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COMBUSTION ANALYSIS

The environment has to deal with ever larger concentrations of pollutants due to the use of all types of combustion processes. Smog formation, acid rain and the constantly increasing number of allergies are a direct result of this development. The path to environmentally friendly energy production must therefore lead to a reduction in the emission of pollutants, which is only possible when the existing equipment is working correctly and defective equipment is taken off line. Flue gas analysis and a flue gas analyser enable you to measure the concentrations of the pollutants present and to adjust your burners for optimal combustion.

This branch can be seen as connected to several very different industries. It has a function as environmental control, as simple air pollution control equipment for its own sake. It can be seen as a supplement to general maintenance services and hence the protection of an investment, and it is also a valuable tool for reducing fuel costs. Known under many names, flue gas analysis, stack emissions monitoring or simply gas analysis. Should it become part of military procedure, we will probably be hearing about gas monitoring, stack as well! If we talk of compliance testing, then the legal aspect of the matter becomes clear, as well as the interest of the EPA in the matter. Without a flue gas analyser, there is no real way of checking your own level of compliance and hence avoiding nasty surprises when official testing with a flue gas analyser is carried out.

Many new sections keep being created. The modern interest in Biogas has been increased by the high cost of fuel in recent times and the greenhouse effects caused by simply venting these gases to atmosphere. NO₂ has become more of a topic, now that carbon monoxide has generally been reduced. Basically, stack testing is a growing business and will be with us for as long as we burn fossil fuels. Most of this site will employ the British expression, flue gas analyser and not the American flue gas analyzer, although there are some mixtures to be found. The two terms are, of course, identical in meaning. There are many other synonyms in common usage, and these will be mixed freely in some places. I apologise in advance for what may be seen as inconsistency. It is more a planned attempt to make everybody feel at home!

Topic Index : The topic index is a short list of the various subject matters covered by this site such as biogas, biomass, landfill technology, sample conditioning systems, stationary monitors, indoor climate control and other carbon dioxide applications.

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1) WHAT IS COMBUSTION ?

Combustion is the act or process of burning. For combustion to occur, fuel, oxygen (air), and heat must be present together.

Per definition combustion is the chemical reaction of a particular substance with an oxidant. Generally this will mean atmospheric oxygen and will be treated as such in the rest of this site.

The combustion process is started by heating the fuel above its ignition temperature in the presence of oxygen. Under the influence of heat, the chemical bonds of the fuel are split. If complete combustion takes place, the elements carbon (C), hydrogen (H) and sulphur (S) react with the oxygen content of the air to form carbon dioxide CO_2 , water vapour H_2O and sulphur dioxide SO_2 and, to a lesser degree, sulphur trioxide SO_3 .

If not enough oxygen is present or the fuel / air mixture is insufficient then the burning gases are partially cooled below the ignition temperature (too much air or cold burner walls), and the combustion process stays incomplete. The flue gases then still contain burnable components, mainly carbon monoxide CO , carbon C (soot) and various hydrocarbons C_xH_y . Since these components are, along with NO_x , pollutants which harm our environment, measures have to be taken to prevent the formation of them.

To ensure complete combustion, it is essential to provide a certain amount of excess air. Combustion optimisation saves money!

The quality of a combustion system is determined by a maximum percentage of complete combustion, along with a minimum of excess air (commonly 5 to 20% above the necessary level for ideal combustion)

AIR	+	FUEL	>>>	FLUE GAS
Oxygen (O_2)		Carbon (C)		Carbon dioxide (CO_2)
		Hydrogen (H_2)		Carbon monoxide (CO)
Nitrogen (N_2)		Sulphur (S)		Sulphur dioxide (SO_2)
		Oxygen (O_2)		excess O_2
Water vapour		Nitrogen (N_2)		Nitrogen oxides (NO_x)
		Water (H_2O)		Nitrogen (N_2)
				Water vapour
				Soot

Flue gas will generally contain a certain amount of CH_4 (methane) if the combustion was not complete. Other hydrocarbons will not occur under normal conditions. higher hydrocarbons are only produced under conditions of high pressure and high temperature such as occur in an internal combustion engine.

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2) WHAT IS COMBUSTION EFFICIENCY ?

Combustion efficiency is a calculation of how well your equipment is burning a specific fuel, shown in percent. Complete combustion efficiency would extract all the energy available in the fuel. However 100% combustion efficiency is not realistically achievable. Common combustion processes produce efficiencies from 10% to 95%. Combustion efficiency calculations assume complete fuel combustion and are based on three factors:

1. The chemistry of the fuel.
2. The net temperature of the stack gases.
3. The percentage of oxygen or CO₂ by volume after combustion.

COMBUSTION PROCESSES AND THEIR COMBUSTION EFFICIENCY RANGES	
PROCESS	TYPICAL COMBUSTION EFFICIENCY RANGE
HOME FIREPLACE	10-30 %
SPACE HEATER	50-80 %
COMMERCIAL GAS BOILER	70-82 %
RESIDENTIAL GAS BOILER WITH ATMOSPHERIC BURNER "LOW EFFICIENCY"	70-82 %
OIL BURNER HEATING SYSTEM	73-85 %
INDUCED DRAFT FURNACE "MEDIUM EFFICIENCY"	74-80 %
BOILER WITH GAS BURNER	75-85 %
CONDENSING FURNACE (GAS & OIL) "HIGH EFFICIENCY"	85-93 %

If your calculation shows that your equipment is losing 20 % of the heating energy of the fuel through stack losses, your equipment is running at 80 % efficiency.

Combustion Efficiency : relates to the part of the reactants that combine chemically. Combustion efficiency increases with increasing temperature of the reactants, increasing time that the reactants are in contact, increasing vapour pressures, increasing surface areas and increasing stored chemical energy. One way of increasing the temperature of the reactants and their vapour pressures is to preheat them by circulating them around the combustion chamber and throat before being injected into the combustion chamber. The specific heat of combustion is a chemical property that refers to the amount of energy that can theoretically be extracted from a fuel at 100 % combustion efficiency. The heating value is a more realistic term and does not include the condensation of the water vapour produced. It is thus more easily applied to real combustion processes.

Air preheating is one method used in steel works, for instance, to increase combustion efficiency. This uses the heat in the flue gases to heat one of a pair of chambers and the inlet air passes through the other one. The use of the chambers is switched as soon as the one chamber has reached temperature, so the air passes through the heated

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chamber. This is one of the simplest and best methods of increasing combustion efficiency in this kind of process. Such preheaters are standard equipment these days for larger systems.

The introduction of the condensing burner has led to the strange situation where combustion efficiencies in excess of 100 % are reported. These devices also use the specific heat of vaporisation as a source of energy and therefore have an increased yield, provided they are operated in the appropriate temperature range.

3) What needs to be measured for combustion efficiency?

Assuming that the fuel parameters are known, only the oxygen or carbon dioxide concentration, ambient temperature and flue gas temperature have to be determined. Since that does not give a 100% certain reading (see chart sections 8 & 9), it is really necessary to measure CO as well.

Combustion efficiency is a simple (and occasionally misleading) measure of the heating efficiency of a boiler. It is equal to 100 percent minus the percentage of heat lost up the vent (called "flue loss" or "stack loss"). The formal methods for measuring flue loss vary by furnace or boiler type, but, in essence, the combustion efficiency measures the total heat energy that is spread through the heating system or escapes from the boiler jacket itself (jacket loss) instead of going up the stack or flue to warm up the environment. Certain factors may place a limit on the combustion efficiency that can be reached. In particular, the need to keep the gases above the dewpoint for sulfur dioxide may be a major factor. Such considerations must be borne in mind at all times when adjusting a burner system.

Combustion efficiency is based on the flue gas temperature and inlet air temperature. These must be measured in an appropriate fashion. The inlet air at the air inlet, avoiding any wind chill factor that the air movement might produce. This is a relatively simple, but important factor. The flue gas temperature must be measured in the hottest part of the gas stream. Generally this will be in the centre of the flue, but eddy effects may cause it to be slightly displaced. It is vital to have the correct fuel programmed into the flue gas analyser before measuring combustion efficiency. The fuel parameters have a noticeable effect on the value of combustion efficiency, and failure to follow this step will result in erroneous data.

Combustion efficiency measures the so-called "steady-state" efficiency of a boiler, which may or may not be appropriate in specific cases, especially where a burner is used as back-up and only ever operates for short periods of time to cover peak usage. many burners operate on a short cycle which is intrinsically less efficient than continuous use at full power.

As stated above, combustion efficiency may be limited in certain cases and with the condensing boilers it is a definite problem. Here the quantity of condensate produced in a set time must be measured for any calculation of efficiency. The high specific heat of evaporation for water makes this a major factor in any true calculation of efficiency.

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Nevertheless, it is a useful factor for seeing changes made by adjustments. Generally this data is also required when annual checks are made on equipment.

4) WHAT IS FLUE GAS ?

When fuels are burned there remains, besides ash, a certain number of gas components. If these still contain combustion heat, they are called heating gases. As soon as they have conveyed their energy to the absorbing surfaces of a heat exchanger, they are called flue or stack gases.

The various common flue gas contents were already mentioned in section 1.

4.1) WHICH UNITS ARE COMMONLY USED ?

The presence of pollutants in a flue gas stream can be expressed in terms of the concentrations of the individual gas components.

The following units are the most common:

ppm (parts per million)

Like the reading "percent (%) ", ppm expresses a ratio. If there is a concentration of 333 ppm CO in a cylinder and you take one million particles out of that cylinder, 333 particles would be carbon monoxide particles.

For convenience, higher concentrations are generally expressed as a percentage (%). The conversion is as follows:

$$10000 \text{ ppm} = 1 \%$$

$$1000 \text{ ppm} = 0.1 \%$$

$$100 \text{ ppm} = 0.01 \%$$

$$10 \text{ ppm} = 0.001 \%$$

$$1 \text{ ppm} = 0.0001 \%$$

An oxygen concentration of 21.95 vol.% would equal 219 500 ppm O₂, and 10% CO is identical with 100 000ppm CO.

mg/Nm³ or mg/m³ (milligram per cubic meter)

When using the unit mg/Nm³, the standard volume (standard cubic meter, Nm³) is used as a reference and the mass concentration of the flue gas is given in milligrams (mg). Since this unit is pressure and temperature dependent, the volume is expressed at standard conditions. There are different sets of standard conditions used for different purposes. Flue gas analysis commonly uses the following standard conditions:

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Temperature: 0°C
Pressure: 1013 mbar (hPa)

Conversion to mg/Nm³ from ppm

$\text{CO (mg/m}^3\text{)} = (21 - \text{O}_{2\text{ref}}/21 - \text{O}_2) \times \text{CO (ppm)} \times 1.25$
$\text{NO}_x \text{ (mg/m}^3\text{)} = (21 - \text{O}_{2\text{ref}}/21 - \text{O}_2) \times (\text{NO} + \text{NO}_2 \text{ in ppm}) \times 2.05$
$\text{SO}_2 \text{ (mg/m}^3\text{)} = (21 - \text{O}_{2\text{ref}}/21 - \text{O}_2) \times \text{SO}_2 \text{ (ppm)} \times 2.86$

The conversion factors used in the formula come from the density of the gas components at standard conditions.

5) WHY IS IT IMPORTANT TO CARRY OUT COMBUSTION TESTING ?

By using a flue gas analyser you can make sure that your equipment is operating safely and at maximum efficiency, and that it fulfils environmental legislation. EPA compliance testing is very important now.

This question can be divided into sections: There is the legal requirement to remain below a certain level of pollutant output and to operate the equipment inside the safety limits at all times. Failure to adhere to these points may well result in heavy fines or the closure of all the equipment until service has been carried out and it can be proved that the safety limits are no longer exceeded or until EPA compliance testing has been repeated successfully. These procedures are always costly and may lead to long delays and shutdown of a plant, possibly at a very inopportune moment. The safety aspect will, of course, be clear to anyone who has had discussions with the local Safety at Work or equivalent officials. Safety is important for many reasons, not just financial ones.

There is then the financial question of use of efficient use of fuel. Even if this is a waste product, it is still financially important to use it carefully. If there is sufficient excess, then it can be sold or used for other purposes, or stored for times when a higher output is required, avoiding the use of alternative and costly fuels.

Both EPA compliance testing and optimal fuel use can be seen as a purely financial matter if necessary, allowing them to be quantified and entered into a profit and loss sheet. This can mean that they will be taken seriously by non-technical people, who are often involved in major decisions in industry. It is preferable, however, to also see them from the point of view of ecology and of worker satisfaction. It is generally known, that the feeling, management is trying to reduce risks will improve the morale and hence output of most people, so keeping equipment safe has other benefits as well. EPA compliance and efforts made to keep systems ecologically friendly are, today, good advertising points, a fact which should not be underestimated.

To perform an analysis, the equipment must be clean and operating properly. After you have serviced the equipment, let it run for 15 to 20 minutes. This will allow the unit to warm up and vent properly. This is especially important after cleaning soot out of the flue, since the particle left will burn inefficiently and will falsify the result. Each

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furnace manufacturer dictates how to do the actual testing on their products. If the service manual does not indicate how, refer to general guidelines set up by the manufacturer of the testing equipment you use. Most modern equipment will come with suggestions as to the pollutant limits typical for the system, so this should increasingly be less of a problem. In any case, the EPA or equivalent national standard compliance limits represent a maximum level of pollution allowable.

6) What is the difference between traditional (mechanical) instruments and continuous sampling flue gas analysers?

The information traditional instruments will give you is comparable in accuracy to electronic instruments, though electronic instruments have very important advantages.

The expression "traditional" is perhaps now misleading, since the electronic instruments have now more or less become the standard for use in most countries. The chemical and mechanical analysers have, fortunately, become the exception to the rule.

For example, contrary to traditional instruments, flue gas analysers monitor on a continuous basis. That ensures you that you will not oversee the most important value, because you can follow the changes automatically and rapidly, and provide a printout of the measured and stored data, and furthermore you have the opportunity to transfer the data to a computer. Stack testing is no longer a game. It is carried out for a number of legal and financial reasons. Satisfying local regulations is an important factor in the continued existence of a company, and nobody will take such matters lightly. The chemical methods leave many factors out of the equation, such as cross-sensitivity effects and transient changes. Since the regulatory authorities are almost all equipped with electronic instruments that will take all these factors into account, there is little advantage in remaining with the ancient methods. In the long run, these are more expensive, since the chemicals must be bought and stored. These are often classified as dangerous liquids for very good reasons and will require the operators to use protective equipment when handling them as well as posing serious storage problems.

Flue gas analysers have also been reduced dramatically in size from the old type of cased instrument weighing around 20 kg to an instrument that can truly be designated a hand held analyser. Weighing less than one kilogram in most cases they are powerful and less expensive relatively than they ever were. The flue gas analyser has really ceased to be an expensive laboratory instrument and is now a medium priced field instrument, in use on building sites and on the factory floor. Laboratory style flue gas analysers do still exist, of course, but they are more used for experimental work or as standard for comparison to other flue gas analyzers.

Overall, electronic flue gas analysers have many important advantages, such as ease of use and speed, automatic sampling, calculations and report generation. The ability to connect them to a computer and download stored results has made their use much quicker and simpler. Most common flue gas analysers have enough memory capacity

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to store the results from a day's work, which can then be collected in one package afterwards, complete with comments and date/time etc. Cordless communication is here also coming into use. A Bluetooth connection can easily be applied to an existing interface enabling wireless communication with a range of different instruments.

7) What is the best place to take a sample?

The measurement for gases and (gas) temperature should be taken at the same point. The sample point should be before draft diverters and barometric dampers so that the gases are not diluted and the temperature has not been decreased by the addition of outside air.

Use the following guidelines for residential or light commercial/industrial equipment.

Oil Burners / Gas Burners - at least 15 cm upstream from the furnace side of the draft regulator (diverter), and as close to the furnace breeching as possible.

For larger Equipment - downstream from, and as close as possible to, the last heat exchange device. This insures that the net temperature change (flue gas temperature minus ambient air temperature) will provide an accurate indication of the efficiency of the heat exchangers.

This question is not easy to answer due to the great differences in the equipment on the market these days and the varying uses the systems are put to. Many burners now carry out a number of purposes, being designed for one basic operation, but with the added function of producing hot water, for instance. The important facts to take into consideration are that there may be no dilution of the sample, and that there should be negligible heat loss since the last point, where useful heat is extracted from the system. Many new systems will have a measurement point already present in the flue, making life very much easier. If it is not present, then a hole will have to be bored in some way. Care must be taken with lined or other double flue pipes to preserve the integrity of the system. Judgement is needed and manufacturer's recommendations must be followed at all times to preserve the warranty on new equipment. Since measurement is compulsory in most areas, the manufacturer must make it possible to carry out measurement at some appropriate point in the system.

In almost all cases, the flue temperature will be measured at the same point as the gas sample is taken. If there are sufficient heat exchangers obstructing the stack, then the gas may be almost homogenous, but care should be taken to check the gas stream for the presence of a core of high temperature gas with a differing composition. This is the gas which should be sampled, both for pollutants and for the true flue gas temperature.

It is regrettably very common for measurements on small domestic heaters to be taken in the existing air flap. Although quick and convenient, this result will have no relation to reality. Either the sample must be taken before the flap or the flap must be held closed during measurement. Such practices are sometimes the result of poor training

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but more often simple laziness on the part of the measuring personnel. These are generally trained maintenance technicians for some sort of heating equipment, and this shows a simple lack of interest in all aspects except being finished on time.

8) **How important is it to measure CO ?**

The concentration of carbon monoxide is an essential part of determining optimum boiler efficiency. An operation near trace levels about 100 ppm and a slight amount of excess air indicates conditions near optimum. No burner is able to mix fuel and air perfectly. The consequence is that there will be products of incomplete combustion present. Where CO begins to be produced in volume, maximum efficiency is achieved. By providing continuous monitoring of CO and O₂ MRU flue gas analyzers make it easy to determine maximum efficiency and optimum boiler operation. In addition, keeping the level of carbon monoxide in the flue gas low will prevent leaks to the surroundings.

It is also possible to measure the level of ambient carbon monoxide with many flue gas analyzers. The exact method will be found in the operating manual. Generally a level of less than 20 ppm is to be expected in any area where people are regularly. Although the safety limits are considerably higher, thought must be given to the source of the carbon monoxide at this level. Ambient outside levels are very much lower, so it must be the result of some process. If it is leakage from a combustion system, then the chances are very high that the problems will get worse, not better. It is then essential to check the integrity of the flue system and to ensure that the draught in the flue is sufficient to exhaust all the waste gases efficiently. A blockage of the flue will have this effect, for instance. Rust may occur on the flue pipe, particularly if it is only in use for a limited time every year and operates at a lower temperature, allowing condensation to form inside the pipe. This is a typical problem for gas fired systems that are used to cover peak loads. They often never operate for long enough to reach the full temperature, allowing acidic condensation to pool.

Carbon monoxide is poisonous because CO robs your blood of oxygen. When you inhale carbon monoxide, it bonds with the haemoglobin in your blood, displacing life-giving oxygen. This produces a toxic compound in your blood called "Carboxyhaemoglobin" (COHb). Over time, exposure to CO can make you sick. Victims exposed to enough carbon monoxide can suffer brain damage, or even die.

One of the long-term exposure limits is set at 9 ppm with a maximum of 35 ppm for one hour. These low concentrations show just how dangerous carbon monoxide really is.

According to the Journal of the American Medical Association (JAMA), 1500 people die each year because of CO poisoning, and another 10,000 become ill. Since you can't see, smell, or taste carbon monoxide, it can make you sick before you even know it's there.

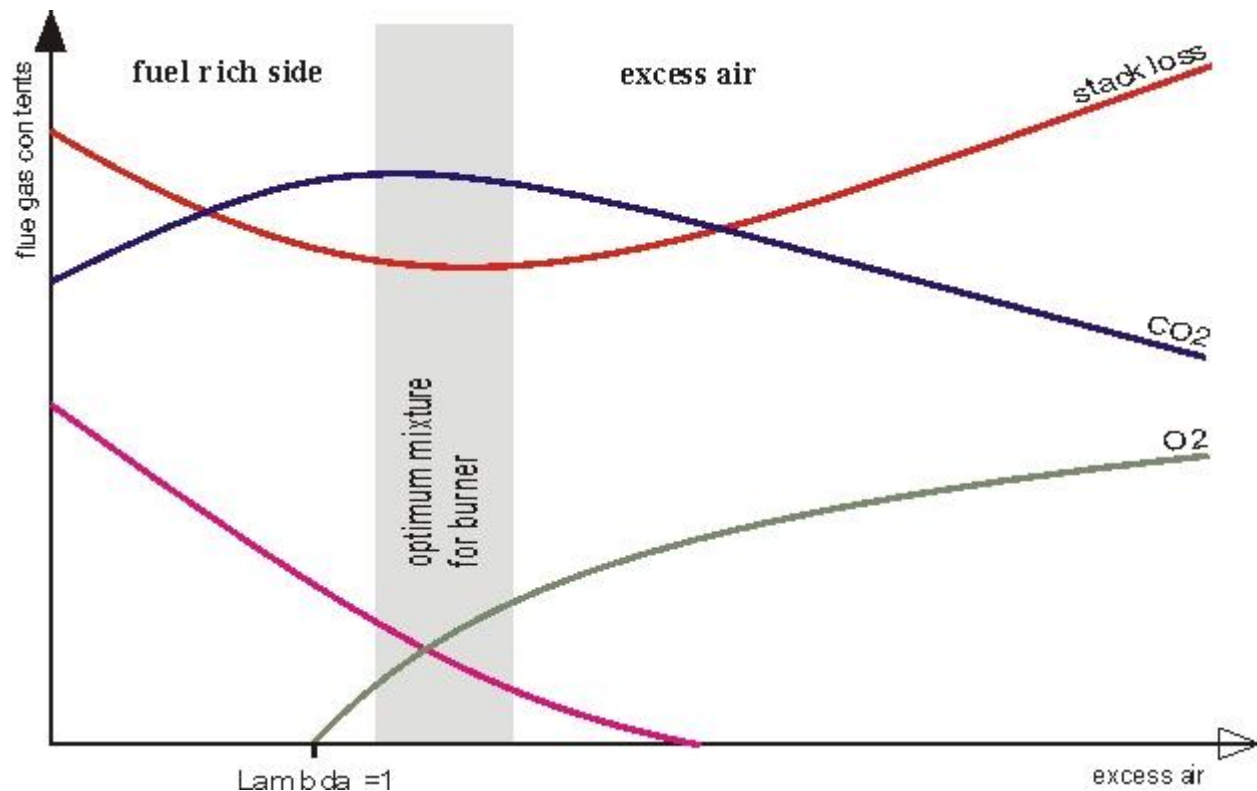
Carbon monoxide becomes particularly dangerous when problems with the draught regulation occur. As stated above, blockages of the flue channel, or poor design can

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lead to downdraughts, which can also occur as a result of later building work. One of the worst sources of carbon monoxide is to be found in the open fireplace that is allowed to die down overnight. Cooling reduces the draught in the chimney greatly, and the dying fire will tend to produce large quantities of carbon monoxide, partly due to the reduced draught, but also because the colder wood or coal is no longer burning efficiently.

In the framework of gas analysis, the main reasons for measuring carbon monoxide are compliance with regulations and the efficiency of combustion. Carbon monoxide is a loss of possible heating value from the material being used as fuel. It is not just an unnecessary load on the environment, it is a cost factor that should not be ignored.

9) How do relevant combustion parameters like O_2 , CO , CO_2 , temperature, and smoke (soot) relate to efficiency?



If it were possible to have perfect combustion, CO_2 would be maximised and O_2 would be at, or close to, zero in the flue gas stream. Since perfect combustion is not practically possible due, in part, to incomplete mixing of the fuel and air, most combustion equipment is set up to have a small percentage of excess oxygen present. The lower the temperature for a given O_2 or CO_2 value the higher is the combustion efficiency. This is because less heat is carried up the stack by the combustion gases.

As can be seen, the optimal combustion mixture is not displayed as a single point, but as a band of possibilities. The optimal combustion will depend on a number of factors and gives the possibility of adjusting for a reducing or oxidising gas, both of which

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can be necessary in an industrial process. The maximum allowable CO value is also an important factor. This may not be exceeded at any time and may limit the adjustment of the burner for maximum efficiency. This should not be the case, but may occur on some older equipment, particularly when solid fuel is involved.

Smoke is the usual indicator of incomplete combustion in oil burners. In addition to indicating poor combustion, smoke can deposit soot on the heat exchangers, further reducing fuel efficiency as well. The real problem is the soot layer, but this is seen by the public and operators as the smoke coming from the stack. The presence of smoke is a good indication that sooting will occur, hence the test for smoke is often referred to as a soot test.

Soot or smoke is one of the factors that will cause complaints from the general population. Carbon monoxide is invisible, but smoke can be seen from a long way away. Often it looks worse than it is due to the inclusion of water vapour in the stack gases. This will condense shortly after the exit from the stack and add to the smoke that is visible. Smoke is thus one of the factors that should be tackled also for good public relations and not just for the damage soot will do to the burner system. Soot can generally be removed fairly easily, but will require that the burner is switched off to do so. Some types of fuel will produce sooting to a certain degree regardless of all attempts to optimise the combustion, but this should be obvious and easily removed at the standard maintenance intervals. Burners that use a high level of excess air will naturally produce less obvious smoke than units operating in the most efficient zone. This may be one way of improving public relations, but this can probably be done at a lower cost in other ways.

10) Why measure draft?

This is important because draft measurement shows how rapidly the gases pass through the furnace or boiler. Draft measurements ensure that there is continuous negative pressure (systems without forced ventilation) in the combustion system. Excessive draft increases stack temperature and therefore decreases combustion efficiency.

Draft is critical. New furnaces use a pressure switch to test for correct draft, and if the draft is off, you will have a callback. A pressure switch will very rarely fail, so before replacing a pressure switch, check the draft.

It is important to measure draft on the chimney side, well downstream from a draft diverter. This measurement will inform you whether there is enough draft to move the flue gases up the chimney and vent them to the outside air.

Draft will be affected by a number of factors, including the outside air temperature. Normally, when a burner is running, there will be enough temperature difference to ensure that there is a measurable pressure difference capable of removing the waste gases safely, but there may be problems at start-up when the ambient temperature is high. Such factors should be borne in mind when designing a system, but the replacement of an older burner with a newer type may cause starting problems. Newer

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types have safety switches that demand a certain level of draught before they will start. This may make it necessary to add some form of forced draught system to solve the problem. Some such systems can be organised to only work during the first part of operation, before working temperature has been reached. Adjustments to safety equipment to solve such problems should not even be considered. These burners require this level of draught and will not work properly without it.

The term draft was chosen instead of draught to show there is no national bias on this site. Draught seems to have gone out of usage, perhaps because it is the longer word. The dictionary still mentions draught.

The matter is slightly different when a forced draught system is used. You then expect a positive pressure in the stack, which will be higher just by the combustion chamber. All the items that obstruct the flow will cause a pressure drop. A differential pressure measurement can be carried out across these obstructions to see which item is causing the most pressure drop, possibly due to breakage or other defect.

Typical values for draft:

Burner with fan 0.12...0.20 hPa (mbar)

Oil burner and gas burner without fan - 0.04...- 0.10 hPa (mbar)

The typical problem that used to occur was bird nests being built in chimney that were only used in winter. With central heating systems now being generally combined with hot water systems the chimneys are in use the whole year, reducing this standard hazard. Nevertheless it still occurs regularly in some countries. A sudden change in draught values will probably be caused by this type of problem. Naturally there are other factors that can cause a blockage and hence a dangerous change in draft values, it does not have to be our feathered friends! Again, modern chimneys tend to be lined, so the old problem of blockages caused by fallen bricks is no longer so likely to be the reason for a change in draft.

The old measurement methods of inclined manometers, whilst theoretically perfectly accurate have given way to electronic measurements in almost all cases. sometimes an old burner will have a permanent draft display in the form of a water column, but this is really an anachronism and has no real use for any purpose. It is a bit like the button in a lift that is supposed to close the doors. It is not connected to anything, but you feel better after pressing it! Burner draft should remain constant throughout the operating life of the system.

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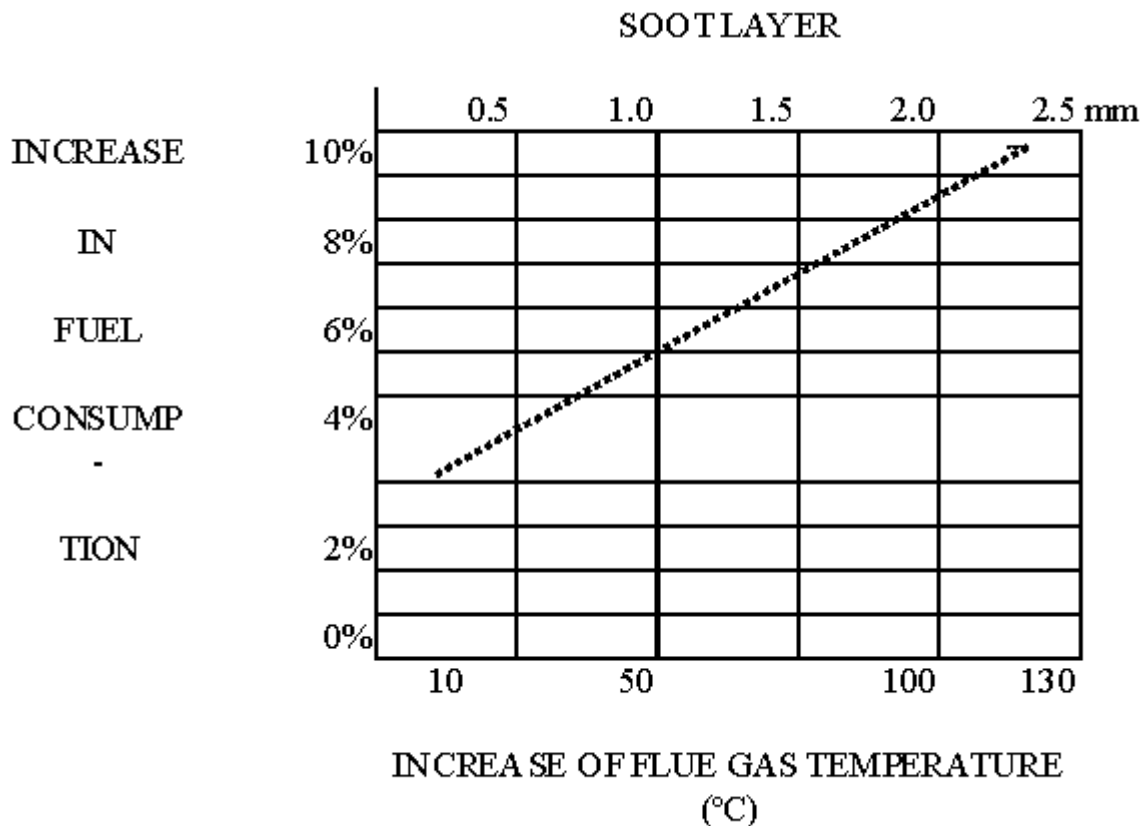
11) Is it important to measure smoke in oil-fired furnaces?

As already mentioned, smoke is a primary sign of incomplete combustion since it is basically composed of very small unburnt carbon particles, therefore it is important to determine the smoke (soot) content of the flue gas. Using MRU portable flue gas analysers gives you the opportunity to perform a soot test and determine oil burner condition and operating efficiency and safety. However, smoke spot testing will not indicate the presence of CO. Since smoke and CO will almost certainly coexist, both tests are necessary.

A smoke test is important. This procedure is generally done when servicing fuel oil furnaces or setting up power burners. If the air/fuel mixture is not correct, you will see it in the flue gas as smoke or soot. Generally, equipment is adjusted for a trace or less of smoke (some manufactures will tell you to set their units up for a trace of smoke, then back it off). Smoke in the flue gas eventually will create a soot build up in the furnace, and that will cause a whole list of problems, including difficulties with draft, efficiency, and carbon monoxide. The use of the flue gas analyser will then allow this somewhat empirical formula to be improved and correctly implemented.

The terms soot test and smoke test are used in different ways in different countries. What you can see and measure is the smoke in the flue gas, but this causes the soot layer to form on the inner sides of the burner. No soot without smoke could be the catch phrase!

EFFECT OF SOOT ON FUEL CONSUMPTION



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Smoke Scale Reading	Burner Performance
1	Excellent - Little, if any, sooting of furnace or boiler surfaces
2	Good - May be slight sooting with some types of furnace or boiler but little increase in flue gas temperature or consumption
3	Fair - Substantial sooting with some types of furnace or boiler and will require cleaning more than once a year on most types of furnace or boiler.
4	Poor - This is a borderline smoke reading, some units may soot only moderately, others may soot rapidly.
5	Very Poor - Heavy sooting in all cases - may require cleaning several times during the season.
6	Extremely Poor - Severe and rapid sooting may result in damage to stack control and reduce overfire draft to danger point.

12) Does frequent testing increase fuel savings?

By adjusting the combustion process and therefore improving combustion efficiency one ultimately saves fuel.

Although some combustion experts do weekly tests others consider three or four checks a year an acceptable level of testing. The appropriate level for a particular unit can only be determined by experience, and is partly dependent on the fuel consumption of the burner. The higher the consumption, the more important it is to optimise the process. Fuel consumption will be affected by a number of factors that can be measured with a flue gas analyser. The air/fuel ratio is an obvious candidate, together with the pressure drop in the stack. The carbon monoxide produced and a few other factors all add up together to change the efficiency of the burner. What works at low load may not work so well at full or half load.

It is relatively easy to work out a programme of testing frequency. It is common to start with frequent testing and find the rate of change of the process. Testing will be necessary after any major changes, such as a different fuel type or large-scale maintenance work. It is important to get an idea of the performance of the burner at different levels of load and varying fuel composition (if applicable). This will make it fairly simple to work out a plan for optimal testing, without unnecessary use of manpower.

The stability of the combustion process is perhaps the biggest factor here: a stable combustion process will require less testing than a system where constant changes are being made. Fuel savings are possible with both systems, perhaps more with unstable processes, since there may be factors that make the combustion process much less than ideal under certain circumstances. Fuel savings will depend to a great deal on discovering these conditions and either avoiding them or changing the combustion process to take account of them. In point of fact, these unstable conditions give the biggest potential for fuel savings, since they may be a long way from the ideal state.

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In countries with large differences in relative humidity and other factors, these must be taken into account when testing. These can have a large effect on fuel consumption and hence provide the potential for large fuel savings. In general, fuel savings are always theoretically possible and can be realised in most cases. There may be certain cases where the efficiency of the combustion process is secondary to another factor, such as a requirement for a reducing atmosphere, or a necessity to keep the stack temperature above the dewpoint for a certain component, but, even in these cases, it is often possible to achieve a small but noticeable fuel saving.

As can be seen from the discussion above, this question is not easy to answer. The best answer is perhaps, yes, but is it worth it? As fuel prices rise it will become more and more worthwhile to take advantage of any chance to save fuel. It is also not just a question of money. Fuel is an import commodity and is limited in supply. When it has been used up, there is no more. At the moment we still have a reasonable amount available, but there is no real sign of new technology to replace the present fossil fuels. This would imply that we should save as much as possible or risk the consequences.

It is also not in the interest of many countries to be dependent on imports of fuel or other materials any more than is strictly necessary. The potential for political blackmail in this branch was amply demonstrated in the 1970s with the oil crisis paralysing an unprepared Europe. Hopefully, the lesson has been learnt, but reserve stocks of fuels are still very low in many countries. Fuel saving will reduce this dependence and free resources to combat other internal problems. The potential is there and need not be very expensive or complicated at first.

13) How to calculate savings through higher efficiency

First of all, the relevant combustion parameters are measured. After that, starting off with high excess air, the air supply is reduced, until an increase in CO is realised. Now the burner is adjusted to a small amount of excess air, and the following result appears:

(EXAMPLE)

Readings X are before adjustment and Reading Y are carried out after adjustment of the system:

Readings X (before adjustment):	Reading Y:
Oxygen 8 %	Oxygen 3 %
$\Delta T (T_{\text{gas}} - T_{\text{amb}})$ 250°C	$\Delta T (T_{\text{gas}} - T_{\text{amb}})$ 190°C
Efficiency 85 %	Efficiency 91 %
CO 0 ppm	CO 99 ppm

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With assumed annual fuel costs of USD150.000 the savings would be as follows:

$$\frac{91 (Y) - 85 (X) \times 150.000}{85 (X)} = \text{USD}10.588,-$$

These fuel costs are by no means extreme examples. Obviously, the price of the flue gas analyser is much less than the annual saving quoted. In general, a return on investment is calculated for three or even five years. Here we have the price of the instrument within one year. Naturally there will be maintenance of the instrument and other factors involved, but the rough calculation clearly shows the potential value of a flue gas analyser in any industry branch where fuel costs are a definite factor.

Not just the cost of the fuel, but its availability should be considered. Fuel of any sort is a major strategic factor and no country wishes to be entirely dependent on outside sources. Since this is a naturally limited resource, care should be taken to use it as sparingly as possible to improve the balance of payments and to ensure an adequate supply in the future. Short-term subsidies of fuel costs to aid industry should be kept as short-term as possible, if they are granted at all. No effort should be spared to reduce the consumption, which will provide a long-term reduction in fuel costs.

Fuel saving is not just a question of reducing the outlay of a company, in many cases it is also a reduction of the dependence of the country on imports. Most fuel is nowadays imported and oil or gas make up a substantial section of the balance of payments, on the wrong side. The dependence on imports has serious political ramifications, as was seen in Europe for the first time during the oil crisis in the 1970s. Reducing the fuel imports would have a very noticeable effect on the balance of payments as well as the political status of most countries.

Fuel taxation varies very widely between countries for the consumer sector, but the greatest users of fuel are to be found in heavy industry or power generation, where taxation is generally much lower to ensure the competitiveness of the indigenous industry. No country wishes to be fully dependent on outside supply in the major sectors such as iron and steel, power generation, agriculture or general metal-working.

Combustion efficiency is also not the only factor involved in the equation. Ineffective lagging of pipework and burner can lead to immense losses far in excess of any losses due to incomplete combustion or stack loss. These factors are often ignored and this type of maintenance should be carried out assiduously before trying to find extra efficiency in the combustion processes. Fuel savings can be very high in this direction as well.

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14) The difference between "Wet" and "Dry" analysis

"Wet-Basis" is analysis without removing the water from the flue gas

"Dry-Basis" is the analysis after the water has been removed (theoretically completely, but usually in part)

A typical "Wet-Basis" measurement would be an In-Situ or across the stack measurement

"Dry-Basis" measurement is performed with extractive system such as a portable flue gas analyser with condensation trap and /or built in gas cooler/dryer.

A look at a typical flue gas composition could show the following values.

oxygen	2.20 %
carbon dioxide	13.20 %
nitrogen	71.10 %
water vapour	13.34 %
sulphur dioxide	0.04 %
carbon monoxide	0.10 %
oxides of nitrogen	0.02 %

If the water vapour is removed now, the volume of the gas decreases and the concentrations of the other components increase. If the sample is conditioned at +4°C the partial pressure of water vapour at 4°C should be used to determine the water content of the gas. However, we can ignore this concentration for our example, since this is an extremely small error well within normal measuring accuracy limits.

COMPOUND	WET BASIS	DRY BASIS
Oxygen	2.2 %	2.53 %
Carbon dioxide	13.2 %	15.23 %
Nitrogen	71.1 %	82.05 %
Water vapour	13.34 %	NIL
Sulphur dioxide	0.04 %	0.047 %
Carbon monoxide	0.1 %	0.115 %
Oxides of nitrogen	0.02 %	0.023 %

As we see, one can obtain different results depending on the methods used. This is not a problem as long as the methods used are stated and not compared with those made under another basis without correction.

Some authorities require results to be reported on a dry basis and others leave it open as long as the basis employed is stated clearly.

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15) What type of sensors are used in MRU instruments?

Most of the sensors used in MRU flue-gas analysers are of the electrochemical type.

The major elements of Toxic Gas electrochemical sensors are three coated electrodes (sensing, counter, and reference) and a small volume of an acidic or alkaline solution.

In use, the gases diffuse through an orifice on the sensing face of the sensor onto the electrode surface and cause a small electrical current. This current is amplified and measured by the electronics. The measured value is then displayed and available for printing, storing or downloading to a computer.

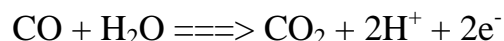
In its simplest form, a sensor operating on electrochemical principles requires two electrodes x a sensing and a counter x separated by a thin layer of electrolyte. Gas diffusing to the sensing electrode reacts at the surface of the electrode either by oxidation or reduction. This reaction causes the potential of the electrode to rise or fall with respect to the counter electrode. With a resistor connected across the electrodes, a current is generated which can be detected and used to determine the concentration of gas present.

One of the conditions required for the above sensor to work accurately is that the potential of the counter electrode should remain constant. In reality, however, the surface reactions at each electrode causes them to polarise. This effect may be small initially, but it increases with the level of reactant gas and effectively limits the concentration range the sensor can be used to measure. This effect can be counteracted by the introduction of a reference electrode of stable potential.

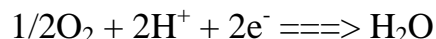
The reference electrode is shielded from any reaction, and so maintains a constant potential. Instead of the signal therefore being measured between the counter and sensing electrodes, it can now be more accurately measured between reference and sensing. With this arrangement, the change in potential of the sensing electrode is due solely to the current generated at the electrode by the reactant gas.

As the reference electrode must maintain a constant potential for correct operation, it is important that no current is drawn from this electrode. In order therefore to measure the potential difference between sensing and reference, it is not sufficient just to place a load resistor across them, as this would draw current. For this reason a potentiostatic feedback operating circuit is used.

The oxidation of carbon monoxide, for example, at the sensing electrode can be represented by the equation:



The counter electrode acts to balance out the reaction at the sensing electrode by reducing oxygen in air to water:



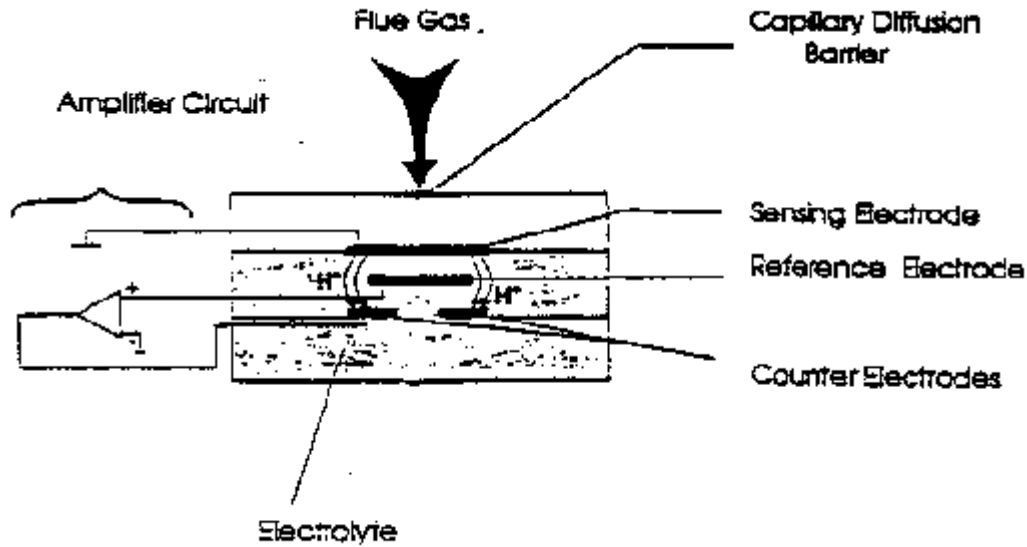
A similar equation can be given for other sensors depending on the reaction of the gas they are designed for on the sensing electrode:

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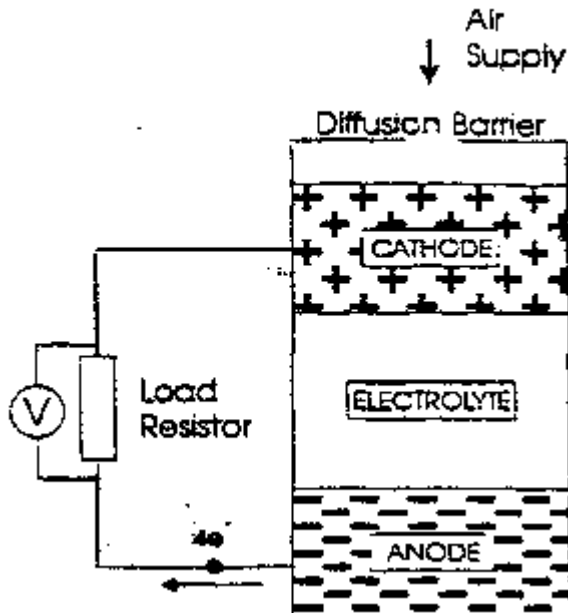
Sulphur dioxide: $\text{SO}_2 + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$

Nitric oxide: $\text{NO} + 2\text{H}_2\text{O} \rightleftharpoons \text{HNO}_3 + 3\text{H}^+ + 3\text{e}^-$

Nitrogen dioxide: $\text{NO}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{NO} + \text{H}_2\text{O}$



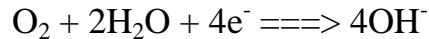
Oxygen sensors are slightly different. In use, oxygen diffuses through a membrane and the gas contacts the sensing electrode and the base solution and reacts at the wet surface of the electrode, this reaction consumes the counter electrode. The chemical change in the counter electrode allows a circuit in the instrument to measure a potential (voltage) between the electrodes. In reality, the oxygen sensor acts as a current source, so the voltage measurement must be carried out over a load resistor. This should not be large, otherwise the balance of the oxygen circuit will be upset.



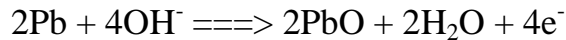
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All oxygen sensors used are of the self-powered, diffusion limited, metal-air battery type comprising an anode, electrolyte and an air cathode as shown below.

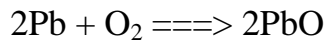
At the cathode oxygen is reduced to hydroxyl ions according to the equation:



The hydroxyl ions in turn oxidise the metal anode as follows:



Overall the cell reaction may be represented as:



The oxygen sensors used are current generators, and the current is proportional to the rate of oxygen consumption (Faraday's Law). This current can be measured by connecting a resistor across the output terminals to produce a voltage signal. If the passage of oxygen into the sensor is purely diffusion limited, this signal is a measure of oxygen concentration.

Other types of sensors may also be used, such as infrared (IR) sensors.

15.1) Cross-sensitivity of electrochemical sensors and how to handle it.

At first there was the idea of eliminating the influencing agents. That was, and still is, done by means of an NO_x/SO_x filter to eliminate their respective interferences caused on the CO cell. Furthermore, the supplier of the sensors equipped the sensors directly with the respective filters. The problem that occurred when using filters is that they used to be clogged long before the sensors were consumed. That is a particular problem when the filter is incorporated in the sensors. Since they can not be replaced, the whole sensor is useless when the filter is gone.

The need to eliminate the H_2 interferences on CO sensors was initiated by the TÜV in Germany. This is partly done using filters, but there are also sensors where the hydrogen concentration is measured independently of the CO and the compensation carried out electronically. These are then manufactured as 4-electrode sensors with a second sensing electrode.

MRU was one of the first suppliers of instruments equipped with electrochemical sensors to introduce a cross-sensitivity calculation in their instruments.

When calibrating the instrument (GA-20plus, GA-21plus, GA-40plus, GA-40Tplus and GA-60), every influence detected is stored and goes into that particular calculation. That gives MRU flue gas analysers an outstanding performance in

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comparison to most other instruments, although it is often difficult to convince people that the new instrument is correct when they have been used to incorrect readings for years.

The main problem with this method of calculating and then compensating for the effects of other gases present is that the cross-sensitivities can, of course, only be calculated for the gases measured directly i.e. no cross-sensitivities can be calculated between gas components the respective instrument is not equipped to measure directly.

As more and more of the exotic gases are becoming interesting due to legislation, so the problem of cross-sensitivity is becoming more apparent. These gases often have a large number of serious cross-sensitivities to other components and it is no longer possible to simply assume that the effects are negligible.

15.2) What is the expected lifetime of electrochemical sensors?

The expected lifetime of **oxygen** sensors used to be two years. New developments made possible an oxygen sensor with **four** years expected lifetime. There are some manufacturers who claim a much longer life-time for their oxygen sensors, but this can only be at the cost of sensitivity, since the signal is caused by consumption of the material of the sensor. To make an electrochemical sensor last longer, one must either reduce the rate of consumption and hence resolution or increase the size of the sensor.

For **toxic** sensors (CO, NO, NO₂, SO₂ etc.) **two** years lifetime is common. Experience shows that one can expect these electrochemical sensors to last about three years if the instruments are maintained properly, and the concentrations the sensors are exposed to are within the range regulations in most developed countries require.

There are, however, a number of factors that will affect the lifetime of electrochemical sensors. They will keep longer if stored at a lower temperature. It is advisable to keep them at a temperature of 20°C or less. Spare sensors are often stored in cellars (basements) or even in refrigerators. They must not be frozen, or the electrolyte will split the housing, but it is quite possible to keep them at about 4°C. Oxygen sensors will react with the atmospheric air. Since this has a high concentration of oxygen, they will, perversely, wear out quicker in storage than in use. If an oxygen sensor is to be out of use for a longer period of time, then it can be removed from the instrument and stored in nitrogen. Theoretically, the whole instrument may be stored in nitrogen, but this is seldom practicable.

The toxic sensors will last longer if the system is thoroughly flushed with fresh air after measurements have been carried out. The time they last will be very dependent on the ranges they have to measure. If they are constantly at the limit of range, then the lifetime will be reduced dramatically. In such cases it may be possible to use a sensor for a higher range, although this will necessarily reduce the sensitivity and hence the resolution of the system. An electrochemical sensor requires a certain level of humidity, otherwise the electrolyte will dry out and the membrane will be damaged. In flue gas applications this is not a problem, since there is sufficient water vapour present, but may be a factor in other applications. Here, it is probably possible to

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switch the air flow to ambient air at regular intervals and hence supply the essential water vapour pressure for a certain period of time. Failure to do so will lead to premature failure of the electrochemical sensor and unreliable results in the time beforehand. The sensor does not require much moisture, but completely dry gas is definitely not good.

Another factor that affects the lifetime of these sensors is cross sensitivity. If a component is present in high concentrations which causes a signal to be produced by the sensor, then this will consume the electrolyte of the sensor and reduce the lifetime accordingly. This may not be noticed if the instrument has a cross sensitivity compensation. It is nevertheless a much underestimated factor, as is the effect of extreme temperatures. The active part of a sensor is an electrode and electrolyte. If the electrolyte dries out, then the sensor will no longer function. For this reason, systems using electrochemical sensors should not be operated with completely dry gases. The level generally quoted is 5 % rH. This will keep the sensor in best condition and operating accurately.

15.3) How often do electrochemical sensors need to be calibrated?

Zero calibration is carried out automatically every time the instrument is switched on, or, as is possible in some MRU instruments, every time the auto-calibration of the oxygen sensor is performed (usually used for continuous measurements over a couple of hours - in connection with a gas cooler/drier).

Span calibration, for toxic sensors, is recommended to be performed at least every six months. Basically, it is dependent on the expectations in regard to accuracy one has and the amount of use the analyser sees. Some companies perform a span calibration every other week. Therefore they are able to achieve accuracies around +/- 2%. An auto-calibration for the oxygen sensors to 20.9% O₂ in air is performed every time the instrument is switched on. Or, as is possible in some MRU instruments, at pre-set intervals to ensure good readings during continuous measurement sessions.

Calibration is an important factor in the accuracy of an analyser reading. The instrument refers to the calibration results as the standard value at every measurement and has no other way to compensate for changes in the characteristics of the sensors. These do remain reasonably stable over fairly long periods, but a certain drift and tendency to a reduced signal with time is unavoidable. The quality of the calibration gas is also important, as is its homogeneity.

Calibration should be carried out at a set temperature and pressure. The signal from the sensors is defined at 20°C, so a calibration at or near this temperature is to be recommended. Better instruments, including those from MRU electronics, have a temperature sensor near the electrochemical gas sensors to allow these effects to be compensated electronically.

Electrochemical sensors have a fairly wide range of tolerance on the output at a set concentration, so they cannot be used without calibration. These tolerances do not have anything to do with the quality of the sensors, they are rather a result of the complicated chemical processes involved. Having a rough idea of the calibration value

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to be expected will allow an experienced service technician to immediately see when a sensor is nearing the end of its useful operating life.

If an analyser is used for extended periods of time it will probably prove necessary to repeat the zero calibration at regular intervals to neutralise any changes that occur with time. Particularly the zero point will tend to drift to a certain degree with time. This can not always be compensated electronically since certain factors are random and a drift that produces a negative result will be atomically treated as zero, since negative concentrations are obviously impossible. For this reason, stationary equipment will generally have a programme feature to do this automatically. This will show up as a sudden zero on the results, but such factors can easily be removed later by software.

16) Types of analyser produced by MRU electronics

For every job there is the correct tool. This old piece of wisdom applies equally well to flue gas analysis. For this reason there are hand-held analysers, analysers in soft or hard cases, 2 gas analysers, 4 gas analysers and so on. Somebody doing a quick boiler tune up on residential equipment will not need a 5 gas analyser and somebody doing an annual inspection of a 600 MW coal-fired power station will be lost with a 3 gas analyzer. To cover this wide range we also produce a 9 gas analyser, both stationary and portable for various ranges and working conditions. The infrared gas analyser is now more common and is integrated into the portable equipment as option where possible. A 6 gas analyzer may easily include 3 infrared sensors for CO₂ or CH₄. These work on the principle of infrared absorbance (absorption). Customer feedback is one of the most important factors in determining what equipment is to be developed or improved, and a series of requests for a 7 gas analyser will lead to optimisation of these types. We take pride in being at the forefront and offering what is required, from simple oxygen analyser to portable infrared or stationary equipment, otherwise known as CEMS (Continuous Emissions Monitoring Systems). Data transfer is essential with this type of flue gas analyser and a range of industry standards exist, most of which are offered such as RS232 (the standard serial communication protocol), RS485 (industry standard allowing 256 instruments to be connected in a bus). Analogue outputs for both current and voltage are to be had and the newest developments are also Ethernet compatible. This allows for an easy connection to the global internet.

There are, nevertheless, certain points that should be borne in mind when choosing a flue gas analyser. Many are constructed in a modular fashion, so there may be the possibility of expanding the capabilities of the instrument to comply with future regulations. It may be also possible to add a gas conditioning system to an existing analyser rather than replacing the entire flue gas analyser. The instrument chosen should be at least capable of covering present needs comfortably to be of any real use for future needs. There is no likelihood of regulations becoming less restrictive in future, but every chance that they will become more restrictive. The flue gas analyser will become more accurate and capable of measuring more components as these become required for EPA compliance testing or the national equivalent. The general expansion of EPA compliance testing to cover further components is a challenge to the flue gas analyser industry to produce modular instruments that will be able to meet

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future necessities. The increased number of suppliers is also a challenge to produce a low cost flue gas analyser that is efficient and accurate. The flue gas analyser will become part of all industries that are involved in the design, production or maintenance of combustion facilities.

17) Sample conditioning

There are several portable sample conditioners available on the market. Other types of sample conditioning systems are also available for other purposes, which may be more suitable for specific cases.

These range from a simple panel containing a knock-out pot and silica gel drier, (only suitable for very short term operation without the risk of damage to the analyser and not at all suitable for the measurement of soluble components such as NO_2 and SO_2 to mains powered units which combine Peltier coolers, filters, sample and condensate pumps and simple sample probes. More sophisticated units are becoming available which include heated sample probes and heated sample lines. The permeation dryer is also becoming interesting, since measurements with infrared sensors require that the water be completely removed from the system. Even low levels of water vapour will produce false peaks on the sulphur dioxide and nitric oxide measurements.

Most of these sample conditioners, with good portable flue gas analysers, are very useful tools for checking permanent installations, for use where permanent analysers are not justifiable, or technical problems exist in a particular process or furnace prohibiting the installation of a permanent system.

The success of sample systems and their associated analysers is entirely dependent on good maintenance. Any analyser system requires a maintenance schedule which must be adhered to. Experience shows that over 97% reliability is achievable with good preventive maintenance. The fuel saved because of that can alone often pay for the analyser and its maintenance, not to mention the positive effects on our environment.

Analyser maintenance is part of the cost of ownership.

In the conventional flue gas system the sample is cooled rapidly and transported to the analyser. This is satisfactory for oxygen, carbon monoxide and nitric oxide analyses.

When the gases being analysed include sulphur dioxide, nitrogen dioxide, hydrogen chloride or ammonia the sample is transported hot (heated sample line) to the sample cooler and then rapidly cooled. There are various types of sample conditioner available for this purpose. These can be separated roughly into two types: refrigerant and solid-state Peltier coolers. This is not the place for a discussion about sample conditioners. Both types work satisfactorily, but the refrigerant type is less portable and therefore seldom used with the portable equipment.

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It is preferable, but not essential, that the temperature of the sample line is capable of being controlled. It is only necessary to remain above the dew-point of the components of the gas stream. Prevention of condensation is essential and a temperature above the sample dew-point aids good reproducibility of analysis as well as accuracy. Where ammonia is to be analysed, a temperature control must be used and kept at a higher temperature. One main advantage of a temperature control is that the temperature can then be reduced when not needed. This is not really meant as a means of saving power costs, but of reducing the loading on power supply and extension cables when operating far from the high capacity cables and power sockets of the main supply. Gas analysis with portable instruments is carried out at intervals, so there is no impetus to provide a complete infrastructure for this.

The cost of these sample lines is high and may be considered a luxury. This is a mistake, and their omission may cost more in maintenance than their initial cost. Analysis errors will also result which may be the subject at a later date of litigation due to breach of legislation.

17.1) Sampling for sulphur dioxide

Like all sample systems the requirements for flue-gas analysis follow certain basic rules. There are, however, some extra points which must be borne in mind if consistent and accurate results are to be obtained.

In all cases the probes should have built-in filters, preferably heated at the exit of the probe prior to the sample line.

The next item in the sample system is the sample line. If the dew-point is high, as is the case with most flue gases then it should be heated to about 120°C, (better 180°C for some flue gas measurements). For sulphur dioxide (SO₂), nitrogen dioxide (NO₂) and other acidic gases a sample transport line with a core tube of PTFE is preferable as this will not react with the aggressive gases in the sample line.

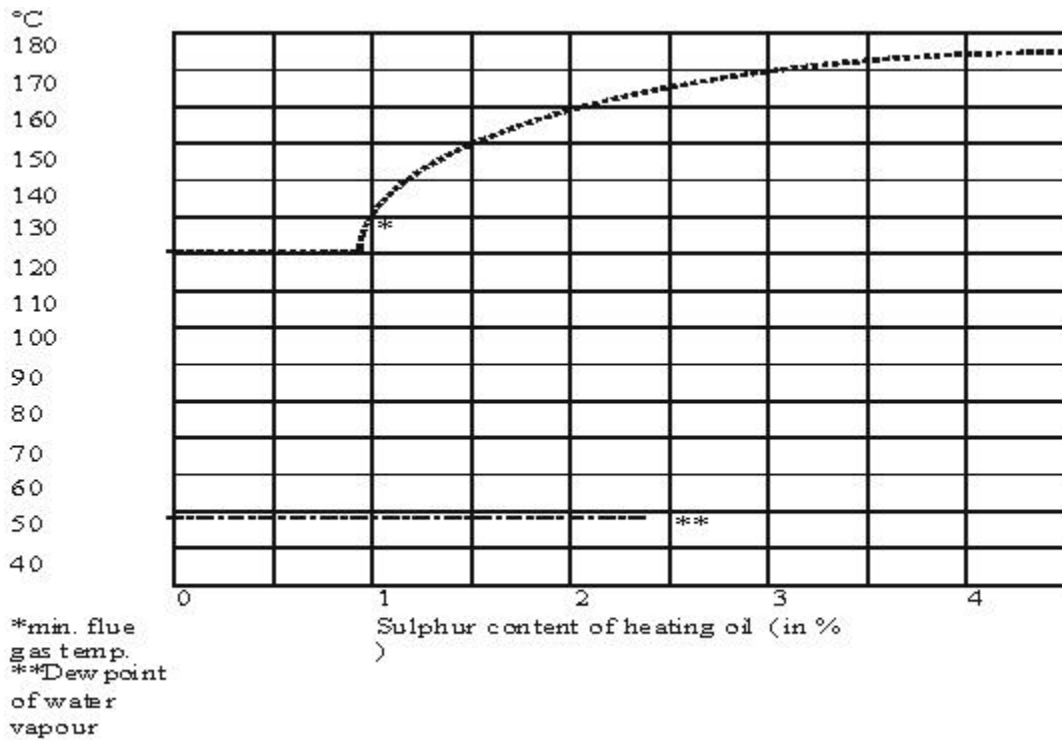
An unheated sample line may be used if the sample is already dry or deliberate cooling from the probe to the analyser desirable. In this case the sample line must fall to the analyser and incorporate a drain, usually automatic, at the lowest point. Entry of condensation into the analyser must be avoided at all costs, since this will cause damage to pumps and sensors. One larger continuous systems it is common practice to split the system, with the cooler being close to the stack and the analyser at a more convenient location. This avoids the expense and maintenance work involved with long runs of heated hose.

The sample is then rapidly cooled to + 4°C using a Peltier cooler. The sample may be either pumped to the cooler or preferably drawn by suction from the flue through the probe, sample line and cooler.

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In either case the pump requires the protection of a filter. When the sample is pumped to the cooler the condensate has to be removed. Possible ways are a peristaltic pump or (less effectively) a catch-pot.

Relationship between the dew point of flue gases and the SO₂ content



When sulphur dioxide is involved, the option of using a catch-pot or automatic drain is not really available. Sulphur dioxide is highly soluble in water and the presence of condensate will lead to grossly falsified results. This may produce the desired result for someone trying to keep an old system running where the levels of sulphur dioxide are above permitted maximum levels, but this is not really the purpose of gas analysis!

As the graph above shows, sulphur dioxide has a marked effect on the dewpoint of the gas, which is not only relevant for the measurement, but also places a lower limit on the temperature of the flue gas when it exits the stack. Temperatures below this limit will lead to the formation of sulphurous acid and sulphuric acid, which will corrode the inside of the stack extremely quickly. Measuring the concentration of sulphur dioxide to ascertain the dewpoint accurately is one of the important uses for the flue gas analyzer. It will also be necessary to mount a temperature sensor at the top of the stack to keep a watch on the dewpoint precisely. This is one of the points where a careful watch is essential to ensure that the dewpoint is not reached and that the efficiency does not become too low as a result.

The fuels used in many countries are now low in sulphur, but there are still many cases where the sulphur content cannot be reduced. The only real answer to this is to fit filters and scrubbers to the stack to remove the sulphur compounds that are formed. On large systems the sulphur can be collected and used for other purposes. It is an

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important chemical in use in many industries. Again, all the parts of the sulphur separation will have to be kept above the dewpoint to prevent droplet formation.

17.2) Nitrogen Analysis

What are the different sources of NO and NO₂ in stack gases?

Nitric oxide (NO) and nitrogen dioxide (NO₂) are the main components of NO_x, which all combustion processes involving atmospheric air can produce.

NO_x emissions contribute to the formation of acid rain and, additionally, can react with hydrocarbons in sunlight to produce a potent respiratory irritant that is commonly called smog.

There are three different sources of NO_x in combustion processes: thermal NO_x, prompt NO_x, and fuel bound NO_x.

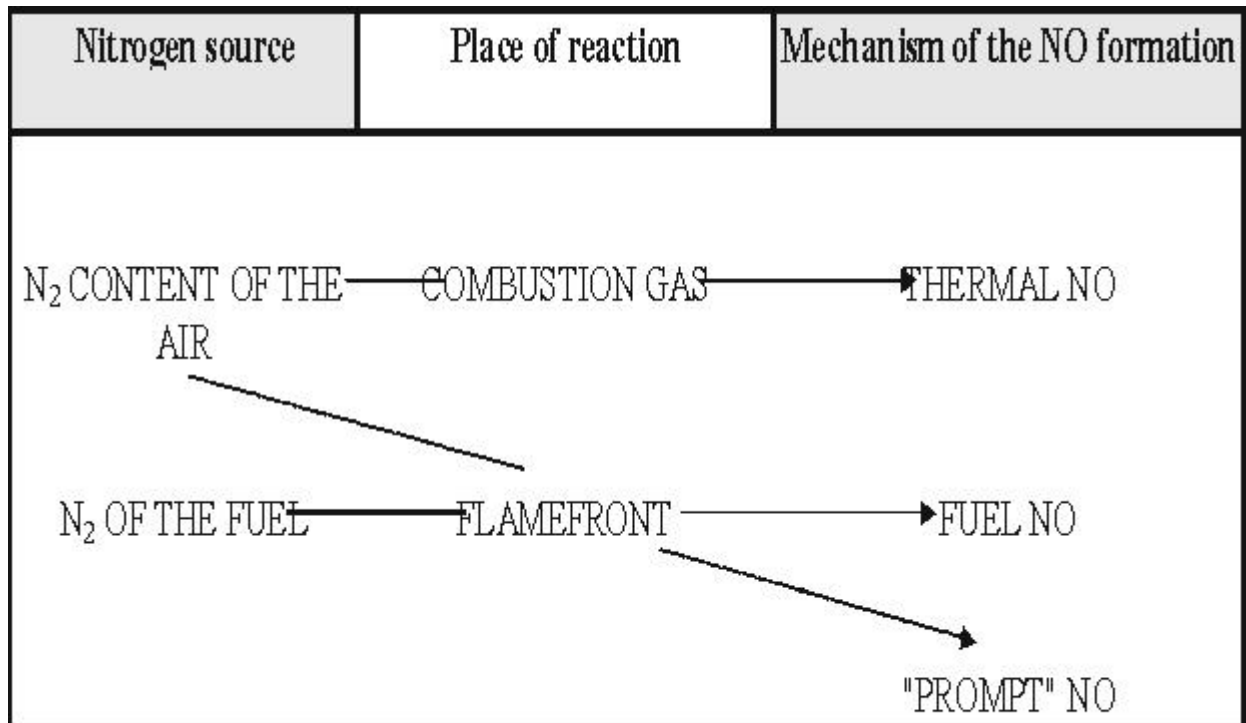
In boilers and furnaces which burn fuels low in nitrogen (gas and light oils), thermal NO_x predominates. By burning nitrogen-rich fossil fuels (heavy oils), higher concentrations of fuel NO_x are generated. Typically, nitric oxide (NO) comprises over 95% of the NO_x found in stack gases, however, a significant amount of NO converts to NO₂ in the atmosphere.

Prompt NO_x is a small amount of total NO_x, emissions that occurs during the low temperature stages of combustion. Since NO_x contributes to smog and acid rain, legislation to reduce these emissions has become much tougher.

To a lesser extent there will be formation of NO₃ (nitrogen trioxide), N₂O₄ (dinitrogen tetroxide) and N₂O (commonly known as laughing gas). These form a thermal equilibrium dependent on temperature and pressure, but are not generally present in quantities that cause serious concern.

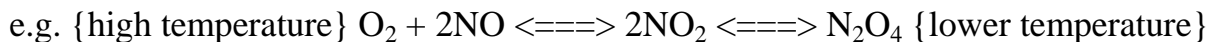
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The three mechanisms of NO formation



17.3) Sampling for oxides of nitrogen

The general principles involved are the same as for sulphur dioxide, however the relationship between nitric oxide (NO), nitrogen dioxide (NO₂), dinitrogen tetroxide (N₂O₄), and air (oxygen O₂) is a complex temperature dependent equilibrium.

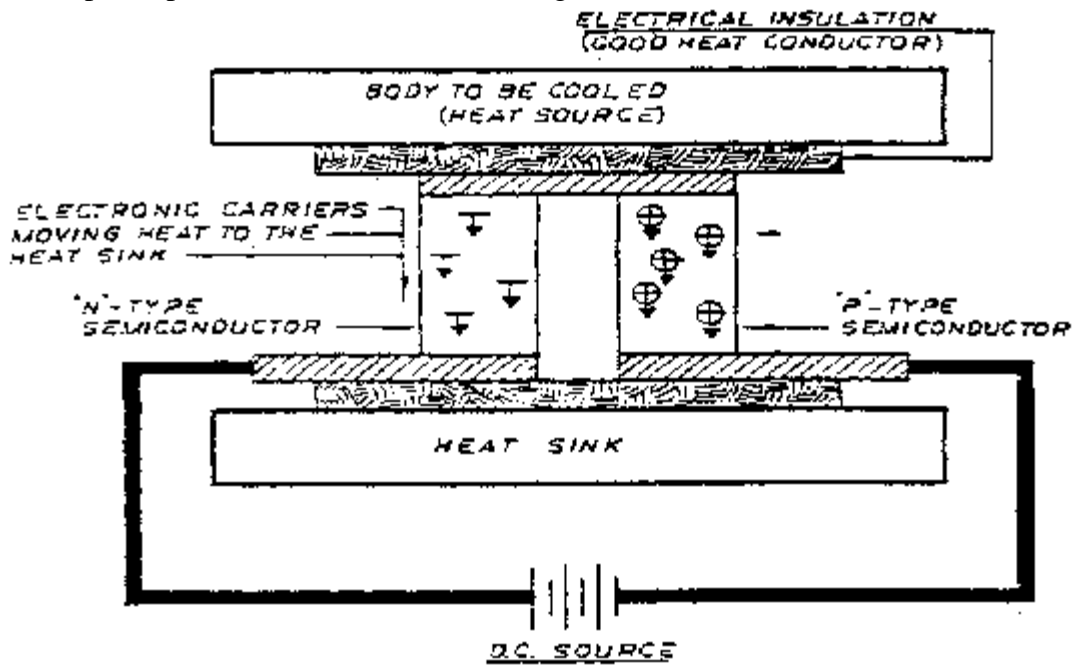


This makes life difficult for all types of spectrophotometer and hence the basic reason for calling this measurement (NO_x)

Most of the oxides of nitrogen become strong acids in the presence of oxygen and/or water. It is therefore important to keep them in the vapour state. For conventional sample systems this is best achieved by using a heated probe and sample line controlled at temperatures around 130°C. Since the common components of NO_x are nitric oxide and nitrogen dioxide, only these two are generally measured. This approximation will be accurate enough for all practical purposes.

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18) Principle of peltier modules used in MRU gas coolers / driers



The basic function of a peltier element is the reversed thermoelectric effect that is used to measure temperatures with thermocouples. The so-called Seebeck effect causes two different metals, if welded together or held in close contact, to produce a particular voltage depending on the temperature.

A peltier element uses this effect to transport heat from one side of a particular body to the other side when a current is applied.

This is used in the Peltier cooler to bring the gas quickly to the dew point. The Peltier element is not a very efficient means of cooling something, when the purely energetic efficiency is considered. It has certain advantages that lead to its use in this type of equipment. It is small and light, making it ideal for any type of portable instrumentation. It contains no coolant which may be either flammable or of a type that is restricted due to environmental considerations. The time between set-up and operational temperature is relatively short due to the low mass and lack of any medium. There is no liquid medium to create airlocks or other problems that can lead to a shortened lifetime. In the case of damage, the semiconductor element can be simply replaced with no worries about refilling a coolant system and checking for leaks, which would be practically impossible in the field. The element is also relatively inexpensive, especially when compared to systems consisting of pump, evaporator and condenser. As spare part it will be available easily worldwide, not requiring specialised parts from the original manufacturer. The major disadvantages are the relatively high current consumption and the necessity of connecting several Peltier elements after each other to achieve the desired cooling effect. A heat sink with fan will be needed to transport the temperature away from the body. The ambient temperature will therefore play a major role in the cooling effects that can be achieved with this equipment. The Peltier element will only achieve a temperature differential, there is no way of programming an exact temperature into the device. Any temperature control desired must be applied separately.

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To increase the cooling effect it is common practice to build a bank of Peltier elements, with the cold side of one in contact with the hot side of the next. Greatly increased cooling can be achieved in this way, but the power consumption will rise accordingly.

Peltier elements are used in many industries where size and weight are at a premium over power consumption. These articles are to be found in all those newest computers with extremely fast processors as an extra aid to cooling.

19) Flue gas contents

The components to be found in flue gases are shown below in the order of their usual concentrations.

Nitrogen (N₂)

Nitrogen is a colourless, odourless and tasteless gas and it does not take a major part in the combustion process. It is the main component of air (79 %) and it reduces the efficiency of the burning process since it is heated and blown out of the stack without actual function for the process.

typical flue gas content: approx. 78 to 80%

Carbon dioxide (CO₂)

Carbon dioxide is also a colourless and odourless gas that is to be found in human breath as well as in every common combustion process. The maximum allowed concentration of carbon dioxide in offices in Europe is 5000 ppm. A carbon dioxide level of 1000 ppm will reduce the ability to concentrate by about 30%. Concentrations above 15% (150000 ppm) cause immediate unconsciousness.

typical flue gas contents: gas burners / boilers 10 - 12%

oil burners / boilers 12 - 14%

Oxygen (O₂)

Is, of course a very important part since otherwise combustion could not take place. The oxygen content of the air partly reacts with the hydrogen (H₂) content of the fuel and forms water (H₂O). This water content is, dependent on the flue gas temperature, condensed and collected in a water trap or it remains in the flue gas as water vapour. The rest of the consumed oxygen reacts with the carbon in the fuel to form carbon

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dioxide and, less desirable, carbon monoxide. These escape as heated gases through the flue pipe.

Typical flue gas oxygen concentrations: gas burners / boilers 2- 3%

Oil burners / boilers 2 - 6%

Carbon monoxide (CO)

A highly toxic gas which is very nasty because it is also colourless and odourless. The maximum permitted concentration in offices is 50 ppm.

typical flue gas contents: gas burners / boilers 70 - 110 ppm

oil burners / boilers 70 - 160 ppm

Nitrogen oxides (NO_x)

Nitrogen oxides occur in all combustion processes where fossil fuels are burned, partly through oxidation of the nitrogen content of the air, as well as the organic nitrogen content of the fuel. (The whole process needs high temperatures, therefore one possibility to reduce NO_x contents is to try to keep furnace temperatures and temperatures at metallic surfaces inside the combustion chamber as low as possible.)

The nitric oxide formed oxidises with time and forms nitrogen dioxide (NO₂).

Nitrogen dioxide is a brown, toxic, water-soluble gas that can seriously damage the lungs if inhaled, as well as contributing to acid rain. In connection with the UV-rays in sunlight it helps to form ozone.

typical flue gas contents: gas burners / boilers 50 - 70 ppm

oil burners / boilers 50 - 110 ppm

Sulphur dioxide (SO₂)

The SO₂ content is pretty much dependent on the type and quality of the fuel being used. It is again a toxic gas which contributes to the formation of acid rain. The maximum allowable concentration in offices is 5 ppm. Together with water, sulphurous acid (H₂SO₃) and sulphuric acid (H₂SO₄) are formed.

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typical flue gas contents: oil burners / boilers 180 - 250 ppm

When poor quality coal is being fired, the SO₂ concentration can sometimes exceed 2000 ppm.

Hydrocarbons (C_xH_y)

Combustibles like methane (CH₄) and butane (C₄H₁₀) occur when incomplete combustion takes place. They are to a large extent responsible for global warming. These are part of a chemical family technically known as alkanes.

typical flue gas contents: oil burners / boilers below 60 ppm

Soot (smoke)

Smoke is another sign that incomplete combustion is taking place. It is measured by comparison with the well-known Bacharach scale (0 - 9). The smoke in the flue gas will cause soot to form on the internal parts of the burner.

20) M e a s u r e d V a l u e s

20.1) Directly measured values

Oxygen (O₂)

Measured to calculate CO₂ and efficiency. The value is used in many of the calculations carried out later using the measured values.

Ambient temperature (T_A)

The ambient temperature needs to be measured at the air inlet of the burner / boiler. If the air is sucked from somewhere else, the temperature needs to be measured at a point representative for the inlet air temperature, otherwise there will be errors in the calculation of efficiency.

Flue gas temperature (T_G)

The measurement should be taken in the core (hottest region) of the gas stream. That is where the carbon monoxide concentration is at its peak and the oxygen content is lowest. In industrial equipment the measurement should be carried out as soon after

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the last heat-exchanger as is practically possible. In many practical applications this is very much easier said than done, but the measurement is important for accuracy.

Carbon monoxide (CO)

In atmospheric gas installations the CO concentration may need to be detected with a so-called multi-hole probe, because the CO concentration in a chimney varies, and that probe makes it possible to sample across the whole diameter. The further along the flue the measurement is carried out, the better the gas is mixed and when a forced draught system is used, the turbulence is usually enough to mix the gas components homogeneously. Such practices appear to be dying out, and most measurements are now carried out simply in the core of the gas stream. Today's equipment produces much lower levels of carbon monoxide, so a low range sensor may be needed for some applications.

Nitrogen oxides (NO_x)

By measuring the amount of nitrogen oxides (NO, NO₂) the appropriate steps can be taken to minimise the NO_x emissions. This is particularly a factor in some areas, where the NO_x emissions are very carefully controlled and excessive emissions are taken very seriously.

Sulphur dioxide (SO₂)

The SO₂ content of flue gases is dependent on the sulphur content of the fuel and is not related to combustion efficiency. This can only really be altered by a change in the fuel or the use of filter systems. Modern fuels have very low levels of sulphur, but this is not the case with old style coal burners or some of the heavy oils in use for power generation.

Hydrocarbons (C_xH_y)

If incomplete combustion takes place, the (unburned) hydrocarbons in the form of soot can be spotted using a filter paper and, in the case of oil derivatives, detected by means of a special solvent. There are usually some gaseous hydrocarbons present, which can be measured with an appropriate sensor. The most accurate method of measuring hydrocarbon gas is an infrared sensor. This does, however, have the disadvantage of being only sensitive to one specific type of hydrocarbon, such as alkanes. There are also catalytic sensors available which react to all hydrocarbons. These have the drawback that they basically operate by combustion and hence require a certain level of excess oxygen to operate. The result will also be increased if any other combustible components of other types are present. In general, they are not

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especially accurate and the thin filament inside is very prone to damage. These catalytic (Pellistor) sensors are no longer acceptable for most flue gas applications due to the poor accuracy and the fragility of the element. Such a sensor is really designed for safety applications where there is no movement of the sensor and hence no danger of breakage. The poor accuracy of the Pellistor sensor is also less of a factor since a healthy safety margin is left in all cases. Although they react primarily to hydrocarbons and carbon monoxide, the Pellistor sensors will include any other material that can burn in oxygen, such as H_2S . This type of cross-sensitivity is unpredictable and hence cannot be compensated. The reaction of the Pellistor sensor to sulphur dioxide, SO_2 , is extreme. The sensor will be poisoned very quickly with no way of regenerating it. Pellistor sensors have now disappeared from quality instruments almost entirely for these reasons. The only thing that still speaks for the Pellistor sensor is the low price, but this stands in no relationship to the other disadvantages.

Carbon dioxide (CO_2)

For many years, carbon dioxide has been calculated from the oxygen concentration and the maximum CO_2 value for the fuel. Increasingly people are interested in directly measuring this component, partly in a drive for higher accuracy in the face of special regulations about this particular gas and partly due to the use of "indefinable" mixtures of gases that may be available as a waste product from another process. Here it is clearly not possible to calculate the CO_2 concentration with any acceptable degree of accuracy. Attempts have been made to develop an electrochemical sensor for this purpose, but the accuracy was poor, so the only real alternative is to use an infrared sensor. These may be slightly more expensive, but they do not have the disadvantages of limited operational life and regular calibration. They are a legal requirement in some countries nowadays. This information is available from your local government representatives.

Soot (smoke)

According to TÜV Standards a particular gas quantity (1.63 l) has to be sucked through a filter paper within a period of 60 seconds in order to provide accurate and comparable readings. It is generally also necessary to heat the area around the filter paper to prevent condensation altering the result. This is called Bacharach testing.

20.2) Calculated values

Carbon dioxide (CO_2)

Is an indicator for the quality of the combustion process. If there is a high CO_2 content together with low excess air, then the stack loss is at its minimum. CO_2 levels will naturally depend on the ratio of hydrogen to carbon in the fuel.

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Excess air factor (λ)

This is the ratio of the actual quantity of air present to the quantity of air that would be needed for complete combustion to take place under ideal conditions.

In real combustion processes it is necessary to have a slight excess of air present ($\lambda > 1$) in order to burn the fuel completely. This is due to imperfect atomisation of the fuel and less than ideal mixing with the combustion air.

Excess air reduces efficiency and should therefore be kept to a minimum.

Stack loss (S_L)

To be calculated after measuring the oxygen content and the difference between the flue gas and ambient temperatures.

Instead of the oxygen content, the CO_2 value can be used for the calculation as well.

Efficiency (ETA, η)

This is the percentage of the energy produced by the fuel that is available for use, not wasted.

It is calculated from the stack loss by subtracting from 100%. A further calculation is possible which takes account of the losses from incomplete combustion caused by the formation of CO.

Modern developments in the field of heat exchangers, especially the introduction of condensing burners has led to the strange condition of some heating units showing efficiencies above 100%. This is explained later.

Dewpoint

This is calculated from a number of factors, such as oxygen content, fuel type and SO_2 concentration, if known. This is the temperature at which the water in the flue gas will commence condensation. The formation of water within the stack is generally undesirable, since this will combine with corrosive gas components to form acid and attack the structure of the flue. This damage occurs more quickly than many people realise.

Flow velocity

The flow velocity can be measured in a number of ways. The two most common methods are pitot tubes and impellers. The impellers are not usually capable of

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withstanding the high temperatures met in flue gas applications, so the pitot tube is seen most often. The differential pressure connections measure the difference between static and dynamic pressure, producing a value that can be used for the velocity calculation. Theoretically, there may be a velocity profile across the width of the stack, particularly in the case of low flow rates, but higher flow rates and turbulent flow are to be expected in most cases. Turbulent flow gives a very flat and nearly constant velocity profile, reducing the errors to an insignificant level. The cross-sectional area of the stack can then be used to calculate the mass flow-rate for all components.

21) BASIC PRINCIPLES OF CALCULATING RESULTS

21.1) Quantities obtained from direct measurements (O_2 , CO, NO, SO_2)

In direct measurements the temperature values and also the concentration of those gas elements which are detected by independent electrochemical sensors are obtained. The electrochemical cell indications are proportional to the volume concentration of the detected elements expressed in ppm (parts per million).

Ambient temperature is mostly measured using a thermistor. This is a material that changes its resistance proportional to the temperature. The commonest type is probably the platinum thermistor. Flue gas temperature is generally measured with a thermocouple. A thermocouple produces a tiny electrical potential proportional to a temperature difference between two points. There are different types of thermocouple available for different temperature ranges, but most of them cover the combustion gas range.

The following quantities are obtained by means of direct measurement:

flue gas temperature T_{gas} and ambient temperature T_a , expressed in $^{\circ}\text{C}$]

volume concentration of CO [ppm]

volume concentration of NO [ppm]

volume concentration of SO_2 [ppm]

volume concentration of O_2 [%]

volume concentration of optional cells NO_2 , H_2S , H_2 , (ppm)

In addition to these standard results it is possible that carbon dioxide, CO_2 or methane CH_4 may also be measured. With these main factors all the other parameters for flue gas are calculated. There are certain sensors that have a different method of measuring to the standard volume concentration indication generally used. This is particularly common with oxygen. Here, the sensor shows the partial pressure of the gas instead of a volume concentration. Naturally it is then necessary to know the ambient pressure in order to calculate the volume concentration if needed. Generally it is enough to know the height above sea level and to calculate the ambient pressure on this basis. These sensors are used in medical equipment where the partial pressure reading is most

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important, hence the difference in technology. More accurate readings will require exact knowledge of the ambient pressure, however. This is also important when using infrared or similar technology. Here, the sensor basically "counts" the number of molecules in the light path, which will also be a function of pressure. More sophisticated infrared analysers are therefore also fitted with a sensor for ambient pressure to correct for these effects.

Some instruments have connections for external sensors or current/voltage analogue inputs. These results can then be shown on the display or stored with the concentrations and temperatures obtained from the standard sensors. These may show the fuel flow rate or gas flow velocity measured with an anemometer.

21.2) Calculating the concentration of carbon dioxide

The volume concentration of carbon dioxide, expressed in [% vol], is not usually obtained by direct measurement, but is calculated on the basis of measured oxygen concentration and the $\text{CO}_{2\text{max}}$ parameter, characteristic for the given fuel.

Formula 1 shows the formula according to which the analyser calculates volume concentration of CO_2 :

$$\text{CO}_2 = \text{CO}_{2\text{max}} \cdot \left(1 - \frac{\text{O}_{2\text{meas}}[\%]}{20.95\%} \right)$$

Some flue gas analysers are fitted with an infrared sensor for carbon dioxide, but this practice is not yet widespread. The only real deficiency in the calculation of carbon dioxide is that there is a slight but noticeable cross-sensitivity of the oxygen sensor for carbon dioxide. This effect can be compensated electronically, but it is dependent on a correct setting of $\text{CO}_{2\text{max}}$ to be effective.

Setting a fuel incorrectly will hence lead to very false readings. This also means that attempts to check the zero point of the oxygen sensor require that a special fuel be programmed with a $\text{CO}_{2\text{max}}$ value of zero. If this is not done, then the sensor will show a rest value of around 0.4% even when the oxygen concentration is zero. An analyser which does not show this error will also not display oxygen in the presence of carbon dioxide correctly, since it is not compensating for the cross-sensitivity.

One of the problems often encountered when measuring CO_2 is flue gas recirculation. Here, a proportion of the flue gas is returned to the air inlet to ensure complete combustion of the carbon monoxide or hydrocarbons. This technology was common in the automobile branch years ago before the introduction of the catalytic converter. This is not the best way to reduce emissions. It is only used to reduce a poor level of pollution under a certain border line, and is not really an attempt to address the problem of pollution production. Flue gas recirculation will also produce a higher than expected level of CO_2 and is not really suitable for calculating systems. It is mostly used to reduce the levels of NO_x in the gas outlet. Here, quite a small amount of

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recirculation can have a significant effect on NO_x due to cooling of the combustion process

The carbon dioxide value has taken on a new meaning since the Kyoto Protocol became reality. Carbon dioxide was earlier a measure of how well a combustion process was functioning, now it is recognised as a pollutant in its own right and one of the causes of global warming. Carbon dioxide will be unavoidable, so long as we are dependent on fossil fuels, but all attempts to measure the quantities produced are a start towards a future reduction. This is also one of the arguments for the increasing attention paid to renewable fuel sources. The carbon dioxide produced during combustion would be produced anyway during the decomposition of the material, and has been absorbed from the atmosphere in the first place. This makes the net balance of carbon dioxide production zero. The argument becomes slightly flawed when talking about the combustion of larger trees and other slow growing plants. There is evidence that these store a quantity of atmospheric carbon dioxide, over and above what they require for growth and the production of cellulose and other sugars. This carbon dioxide is then released during burning. True, it was absorbed from the atmosphere to start with, but it does still contribute excessively to the global production of carbon dioxide. The argument is that it was absorbed a long time ago, so is not really a part of our present carbon dioxide cycle. When talking of biomass combustion, these are generally fast-growing plants that are only one or two years old.

21.3) Calculating the concentration of nitrogen oxides NO_x

In addition to nitric oxide NO , combustion gases contain also higher oxides of nitrogen (mainly NO_2). Not all MRU portable flue gas analysers have the nitrogen dioxide sensor in the basic version. But it is possible to calculate the NO_2 contents on the basis of the measured NO . It is generally assumed that nitric oxide NO contained in combustion gases makes up about 95% of the total amount of nitrogen oxides NO_x . Some MRU combustion analyzers calculate the total concentration of nitrogen oxides NO_x according to the following formula:

$$\text{NO}_x[\text{ppm}] = \frac{\text{NO}[\text{ppm}]}{0.95}$$

If the gas analyzer is fitted with NO and NO_2 sensors, there is no need to calculate the amount of NO_2 . The NO_x concentration is calculated by the analyser as a simple sum of measured NO and NO_2 concentrations. This may be a requirement in some areas. Calculation of NO_x from NO is only possible if there is a reliable and known ratio between NO and NO_2 in the gas measured. This may not always be the case.

$$\text{NO}_x[\text{ppm}] = \text{NO}[\text{ppm}] + \text{NO}_2[\text{ppm}]$$

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In general there is a common ratio fixed in the standards of most countries. This ratio is not always the same in all countries and NO_x measurements must therefore state clearly what ratio of nitric oxide to nitrogen oxides or nitric oxide in NO_x was applied for the results. The value will lie around 3 - 5 % NO in NO_x in most cases. Cases where the NO_x proportions are thought to be very much different will require measurement of both nitric oxide and nitrogen dioxide. The higher oxides of nitrogen can generally be ignored for most stack applications, although the measurement of N_2O (nitrous oxide or "laughing gas") is becoming more common in certain countries.

The tendency is now growing to insist on a separate measurement of NO and NO_2 in many countries. The low levels of NO_2 that are generally encountered make this slightly difficult, but sensors for low ranges are becoming available and reliable. The move is probably to be greeted favourably. The older methods and the rules of thumb that have been used for years are not always accurate and measurement is generally to be chosen over guesswork!

21.4) Concentration of "undiluted" carbon monoxide CO_{undil}

To make the calculation of the carbon monoxide concentration in combustion gases independent of excess air with which the combustion process is conducted, the idea of "undiluted" carbon monoxide CO_{undil} was introduced (it is also called the CO concentration calculated for 0% O_2). The value of CO_{undil} is calculated according to the formula below:

$$\text{CO}_{\text{undil}} = \text{CO} \cdot \lambda$$

where:

CO - volume concentration CO[ppm]

λ - excess air number

Other gases can also be displayed as undiluted values. The great value of this value is that it defeats all attempts to disguise a high level of pollution by increasing the airflow and hence diluting the waste gases. Undiluted carbon monoxide is a good measure of the "true" pollution value of a burner. It shows how high the concentration would be if the burner was working at full efficiency. It is also useful in those cases where it is not possible to measure the gas concentrations before a gas dilution takes place. This is often unavoidable and the undiluted carbon monoxide is the only way to see what is really happening in the burner unit. The dilution of the flue gases is not necessarily an attempt to disguise something, but simply a part of some processes. Heated gas is often needed in industry, and often an oxidising atmosphere is essential, just as a reducing atmosphere can also be required. A reducing atmosphere would naturally be rich in carbon monoxide, whilst an oxidising atmosphere should contain as little as possible to prevent undesirable reactions.

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As can be seen, the undiluted carbon monoxide is dependent on the measurement of oxygen concentration and the knowledge of the correct fuel type. This is not always so easy, especially where non-standard or mixed fuels are used. Nevertheless, a reasonable approximation must be made to calculate the undiluted carbon monoxide with any form of accuracy. The undiluted carbon monoxide is a value that is often quoted and may be requested on official forms.

Care must be taken with this measurement should the airflow be reduced to a level producing an oxygen concentration below the official value for excess air. This can happen in certain systems with very slow control systems. Here, there will be no adjustment for the level of oxygen and the measured volumetric concentration will be shown. If needed, the result may be converted by hand afterwards. This is, nevertheless a potentially dangerous situation with the burner operating in a manner that will possibly cause the production of large quantities of unburnt products such as carbon monoxide, methane and hydrogen. Such situations should be avoided whenever possible, unless required by a particular process as discussed above.

Undiluted carbon monoxide becomes difficult to measure in systems operating on high levels of dilution due to the many inaccuracies which will all add up. This is particularly true when only trace levels of the gas can be measured. For this reason, all attempts must be made to find a measuring point as close as practically possible to the burner.

21.5) Mass concentrations of gas components

MRU flue gas analysers also make calculations of mass concentration expressed in [mg/m³] from the concentration expressed in [ppm]. Mass concentration of gas elements depends on the gas pressure and temperature. To make comparison of results possible, the idea of standard conditions was introduced, that is standard temperature and pressure values at which the mass concentration of the elements is calculated. The MRU flue gas analyser uses standard conditions of 1000 hPa and 0°C.

The screen displaying, amongst others, mass concentration of the measured gases is shown below. It should be noticed that the analyser indicates two different values expressed in [mg/m³], they are the so called absolute mass concentration and mass concentration in relation to oxygen. These values are often confused - in the next section the way they are calculated and the differences between them are explained.

* CURRENT VALUES *				

GAS	[ppm]	[mg/m ³]	[mg/m ³]	O ₂ rel= 5%
-----+-----+-----+-----				
CO	178	219	415	max 1000
NO	56	119	246	! max 200
NO _x	78	165	323	! max 250
SO ₂	115	312	240	max 400

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21.5.1) Absolute mass concentration of gas components

Absolute mass concentration defines how many milligrams of a given gas is contained in 1 m³ of combustion gas at standard conditions (1000 hPa, 0°C). The concentration value is calculated from the concentration expressed in ppm using the factor A from table 5. The following formula shows how the absolute mass concentration is calculated (here CO concentration):

$$\text{CO} \left[\frac{\text{mg}}{\text{m}^3} \right] = \text{CO}[\text{ppm}] \cdot A_{\text{CO}}$$

where:

CO[mg/m³] -absolute CO mass concentration in combustion gas (at standard conditions).

CO[ppm] -absolute CO volume concentration in combustion gas (from measurement).

A_{CO} -correction factor from table 5.

Gas	A - $\left[\frac{\text{mg}}{\text{m}^3 \cdot \text{ppm}} \right]$
CO	1.250
NO	1.340
SO ₂	2.860
NO ₂ , NO _x	2.056
H ₂ S	1.520
H ₂	0.089
Cl ₂	3.220
HCl	1.693
HCN	1.205

Table 5: Factors to convert concentration in [ppm] into mass concentration in [mg/m³] (at standard conditions 1000 hPa, 0°C).

Note: mass concentration of nitrogen oxides (NO_x) is calculated by the analyser (according to the standards) using the nitrogen dioxide (NO₂) factor.

Mass concentration calculated by a MRU portable flue gas analyzer is comparable with the results obtained by other methods (or different types of analysers) only when the calculations have been carried out based on the same standard conditions.

21.5.2) Mass concentrations in relation to the concentration of oxygen in combustion gases

As well as absolute mass concentration, the mass concentration in relation to the oxygen concentration in the combustion gases is calculated. The concentration of a given component in relation to the oxygen concentration is expressed by the following formula (as an example for CO value):

$$\textcircled{6} \quad \text{CO}_{\text{rel}} \left[\frac{\text{mg}}{\text{m}^3} \right] = \frac{20.95\% - \text{O}_{2\text{ref}}}{20.95\% - \text{O}_{2\text{meas}}} \cdot \text{CO} \left[\frac{\text{mg}}{\text{m}^3} \right]$$

where:

CO_{rel} - CO concentration in relation to oxygen expressed in [mg/m³]

O_{2ref} -reference oxygen, conventional parameter (chosen by selecting fuel or entered independently from keyboard) expressed in [% vol]

O_{2meas} - the measured concentration of O₂ in combustion gases expressed in [% vol]

20.95% - oxygen concentration in pure air

CO - the measured concentration of CO in combustion gases expressed in [mg/m³] (absolute mass concentration)

Using similar formulae, the concentrations in relation to oxygen concentration of sulphur dioxide SO₂, nitrogen oxides NO_x and other gases are calculated. The concentration related to oxygen concentration was introduced to make the evaluated concentration independent of the way the combustion process is carried out. The absolute value (expressed in [ppm]) can be lowered artificially in the combustion process with an increase in excess air (large amount of O₂ in the combustion gases). It does not have to be a decrease of the total emission. The formula which calculates concentration related to oxygen takes into account the oxygen concentration of the combustion gases, making the results independent of the excess air factor.

The parameter O_{2ref} - reference oxygen is a standard value. Standards recommend different values of this parameter for various types of fuel. In MRU flue gas analysers the value of reference oxygen can be accepted automatically in the process of fuel selection (the so-called automatic reference oxygen choice) or entered by the operator from the keyboard (the so-called manual selection of reference oxygen). Relative mass concentration calculated from two different measurements are

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comparable only if the same reference oxygen and the same standard conditions have been used.

Note : *If $O_{2meas} < O_{2ref}$ then relative concentration CO_{rel} calculated from formula is less than absolute concentration. In such a case, the analyser replaces the value of relative concentration with the value of absolute mass concentration.*

21.6) Calculating combustion parameters

Beside calculating gas component concentrations, the analyser calculates some parameters describing the combustion process. The formulae for calculating combustion parameters are empirical formulae - analysers calculate the parameters of the combustion process according to the principles predicted by DIN standards.

The most important parameter is the amount of heat convected by combustion gases to the environment - the so-called chimney loss (stack loss) S_L . Chimney loss is calculated on the basis of an empirical formula known as Siegert's formula:

$$S_L = (T_{gas} - T_{amb}) \cdot \left(\frac{A1}{CO_2} + B \right)$$

where:

S_L -chimney loss - the percentage of heat produced in combustion process which is convected with the combustion gases.

T_{gas} - flue gas temperature

T_{amb} -the temperature of the boiler inlet air (it is assumed by the analyser to be the ambient temperature)

CO_2 -the calculated (on the basis of oxygen concentration and CO_{2max}) amount of CO_2 in combustion gases, expressed in [% vol]

A1, B - factors characteristic for a given fuel type (see Table 6)

Based on the calculated chimney loss the analyser estimates the efficiency of the combustion process η (this should not be confused with total boiler efficiency)

$$\eta = 100\% - S_L$$

where: η - combustion efficiency

The above formula assumes that the only quantity decreasing combustion efficiency is stack loss. Thus, it omits incomplete combustion losses, radiation losses etc. Such a simplification is a result of the inability to measure the size of other losses with the gas

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analyser. Because of this gross simplification in the formula above it should be remembered that the efficiency calculated in this way can not be treated as precise.

However, efficiency calculated like this is very convenient as a comparable parameter when regulating the furnace.

The formula, though simplified, reflects precisely the tendencies of efficiency change, thus it is possible to observe whether the efficiency increases or decreases. It is sufficient information for the regulation process.

It is possible to take into account the efficiency reduction caused by incomplete combustion. This loss is represented by a quantity called the loss by incomplete combustion I_L . It determines the percentage of energy loss caused by the presence of flammable gases (in this case mainly CO) in the combustion gases. There will be some formation of methane in the flue gases, which will also add to the level of incomplete combustion. In most cases, however, this will be a negligible amount and can generally be ignored. The loss caused by incomplete combustion is calculated on the basis of the measured CO concentration in the combustion gases according to the following formula:

$$I_L = \frac{\alpha \cdot \text{CO}[\%]}{\text{CO}[\%] + \text{CO}_2[\%]}$$

where:

CO, CO₂ - volume concentrations of CO and CO₂ in the combustion gases

α - the factor specific for a given fuel

Calculating I_L enables correction of the previously calculated (formula 8) combustion efficiency. Then the so-called corrected efficiency η^* is calculated:

$$\eta^* = \eta - I_L$$

The last combustion parameter calculated by MRU instruments is the excess air factor λ . This factor expresses how many times the amount of air supplied to the boiler is larger than the minimum amount which is theoretically necessary to burn the fuel completely. The system calculates the λ factor on the basis of the known CO_{2max} value for the given fuel and the calculated concentration of CO₂ in the combustion gases using the formula:

$$\lambda = \frac{\text{CO}_{2\text{max}}}{\text{CO}_{2\text{meas}}}$$

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The above formula may be transformed into the form:

$$\lambda = \frac{20.95\%}{20.95\% - O_{2meas} [\%]}$$

21.7) Fuel components

The basis for correctly determining the quantities describing the combustion process is the knowledge of fuel parameters. MRU - instruments have stored parameters for several standard fuels. Table 6 presents parameters for all the standard analyser fuels.

Some of these parameters are not used at present in the calculations carried out by the analyser. They are simply present to enable them to be used in the future, should it be necessary. This may seem strange, but makes life easier for software development.

No.	Fuel	CO _{2max}	A1	B	α	O _{2ref}	Heating value
1.	Light oil	15.4	0.500	0.007	52	3	37.80 MJ/kg
2.	Natural gas	11.7	0.370	0.009	32	3	37.35 MJ/m ³
3.	Town gas	13.1	0.350	0.011	32	3	16.34 MJ/m ³
4.	Coke-oven gas	10.2	0.290	0.011	32	3	
5.	Liquid gas	14.0	0.420	0.008	32	3	
6.	Bio-diesel	15.7	0.457	0.005	52	3	37.40 MJ/kg
7.	Extra light oil	15.3	0.590	0	52	3	42.70 MJ/kg
8.	Heavy oil	15.9	0.610	0	52	3	39.90 MJ/kg
9.	Coal-tar oil	18.0	0.650	0	52	3	38.80 MJ/kg
10.	Natural gas with fan	12.1	0.460	0	32	3	37.35 MJ/m ³
11.	Town gas with fan	10.0	0.380	0	32	3	16.34 MJ/m ³
12.	Propane with fan	13.7	0.500	0	32	3	93.60 MJ/m ³
13.	Propane	13.7	0.475	0	32	3	93.60 MJ/m ³
14.	Butane with fan	14.1	0.500	0	32	3	128.00 MJ/m ³
15.	Butane	14.1	0.475	0	32	3	128.00 MJ/m ³
16.	Biogas with fan	11.7	0.780	0	32	3	24.00 MJ/m ³
17.	Biogas	11.7	0.710	0	32	3	24.00 MJ/m ³
18.	Mineral coal HV 31.5	18.8	0.683	0	69	11	31.50 MJ/kg
19.	Mineral coal HV 30.3	18.5	0.672	0	69	11	30.30 MJ/kg
20.	Lignite HV 8.2	19.1	1.113	0	69	11	8.20 MJ/kg

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21.	Lignite HV 9.4	19.1	0.988	0	69	11	9.40 MJ/kg
22.	Dry wood	19.4	0.650	0	69	11	15.30 MJ/kg

Table 6: Parameters of fuels stored in the memory of MRU analysers.

Table 6. shows the following parameters:

$\text{CO}_{2\text{max}}$ -the maximum concentration of carbon dioxide in the combustion gas, a quantity specific for a given type of fuel. The parameter determines the amount of carbon dioxide in the combustion gases if the combustion process is carried out with excess air factor λ equal 1.

A1, B - factors which appear in Siegert's empirical formula

α - the factor used to calculate loss caused by incomplete combustion.

It should be assumed

$\alpha = 69$ for solid fuels

$\alpha = 52$ for liquid fuels

$\alpha = 32$ for gaseous fuels

$\text{O}_{2\text{ref}}$ -reference oxygen - the parameter used to calculate relative concentrations of components (formula 4). It is a standard quantity. In the table, it has been assumed as in DIN standards that it is 11% for solid fuels and 3% for gaseous and liquid ones.

H_V - fuel quality - the amount of energy produced during the complete combustion of 1 kilogram (or 1m^3 in the case of gas) of fuel. This is the lower energy of combustion.

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21.8) The influence of fuel parameters on the accuracy of result calculations

As has already been mentioned, MRU combustion gas analyzers do not generally measure the concentration of carbon dioxide, but calculate it from the measured oxygen concentration and the $\text{CO}_{2\text{max}}$ parameter. On the basis of CO_2 concentration calculated in this way, the chimney loss, combustion efficiency and loss by incomplete combustion are calculated. Obviously, the fuel parameters (especially $\text{CO}_{2\text{max}}$), have a fundamental influence on calculations of combustion processes. The following results calculated by MRU combustion gas analyzers are affected by fuel parameters:

CO_2 content - depends on $\text{CO}_{2\text{max}}$

λ (excess air) - depends on $\text{CO}_{2\text{max}}$, but is cancelled out in the calculation, as is explained below.

η and η^* - depend on $\text{CO}_{2\text{max}}$, A1 and B

S_L chimney loss- depends on $\text{CO}_{2\text{max}}$, A1 and B

I_L loss by incomplete combustion - depends on $\text{CO}_{2\text{max}}$ and α .

As can be seen from the formula, the value of the excess air factor does not depend on the fuel parameters. The calculated results of gas quantities (except CO_2) and the results of temperature measurements and power quantities do not depend on fuel parameters either. The undiluted gas concentrations is an exception to this rule. Since the excess air is a factor in this calculation, it will be affected by the type of fuel chosen. In general, the fuel parameters should not be underestimated and setting the wrong fuel will often produce very incorrect results. This is a great problem in cases where the fuel is not easy to define or a mixture of fuels is in use at load-dependent ratios. The classic case is an oil refinery, where the excess process gas is used for reheating and extra oil or natural gas are added to make up any shortfall. This is discussed under a separate section as process gas, a generic term for all forms of gas produced as by-products of a chemical process and used for heating purposes. Clearly, the fuel parameters stored in a flue gas analyzer are of very fundamental nature, and it is a shame that there is no international agreement about their values. This is mainly due to the historical fact that countries have different suppliers for fuels in general, but these differences are slowly disappearing, and a time will come when the commonest fuels are identical in all countries.

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22) RECENT DEVELOPMENTS :

There have been many developments in the field of combustion technology in the last few years. This is especially true for gas burners. The newest gas burners are of the condensing type, where the flue gas temperature is below the dew-point of the gases, which lies by about 57°C for flue gases from gas burners. The water in the gas condenses on a set of special heat exchangers mounted in the gas stream. This enables the evaporation energy to be extracted from the gas as well, raising the efficiency greatly at no extra cost.

Care has to be taken to use corrosion-resistant materials, since the condensate is relatively aggressive and the flue channel has to be fitted with a stainless steel liner or equivalent, otherwise it will be destroyed fairly quickly.

The traditional calculation of combustion efficiency uses the temperature of the gases at inlet and in the stack for the calculation. A separate correction must be made to take account of the specific heat of evaporation when working with condensing equipment. This correction is of interest for the owner of the equipment, but may not be accepted officially as a measure of efficiency. Regulations in most countries specify how these parameters should be calculated and may not allow a different method.

Another new and related matter is carbon monoxide detection in and around the burner. This can be done with the same basic equipment if the hardware and software is prepared for the job.

As has been discussed above, the function as an air pollution control device is just part of the job carried out by this equipment. A flue gas analyser is even more necessary with the modern equipment. The operating data often specifies the adjustment of the burner in terms of the waste gases and it is simply not possible to adjust it in any other way. The adjustment of a condensing boiler for high efficiency is very critical. Condensation should occur in as much of the range as possible, without losing the capability to reach maximum output when necessary.

Flow Measurement to determine the exact quantity of pollutants produced is becoming more common. Many instruments are being equipped for this purpose now. Flow measurement allows the total level of pollution to be calculated. As has often been said: you can't eat a percentage, and this is just as true in reverse when talking about pollution. A cigarette lighter produces a very high level of carbon monoxide, but the total quantity is minimal. There have therefore been no serious attempts to limit the emissions from cigarette lighters! As can be seen from the linked pages, flow measurement has some aspects that make it more complicated than might appear at first sight, but the result is essential to know the amount of pollution that is produced yearly or monthly from a specific stack. Again, these methods were common for stationary equipment for a long time before being applied to portable instruments, but such additions increase the range of operation for the equipment and also provide an alternative should the CEMS be out of operation for maintenance or other reasons.