or in ppm without any reference, e.g. 140 ppm

Expression	Written as	
Grams	g	
Milligram	mg	10^{-3} g
Microgram	μg	10^{-6} g
Nanogram	ng	10^{-9} g
Picogram	pg	10^{-12} g
Femtogram	fg	10^{-15} g

Tab. 15: Unit of mass g with subdivisions

Expression	Written as	
Parts per billion	0.001 ppm	0.0000001%
Parts per million	1 ppm	0.0001%
	10 ppm	0.001%
	100 ppm	0.01%
	1000 ppm	0.1%
	10000 ppm	1%

Tab. 16: Particle concentrations ppm and % with subdivisions

Note

Due to the general dependency of a volume of gas on its temperature and pressure, it is also necessary for the unambiguity of a reading when using the mass concentrate to

- Either specify the current values for the pressure and temperature of the gas applicable at the time of measurement, or
- Convert the current readings to what are regarded as the standard conditions, see next section. Following this kind of conversion, the volume is then specified in standard cubic metres (described as Nm^3 or m^3N).

Standard conditions; standard volume of a gas (VN)

The volume of a gas is dependent on its temperature and how pressurized it is.

For the purposes of comparison, a standard volume was defined:
A gas has its standard volume if its temperature and pressure are identical to the values defined as the standard conditions of 273 K (corresponding to 0°C) and 1013 mbar (hPa).

Conversion of concentration figures

Conversion of a reading to standard conditions

The conversion of a current reading (status 1) to standard conditions (status 2) is carried out according to the formula

$$C_2 = C_1 \times \frac{T_1 \times P_2}{T_2 \times P_1}$$

where the variables in the formula have the following meanings:

Status 1: Measurement status	T_1: Temperature of gas on measurement (273 K + current temperature in °C) P_1: Pressure of gas on measurement in hPa C_1: Measured concentration
Status 2: Standard status	T_2: Standard temperature (= 273 K) P_2: Standard pressure (= 1013 hPa) C_2: Concentration converted to standard conditions

Example:

200 mg/m³ at 35 °C and 920 hPa after conversion is 248.4 mg/Nm³ in standard conditions

Conversion of ppm to mass concentration [mg/Nm³]

ppm (abbreviation for parts per million) is a commonly used unit of concentration in the form of a mixing ratio; it has an equally common counterpart unit of mass concentration.

A specification in [ppm] can be converted to the corresponding unit of mass concentration [mg/Nm³] using the standard density of the gas in question as the factor for the formulae shown below. The "dilution" of the flue gas by air (from the excess air and where necessary from targeted additions of air or through possible leaks in the plant), of which the oxygen con-

centration is a measure, must also be taken into account. The readings must therefore generally be converted to a certain oxygen portion (called the "O_2 reference"). Only specifications with the same oxygen reference value are directly comparable! For this reason, the corresponding oxygen reference values are also always specified in the official requirements alongside the pollutants. In addition, the actual oxygen portion measured, which is a measure of the actual dilution, is also required for the conversion (O_2 in the denominator of the formula).

The conversion formulae for the gases CO, NO_X and SO_2 are:

$$CO\ (mg/m^3) = \left[\frac{21 - O_2 - reference}{(21 - O_2)} \right] \times CO\ (ppm) \times 1.25$$

$$SO_2\ (mg/m^3) = \left[\frac{21 - O_2 - reference}{(21 - O_2)} \right] \times SO_2\ (ppm) \times 2.86$$

$$NO_X\ (mg/m^3) = \left[\frac{21 - O_2 - reference}{(21 - O_2)} \right] \times (NO\ (ppm) + NO_2\ (ppm)) \times 2.05$$

Note

The numerical factor (1.25 etc.) used in the formulae corresponds to the standard density of the respective gas in mg/m³. The following should be taken into account:

• Standard density values of 2.86 - 2.93 kg/m³ are specified for SO_2 in literature (difference between ideal and actual gas behaviour of SO_2)

• The standard density of NO_2 of 2.05 is used for NOx, as NO_2 is the only stable compound (NO bonds with oxygen extremely quickly after its production to form NO_2)

• The factor 1.52 must be used for H_2S with the rest of the formula unchanged

If the conversion is to be carried out without reference to the oxygen content, the formula is simplified by omitting the expression in brackets for CO, to leave

CO in [mg/m³] = CO in [ppm] x 1.25

This applies to the other gases analogously.

Conversion of ppm to energy-related units

To represent the concentration of pollutants in the two energy-related units g/GJ and mg/kWh (1 kWh = 3.6 MJ), conversions using fuel-specific factors (FBr) are required; refer to formulae below and Table 17 for the FBr factor.

The conversion from ppm to g/GJ is carried out according to the following formulae:

$$CO \text{ (mg/kWh)} = \frac{21}{21-O_{2 \text{ measured}}} \times CO \text{ (ppm)} \times FBr \times 1.25$$

$$NO_X \text{ (mg/kWh)} = \frac{21}{21-O_{2 \text{ measured}}} \times NO_X \text{ (ppm)} \times FBr \times 2.05$$

$$SO_2 \text{ (mg/kWh)} = \frac{21}{21-O_{2 \text{ measured}}} \times SO_2 \text{ (ppm)} \times FBr \times 2.86$$

Fuel oil EL	0.2434	Town gas	0.2238
Heavy fuel oil	0.2460	Briquettes	0.2685
Natural gas	0.2525	Lignite	0.2661
LPG	0.2332	Hard coal	0.2643
Coke oven gas	0.2220	Coke, wood	0.2633

Tab. 17: FBr factor for different fuels

The applicable factor of 3.6 must be included when converting from ppm to mg/kWh with the rest of the formulae remaining unchanged:

$$CO \text{ (mg/kWh)} = \frac{21}{21-O_{2 \text{ measured}}} \times CO \text{ (ppm)} \times FBr \times 3.6 \times 1.25$$

$$NO_X \text{ (mg/kWh)} = \frac{21}{21-O_{2 \text{ measured}}} \times NO_X \text{ (ppm)} \times FBr \times 3.6 \times 2.05$$

$$SO_2 \text{ (mg/kWh)} = \frac{21}{21-O_{2 \text{ measured}}} \times SO_2 \text{ (ppm)} \times FBr \times 3.6 \times 2.86$$

3.1.2 Sampling, gas conditioning

Extractive sampling

In most gas analysis methods, the measurement gas is extracted as a representative portion of the process gas (hence the term extractive methods, in contrast to in-situ methods), conditioned and fed to the analyzer. Conditioning, also referred to as sample preparation, is understood to mean cleaning the gas using a filter and primarily cooling, and therefore drying, the gas to a defined constant value.

The advantages of this measurement concept are

- Separation and protection of the sensitive analyzer technology from the extremely harsh conditions in the process stream
- Via the conditioning procedure, the sample gas can be transformed into a practicable and constant (and therefore comparable) condition
- More than one analyzer may be operated with one sampling unit or one analyzer may be connected to several sampling points (via a changeover switch).

Gas sampling and conditioning
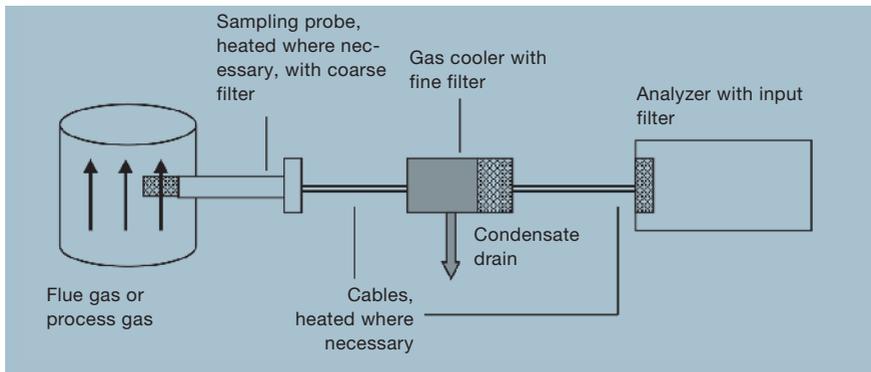
Figure 9: Sample gas extraction and conditioning (schematic)

Instruments for extracting and conditioning the gas are either designed as separate units or combined in one or two compact units. In simple terms, the functions are as follows:

• Gas sampling is carried out via a heated or unheated sampling probe made of different materials and for different temperature ranges (up to 1200 °C and above). A coarse ceramic filter is built into the probe head, and some probes (e.g. the Testo multifunction probe) have additional sensors for determining the pressure and temperature.

• The measuring gas cooler is located between the probe and analyzer. Flue and process gases always carry a certain amount of water, which at high temperatures (above the dew point) exists as water vapour and at low temperatures (below the dew point) as water droplets. In both cases, the measuring result is distorted by chemical reactions between other components of the measuring gas and the water. Furthermore, the measuring equipment may be attacked and destroyed by

aggressive solutions formed, for example, through the reaction of SO_2 with water. Measurement gas coolers are used to remove the majority of water vapour (humidity) from the measuring gas by cooling it to a fixed temperature, e.g. 4°C and to keep the remaining level of humidity constant, and therefore comparable, by maintaining a constant temperature. The resulting condensate is usually discharged via peristaltic or diaphragm pumps.

• The measuring gas lines or hoses are either unheated (in the case of non-critical gases or extremely high ambient temperatures) or heated to keep the gas above the dew point and thus to prevent the formation of condensate.

• Depending on the manufacturer, the analyzer may also have a gas filter and in some cases a condensate separator or an internal heater.

The gas humidity content is an extremely critical variable when it comes to gas analysis,
in two respects:

• As vapour, it dilutes the flue gas, and if the humidity should fluctuate, this dilution will also fluctuate, as will the readings.

 • As water, it forms compounds with certain components of the gas, changing their concentration and consequently the readings too.

Remedial measures:

• Always measure the humidity level, which is an important variable, simultaneously.

• Bring the humidity to a defined, and therefore comparable level using a measuring gas cooler.

• Always prevent the formation of condensate over components or all of the measuring equipment by using a heating system throughout!

3.1.3 Cross-sensitivity

The cross-sensitivity of a detection system is caused by the fact that its specific resolution is not unlimited. The detection system is therefore often sensitive not only to the component of interest that is being measured, but also to a certain extent to other (associated) components present in the measuring gas. Changes in the concentrations of these components will have an effect on the reading of the component actually being measured, which must be corrected within the device or retrospectively. To this end, the associated components must also be measured. Cross-sensitivity is expressed by the effect (increase or decrease) that an associated component of the measurement gas has on the reading of the component being analyzed. The extent of cross-sensitivity depends on the type of detection system (i.e. it is instrument-specific!) and on the concentration of the associated components. Please refer to Table 18 for the testo 350.

Cross-sensitivities

This table is valid for new sensors with possibly unused filters, and for transverse gas concentrations in the ppm range (down to less than 1000 ppm). The value "0" means: <1% cross-sensitivity.

Target gas	Transverse gas									
	CO	NO	SO_2	NO_2	H_2S	H_2	Cl_2	HCl	HCN	CO_2
O_2	0	0	0[8]	0	0	0	0	0[8]	0	see[9]
$CO(H_2)$	-	0[5]	0[5]	0[5]	0	0[10]	0	0	0	0
$CO(H_2)_{low}$	–	0[5]	0[5]	0[5]	0	0[10]	0	0	0	0
NO	0	–	0[5](r)[6]	6%[7]	0	0	0	0	0	0
NO low	0	–	0[5]	<5%[7]	0	0	0	0	0	0
NO_2	0	0	<-2%	–	-20%[7]	0	100%	0	0	0
SO_2	<5%[7]	0	–	-110%[7]	0[5]	<3%	-80%	0[5]	30%	0
SO low	<5%[7]	0	–	-110%[7]	0[5]	<3%	-80%	0[5]	30%	0
C_XH_Y	35%[5]	0[5]	0[5]	0[5]	0	130%[11]	no data	no data	no data	0
H_2S	<2%[7]	<15%[7]	<20%[7]	-20%[7]	–	0	<10%	0	0	0

[5] With non-saturated filter.
[6] w = replaceable filter
[7] Is compensated if the transverse gas in the instrument is also measured (i.e. if the instrument is equipped with the relevant sensors).
[8] No influence up to a few 1000 ppm; for cross-concentration in the %-range 0.3% O_2 per 1% SO_2 / HCl.

[9] 0.3% O_2 per 1% CO_2; is compensated
[10] After H_2 compensation
[11] Is compensated with indication H_2 by the $CO(H_2)$ sensor.

Tab. 18: Cross-sensitivities in the testo 350 analyzer

- No sign signifies a positive effect (increase in the reading)
- "-" sign signifies a negative effect (reduction in the reading)
- CO_2 and NH^3 as well as saturated hydrocarbons do not produce cross-sensitivities

Further information regarding the effects of associated components:

- Higher concentrations of unsaturated hydrocarbons can result in zero drift and reduced response intensity, particularly for the CO and NO measuring cell.
- High concentration levels of aggressive gases such as HCN, HCl or fluorides may attack the sample lines or the cell housing.

3.1.4 Calibration, adjustment

Calibration
As per DIN 1319, Part 1, calibration in measuring technology is understood to refer to the process of determining and recording the existing measurement deviation on the instrument when it is ready and operational. In the case of displaying measuring instruments, the discrepancy between the display and the correct value for the parameter, or the value assumed to be correct, is determined and recorded using factors or functions. Unlike adjustment, calibration does not involve making any changes to the measuring instrument.

Calibration is an essential element of quality assurance in emissions monitoring. Reference materials whose composition is known very precisely within certain margins are used for calibration. Calibration gases (also called test gases) are used for gas analysis.

Adjustment
In line with DIN 1319, Part 1, adjustment in measuring technology is understood to refer to the process of adjusting a measuring instrument so that the error of measurement is as small as possible. This process involves making changes to the instrument.

Official Calibration
Official Calibration of a measuring instrument is very similar to calibration, but it may only be carried out by official bodies. Official Calibration is a legally defined and protected term for an official quality inspection, with appropriate labelling.

Test gas
A gas whose composition is known with a high degree of precision, and certified. Test gases are used to calibrate a gas analyzer.

Zero gas
Test gas is used to adjust the zero point of a gas analyzer. It must not contain the component being analyzed (process gas without the component being analyzed, or e.g. nitrogen).

Associated gas
Measuring gas without the component to be analyzed.

3.2 Gas analyzers

3.2.1 Terminology and use

Process analysis
Process analysis, as distinct from laboratory analysis, refers to the usually continuous measuring processes used to determine the physical or chemical properties and concentrations of chemical components in process media on site in a plant.

The most common process analysis applications are those in plants for the chemical and petrochemical industries, power generation, metals and minerals, foodstuffs and luxury foods, paper and pulp, non-metallic minerals, but also in engine construction and research and development, for example. In the case of gaseous process media (i.e. combustion gases, process gases, flue gases, also air), this is referred to as process gas analysis.

Measuring points with the continuous sampling and the measuring instruments (gas analyzers) are distributed throughout the plants (at the boiler, stack, cement kiln, upstream of the electrostatic precipitator, at a distillation tower, etc.) in extremely harsh operating conditions in some cases. From this, the differences to laboratory analysis, where discrete samples are taken from a process and examined centrally in a laboratory under controlled and stable laboratory conditions, are clear.

The measuring results are used
• To control the process by, for example, measuring additives and optimizing processes
• For plant safety, by checking for explosive gas mixtures
• For product quality, by monitoring processes and product specifications, and
• For environmental protection, by monitoring the flue gases for compliance with permissible emission limits for pollutants.

Analyzers

The core element of every analyzer is made up of substance-specific sensors or sensor systems. Their function is based on physical or chemical principles such as absorption, adsorption, transmission, ionization, heat effect or paramagnetic or electrochemical properties. The sensors react to a change in the measurement parameter with a corresponding change in their properties (e.g. increased light absorption or reduced conductivity), from which a measurement signal can be obtained.

In terms of design, a distinction is made between:
• Mobile, lightweight and portable analyzers for short-time measurements at a range of different 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" instruments) and
• Analyzers to which a sample that is extracted from the process stream and prepared is brought for measurement ("extractive" instruments).

Thanks to recent developments, instruments that combine mobility with the suitability for stationary continuous measurements are also available: One example of this is the testo 350 analyzer, which is easily transportable yet also suitable and approved for long-term measurements over several weeks.

Areas of application

Process gas analyzers have mainly three application areas:

1. Optimization of combustion processes in order to reduce operating costs, to protect the plants and to minimize pollutant emissions (combustion optimization)

2. Generating and monitoring a specific gas composition within a production process in order to create and maintain certain product qualities (process control).

3. Monitoring the functions of flue gas cleaning plants and monitoring the flue gases released into the atmosphere for compliance with the legally permissible pollutant concentrations (emission control).

Table 19 provides examples of these three areas of application and their metrological objectives with reference to typical areas of application.

Areas of application and objectives of gas analysis		
1	2	3
Optimizing a combustion system	Monitoring the composition of a defined gas atmosphere	Checking the function of gas cleaning plants and monitoring flue gases to check for gaseous pollutants
Minimizing operating costs and pollutant emissions	Establishing and ensuring defined product quality	Compliance with legal requirements
Combustion optimization	Process control	Emission control
Applications		
Non-metallic minerals/glass	X	X	X
Metal production	X		X
Metal treatment	X	X	X
Heat generation	X		X
Waste disposal	X		X
Research and development	X	X	X
Chemical/petrochemical industry	X		X

Tab. 19: Areas of application and objectives of gas analysis

Sensors

The term sensors generally refers to all kinds of instruments that provide information about a physical or chemical quantity. A sensor consists of the actual sensing element (also called the elemental sensor) and a transmitter. The sensing element must have a feature, e.g. conductivity, that also changes as the variable to be measured, for example a temperature, changes. This "reaction" of the sensor is then transformed by the transmitter (usually an amplifier) into an electrical measuring signal.

The main groups of sensors are:

• Sensors for determining temperature
• Sensors for determining pressure
• Sensors for determining flow rate
• Sensors for determining substance concentrations and properties (analysis technology)

Note: In analysis technology, the term sensor is often used colloquially only for those sensing elements that are particularly small in size, while larger sensors are described as "analyzers".

Some of the sensors commonly used to determine components in gases are shown in Table 20.

Sensor type/measuring principle	Effect measured
Semiconductor sensors	Change in conductivity
Solid-state electrolyte sensors Liquid electrolyte sensors	Interaction between chemical reaction energy and electrical energy
Optical sensors	Change in optical properties
Calorimetric sensors	Reaction heat from interaction with gases
Photometric sensors (instruments)	Absorption of infrared (NDIR) or ultraviolet (UV) radiation, for example
Paramagnetic sensors (instruments)	Paramagnetic properties of oxygen
Chemiluminescence sensors (instruments)	Chemical reaction with formation of luminescence radiation
Flame ionization (FID) (instruments)	Ionization in a flame with current measurement
Biosensors	Bioreactions

Tab. 20: Common sensor types (selection)

Portable devices

The demands placed on portable analyzers in the process industry present a particular challenge for the instrument manufacturer. The usually extremely harsh measuring environment and the level of measuring accuracy and reliability required, set against the instrument's small dimensions and low weight, create a profile of requirements that was impossible to fulfil only a few years ago. The design of the testo 350 and predecessor models have set new standards in this regard, which have been impressively proven by the fact that these instruments have been granted official approvals.

The testo 350 is a portable extractive measuring instrument which, due to its specific features (measuring gas cooler, automatic calibration, etc.), can also be used for stationary installations over a certain period of time. With this, it therefore opens up a new area of application and offers the user an extremely cost-effective solution for lots of tasks. Ideally, electrochemical gas sensors, which are well suited to portable devices in terms of their weight, space requirement and power consumption, are used. However, its functional principle requires a considerable level of expertise in order to ensure the requisite accuracy, reliability, operating life and operability when designing the appropriate sensor environment.

3.2.2 Measuring principles for determining gas concentrations (selection)

A variety of measuring principles are used to determine the concentration of different gases in gas mixtures. Tab. 21 provides an overview with reference to the principles used by Testo.

Electrochemical sensors (potentiometric titration)

The electrochemical sensors suitable for determining oxygen and harmful gas components such as CO, SO_2 or NO_X operate according to the principle of ion-selective potentiometry. The sensors are filled, specifically for their measuring task, with an aque-

Measuring principle	Components being analyzed						
	SO_2	CO	CO_2	NO_X	H_2S	O_2	HC
Conductimetry	•	•					
NDIR	•	•	X	•			•
NDUV	•			•			
Paramagnetic method						•	
Chemiluminescence				•			
Heat effect		•					X
Flame ionization							•
Potentiometric titration	X	X		X	X	X	
Solid-state electrolyte						X	

• suitable measuring principles   X used by Testo   HC hydrocarbons

Tab. 21: Components being measured and appropriate measuring principles for verifying these

ous electrolytic solution. Two or three electrodes, likewise task-specific, are placed in the solution with an electrical field applied to them. On the outside, the sensors are sealed with gas permeable membranes. Please refer to Figures 10 and 11. The specific design and function of the sensors differ depending on the gas component to be measured, as shown in the following two examples.

Example 1: Oxygen sensor (two-electrode sensor)
The flue gas and the oxygen molecules contained therein pass through the gas-permeable membrane to the cathode. Due to its material composition, a chemical reaction takes place in the cathode resulting in the formation of OH^- ions (ions are charged particles). These ions migrate through the liquid electrolyte to the anode, generating a current flow that is proportional to the O_2 concentration. The drop in voltage triggered at a resistor located in the circuit then serves as a measuring signal that is used for further electronic processing.

The built-in resistor with a negative temperature coefficient (NTC) is used to compensate for temperature influences and thus ensures thermally stable sensor performance.
The operating life of an oxygen sensor of this type is about 3 years.

Fresh air

O_2

Cathode

Gas-permeable membrane

Ionic migration

OH^- OH^- O H OH^- OH^- OH^- OH^- OH^- OH^-

Connecting line for cathode

Anode

NTC resistance with negative temperature coefficient

Aqueous electrolyte

$+$ $-$

External circuit
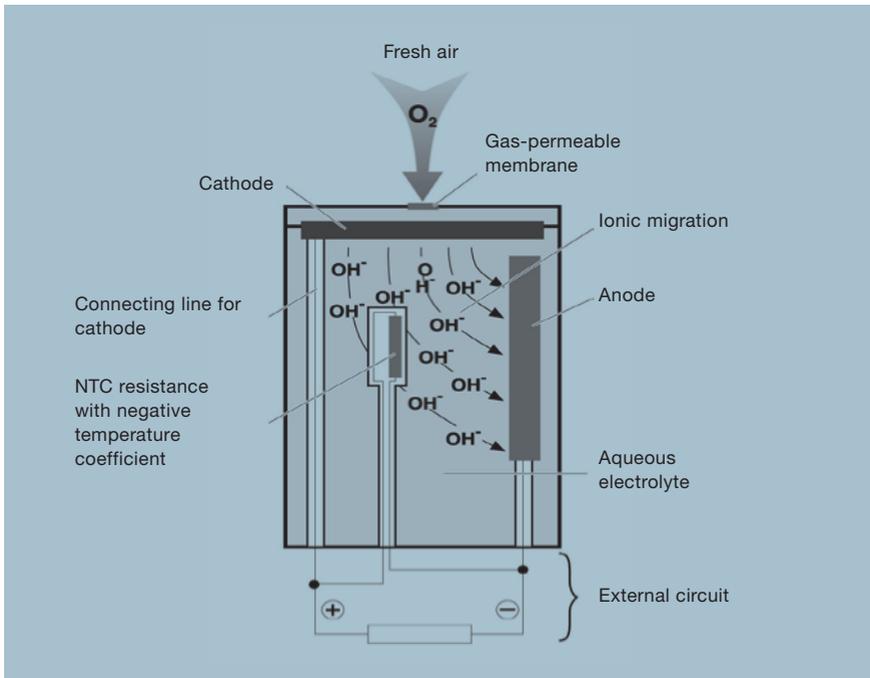
Figure 10: Oxygen sensor (schematic)

Chemical equations of the oxygen sensor:

At the cathode:

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

At the anode:

$2Pb + 4OH^- \longrightarrow 2PbO + 2H_2O + 4e^-$

Overall:

$2Pb + O_2 \longrightarrow 2PbO$

Example 2: Sensors for CO, SO$_2$ and NO$_X$ (three-electrode sensor)
Sensors with three electrodes are used to determine gas components such as CO, SO$_2$ or NO$_X$. The function is explained using a CO sensor; transfer to the other components is evident from the chemical equations.

The carbon monoxide (CO) molecules pass through the gas-permeable membrane to the sensing electrode, where H$^+$ ions are formed as a result of a chemical reaction. In the electrical field, these migrate 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 that is also supplied. The third electrode (reference electrode) is used to stabilize the sensor signal. The operating life of this type of sensor is about 2 years.
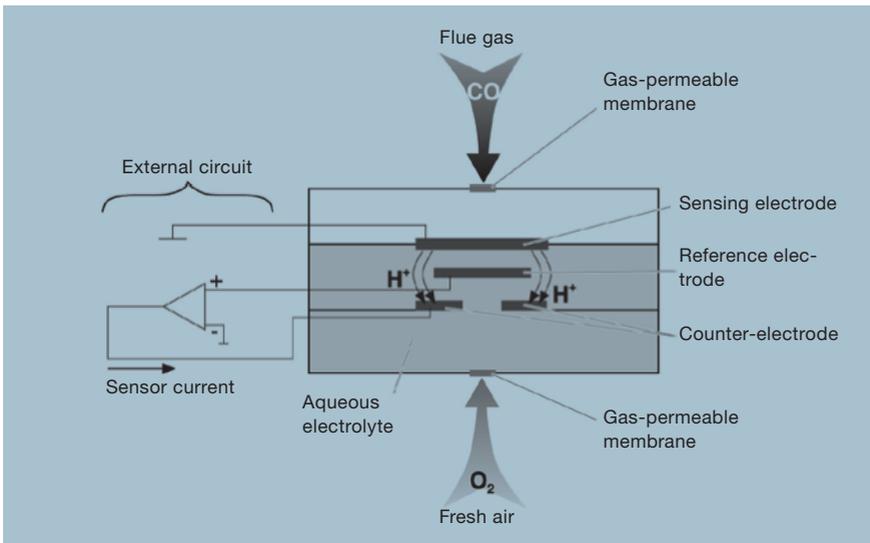
Figure 11: Sensor for CO and other gases (schematic)

Chemical equations for CO
Anode:
$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e^-$$
Cathode:
$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$
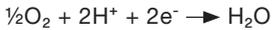
Further chemical equations
$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H^+ + 2e^-$$
$$NO + 2H_2O \longrightarrow HNO_3 + 3H^+ + 3e^-$$
$$NO_2 + 2H^+ + 2e^- \longrightarrow NO + H_2O$$
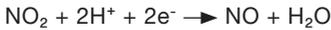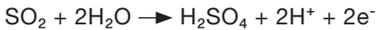
Infrared absorption (IR method)

Infrared radiation is absorbed by gases such as CO, CO_2, SO_2 or NO at a wavelength that is typical for each component (wavelength range several µm). The weakening of a particular infrared radiation range as a volume of gas passes through is therefore a measure of the concentrations of the gas component in the measuring gas that has passed through. There are two methods for selecting only one component:

In the dispersive method, the radiation is spectrally dispersed by prisms or gratings before passing through the volume of gas, and then only radiation with the wavelength that is typical of the component in question to be analyzed is conducted through the volume of gas (measuring chamber). This principle is mainly used in laboratory equipment.

In the non-dispersive methods (NDIR method), the previous spectral dispersion is dispensed with. After modulation, such as by a rotating diaphragm wheel, broadband radiation passes through the measuring chamber. There are then two methods for detecting the level of absorption:

- A detector filled with the component to be analyzed measures the residual radiation remaining after passing through the measuring chamber, where necessary in comparison with unattenuated radiation. The resulting pressure fluctuations (caused by variable heating of the volume of gas due to absorption) are detected via a membrane capacitor or a microflow sensor and converted into an electrical signal.
- Alternatively, however, the radiation passes through the absorption section and is subsequently restricted by an interference filter to the wavelength range required for CO_2, for example, and detected with an IR radiation detector. As the gas concentration increases, more radiation is absorbed and the detector signal is reduced accordingly.
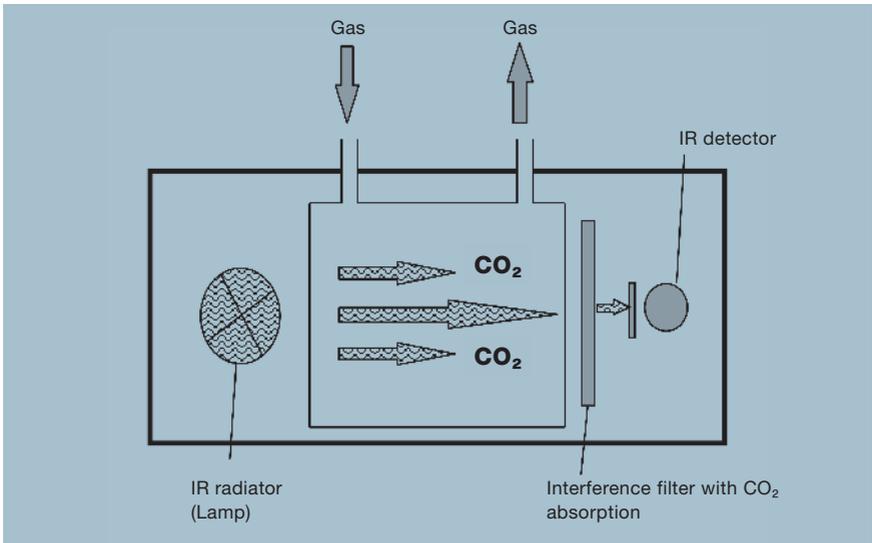
Figure 12: NDIR sensor (compact design) for measuring CO_2

Ultraviolet absorption (UV method)

Ultraviolet radiation is also specifically absorbed by certain gas components, such as SO_2 or NO. The UV method is therefore in competition with the NDIR method, and has the advantage in that there is no cross-sensitivity to water vapour. However, the light sources are more expensive than with the NDIR method. The UV method is therefore only used for particular applications.

Chemiluminescence method (CLD method)

This method, which was specifically developed for the sensitive detection of NO, uses the features of NO to emit characteristic radiation (chemi-luminescence) on reacting with ozone (O_3). The intensity of this radiation is proportional to the NO mass concentration. CLD instruments are customary for the selective detection of low NO concentrations, e.g. in engine exhaust gases. They comprise an ozone generator, an enrichment and reaction chamber and a photomultiplier detector.

Paramagnetic method

Oxygen is the only gas that is strongly paramagnetic, i.e. oxygen molecules are highly attracted by a magnetic field. This effect is used to determine the oxygen concentration. Modern instruments are available primarily in two different designs:

In the case of dumbbell type analyzers, a dumbbell with two nitrogen-filled glass spheres is mounted on a rotating suspension in the measuring chamber, which in turn is placed in an inhomogeneous magnetic field. When oxygen is present in the measurement gas, the O_2 molecules are drawn into the magnetic field, which causes a force to act on the dumbbell. This force is compensated by a spring acting against it, which results in a usable measurement parameter.

Differential pressure analyzers use the effect whereby a pressure difference is generated between two gases with different magnetic characteristics when the interface of both gases is exposed to a magnetic field. This feature is used for determining oxygen in a measurement gas in interaction with an oxygen-free reference gas, e.g. nitrogen. The resulting pressure difference generates a gas flow, which is detected by a flow sensor and converted into a measuring signal.

Thermal conductivity

Thermal conductivity analyzers (standard thermal conductivity detectors) use the different thermal conductivity values of measurement and reference gas. A filament measuring bridge is flushed in sections, both by the measurement gas and also by a reference gas with a thermal conductivity that is appropriate to the measuring task. The different cooling of the filaments results in a detuning of the bridge, which is used as the effect measured.

Heat effect

This measuring principle is based on the combustion heat of the combustibles in the measurement gas. These are catalytically converted on an electrically preheated body (wire or bead) and as they burn they increase the temperature of the body, altering its electrical resistance. This measuring principle will only work if there is sufficient oxygen available in the measurement gas for the combustion.

The change in resistance is a measure of the content of (all!) combustibles in the measurement gas. These are mainly hydrocarbons (abbreviated HC, also referred to as CXHY), but also CO or H_2. Cross-sensitivities therefore exist

between these components, and these must be taken into account when measuring or evaluating the readings.

Example:
The hydrocarbon methane reading is increased by CO, which is present simultaneously in the measurement gas, by 0.27 vol. % per 1 vol. % CO. For hydrogen, there is a corresponding increase of 1.5 Vol% per 1Vol% H_2.

Furthermore, there is cross-sensitivity to water vapour.

Testo's module for detecting hydrocarbons, which is used in some of its instruments, is based on this principle. Figure 13 offers a schematic view of its structure. A current flows through the platinum wire, heating the wire and the catalytic material to a temperature of approx. 500 °C. The combustibles in the measurement gas are burnt at the surface (as long as sufficient oxygen is available), which increases the temperature of the catalyst and platinum wire, and this in turn changes the electrical resistance of the wire and generates a measurement signal on a "Wheatstone bridge circuit".
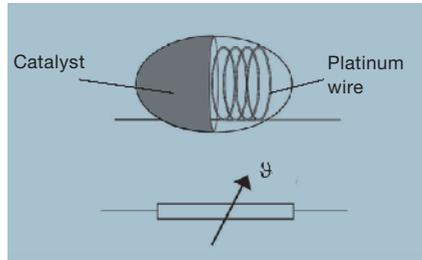
Figure 13: Sensor according to the heat effect principle

Use of the Testo HC module requires special attention due to its cross-sensitivity and possible impairment of its function due to substances contained in the measurement gas, such as H_2S, silicones or sulphurous hydrocarbons. Please refer to the instruction manual for the instrument for the relevant information.

Flame ionization detector (FID)

The organic carbon compounds contained in the measurement gas are introduced into a flame (usually hydrogen/helium), where they are burned and ionized. The ions generated are measured as an ion stream, which as a first approximation is proportional to the organic carbon atoms involved in the process. The varying degrees of sensitivity of the process to different organic compounds is taken into account by applying response factors.

Solid-state electrolyte sensor

A unique but very common oxygen measuring principle in rough operating conditions uses a solid-state electrolyte made of doped zirconium dioxide ceramics, on whose opposing surfaces electron-conductive layers are deposited as electrodes. As a specific property, this solid electrolyte contains oxygen vacancies in its crystal lattice that facilitate conductivity for oxygen ions at high temperatures. The oxygen (O_2) molecules in the process gas to be measured are converted to oxygen ions on contact with the electrode material; at a sufficiently high electrolyte temperature (>500°C), these trigger a current through the electrolyte. If the oxygen concentration is the same on both sides, the effects are eliminated, and at different concentrations a usable electrical signal is generated. If there is a reference gas with a known O_2 concentration on one side, the O_2 content in the measuring gas can be determined from this signal.

Instruments operating according to this principle are known as "zirconium oxide probes" or "oxygen probes". They are generally installed directly in the hot flue gas (in-situ principle) and therefore measure the gas in its original state, i.e. including its humidity! However, since humidity has a diluting effect on the other gas components, the O_2 readings of these probes are generally lower than O_2 readings which, using any method whatsoever, are measured on the same flue gas but at lower gas temperatures, i.e. drier flue gas.

Oxygen readings from zirconium probes are usually lower than those obtained on the same gas using other methods, but both values are correct! The difference is caused by the different degrees of dilution (temperatures) of the gas during measurement; when referencing identical gas temperatures (i.e. equal dilutions), the values will be equal!

Testo uses this effect in some analyzers to determine the level of humidity in the flue gas, as follows:
• Measuring the oxygen in humid flue gas using a ZrO_2 sensor
• Cooling and drying the flue gas in a gas cooler
• Measuring the oxygen in dry flue gas using an electrochemical sensor
The original humidity content of the flue gas can be calculated from the difference between the two readings and the temperature of the cooler.
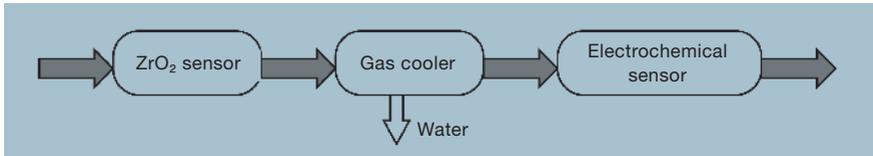
Figure 14: Set-up for humidity measurement in flue gas

4. Application examples

Preliminary comment

- The gas analysis applications described below should be considered as examples. The objective is to demonstrate in concise form the many different processes and methods and the associated gas analysis application options (motives, benefits). The respective plants and methods can only be displayed schematically and mentioned briefly. In reality, deviations from these can be assumed in all cases, in view of the variety of different processes, the plant constructors, the local conditions and the specific concepts of the operating company. The same applies to the indicated measuring point positions.

- Furthermore, components being analyzed with typical concentration ranges are listed, along with certain limit values according to the regulations valid in Germany. These examples, too, are only intended as a guide; they are based on practical experience of using Testo gas analyzers, although it is often the case that not all possible components have been measured. As a result, the reading and measuring range information is incomplete in some illustrations, and in a few cases this was completely dispensed with.

- In practical applications, the actual situation should always be referred to.

4.1 Power generation

4.1.1 Solid-fuel firing systems

Solid-fuel firing systems are facilities for generating heat by burning solid fuels such as hard coal, lignite, wood, etc. Usually the fuels are broken down substantially, coal is even ground into pulverized coal and fed into the combustion chamber, where it is burnt either in a fixed bed, a fluidized bed or an entrained dust cloud. The combustion air is supplied by powerful fans, sometimes already mixed with pulverized coal. In terms of pollutant concentration, the flue gases must comply with the regulations of TI Air, and plants with a thermal output of more than 50 MW must comply with the regulations of the 13th German Federal Immission Control Ordinance (BImSchV).

Use of gas analysis, e.g. for
• Optimum adjustment of the plant
• Drawing up the energy balance
• Monitoring compliance with limit values in the flue gas

**Process flow chart and measuring points**
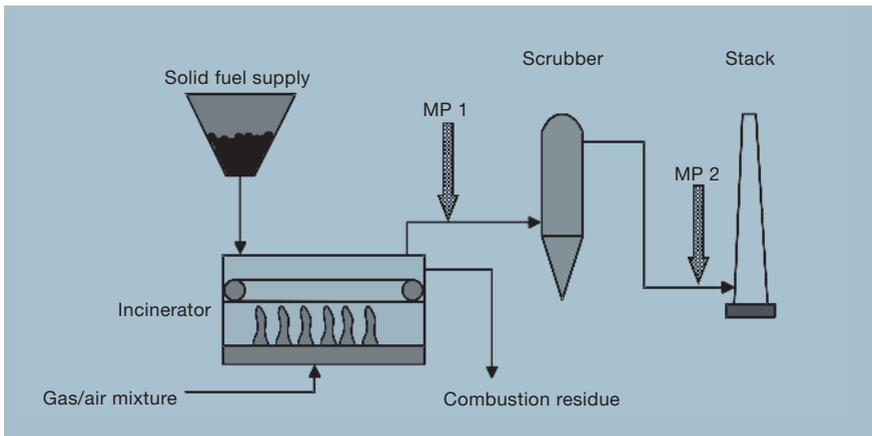
Figure 15: Process flow chart for a solid fuel combustion system with measuring points

Measuring points and measuring tasks

- MP 1 at the boiler outlet for optimum burner adjustment (fuel savings, economic efficiency), identification of CO pockets, operational reliability
- MP 2 in the clean gas at the stack for monitoring compliance with limit values

Measurement parameter	Typical values	Limit values
	MP 1	MP 2
CO	150 to 170 mg/m³	
NO		
NO_2		
NO_X (as NO_2)	650 to 750 mg/m³	Limit values in accordance with national regulations
SO_2	25 to 35 mg/m³	
O_2	7%	
Gas temperature	250 °C	

Tab. 22: Typical values and limit values for a solid fuel combustion system

Information relating to this application:

1. High concentrations of soot may be present in the flue gas
2. In the case of complete combustion, there are considerable fluctuations in CO concentrations
3. Depending on the fuel, the SO_2 content can vary considerably, and HCl and HF may also be present

4.1.2 Gas-fired installations

Gas-fired installations are facilities for generating heat by burning gaseous fuels such as natural gas, industrial gas, blast furnace gas, etc. They facilitate combustion that is largely free of pollutants and residues. In small-scale plants, the fuel and air is supplied by gas blowers, and in larger plants by high-pressure burners. In terms of their pollutant concentration, the flue gases must comply with the regulations of TI Air, and where applicable to those of the 13th German Federal Immission Control Ordinance (BImSchV).

Use of gas analysis, e.g. for
• Optimum adjustment of the plant
• Drawing up the energy balance
• Monitoring compliance with limit
  values in the flue gas

Process flow chart and measuring points
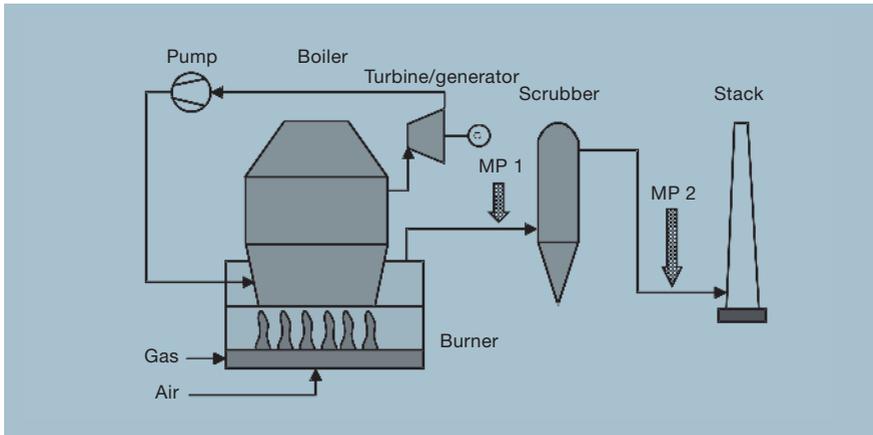
Figure 16: Process flow chart for a gas combustion system with measuring points

Measuring points and measuring tasks

- MP 1 at the boiler outlet for optimum
  burner adjustment
- MP 2 at the stack for monitoring
  compliance with limit values

	Typical values	Limit values
Measurement parameter	MP 1	MP 2
CO	0 to 5 ppm	Limit values in accordance with national regulations
CO_2	9 to 11% (guide parameter)	
NO	30 to 50 ppm	
NO_2	0 to 2 ppm	
NO_X		
SO_2	5 mg/m3 (LPG) 1700 mg/m3 (associated gas)	
O_2	2 to 3%	
Gas temperature	180 °C	

Tab. 23: Typical values and limit values for a gas combustion system

4.1.3 Gas turbine plants

Stationary gas turbines have their origins in the development of aircraft engines and are mainly used to drive generators or machinery. They are used primarily to generate peak-load power, often in conjunction with a downstream waste heat boiler to generate thermal heat. The flue gases correspond to those of gas or oil-fired installations and, in terms of pollutant limit values, must comply with the regulations of TI Air. NOX emissions are subject to the dynamic sampling clause, which proposes low NOX combustion for gas turbines and the injection of water into the combustion chamber. Besides natural gas, landfill gas, mine gas or biogas are also used as fuel.

Use of gas analysis, e.g. for
• Monitoring turbine emissions
• Monitoring compliance with limit values in the flue gas

Process flow chart and measuring points

Burner   Turbine/generator   Waste heat boiler   Stack

MP 2

G

MP 1
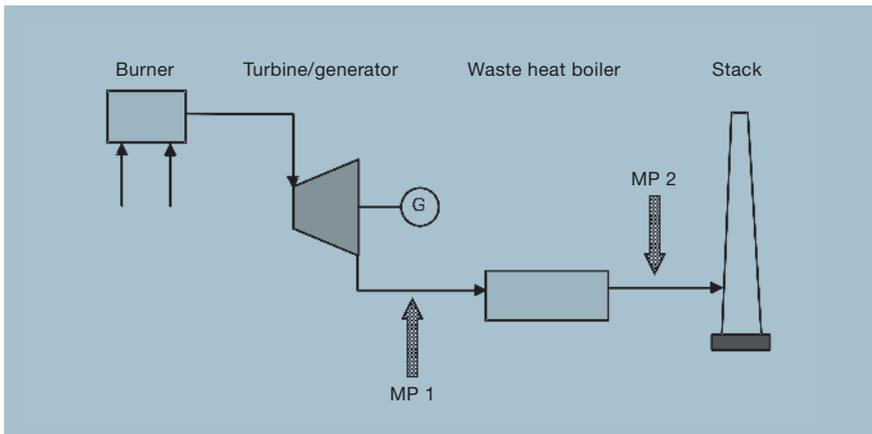
Figure 17: Process flow chart for a gas turbine plant with measuring points

Measuring points and measuring tasks

- MP 1 downstream of the turbine for
  determining the turbine emissions
- MP 2 downstream of the waste heat
  boiler for monitoring compliance with
  limit values.

Measurement parameter	Typical values	Limit values
	MP 1	MP 2
O_2	15 to 18%	Limit values in accordance with national regulations
NO_X	25 to 60 ppm	
CO	0 to 30 ppm	
Gas temperature	300... 400 °C	

Tab. 24: Typical values and limit values for a gas turbine plant

Information relating to this application:

1. There is a dynamic vacuum at the
   MP 1 sampling point. It is therefore
   crucial that the sampling point is
   sealed, otherwise ambient air will be
   sucked in and affect the measure-
   ments.

4.1.4 Oil-fired installations

Oil-fired installations are facilities for generating heat by burning oils of varying quality. Here, fuel and combustion air are brought into the combustion chamber in the form of a fine mist via the burner. Oils burn with almost no residues, and the amount of flue dust is also small. In terms of pollutant concentration, the flue gases must comply with the regulations of TI Air, and plants with a thermal output of more than 100 MW must comply with the regulations of the 13th German Federal Immission Control Ordinance (BImSchV).

Use of gas analysis, e.g. for
• Optimum adjustment of the plant
• Drawing up the energy balance
• Monitoring compliance with limit values in the flue gas

Process flow chart and measuring points
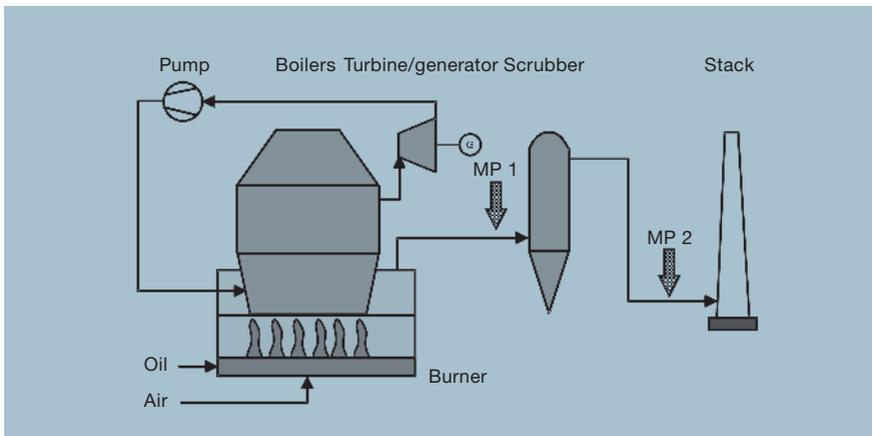
Figure 18: Process flow chart for an oil-fired installation with measuring points

Measuring points and measuring tasks

• MP 1 at the boiler outlet for optimum burner adjustment (fuel savings, economic efficiency), plant balance

• MP 2 in the clean gas at the stack for monitoring compliance with limit values

Measurement parameter	Typical values	Limit values
	MP 1	MP 2
O_2	2.5 to 3.5%	Limit values in accordance with national regulations
CO	0 to 5 ppm	
CO_2	13 to 15%	
NO	50 to 150 ppm	
NO_2	0 to 5 ppm	
NO_X (as NO_2)		
SO_2	50 to 100 ppm	
Gas temperature	200 °C	

Tab. 25: Typical values and limit values for an oil-fired installation

4.1.5 Coal-fired power plant

Coal-fired power plants are thermal power plants in which coal (the primary energy) is used to generate electricity (the secondary energy). Both lignite and hard coal are used as fuel.

The coal is coarsely crushed, dried and finely ground in a coal mill. Together with the air pre-heated in the air pre-heater, it is then blown into the combustion chamber of the boiler in the form of a dust/air mixture and burnt at a temperature of approx. 1000 °C. The steam generator surrounds the combustion chamber and comprises a pipe system with boiler feed water flowing through it. The water is heated until it becomes live steam at a pressure of approx. 200 bar, and in this form it drives the turbine. The flue gases escape upwards, pass through the various gas scrubbers and are discharged via the stack. The steam, which has expanded and cooled down after passing through the turbine, is once again liquefied in the condenser via further cooling and returned to the circuit in the form of water.

In Germany, in terms of their permissible concentration of pollutants, the flue gases from coal-fired power plants must comply with the regulations of TI Air or, as in most instances, plants with a thermal output of >50 MW must comply with the regulations of the 13th German Federal Immission Control Ordinance (BImSchV).

Use of gas analysis, e.g. for
• Optimum adjustment of the combustion system (fuel and emission limitation)
• Monitoring the function of flue gas cleaning plants
• Monitoring compliance with emission limit values
• Safety of personnel and plants (risk of fire and explosion)

Process flow chart and measuring points
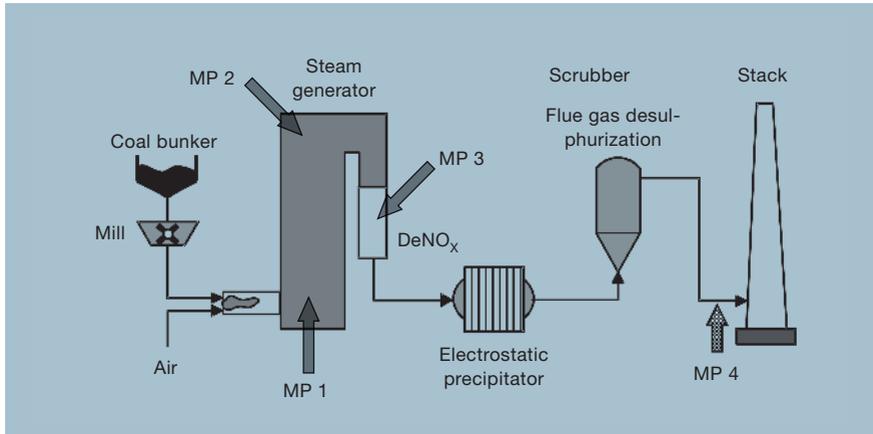
Figure 19: Process flow chart for a coal-fired power plant with measuring points

Measuring points and measuring tasks

- MP 1 in the boiler for monitoring consistent combustion and the air ratio, identification of CO pockets and checking operational reliability
- MP 2 at the boiler outlet for monitoring the combustion process (economic efficiency)
- MP 3 at the denitrification plant for checking the function of the denitrification plant
- MP 4 at the stack for checking compliance with emission limit values

Measurement pa-rameter	Typical values			Limit values
	MP 1	MP 2	MP 3	MP 4
O_2	5 to 9%	5 to 9%		Limit values in accordance with national regulations
CO	10 to 5000 ppm	10 to 5000 ppm		
CO_2		15 to 18%		
NO_X		500 to 600 ppm		
SO_2		500 to 2000 ppm		
Dust		2 to 20 g/m³		
Flue gas temperature	approx. 1000 °C	approx. 1000 °C		
Humidity		10 to 15%		

Tab. 26: Typical values and limit values in a coal-fired power plant

Information relating to this application:

For measurements downstream of the electrostatic precipitator, the probe must be grounded.

4.1.6 Cogeneration plants

Cogeneration plants (CHP) are relatively small, modular energy plants that can be used in the immediate vicinity of a consumer to produce electricity and heat simultaneously. Generators driven by combustion engines or gas turbines are used to generate electricity, while heat is generated by using the waste heat from the prime movers (coolant and/or flue gas heat). This is also referred to as power generation via combined heat and power. In addition to diesel oil, gas (natural gas, landfill gas) is the preferred fuel. The power output of CHP plants ranges from 15 KW to around 30 MW. The flue gases of the prime movers (diesel engines, gasoline engines, gas turbines) must comply with the respective provisions of TI Air, which requires the use of catalysts.

Use of gas analysis, e.g. for
• Optimum prime mover adjustment
• Checking the function of the catalyst
• Monitoring compliance with emission limit values

Process flow chart and measuring points
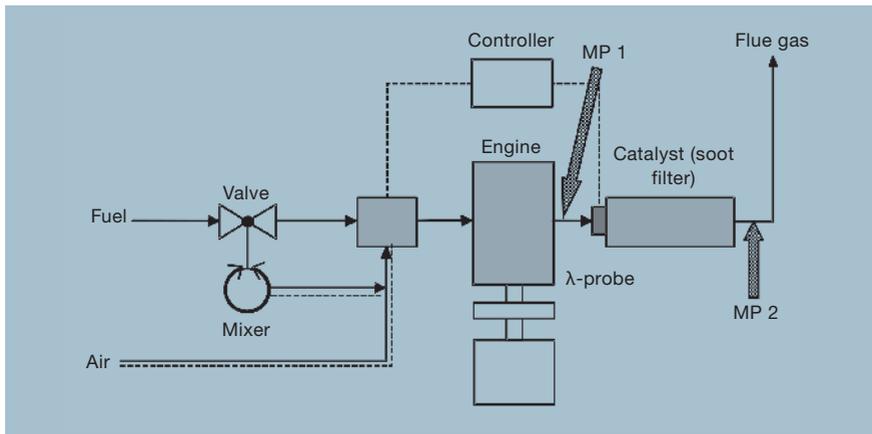
Figure 20: Process flow chart for a cogeneration plant

Measuring points and measuring tasks

• MP 1 upstream of the catalyst for efficiency checking and engine adjustment

• MP 2 downstream of the catalyst for efficiency checking, engine adjustment and compliance with the legal requirements

Measurement parameter	MP 1		
	Typical values for different fuels		
	Natural gas	Landfill gas	Oil
O_2	8%	5 to 6%	8 to 10%
NO	100 to 300 ppm	100 to 500 ppm	800 to 1000 ppm
NO_2	30 to 60 ppm	90 to 110 ppm	10 to 20ppm
CO	20 to 40 ppm	350 to 450 ppm	450 to 550 ppm
CO_2	10%	13%	7 to 8%
SO_2		30 ppm	30 to 50 ppm

Tab. 27: Typical readings in a cogeneration plant (measuring point 1)

Measurement parameter	Type of engine	MP 2 Limit values
CO	Natural gas	Limit values in accordance with national regulations
$NO+NO_2$	Compression ignition <3 MW	
$NO+NO_2$	Compression ignition >3 MW	
$NO+NO_2$	Other 4-stroke	
$NO+NO_2$	Other 2-stroke	
O_2	Reference value	
SO_2	According to DIN 51603	

Tab. 28: Limit values for cogeneration plant flue gases for different engines (measuring point 2)

Information relating to this application:

1. The use of λ-controlled engines may result in extreme H_2 values, with a risk of damaging the CO measuring cell.

4.1.7 Combined cycle power plant (gas and steam power plant)

In combined cycle power plants, fossil fuels are burned to generate electricity via the optimum combination of a gas turbine and a steam turbine process with high efficiency and relatively low emissions. There are several possible combinations; usually, a gas turbine is operated primarily with natural gas or heating oil. The hot flue gases generate high-pressure water vapour

for driving a steam turbine. In other scenarios, hot flue gases from a pressure-loaded coal firing plant drive a downstream gas turbine.

The flue gases of combined cycle power plants must comply with the respective provisions of TI Air.

Use of gas analysis, e.g. for
• Optimum burner adjustment
• Monitoring compliance with emission limit values

Process flow chart and measuring points
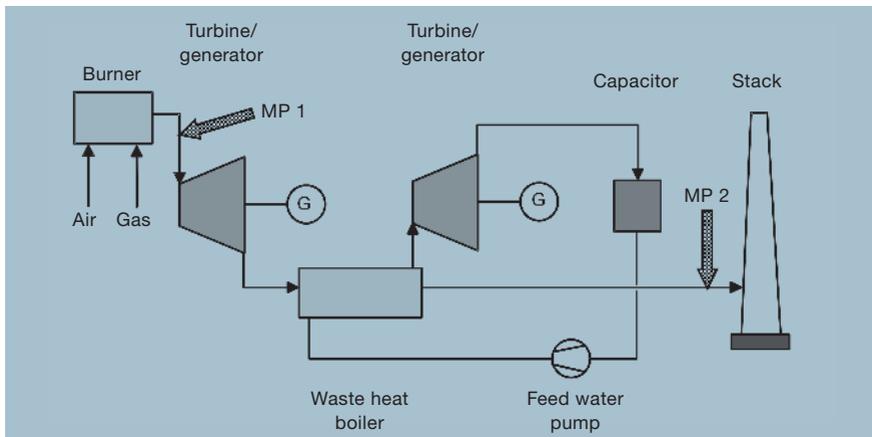
Figure 21: Process flow chart for a combined cycle power plant with measuring points

Measuring points and measuring tasks
• MP 1 at the burner outlet to optimize combustion

• MP 2 in the clean gas at the stack for monitoring compliance with the legal requirements

4.2 Waste disposal

4.2.1 Waste incineration

Nowadays, solid, liquid and paste-like waste materials such as household, hazardous and industrial waste, sludges, used tyres, etc. are disposed of predominantly via thermal treatment (pyrolysis, incineration) using the energy released, rather than landfilling. In pyrolysis plants (see 4.2.2), the waste materials are largely decomposed without oxygen, generating pyrolysis gas for further use. More common are waste incineration plants where the waste is incinerated in rotary kilns, muffle furnaces or fluidized-bed furnaces at temperatures up to 1200°C. The resulting flue gases are cleaned in various stages before being discharged into the atmosphere. In Germany, their permissible level of pollutants is regulated by the 17th German Federal Immission Control Ordinance (BImSchV).

Use of gas analysis, e.g. for
- Controlled waste supply (reduced filter load and emission levels)
- Keeping the gross calorific value constant
- Monitoring the function of the cleaning stages
- Compliance with emission limit values

Process flow chart and measuring points
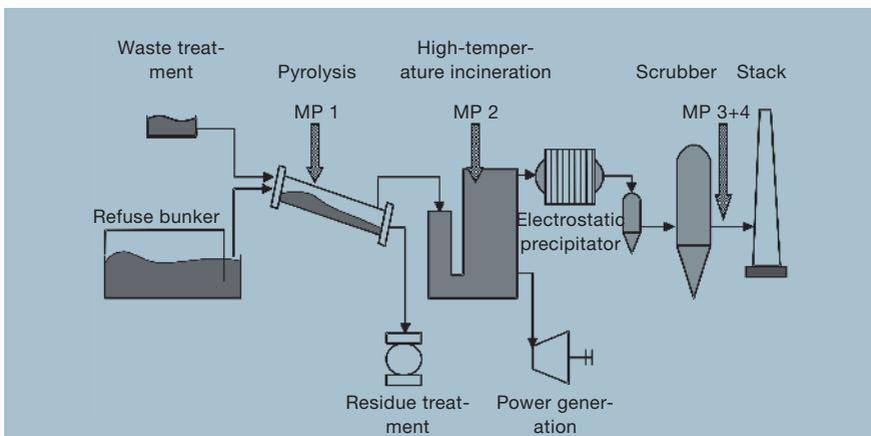
Figure 22: Process flow chart for a waste incineration plant with measuring points

Measuring points and measuring tasks

- MP 1 and MP 2 on the furnace or boiler for optimized waste supply (less strain on the filters and lower emission levels) and for controlling a constant gross calorific value.

- MP 3 downstream of the flue gas cleaning processes to check their efficiency

- MP 4 at the stack to monitor limit value compliance and as backup in the event of the stationary measuring technology failing

Measurement parameter	Typical values		Limit values
	MP 1 and 2 in the crude gas	MP 3 and 4 in the clean gas	
O_2	8 to 11%	7 to 9%	Limit values in accordance with national regulations
NO	150 to 200 ppm		
NO_X	10 to 40 ppm	50 to 70 mg/m³	
CO	15 to 25 ppm	11 to 17 mg/m³	
CO_2	10 to 12%		
SO_2	40 to 60 ppm	5 to 11 mg/m³	
HCl	… 500 ppm		
HF	… 30 ppm		
Dust	2 … 3 g/m³		
Gas temperature	300 °C		

Tab. 29: Typical values and limit values for a waste incineration plant

Information relating to this application:

1. The crude gas (upstream of the cleaning processes) usually contains aggressive associated components such as HCl, HF and HCN. A heated sampling system must be used for this. Furthermore, the cross-sensitivity of the SO_2 sensor to Cl_2 (80%) and HCl (15%) must be taken into account.

2. The fuel (waste) composition will often vary depending on delivery. This can also result in major fluctuations in the readings.

3. For measurements downstream of the electrostatic precipitator, the probe must be grounded.

4. For plants in which waste is only a portion of the fuel supplied, the limit values of the 17th BImSchV must only be applied to the corresponding portion of the entire amount of fuel! In relation to the total flue gas quantity, this results in considerably lower limit values, which must be complied with and verified via measurement.

4.2.2 Waste pyrolysis

Waste pyrolysis is a process that decomposes organic substances (contained in waste), largely in the absence of oxygen. The most suitable input substances are plastics, used tyres, rubber, but also household waste. Pyrolysis gas and pyrolysis coke are generated as reaction products, both of which can be reused for energy. The advantages of this process compared to waste incineration are much smaller volumes of flue gas (no combustion air!) and associated smaller plant dimensions. However, problems have recently arisen in the operation of such plants.

Waste pyrolysis plants must comply with the limit values specified in TI Air, which are comparable to those of the 17th BImSchV; however, the oxygen reference value has been reduced to 3%.

Use of gas analysis, e.g. for
• Monitoring the function of the cleaning stages
• Compliance with emission limit values

Process flow chart and measuring points
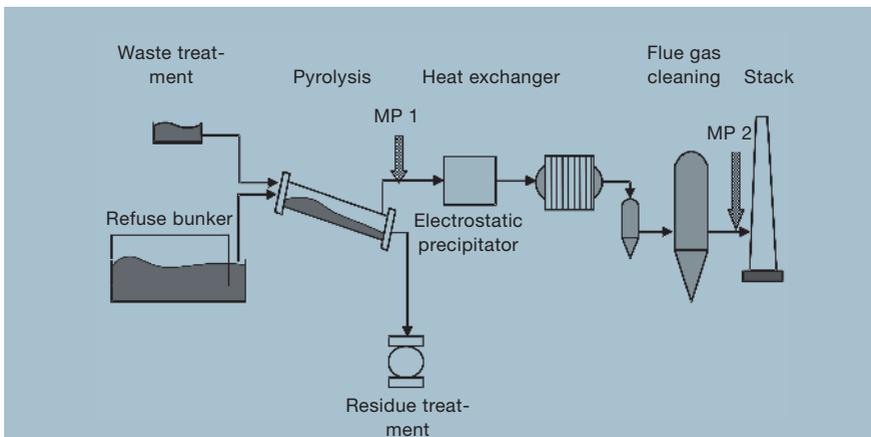
Figure 23: Process flow chart for a waste pyrolysis installation with measuring points

Measuring points and measuring tasks

- MP 1 in the flue gas of the pyrolysis furnace to monitor optimum waste supply and the pyrolysis process
- MP 2 at the stack to monitor compliance with limit values in accordance with national regulations

4.2.3 Thermal afterburning

During thermal afterburning, also known as thermal flue gas cleaning, the flammable air pollutants contained in the flue gas are burned with atmospheric oxygen at temperatures between 700 and 900 °C. This generates CO and water, however depending on the pollutants, also SO_2, HCl and others. Thermal afterburning is not to be confused with flame combustion, which works at 1300 °C and catalytic combustion, which is operated at 250-500 °C.

Thermal afterburning furnaces generally require a large amount of energy (supplementary furnaces) and are therefore only used where other processes do not offer sufficient efficiency or where particular constituents need to be destroyed.

In most plants, emissions are restricted by the regulations of TI Air.

Use of gas analysis, e.g. for
• Monitoring the crude gas
• Optimization of combustion
• Compliance with limit values

Process flow chart and measuring points
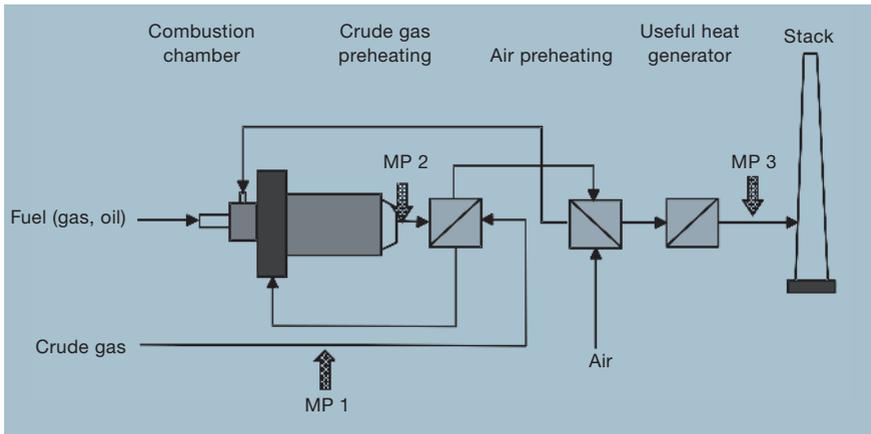
Figure 24: Process flow chart for a thermal afterburning plant with measuring points

Measuring points and measuring tasks

- MP1 for monitoring the inflowing crude gas
- MP 2 to optimize combustion
- MP 3 for monitoring compliance with limit values

Measurement parameter	Typical values
O_2	
NO_X	10 to 100 mg/m³
CO	10 to 100 mg/m³
CO_2	
SO_2	
C_{total}	5 to 20 mg/m³

Tab. 30: Typical values for a thermal afterburning plant

4.3 Non-metallic minerals industry

4.3.1 Cement production

The material known as cement consists of ground cement clinker mixed with gypsum. It is the end product of a firing process in a cement kiln. The raw materials used are limestone ($CaCO_3$) and additives such as clay, ash or sand. The fuels used are coal dust, oil and also waste material such as waste oil and used tyres. The essential process steps and plant components are:

Grinding of the raw materials, drying of the ground material (this generates what is known as raw meal), heating of the raw meal and removal of CO_2 (calciner), firing in a rotary kiln, cooling, mixing with gypsum and grinding. The flue gases pass through an evaporative cooler and requisite cleaning stages, primarily an electrostatic precipitator, before they are released into the atmosphere.

Use of gas analysis, e.g. for
• Optimizing the evaporative cooler operation
• Determining the efficiency of the electrostatic precipitator
• Monitoring the probe position of the stationary analyzer
• Compliance with emission limit values

Process flow chart and measuring points
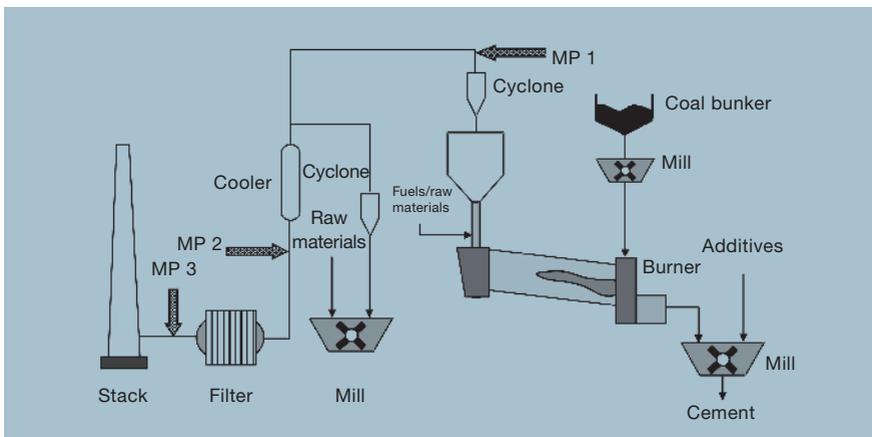
Figure 25: Process flow chart for cement production with measuring points

Measuring points and measuring tasks

- MP 1 between calciner and evaporative cooler to draw up a plant balance
- MP 2 upstream of the electrostatic precipitator to draw up a plant balance and to record efficiency
- MP 3 in the clean gas at the stack to monitor compliance with emission limit values

Measurement parameter	MP 1 in the crude gas		MP 3 and 4 in the clean gas		Limit values
	Typical values	Measuring range (MR extension)	Typical values	Measuring range (MR extension)	
O_2	Up to 10%	0 to 21%	Like crude gas		Limit values in accordance with national regulations
CO	100 to 10000 ppm	0 to 10000 ppm (0.1 to 20%)	Like crude gas		
CO_2	Approx. 20 to 40%	0 to 25% (0.1 to 100%)	Like crude gas		
SO_2			low	0 to 5000 ppm	
NO_X			200 to 700 ppm	0 to 5000 ppm	
Dust	Up to 100 g/m^3	Up to 100 mg/m^3			
Temperature	300 to 400 °C		100 to 150 °C		

Tab. 31: Typical values and limit values for cement production

Information relating to this application

1. Very high dust load in the crude gas and sometimes in the ambient air
2. Very high CO_2 concentrations, partially outside the measuring range.
3. At high O_2 concentrations, the O_2 sensor is cross-sensitive to high CO_2 concentrations!
4. Flow measurement is not possible with high dust loads and high gas velocities
5. The probe must be grounded when mounted at a stack built of bricks!
6. Depending on the fuel, limit values for lead (as dust) as well as for thallium and cadmium also need to be complied with.

4.3.2 Production of ceramics/ porcelain

The term ceramic describes products made of clay and additives, solidified by firing (not by air drying). The raw materials are kaolin (i.e. a clay of a certain composition), quartz (SiO_2) and feldspar (rock made up of different silicates). These materials are processed via mills, slurry and filter plants as well as sieves and mixers, they then go through the shaping process and are subsequently fired in several steps. A distinction is made between pre-firing at approx. 900 °C for solidifi-

cation and subsequent firing at approx. 1400 °C for complete sintering (glazing). The colours are applied either during the sintering phase or in a third firing stage. The firing temperature and composition of the gas atmosphere during the firing process are crucial to the quality (solidity and appearance) of the final product. Before being released into the atmosphere, the furnace flue gases go through several cleaning processes, sometimes these include recycling powdered material to the process. The flue gas composition must comply with the regulations of TI Air.

Process flow chart and measuring points
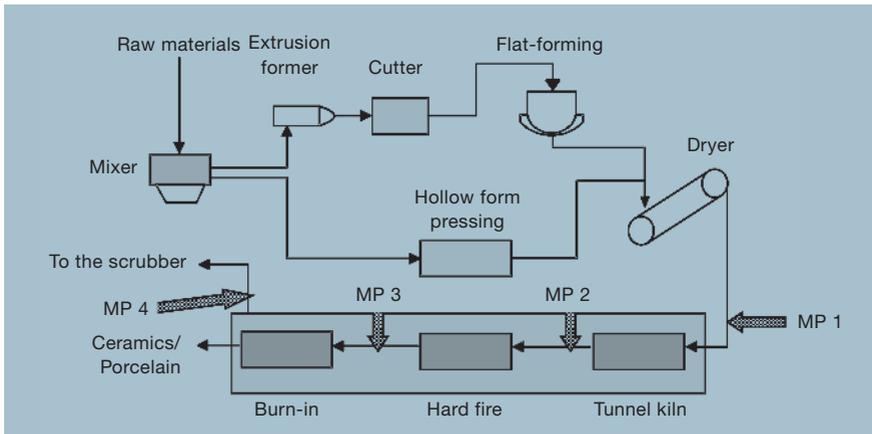
Figure 26: Process flow chart for ceramics/porcelain production with measuring points

Use of gas analysis in ceramic production, e.g. for
- Optimum burner adjustment
- Ensuring product quality (gas composition)
- Monitoring the process sequence (degree of drying)
- Monitoring compliance with emission limit values

Measuring points and measuring tasks
- MP 1-3 in the crude gas at the combustion stations for optimum burner adjustment, high and constant product quality (appearance) and for determining the degree of drying
- MP 2 in the clean gas for monitoring the function of the cleaning stages and for monitoring compliance with the limit values.

Measurement parameter	Typical values		Limit values
	MP 1-3 in the crude gas	MP 4 in the clean gas	
O2	13 to 16%	13 to 16%	
NOx	30 to 40 ppm	30 to 40 ppm	
NO			
NO2			Limit values in accordance with national regulations
CO	40 to 60 ppm	40 to 60 ppm	
CO2			
SO2	700 to 1300 ppm	450 to 900 ppm	
Humidity	10 to 14%	10 to 14%	

Tab. 32: Typical values and limit values for ceramics production

Information relating to this application: Aggressive components (HF, HCl) may be present in the flue gas! We therefore recommend using a heated gas sampling system.

4.3.3 Brick production

Brick is a generic term for building materials made of fired clay, which are usually manufactured in brickworks, directly at the raw material deposit site. The raw materials are prepared by mixing, crushing and adjusting the moisture content, they then go through the moulding process and a drying process before they are finally put on wagons and fired, usually in continuous tunnel kilns at 900 °C to 1300 °C (sintering).

The flue gases mainly contain dust, but also sulphur and nitrogen oxides and possibly HF.

Use of gas analysis in brick production, e.g. for
- Optimum burner adjustment (energy savings)
- Ensuring product quality
- Determining the degree of drying
- Monitoring compliance with limit values

Process flow chart and measuring points
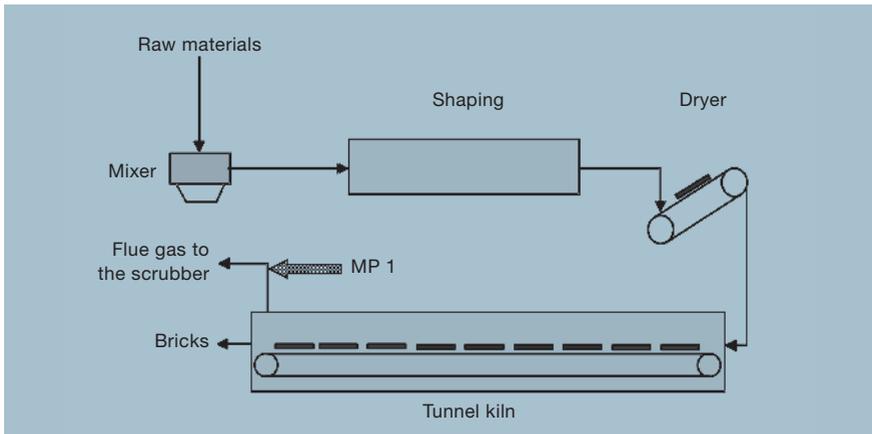
Figure 27: Process flow chart for brick production with measuring point

Measuring points and measuring tasks

- MP 1 at the tunnel kiln for optimum burner adjustment, high and constant product quality (appearance) and for determining the degree of drying
- MP 2 in the clean gas (not shown in the picture!) for monitoring the function of the cleaning stages and for monitoring compliance with the limit values.

4.3.4 Glass production

Glass production includes a wide variety of different products, with the main emphasis on hollow glassware (for containers and all kinds of consumer goods) and flat glass, which is mostly refined into higher quality products.

The raw materials vary considerably depending on the product; in general, sand, soda and limestone are important, with specific substances (e.g. metal oxides) subsequently added to them. Recycled glass is also widely used. The raw materials are crushed, mixed and fed into the melting furnace as a conglomerate. A distinction is made between pot furnaces for discontinuous operation and tank or

tunnel furnaces for continuous operation, with melting temperatures usually at 1500°C or above. Furnace and firing details vary depending on the application. Natural gas, heating oil and electricity are used as energy sources. Additives such as nitric acid are used to homogenize the melt.

The flue gases mainly contain dust, sulphur oxides, nitrogen oxides (resulting from the high temperatures) as well as fluorine and sulphur compounds from the raw materials or waste glass. They have to go through various cleaning processes before being released into the atmosphere, and their composition must comply with the regulations of TI Air.

Process flow chart and measuring points
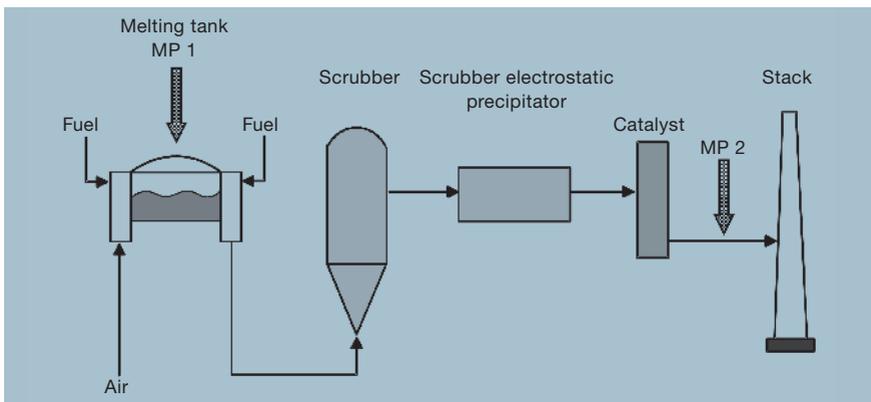
Figure 28: Process flow chart for glass production plant with measuring points

Use of gas analysis in glass production, e.g. for
- Optimum burner adjustment (energy savings)
- Ensuring product quality
- Increasing plant service life
- Monitoring compliance with limit values

Measuring points and measuring tasks
- MP 1 at the melting furnace for increased service life, high and constant product quality, reduced energy consumption, controlling the addition of sulphate.
- MP 2 in the clean gas downstream of the filters for monitoring the function of the cleaning stages and for monitoring compliance with the limit values.

	Typical values	Limit values
Measurement parameter	MP 1 on the tunnel kiln	MP 2 downstream of the filters
O_2	0 to 9%	
NO_X	30 to 40 ppm	
NO	800 to 3000 ppm	
NO_2	0 to 100 ppm	
CO	0 to 1000 ppm	
CO_2	35 to 45%	Limit values in accordance with national regulations
SO_2	0 to 5000 ppm	
Chlorine compounds		
Fluorine compounds		
Dust		
Gas temperature	1400 to 1600 °C	

Tab. 33: Typical values and limit values for glass production

4. Application examples

Practical information relating to this application:

1. The flue gas may be very humid, resulting in abrupt evaporation in the sampling probe. It is therefore essential to use a heated gas sampling system!

2. The CO_2 concentrations are very high and therefore outside of the measuring range.

3. The oxygen content in the vicinity of the plant may drop below 21%. The fresh-air hose should therefore be routed to the outside.

4. The temperature in the vicinity of the plant may rise up to 70 °C. Therefore it is essential to use a heated sampling hose.

5. The dust content in the crude gas is usually very fine-grained and can reach 400 mg/m^3

4.3.5 Lime production

The term "lime" itself is not specific, it is used to describe various substances. Here, what is referred to is burnt lime (CaO), which is produced by burning calcite (calcspar, $CaCO_3$) at 700-900 °C. Different types of continuously operating furnaces (shaft kilns, annular shaft kilns, rotary kilns) are used for lime burning. These differ in terms of how calcite and fuel (coke and gas) are fed in and in terms of the design of the combustion chambers. Burnt lime is used, for example, as an additive in the iron and steel industry, in the chemical industry, in the paper and building materials industry and notably in the field of environmental protection for flue gas cleaning (flue gas desulphurization).

Before being released into the atmosphere, the furnace flue gases go through several cleaning processes, including a scrubber. Their composition must comply with the regulations of TI Air.

Use of gas analysis in lime production, e.g. for
• Process optimization via flue gas analysis (coke savings in the case of shaft kilns, natural gas savings in the case of annular kilns)
• Monitoring for process-related high CO values
• Monitoring compliance with emission limit values

Process flow chart and measuring points
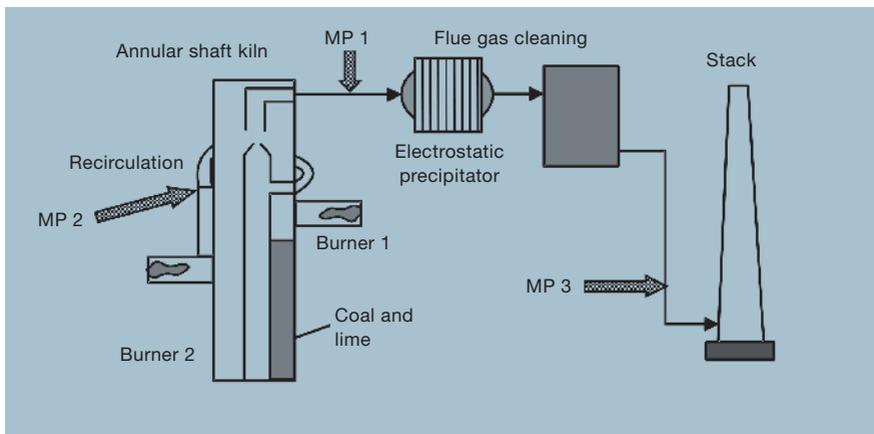
Figure 29: Process flow chart for lime production with measuring points

Measuring points and measuring tasks

- MP 1 in the crude gas for efficiency checking (cost reduction, coke costs) and environmental protection (high CO concentrations)

- MP 2 in the crude gas in the recirculation for determining the plant balance
- MP 3 in the clean gas for monitoring the cleaning stages and compliance with the limit values

Measurement parameter	Typical values		Limit values
	MP 1 and 2 upstream of the scrubber		MP 3 at the stack
Furnace type	Shaft kiln	Annular shaft kiln	
Fuel	Various cokes	Natural gas	
O_2 dry	5 to 6%	5.5 to 6%	
O_2 wet	2 to 3%	5 to 5.5	
CO	6 to 7%	1.5 to 2%	Limit values in accordance with national regulations
CO_2	28 to 32%	24 to 26%	
SO_2	300 ppm	100 ppm	
NO_X	200 ppm	200 ppm	
HF			
Humidity	5 to 8%	5 to 8%	
Dust			

Tab. 34: Measuring ranges and limit values for lime production

Practical information relating to this application:

1. Look out for high dust loading in the ambient air
2. High radiant temperatures may exist, which may require the equipment to be shielded.

4.4 Metal/ore industry

4.4.1 Processing of ores (sintering)

Metals are extracted from their respective metal ores via reduction processes. Prior to this, these ores need to be processed, and a method frequently used for this is sintering or the production of pellets (agglomerates of sintered ore). The raw materials (ores) are first ground and mixed with additives and then formed into pellets. These then pass through a grate furnace with temperatures above 1000 °C, where they agglomerate to form solid pieces via surface melting. In this form, the ore is then suitable for further process-ing, e.g. in a blast furnace to product iron. During the sintering process, particulate and gaseous emissions are generated. The dust may also contain substances such as zinc, lead or cadmium. Gaseous emissions can include SO_2 and NO_X in particular, but also fluorine and chlorine compounds.

In terms of the limit values for pollutants, sintering plants must comply with the regulations in TI Air

Use of gas analyzers, e.g. for
• Optimum operational management (energy costs)
• Monitoring compliance with limit values

Process flow chart and measuring points
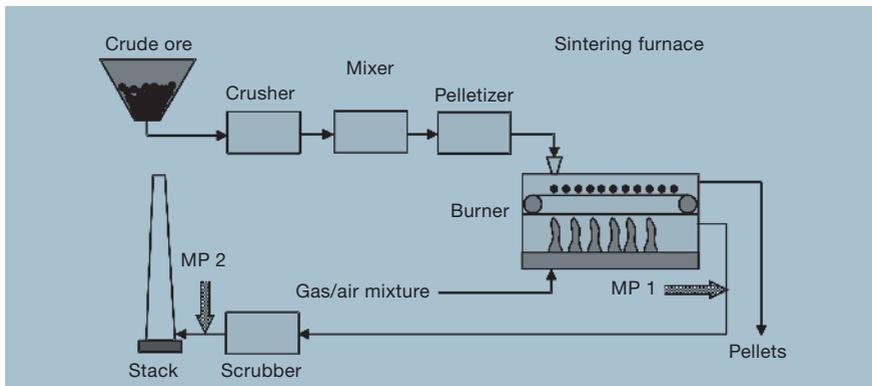
Figure 30: Process flow chart for pellet production (sintering) with measuring points

Measuring points and measuring tasks

- MP 1 in the crude gas downstream of the furnace for furnace optimization

- MP 2 in the clean gas at the stack for monitoring the function of the flue gas cleaning and for monitoring the limit values

Measurement parameter	Typical values	Limit values
	MP 1	MP 2
SO_2	500 to 3000 mg/m³	
NO_X	150 to 350 mg/m³	
Fluorine compounds	2 to 10 mg/m³	Limit values in accordance with national regulations
Chlorine compounds	20 to 60 mg/m³	
Dust	up to 3000 mg/m³	
Temperature	1000 to 1200 °C	

Tab. 35: Typical values and limit values in a sintering plant

4.4.2 Production of pig iron (blast furnace)

Pig iron is obtained through reduction (deoxygenation) of iron ore in a blast furnace or via direct reduction, with coke, natural gas or coal used as reducing agents. In the blast furnace process, the processed ore (pellets, sinter) and the additives, together with coke, are fed to the blast furnace from above (through the top of the furnace). From below, a hot blast of air blows in as an additional energy carrier. The mixture of hot air and reducing gases rises upwards, counter-current to the sinking raw materials, and is extracted at the top of the furnace as blast furnace gas. Together with the slag, the molten pig iron collects at the bottom of the furnace and is then removed at regular intervals and usually delivered to a steel plant for further processing. The flue gas (here referred to as blast furnace gas) still contains large amounts of CO and is laden with dust, and following dedusting, is used for generating hot air and for heating rolling mill furnaces, for example, or is burned in power stations. Only after this further use is it released into the atmosphere, provided that it complies with the regulations of TI Air.

Use of gas analysis in pig iron production, e.g. for
• Optimum operational management (energy and raw material use)
• Monitoring the composition of the blast furnace gas for its further use
• Monitoring the plant for CO leakage
• Monitoring compliance with limit values

Process flow chart and measuring points
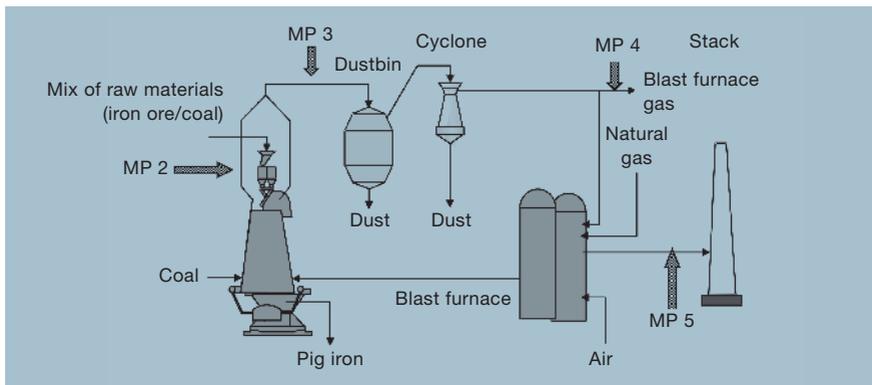
Figure 31: Process flow chart for pig iron production (blast furnace) with measuring points

Measuring points and measuring tasks

- MP 1 (not included in the illustration!) inside the raw material silo for monitoring CO
- MP 2 in the riser pipe of the blast furnace as a guide parameter for furnace operation
- MP 3 in the downpipe, upstream of the dustbin for determining the plant balance and for fire hazard prevention due to CO in the dustbin
- MP 4 at the blast furnace gas discharge downstream of the dustbin for monitoring the composition of the blast furnace gas (plant balance; further use of the blast furnace gas)
- MP 5 at the stack for monitoring compliance with limit values

Measurement parameter	Typical values				Limit values
	MP 1	MP 2	MP 3	MP 4	MP 5
	0 to 50 ppm	0 to 50%	0 to 50%	0 to 50%	Limit values in accordance with national regulations
CO_2		0 to 30%	0 to 30%	0 to 30%	
CH_4		0 to 4%	0 to 1%	0 to 1%	
H_2		0 to 15%	0 to 10%		
Dust			50 to 100 g/m3	1 to 10 g/m3	
Temperature		Up to 1300 °C	100 to 500 °C	100 to 150 °C	

Tab. 36: Typical values and limit values for pig iron production (blast furnace)

Note: At measuring point 2, there are stringent temperature- and dust-related requirements for gas extraction (specialist manufacturer).

4.4.3 Production of crude steel

Crude steel is produced during the first processing stage of pig iron via oxidation with oxygen in converters. The approx. 4% carbon still contained in pig iron is reduced to less than 1% via the reaction with oxygen. The refining process (blowing phase) generates converter gas, a flue gas containing a high level of CO, which is further utilized in the steel plant following removal of the dust content. Only after this further use is it released into the atmosphere, provided that it complies with the regulations of TI Air.

Use of gas analysis in crude steel production, e.g. for
• Optimum operational management of the converter
• Monitoring the composition of the converter gas for further use
• Monitoring compliance with limit values

Process flow chart and measuring points
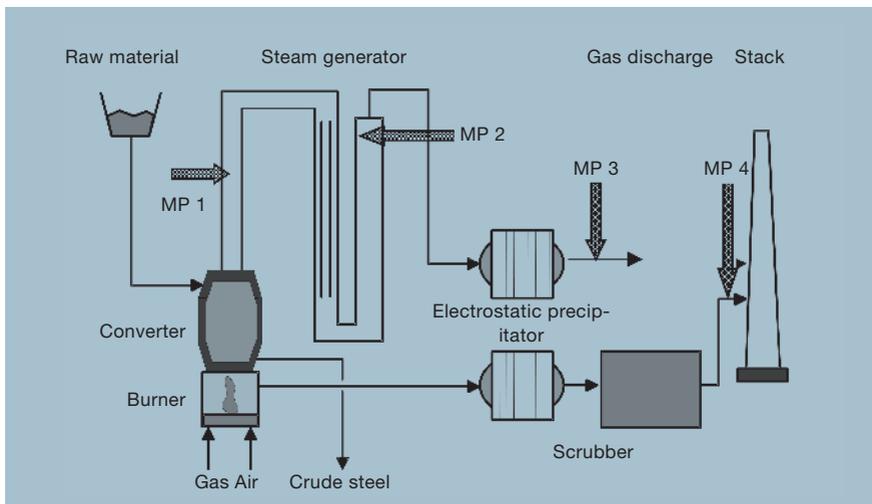
Figure 32: Process flow chart for crude steel production with measuring points

Measuring points and measuring tasks

• MP 1 downstream of the converter for process optimization

• MP 2 downstream of the heat exchanger for process optimization

• MP 3 upstream of the gas discharge for monitoring gas composition

• MP 4 at the stack for monitoring compliance with limit values

Measurement parameter	Typical values			Limit values
	MP 1	MP 2	MP 3	MP 4
CO	0 to 80%	0 to 80%	0 to 80%	Limit values in accordance with national regulations
CO_2	0 to 40%	0 to 20%	0 to 20%	
SO_2				
H_2	0 to 10%	0 to 10%	0 to 10%	
O_2	0 to 1%	0 to 1%	0 to 1%	
Dust	10 to 50 g/m^3	10 to 50 mg/m^3	20 to 50 mg/m^3	
Gas temperature	approx. 1600 °C	approx. 150 °C		

Tab. 37: Typical values and limit values for the production of crude steel

4.4.4 Coking plants

Coking plants are thermal hard coal refining plants, where hard coal is heated to temperatures of 800 °C and above in a dry distillation process, in the absence of air (pyrolysis). The objective of this coking process is to produce coke for industrial use, primarily in metallurgy. Coke features a very high carbon content (>97%) and a very low level of volatile substances. The process generates coke oven gas, which is further used.

Coal of a special quality is distilled ("cooked") in the coke oven in a dry atmosphere for about 15 hours and then discharged into a cooling process.

The wet quenching method used in the past has now largely been replaced by dry cooling in a shaft cooler. This permits the recovery of heat via a waste heat boiler, with a reduction in pollutant emissions. Besides dust, relevant pollutants are primarily SO_2, NO_X, CO and organic components. In terms of the permissible limit values, the flue gases must comply with the regulations in TI Air.

Use of gas analyzers, e.g. for
• Optimizing the coking process
• Analyzing the coke gas prior to its further use
• Monitoring the function of the flue gas cleaning system and monitoring limit value compliance

Process flow chart and measuring points
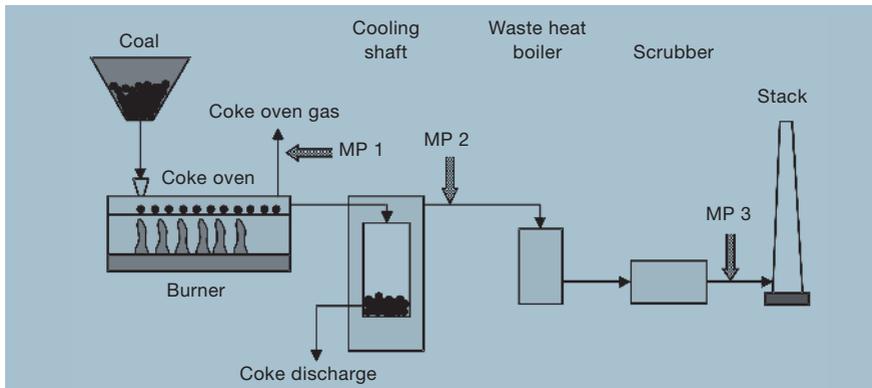
Figure 33: Process flow chart for a coking plant with measuring points

4. Application examples

Measuring points and measuring tasks
MP 1 at the gas discharge for evaluating the coke gas
MP 2 downstream of the cooling shaft for optimizing the coke drying process
MP 3 at the stack for monitoring compliance with the limit values

4.4.5 Production of aluminium

Aluminium is produced through the electrolysis of aluminium oxide. To achieve this, at temperatures of approx. 950 °C the alumina is dissolved in molten cryolite, into which carbon anodes are dipped. As a DC voltage is applied, the aluminium oxide is broken down into aluminium and oxygen. The aluminium accumulates at the bottom of the tank, is discharged and further refined in melting furnaces and finally cast into bars, for example. There are different types of electrolytic furnaces, most of which are now fully encapsu-

lated furnaces. Electrolysis generates mainly dust and fluorine compounds as well as SO_2 and CO, resulting from combustion of the carbon electrodes. The filter dusts are usually recycled.

The permissible emissions must comply with the regulations in TI Air

Use of gas analysis in aluminium production, e.g. for
• Optimum management of the furnace
• Monitoring the sorption reactor
• Monitoring compliance with limit values

Process flow chart and measuring points
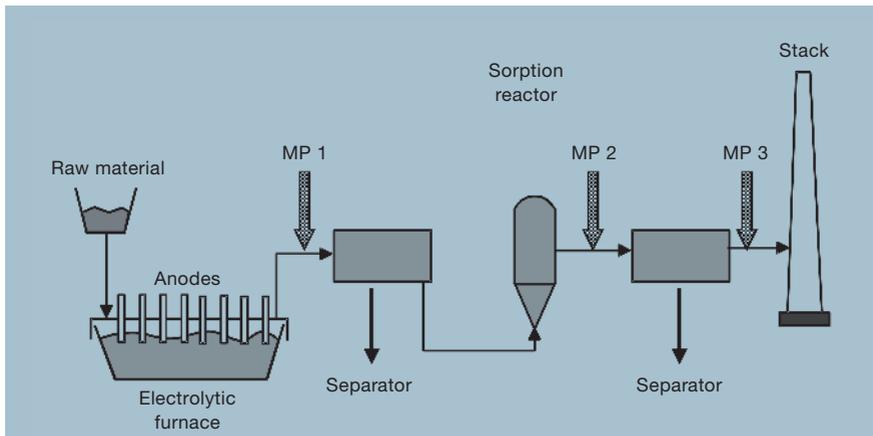
Figure 34: Process flow chart for aluminium production with measuring points

4. Application examples

Measuring points and measuring tasks
- MP 1 downstream of the melting
  tank for plant optimization
- MP 2 downstream of the sorption
  reactor
- MP 3 at the stack for monitoring
  compliance with limit values

4.4.6 Thermal surface treatment

Heat treatment is a collective term for all processes in which workpieces, primarily made of metal, are exposed to temperature changes in order to obtain certain characteristics in the workpiece, specifically in its surface (crystal structure). The composition of the surrounding atmosphere is of vital importance here:

• In some processes, surface oxidation via O_2, CO_2 or H_2O needs to be inhibited during heat treatment (tempering, hardening). This is achieved by maintaining a controlled, neutral gas atmosphere, which has no oxidizing or reducing effects.

• When it comes to other processes, in addition to heat treatment, the objective is to specifically influence the surface properties via a specific atmospheric composition. During carburizing, for example, carbon is implanted into the surface and, during the carbonitriding process, nitrogen is also. For certain applications, the removal of carbon from the surface via decarbonization is also required.

Heat treatment is carried out in furnaces, in batch or continuous operation (continuous belt) at 800-1200 °C, with the processed parts discharged into a quenching bath. Sealing of the furnace (retort) vis-a-vis the conveyor belt, insertion of the defined treatment gas and monitoring the plant for leaks are all key procedures for the plant to be able to function correctly.

Use of gas analysis, e.g. for
• Monitoring the furnace atmosphere
• Analyzing the treatment gas and the heating gas

Process flow chart and measuring points
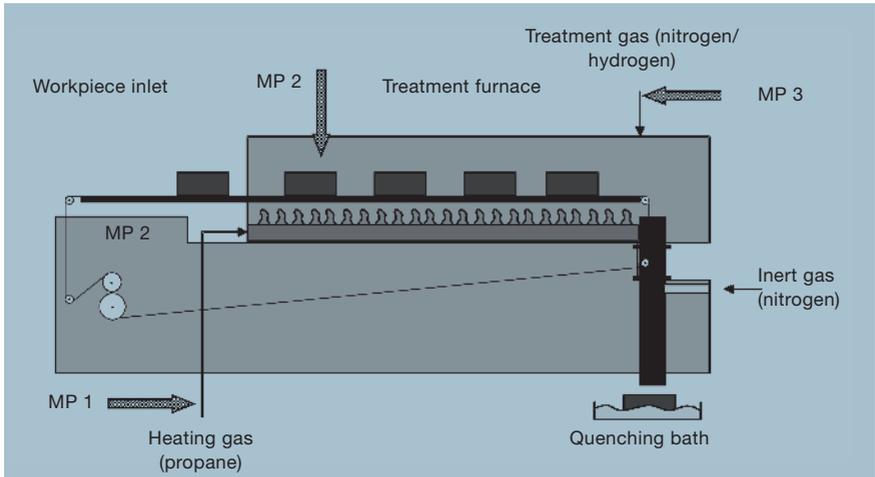
Figure 35: Diagram of a furnace for surface treatment with measuring points

Measuring points and measuring tasks

- MP 1 at the heating gas inlet for monitoring the heating gas
- MP 2 in the furnace for monitoring the furnace atmosphere
- MP 3 at the treatment gas inlet for adjustment and monitoring

The most common components for analysis are O_2, CO, CO_2 and CH_4.

4.5 Chemical industry

4.5.1 Process heaters

Almost all chemical and petrochemical plants require high temperatures to produce final or intermediate products, in most cases using superheated steam. The combustion plants required for this are referred to as process heaters. The figure below outlines this type of plant, where superheated steam is generated in a process heater and used in a double-walled reactor to establish the reaction temperature.

These kinds of combustion systems must comply with the regulations in TI Air or those in the 13th German Federal Immission Control Ordinance (BImSchV).

Use of gas analysis, e.g.
• For optimum adjustment of the burner (fuel savings and emission reduction)
• For optimizing combustion
• For monitoring compliance with emission limit values

Process flow chart and measuring points
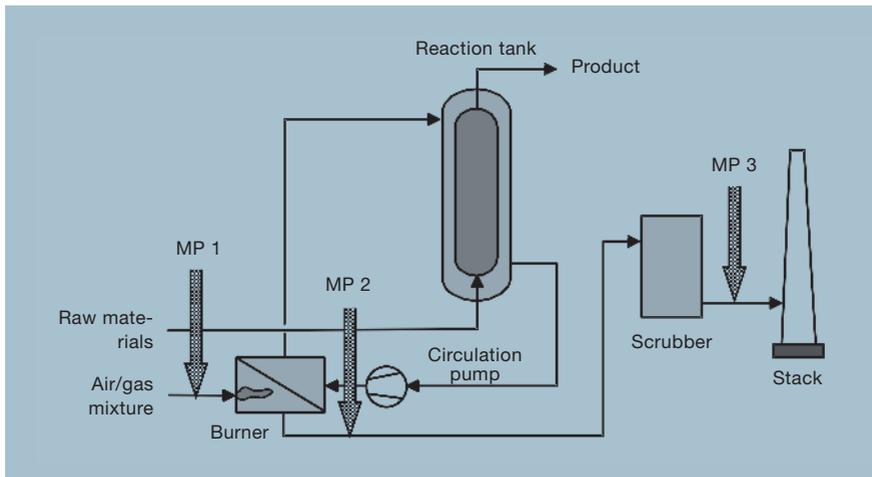
Figure 36: Process flow chart for a process heater with measuring points

4.5.2 Refineries

Refineries (or to be more exact, petroleum oil refineries) comprise a number of processing plants in which marketable petroleum products such as gasoline, diesel oil, plastics, fibres, detergents, solvents, along with many others, are produced from crude oil in several processing steps. These processing stages all run at high temperatures, which requires the use of numerous combustion plants (see 4.5.1).

The processing of the crude oil starts with distillation at atmospheric pressure and approx. 350 °C, whereby gasoline, petroleum and gas oil (diesel fuel), for example, are generated; the residue is made up of components that can be utilized as heavy fuel oil or further processed in a vacuum distillation at approx. 400 °C, e.g. to create lubricating oil or bitumen.

However, the great variety of products required by the market cannot possibly be realized via distillation alone. Special processes are used for this; these break down the heavy petroleum distillates obtained during further processing into lighter hydrocarbons (cracking units) and subsequently refine them (reformer units). Both these processes are carried out using catalysts at temperatures around 500 °C or above, often using fluidized-bed processes. The figure below outlines the distillation columns, the discharge of finished and raw products as well as the treatment of flue gases (tail gas) via incineration and cleaning.

Refineries are emission sources for pollutants such as SO_2, NOX, H_2S, particulate matter and many hydrocarbons. The emissions come from both fugitive and stack (primarily combustion processes) sources. Emission reduction is achieved by using low-emission fuels, taking combustion measures and flue gas cleaning plants.

For example, in Germany, refineries and their individual plants must comply with the regulations in TI Air, and combustion plants specifically may also fall within the scope of the 13th BImSchV, depending on their thermal output.

Use of gas analysis in refineries, e.g. for

- Optimum adjustment of the combustion systems (fuel savings and emission reduction)
- Monitoring the function of flue gas cleaning plants

- Monitoring compliance with emission limit values
- Safety of personnel and plants (risk of fire and explosion)

Process flow chart and measuring points
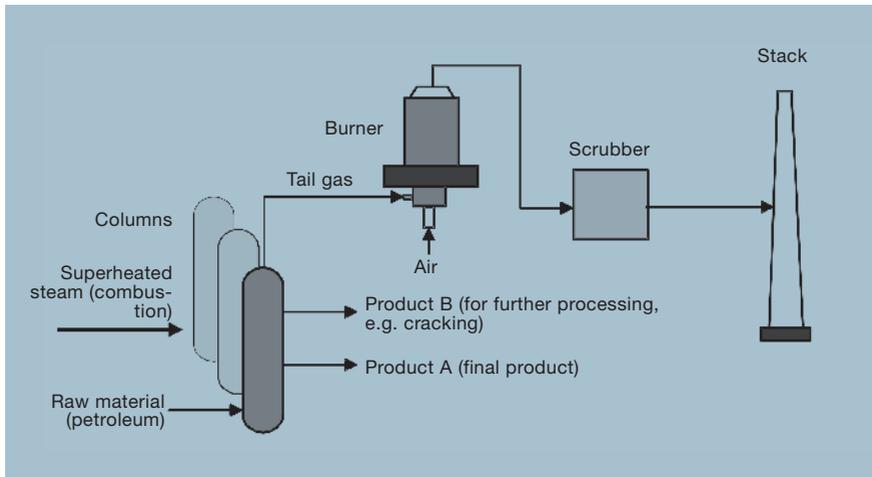
Figure 37: Process flow chart for a refinery (without measuring points)

Measuring tasks

Due to the wide variety of individual plants in a single refinery, no specific measuring point locations or tasks are mentioned here.

However, we would once again make reference to the numerous combustion plants for steam generation and residue incineration, which are operated in a refinery and which offer a wide range of tasks for gas analysis.

4.5.3 Flare stacks

Flare stacks are used for the safe burning of flue gases from oil wells, refineries and other petrochemical and chemical plants or from landfill sites. A distinction is made between flare stacks with regular operation and those that are used as safety installations in case of emergencies, when flammable gases have to be quickly discharged in the event of process malfunctions (explosion prevention). Flare stacks are often equipped with accessories such as steam injectors for smoke suppression or additional heaters for burning lean gases. The possible infiltration of air through leaks or the stack tip is critical because this can result in explosions within the system. This can be remedied via flushing gas or an air deflector at the stack tip.

Use of gas analyzers, e.g. for
• Monitoring the composition of the flue gas
• Detecting leaks

Process flow chart and measuring points
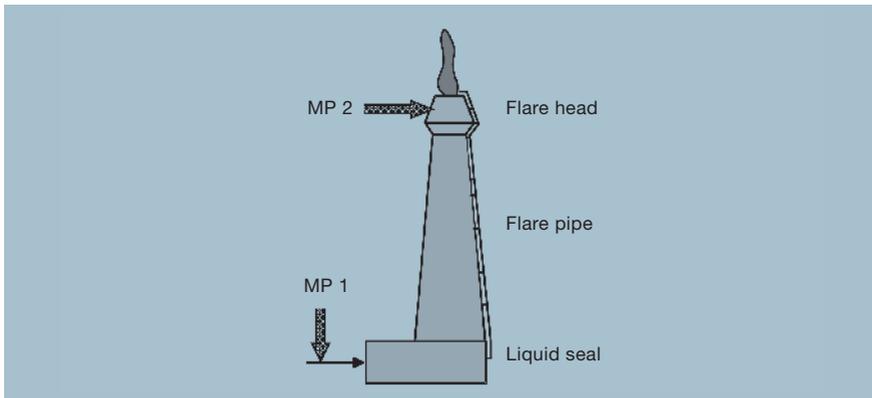
Figure 38: Design of a flare system

4.5.4 Residue incineration

Many industrial processes, for example in the chemical industry, produce liquid or gaseous residues and waste materials whose composition requires incineration as the only possible means of safe disposal. Residue incineration plants are used for this purpose. At temperatures between 900 and 1300 °C, these plants incinerate the residues in rotary kilns, converting the residues to environmentally friendly ash or slag. These plants are very similar to those for waste incineration. Please refer to the application example 4.2.1

The resulting flue gases must go through suitable gas cleaning processes, and in Germany their permissible composition when released into the atmosphere must comply with the regulations in the 17th German Federal Immission Control Ordinance (BImSchV).

Use of gas analyzers, e.g. for
- Optimizing the combustion process
- Monitoring the performance of the flue gas cleaning plants
- Monitoring compliance with limit values

Process flow chart and measuring points
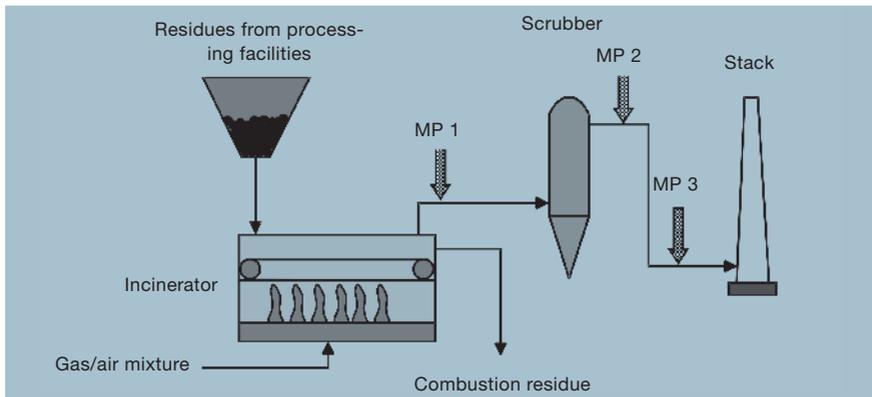
Figure 39: Process flow chart for a residue incineration plant with measuring points

Measuring tasks

- MP 1 at the boiler for optimized material supply and incineration conditions
- MP 2 at or between the flue gas cleaning installations for performance monitoring
- MP 3 at the stack for monitoring compliance with limit values

Information relating to this application
- The crude gas (prior to the cleaning processes) often contains aggressive associated components such as HCl, HF and HCN. A heated sampling system must be used for this. Furthermore, the cross-sensitivity of the SO_2 sensor to Cl_2 (80%) and HCl (15%) must be taken into account.
- The fuel (residue) composition will often vary depending on delivery. This can also result in major fluctuations in the readings.
- For measurements downstream of the electrostatic precipitator, the probe must be grounded.

4.6 Others

4.6.1 Crematoria

For crematoria, the limit values shown in the following table were set out in the 27th German Federal Immission Control Ordinance (BImSchV) in 1997.

Measurement parameter	Limit values
CO	50 mg/m^3
C_{total}	20 mg/m^3
Dust	10 mg/m^3
Dioxins+furans	0.1 ng/m^3
O_2 (reference value)	11%

Tab. 38: Limit values for crematoria

4.6.2 Engine test beds

Engine test beds are used to develop and test new engines, as well as for performance and endurance tests. There is a difference between test beds for vehicle engines and those for stationary engines.

Stationary engines are mainly used for generating electricity and in cogeneration plants. Stationary engines have an exhaust gas emission spectrum similar to that of vehicle engines; the relevant components are NO_X, SO_2 CO and hydrocarbons; diesel engine exhaust gas also contains soot particles. In accordance with the 4th BImSchV, these types of engines are subject to approval above a capacity of 1 MW (unrestricted for engines operated with waste oil or landfill gas!), and corresponding regulations are included in the TI Air. In 1991, limits were tightened up based on the dynamic sampling clause.

Use of gas analyzers, e.g. for
• Measurements within the scope of development work
• Measurements as part of endurance tests
• Measurements within the scope of approval procedures

Process flow chart and measuring points
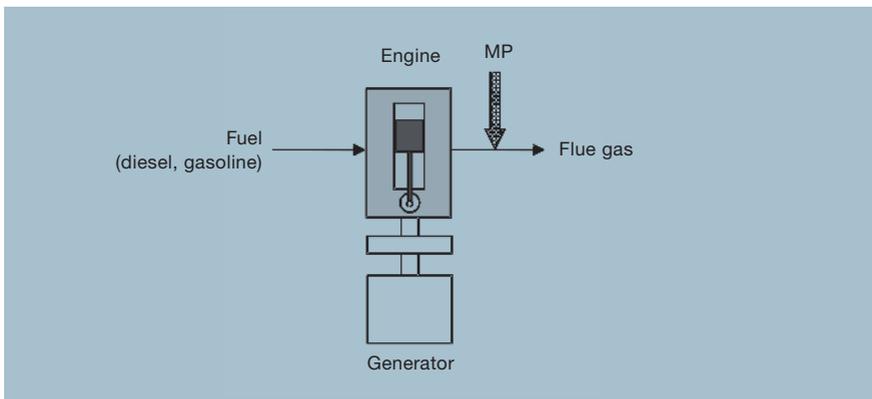
Figure 40: Process flow chart for an engine test bed with measuring point

5. Testo gas analysis technology

5.1 The company

Electronic measurement of physical and chemical parameters with portable instruments.

This has been the focus of the expertise of the Testo Group of Companies in Lenzkirch in the Black Forest, for over 60 years. Ever since it was founded in 1957, Testo SE & Co. KGaA, a medium-sized company, has been involved in the development, manufacture and worldwide distribution of probes and portable measuring instruments for

• Temperature and humidity
• Flow and pressure
• Components in gases (gas analysis)
• Analytics in liquids (liquid analysis)
• Light, sound and speed
• Electrical measurement parameters

With this broad range of applications, Testo is involved in numerous industries such as air conditioning & refrigeration, food, heating, power generation, non-metallic minerals, chemistry and process engineering, with tradespeople and authorities as well as in industry. All over the world, Testo has become a highly respected partner thanks to the performance, quality and user orientation of its products.

Portable measuring instruments differ considerably from stationary instruments which are permanently installed at the place of measurement. The main differences are obvious:

• For stationary instruments, the environment for operating the instrument can be optimally designed (air-conditioned housing or analysis container, stabilized power supply, etc.). and the instruments themselves can be developed to the highest levels of accuracy, operational reliability and ease of use without any significant restrictions in terms of weight or dimensions.
• Mobile devices, on the other hand, are operated in harsh, constantly changing environmental conditions.

In most cases, they have to manage without a power supply and have to meet the demands for portability in terms of their weight and dimensions. This poses a particular challenge for development and production.

In view of these conflicting constraints when it comes to developing and installing the instruments, various fields of application have been established, particularly in the field of gas analysis for portable and stationary instruments, which complement each other well and have thus far seldom overlapped.

However, through consistent development work, Testo has recently succeeded in making portable devices so powerful that they are able to advance into some of the task areas of stationary devices, without sacrificing any "portability". Heated gas ducts, measurement gas coolers, gas sampling probes with automatic air purging, instrument heating and cooling, and the use of laptops and bus technologies for operation, data processing and communication are all examples of this progress.

Testo offers portable gas analyzers which are approved for long-term measurements and have successfully passed demanding qualification tests such as those for the 17th German Federal Immission Control Ordinance (BImSchV) in Germany or approval tests in the USA. As a result, the instruments have a considerably expanded range of application compared with earlier versions, which can best be described as "measurements of combustion exhaust gases in most industrial sectors". Section 4 of this Guide provides numerous examples of this.

The following pages offer an overview of the current product range of Testo gas analyzers. The aim is to illustrate the variety of instruments and their features, and thus help the user to make the right choice for his or her analysis task.

However, for detailed information please always refer to the specific instrument documentation.

5.2 Typical features

General information

For more than 30 years, Testo gas analyzers have proven their worth all over the world in industry, with the authorities and in trade. More than 200,000 instruments are in use, testifying to the performance of this modern measuring technology on a daily basis.

Figure 41: Electrochemical sensor

Testo gas analyzers predominantly use electrochemical measuring cells (Figure 41) to analyze gas components. Through its own research and development, Testo has made this low-cost and space-saving technology, which is nonetheless challenging with respect to its operating conditions, available for the application of routine measuring technology in harsh operating conditions. This applies to both the measuring cells themselves and also their environment, such as optimization of the sample lines, correct allow-

ance for cross-sensitivities, reliable processing of the measurement gas and, last but not least, easy replacement by the user.

Testo takes full account of the fast pace of innovation in measuring technology! 70% of sales are from products that are younger than 3 years old. This innovative capacity is coupled with a marked focus on quality. Testo was awarded the ISO 9001 quality certificate back in 1992, and this was reaffirmed in 1997.

The testo gas analyzers can be characterized as follows:

• The instruments are either handheld or the size of a small suitcase, still with the option of transportation manually or via a transport cart. The instruments measure continuously.

• The product range is extensive and includes instruments for all kinds of purposes, with suitable equipment and appropriate performance data. There are instruments for determining individual gas components and those for the simultaneous determination of multiple gas components.

- The devices have successfully passed numerous certification and suitability tests, including the test known to be particularly demanding with respect to the 17th German Federal Immission Control Ordinance (BImSchV).
- The instruments are remarkably cost-effective compared to other gas analyzers.
- The instruments are very easy to maintain and are therefore inexpensive to operate. Users can do a lot of the maintenance themselves.
- The instruments come with very detailed documentation. In addition, Testo endeavours to support users by providing specialist information (e.g. this Guide).

Performance

The testo 350 gas analyzer successfully passed several qualification tests which demonstrate the high level of performance of the Testo instrument technology:

- The qualification test for continuous emission measurements was carried out on a waste incineration plant for the components NO, NO_2, SO_2, CO and O_2. As a result, the testo 350 was certified unreservedly as suitable for use in continuous operation (maintenance interval 14 days)

at installations subject to the 13th and 17th German Federal Immission Control Ordinance (BImSchV) and TI Air (TA Luft).

- The qualification test in accordance with DIN EN 50379-1 and -2 for portable measuring instruments for carrying out measurements at TI Air plants. This test was also passed unreservedly for the fuels coal, natural gas, digester gas, oil, wood and household waste in these types of plant: steam boilers, gas and diesel engines, gas turbines and waste incineration plants.
- In the USA, testo 350 meets the performance specifications for measuring NO_X, CO and O_2 as well as the requirements of the conditional test method CTM-030 and 034. Moreover, it is approved as a backup instrument in the event of a stationary measuring device malfunctioning.

The measuring accuracy according to the TÜV test for DIN 33962 for all components is less than 1.5% of the MR final value (Table 39) and therefore more than 3 times better than required in DIN 33962 (5%).

5.3 Overview of industrial flue gas analyzers from Testo

The range of instruments for industrial applications currently consists of three types:

1) testo 340 – handheld measuring instrument

The testo 340 is a handheld measuring instrument for industrial flue gas analysis. A compact design, it offers maximum mobility and, thanks to the reliable technology, is ideal for international servicing assignments or during commissioning and control measurements of combustion and power generation plants, for example. In addition to an O_2 sensor, a further three sensors (CO, CO_{low}, NO, NO_{low}, NO_2 or SO_2) can be fitted in accordance with your practical requirements. The testo 340 has built-in flow/differential pressure measurement, single dilution (factor x5) and dilution of all sensors (factor x2).

Figure 42: testo 340 – flue gas analyzer for industry with accessories

2) testo 350 –
Portable analyzer system

The testo 350 is a portable analyzer system for industrial flue gas analysis. It consists of up to 16 analyzer units and a control unit. The 350 analyzer unit(s) can be controlled with the testo 350 control unit, but also with a PC (via USB, Bluetooth or CANCase) or an Android app.

The testo 350 was specifically developed for practical requirements in industrial emissions measurement, for example for measuring emissions from industrial engines, burners, gas turbines, thermal processes, etc.

In addition to an O_2 sensor, a further five gas sensors (CO, CO_{low}, CO_2, NO, NO_{low}, NO_2, SO_2, H_2S or C_XH_Y) can also be fitted in accordance with your practical requirements.

The testo 350 also has built-in flow/differential pressure measurement, temperature probe input Type K NiCr-Ni and Type S, Pt10Rh-Pt, rechargeable battery, integrated combustion air probe (NTC), a trigger input, single dilution factor (x2, x5, x10, x20, x40) and dilution of all sensors (factor x5).

Figure 43: testo 350 – flue gas analyzer system for industrial emissions measurement

3) testo 350 MARITIME – Flue gas analyzer for marine diesel engines

The testo 350 MARITIME is a seaworthy, certified[1]) and portable flue gas analyzer for measuring emissions from marine diesel engines. The testo 350 MARITIME can be used for the following on-board verification surveys in accordance with the NO_X Technical Code 2008:

- For on-board direct measurement and monitoring (e.g. periodic and intermediate surveys), for the simplified measurement method, for instance if any modification or readjustment has been made to an engine.

- Inspection of the NO_X limit values stipulated in MARPOL Annex VI. These are checked during regulatory NO_X controls, for example. The NO_X measurement can also be used to provide proof of NO_X reduction which is required in regional special zones with certain NO_X tax requirements (such as Norway).

The testo 350 MARITIME is fitted with six gas sensors (O_2, CO, CO_2-(IR), NO, NO_2, SO_2) and also includes a gas conditioning unit, measuring range extension for single slot SO_2, fresh air valve for long-term measurement, differential pressure sensor, temperature

Figure 44: testo 350 MARITIME – flue gas analyzer for marine diesel engines

0098/12   37 811 - 12 HH   14DD001B

probe input Type K NiCr-Ni and Type S Pt10Rh-Pt, Testo data bus connection, rechargeable battery, integrated combustion air probe (NTC), trigger input, measurement data memory and USB port.

1) Certificate: Germanischer Lloyd (DNV GL) certificate no. 37811 - 12 HH, according to MARPOL Annex VI and NOx Technical Code 2008 and Nippon Kaiji Kyokai (Class NK) certificate no. 14DD001B. In addition, the testo 350 MARITIME fulfils the directive on marine equipment and has the MED mark of conformity 0098/12.

Gas component	testo 340	testo 350	testo 350 MARITIME
O_2	0 to +25 vol.%	0 to +25 vol.%	0 to +25 vol.%
CO_{low}	0 to 500 ppm	0 to 500 ppm	
CO	0 to 10 000 ppm	0 to 10 000 ppm	0 to 3 000 ppm
CO_{high}	700 ppm to 20 000 ppm	2 500 ... 50 000 ppm	
CO_2 (IR)		0 to 50 vol.%	0 to 40 vol.%
SO_2	0 to 10 000 ppm	0 to 25 000 ppm	0 to 3 000 ppm
H_2S		0 to 1 500 ppm	
NO_{low}	0 to 300 ppm	0 to 300 ppm	
NO	0 to 8 000 ppm	0 to 20 000 ppm	0 to 3 000 ppm
NO_2	0 to 1 000 ppm	0 to 2 500 ppm	0 to 500 ppm
C_XH_Y			
Methane		100 to 40 000 ppm	
Propane min		100 to 21 000 ppm	
Butane min		100 to 18 000 ppm	
Number of sensors	2 to 4	2 to 6	6

Tab. 39: Measuring range and accuracies

5.4 Overview of accessories

With the relevant accessories, the analyzer (handheld measuring instrument or analyzer unit) becomes a functional measuring system. The following table shows the different categories of accessories, which include essential sampling equipment, additional data output options and enhancements and supplements for operating in specific conditions.

Some accessories are analyzer-specific, but others are universally applicable. For details, please refer to the instrument documentation.

Accessories for sample gas extraction and conditioning

Sample taking and preparation is crucial to achieving accuracy and consistency in the measurement results and to the service life of the measuring equipment. The process needs to eliminate two sources of error in particular:

• Damage to the measuring equipment from components of the flue gas (aggressive components and dirt) and

• Falsification of the measurement results due to non-defined elimination of gas components through reactions with the flue gas humidity prior to the measurement

Please refer to the explanatory comments in Section 3.1.2.

Flue gas probes

In line with the fields of application, Testo SE & CO. KGaA has developed innovative flue gas probes which, in combination with the testo 340 and testo 350 flue gas analyzers, can be used in situations involving very high temperatures, aggressive condensate, high dust concentrations or high mechanical stresses.

Modular standard gas sampling probe

The standard gas sampling probes are available for different temperature ranges (500 °C / 1000 °C), in different lengths (335 mm / 700 mm) and even with a pre-filter for dusty flue gas.

Flue gas probe for industrial engines

The flue gas probes for industrial engines are ideal for carrying out measurements on stationary industrial engines (e.g. gas/diesel engines). They are made entirely of metal to prevent

the handle from melting due to radiated heat.

$SO_{2\ low}$ probe

The unheated or heated $SO_{2\ low}$ kit is particularly suitable for measurements following flue gas after-treatment (e.g. scrubbers), in order to be able to determine the effectiveness of reducing SO_2 concentrations. For example, this is how SO_2 concentrations in the crude gas and in the clean gas are measured.

Industrial gas sampling probe

The unheated or heated industrial gas sampling probe is used for measurements involving high temperatures, high dust loads or wet flue gas. The probes can be customized to the measuring task by adding accessories.

Gas conditioning

Without appropriate measures being taken, measurements in humid flue gas would result in SO_2 and NO_2 readings that are too low. This is caused by the reaction of these gas components with water, which is formed via condensation of the flue gas humidity when cooled. The condensate contains significant and undefined (!) quantities of SO_2 and NO_2, which therefore can no longer be measured in the gas.

To prevent or quantify this effect, compact gas conditioning (Figure 45) or the coolers built into the instruments which cool and, in the process, dry the gas via a Peltier cooler, are used. A proportion of SO_2 and NO_2 is still lost via the condensate, but this is now defined by the cooling temperature, which means that the subsequent measurement on the (dry) gas in respect to the cooling temperature provides accurate values.
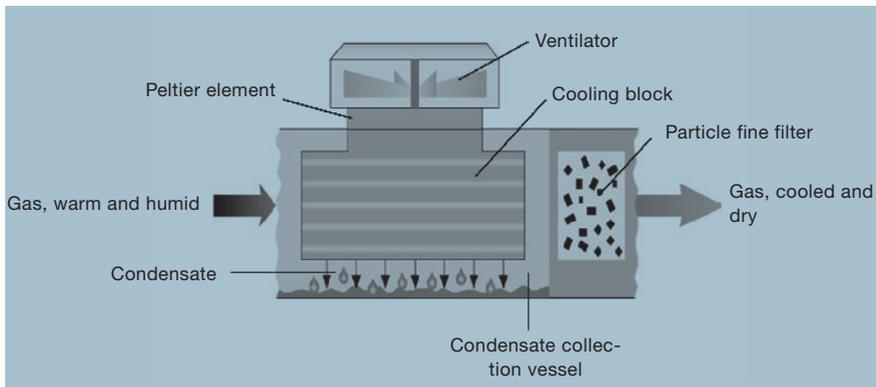
Figure 45: Testo gas conditioning, schematic

Special gas pipes

The formation of condensate and thus the influence on the concentrations of SO_2 and NO_2 also depend on the time that is available for a reaction. High flow velocities have a positive effect here. With this in mind, testo has now undertaken a patented new development in which the hose no longer has to be heated. The hose conducting the gas has a small diameter, which creates high velocities. The material used is PTFE, which is known for its very low absorption.

System solutions

A complete system for sample gas extraction and conditioning consists of a gas sampling probe, gas lines (tubes or hoses), coarse and fine filters and a cooling unit. Testo has coordinated its sampling accessories, so that perfect system solutions can be created by combining the modules. Some of the instruments are already equipped with sample conditioning units, e.g. the testo 350 with its built-in measurement gas cooler.

Be sure. **testo**

Testo's head office

Testo SE & Co. KGaA
Testo-Strasse 1
D-79853 Lenzkirch, Germany
Phone: +49 7653 681-700
Fax: +49 7653 681-701
info@testo.de
www.testo.com

You will find the contact details for our
subsidiaries and agencies all over the
world at **www.testo.com**

Index

Be sure. **testo**

Testo SE & Co. KGaA
Testo-Strasse 1, D-79853 Lenzkirch, Germany
Phone +49 7653 681-700
Fax +49 7653 681-701
e-mail info@testo.de

www.testo.com