# Emission Monitoring Technologies for Combustion and Gasification Plant

dti

**TECHNOLOGY STATUS REPORT**

CLEANER FOSSIL FUELS PROGRAMME

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*Figure 1. Coal-fired power station (courtesy of Signal Group Ltd)*

## SUMMARY

The continuous monitoring of pollutant emissions to atmosphere from industrial processes is a requirement of many environmental regulators worldwide.

Limitations of available monitoring technologies have resulted in the development and application of both improved conventional techniques and novel technologies to monitor these pollutants continuously. There is a lack of adequate information on the robustness, reliability, applicability, accuracy, cost-effectiveness and comparative performance of the various technologies developed and widely used in recent years.

## BENEFITS OF THE TECHNOLOGIES

Assessment of pollutant releases to atmosphere from coal and waste-fired combustion processes may be carried out by periodic manual monitoring techniques, or by instruments that are capable of measuring gases, vapours and particles continuously. Periodic manual monitoring techniques can only provide a 'snap shot' of plant emissions, and do not give an accurate picture of the variation of pollutant release levels with time. Such variations may be due to, for example, changes in fuel composition or changes in the efficiency of pollution abatement equipment.

Continuous emissions monitoring equipment is installed for a number of reasons, for example:

- regulatory compliance
- monitoring of plant performance
- calculation of emissions inventories
- compilation of environmental impact assessments.

As in many countries, the preferred approach of the UK pollution regulators is to fit continuous monitors wherever possible.

## INTRODUCTION

The Department of Trade and Industry (DTI) has, as part of the Cleaner Fossil Fuels Programme, funded a review of the status of on-line emission monitoring technologies for combustion and gasification plant. One of the primary aims of the study was to assess the market potential for exploiting these technologies in power generation applications. The scope of the study covers emissions that are currently subject to national and international directives and/or legislation. The study does not include trace elements, as this is the subject of a separate report.

## OVERVIEW OF ON-LINE EMISSIONS MEASURING TECHNOLOGIES

Continuous emission monitoring (CEM) systems, or automated measuring systems (AMS) as they are more commonly known across the European Union (EU), can be categorised as being either extractive systems (source-level or dilution) or *in situ* systems. *In situ* systems can be further divided into point *in situ*, sometimes referred to as in-stack monitors, and path monitors, which are also known as cross-stack monitors. In coal and waste-fired combustion and gasification plant, the main flue gas parameters that are monitored continuously are:

- sulphur dioxide ($SO_2$)
- oxides of nitrogen ($NO_x$)
- particulates
- carbon monoxide (CO)
- speciated and total organic compounds
- hydrogen chloride (HCl)
- hydrogen fluoride (HF)
- oxygen ($O_2$)
- gas flow rate, water vapour content, temperature and pressure
- carbon-in-fly-ash.

The following sections provide a description of the main types of sampling systems offered by manufacturers and system builders, together with an overview of currently available technologies for measuring the major pollutant releases to atmosphere.

## EXTRACTIVE SYSTEMS

### Source-level Extractive Systems

Source-level extractive systems are those in which a sample of flue gas is continuously extracted and conveyed to the analyser using a sampling line. Three types of source-level extractive systems are marketed commercially:

- hot/wet systems

*Figure 2. Multi-component extractive gas analysers (courtesy of Signal Group Ltd)*

- cool/dry systems with conditioning at the probe
- cool/dry systems with conditioning at the analyser enclosure.

## *IN SITU* SYSTEMS

### Point *in situ*

Point *in situ* systems perform measurements at a single point in the stack, as do extractive system probes. The point, however, may extend over a few centimetres  or to a metre or more. The sampling path will be relatively short compared with the stack or duct diameter, so the sampling location must be carefully chosen to ensure that the sample is representative of the flue gas.

### Path Monitors

Path monitors usually measure over the entire stack or duct diameter. They are based on a beam of a certain wavelength that crosses the duct and is attenuated proportionately to the concentration of the target compound. In some systems a pipe may be used in the stack for support or calibration purposes. There are two basis types of path systems: single pass and double pass. These systems are a much simpler design than extractive systems.

*Figure 3. Point in situ gas analyser (courtesy of Procal Analytics Ltd)*

## CURRENTLY AVAILABLE TECHNOLOGIES FOR MEASURING THE MAJOR POLLUTANT RELEASES TO ATMOSPHERE

Table 1 summarises currently available techniques for the continuous and semi-continuous measurement of gaseous and phase-partitioned species commonly monitored in releases to atmosphere from coal and waste-fired combustion and gasification plant. It should be noted that some techniques, for example mass spectroscopy and ion-mobility spectrometry, are capable of measuring more determinands than are identified in the table. However, these techniques would not normally be used for the measurement of species such as $SO_2$, $NO_x$ and CO owing to their relative cost and complexity.

*Table 1. Currently available technologies for measuring the major pollutant releases to atmosphere*

| **Analysis Technique** | **Pollutant** | | | | | |
|---|---|---|---|---|---|---|
| **Extractive Systems** | **$SO_2$** | **$NO_x$** | **CO** | **VOC** | **HCl** | **HF** |
| Simple non-dispersive infrared (NDIR) | ✓ | ✓ | ✓ | ✓ | ✓ | |
| Luft detector NDIR | ✓ | ✓ | ✓ | ✓ | | |
| Photoacoustic detector | ✓ | ✓ | ✓ | ✓ | | |
| Gas filter correlation (GFC) NDIR | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Differential optical absorption spectroscopy (DOAS) | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Fourier transform infrared spectroscopy (FTIR) | ✓ | ✓ | ✓ | ✓ | | ✓ |
| Non-dispersive ultraviolet (NDUV) | ✓ | ✓ | | | | |
| Ultraviolet fluorescence | ✓ | | | | | |
| Electrochemical cells | ✓ | ✓ | ✓ | ✓ | | |
| Flame photometric | ✓ | | | | | |
| Conductivity (conductometric) analyser | ✓ | | | | ✓ | |
| Chemiluminescence analysers | | ✓ | | | | |
| Flame ionisation detectors | | | | ✓(Total VOC) | | |
| Photo ionisation detectors | | | | ✓(Total VOC) | | |
| Gas chromatography | | | | ✓ | | |
| Mass spectroscopy | | | | ✓ | | |
| Ion-mobility spectrometry | | | | ✓ | ✓ | ✓ |
| Potentiometric analysis | | | | | ✓ | ✓ |
| ***In situ* systems** | **$SO_2$** | **$NO_x$** | **CO** | **VOC** | **HCl** | **HF** |
| Differential optical absorption spectroscopy (DOAS) | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Derivative spectroscopy | ✓ | ✓ | ✓ | | ✓ | ✓ |
| Gas filter correlation (GFC) NDIR | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| High temperature electrochemical cells | ✓ | ✓ | | | | |

The following sections contain a description of the generic technologies identified in the above table.

## Simple Non-dispersive Infrared (NDIR)

Many gaseous pollutants absorb light energy in one or more regions of the spectrum. $SO_2$ and a wide range of other gases absorb both infrared radiation and ultraviolet radiation. Each type of pollutant molecule will absorb light at a characteristic wavelength, and can, therefore, be distinguished from other pollutant species.

Continuous emission monitors using this principle apply the Beer-Lambert Law, which states that the transmittance of light (ie the ratio of the intensities of the transmitted and incident light) through a medium that absorbs it is decreased exponentially.

Heteroatomic gaseous molecules, ie those which contain two or more dissimilar atoms in the molecule, display unique absorption characteristics in the infrared region of the spectrum. Homoatomic molecules containing only one type of atom within the molecule do not produce characteristic vibrations when exposed to light in the infrared region; therefore they cannot be measured by this technique. This is fortuitous, as most flue gas samples contain large proportions of nitrogen and oxygen, which would completely mask absorptions by other gases in the sample. By using this principle an instrument can be designed to measure pollutant gas concentrations. Non-dispersive photometry analysers using infrared (NDIR) and ultraviolet (NDUV) have been developed for a wide range of gases.

Simple NDIR analysers use filters or other methods to measure the absorption of light over a relatively small range of wavelengths centred at an absorption peak of the molecule of interest. In a simple NDIR analyser, infrared light is emitted from a source such as a heated coil or other type of infrared radiator. The light is transmitted through two gas cells: a reference cell and a sample cell. The reference cell contains a gas such as nitrogen or argon that does not absorb light at the wavelength used in the instrument. A sample of the gas is passed through the sample cell of the instrument. As the infrared beam passes through the sample cell, pollutant molecules will absorb some of the light. As a result, when the light emerges from the end of the sample cell it will have less energy than when it entered, and it will also have less energy than the light emerging from the reference cell. The energy difference is detected by, for example, a solid-state detector. The ratio of the detector signals from the two cells gives the light transmittance, which can be related to the pollutant gas concentration.

Simple NDIR analysers are still supplied for applications where only one gaseous species is to be monitored. They are relatively low cost, reliable and robust. A limitation of analysers based on this principle is that gases that absorb light in the same spectral region as the gas of interest will cause a positive interference in the measurement. Water vapour and $CO_2$ are strongly absorbing in the infrared region and must be removed from the sample before the gas enters the analyser. One solution to this problem is to use absorption cells arranged in series, as in the Luft detector.

## Luft Detector NDIR

The Luft type detector or pneumatic detector consists of a reference cell, a sample cell and, in the case of single component analysers, two gas-filled absorption cells arranged in series. The cells are connected in such a way that any pressure difference between the cells can be detected by either a flow sensor, or in some designs, by a type of strain gauge known as a microflow sensor. The cells in the detector are filled with the gas to be measured, in this case $SO_2$. Appropriately filtered infrared light is made to pass through both cells. More light is absorbed in the first cell than in the second cell due to the distribution of energy in the light (higher energy at centre of band, lower at band ‘wings’). The light energy is absorbed by the $SO_2$ in the cells, causing the gas to heat up. Differential heating caused by the difference in incident IR light causes a differential pressure between the two cells in the detector, which is detected either by distortion of the diaphragm (measured by strain gauges) or by flow between the cells. Many different designs of detector are available with various improvements having been introduced over the years to both increase sensitivity and decrease interference. The dual beam analyser has been a standard measurement analyser for $SO_2$ at large combustion plant (LCPs) across Europe and many have received Type Approval in Germany. In recent years, single beam analysers with Luft type detectors have also become available. Analysers with Luft type detectors are more susceptible to problems associated with vibration than analysers with solid-state detectors, although the use of microflow sensors has helped overcome this problem.

## Photoacoustic Detector

A variant of the pneumatic detector technique is the photoacoustic detector. Analysers based on this principle of operation monitor acoustic waves resulting from the absorption of chopped light by molecules in a sealed sample cell.

In a light-absorbing molecule, when vibrational-rotational energy dissipates absorbed light energy into kinetic energy, the pressure will increase in the sealed chamber in which they are confined. If the light beam is turned on and off, the pressure will alternately increase and decrease, producing a pressure pulse or acoustic signal. In practice this is achieved by placing a rotating chopper between the light source and the measurement chamber. When the chopper produces pulses between 20Hz and 20kHz frequency, the pressure pulse can be detected by sensitive microphones.

By placing different optical filters in a carousel located between the chopper and measurement chamber, a range of organic and inorganic compounds can be measured to ppb levels. In the photoacoustic technique light absorption is measured directly, so if there is no absorbing gas in the measurement cell, no pressure pulse will be generated. If some gas is present some sound will be generated and if more gas is present then more sound will be generated. The technique does not provide continuous analysis, as the sample must be sealed in the measurement chamber before the analysis sequence can begin. This cycle typically takes 40 seconds to complete for five determinands plus water vapour. For stack monitoring applications the technique is usually combined with a dilution sampling system.

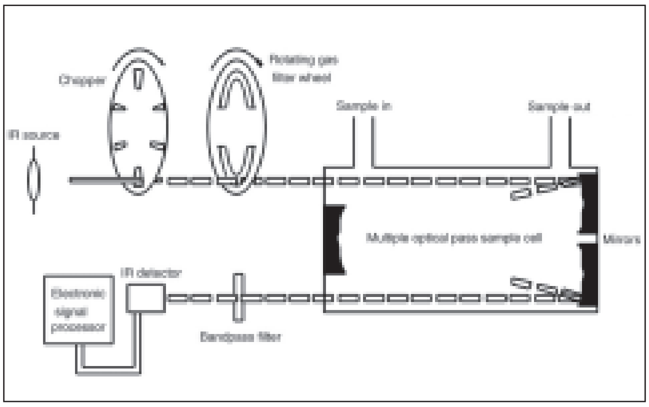

*Figure 4. Gas filter correlation analyser (courtesy of DRC Consultancy Services)*

## Gas Filter Correlation (GFC) NDIR

A type of NDIR technique, which is widely used in *in situ* monitors, is also applied to extractive system analysers. The gas filter correlation (GFC) technique uses a reference cell that contains a 100% concentration of the pollutant, instead of the 0% concentration in the techniques discussed previously. Radiation from an infrared source passes through a filter wheel, which contains a neutral gas such as $N_2$, in one cell and the gas of interest in the other cell. The light is then passed through a modulator that creates an alternating signal. When the instrument is operating, the filter wheel is continuously rotating. When light passes through the gas filter it will be attenuated. The gas filter contains enough of the target gas to remove most of the light at the wavelengths where the target gas absorbs. The wavelengths not absorbed are not removed but are passed on to the detector. The net result is a reduction of light energy reaching the detector. When the light passes through the neutral cell its intensity is not reduced. If a sample of gas containing the target pollutant is introduced into the sample cell, the molecules will absorb light energy at the absorption wavelength of the target gas. Because the gas filter was chosen to absorb energy at the same wavelengths, the absorption is already complete in the gas filter cell beam, and the detector will see the same signal as it did when the sample cell contained zero gas. The beam passing through the $N_2$ side however, will carry less energy because light is absorbed by the target gas in the sample cell. The difference between the two beams is monitored, and can be related to the concentration of the gas of interest in the sample. Other gases having spectral patterns in the same regions as the target gas will not affect the measurement, as they do not correlate. This technique is popular in the UK, with most manufacturers offering analysers based on the GFC principle of operation. Analysers are robust, relatively low cost and less sensitive to vibration effects.

## Differential Optical Absorption Spectroscopy (DOAS)

Another non-dispersive method measures light absorption at different wavelengths, those at which the molecule absorbs energy and those at which it does not. In this system a reference wavelength is used instead of a reference cell as in techniques described previously. The underlying principle behind the method once again is derived from the Beer-Lambert law.

The technique, known as differential absorption spectroscopy or differential optical absorption spectroscopy (DOAS), is applicable to both extractive system analysers and *in situ* systems. In a typical system a light source is used to emit light at many different wavelengths and transmit it through a cell containing the sample gas, or across the stack. The detector signal at the light wavelength where no energy is absorbed is used as a reference measurement for the signal obtained at the wavelength where energy is absorbed.

The differential absorption spectroscopic technique has been used for many years. The earliest designs used filters to select the light wavelengths, but other techniques have since been developed including:

- diode lasers
- photodiode arrays
- moving slits.

The most recent analyser designs use infrared diode lasers. By varying the voltage or temperature across a diode laser it can be made to emit light at different wavelengths. Analysers based on the DOAS principle are popular in the UK for the cross-stack monitoring of multiple components. One of the main suppliers of systems based on this technology in the UK uses analysers manufactured by Opsis of Sweden.

In the Opsis version of the DOAS principle, a high-pressure xenon lamp located in a stack-mounted assembly generates visible, infrared and ultraviolet light. The light is focused and directed across the stack or duct to be monitored. A receiver unit located on the opposite side of the duct collects the light and focuses it on to a fibre optic cable. From here the light is conducted through the optic cable to the analyser, which can be located many metres away. In the analyser the light enters a spectrometer, where it is separated into narrow wavelengths using an optical grating. An optical grating is a polished surface upon which have been etched fine lines. In the UV version of the analyser there are 1200 of these lines per millimetre. The optical grating moves in order to select the wavelength of interest; the resultant light is scanned by a moving slit and is finally converted into electrical signals by a detector.The electrical signal is matched to previously obtained absorption curves, which are stored in the machine's memory. From this different gas concentrations can be calculated.

## Fourier Transform Infrared (FTIR) Spectroscopy

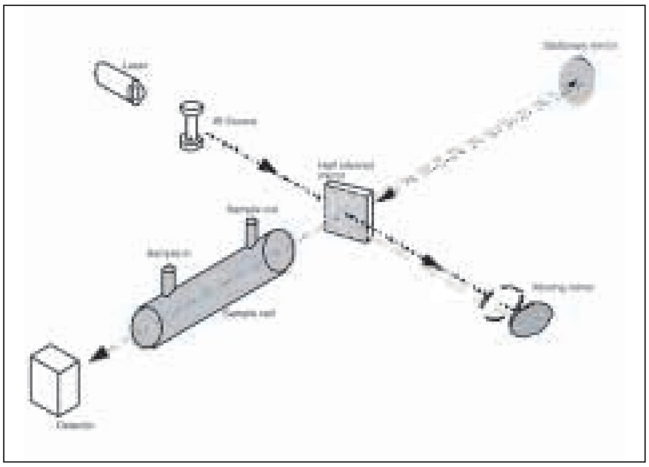

*Figure 5. Fourier transform infrared spectroscopy (courtesy of DRC Consultancy Services)*

The technique of FTIR spectroscopy is growing in popularity for the multi-component analysis of stack gases. Analysers based on this principle of operation are capable of measuring up to 50 determinands concurrently with very fast response times and fewer cross-interferences than NDIR analysis methods. A further attraction of the FTIR technique is that analysers do not require frequent calibration against reference materials. Once the instrument has been calibrated, the calibration data are retained as a spectral library, which is stored as software. Essentially the FTIR technique provides a 'picture' of the total absorption spectrum of the sample gas over a broad spectral range. Instruments typically have a range from 2.5 to 25µm.

The heart of the system is the interferometer, in which light from an infrared source is divided into two beams by a beam splitter. Each light beam is made to travel a different path, and then recombine. One of the beams strikes a moving mirror, which changes the distance over which the beam travels. A helium-neon laser measures extremely accurately the position of the mirror. The light beams recombine, and pass through the sample cell to the detector. As the beams split, travel different distances and then recombine they constructively and destructively interfere, depending on whether they are in phase or out of phase.

The 'picture' or interferogram that is subsequently built up by this process contains all the information required to identify and quantify the gases present in the sample cell. However, the interferogram is extremely complex and cannot be interpreted by direct observation. Instead, the data are subjected to a mathematical procedure known as a Fourier transform, which 'develops' or 'transforms' the data. Instruments contain a library of spectra, and by comparing the sample data with the library the sample can be analysed.

## Non-dispersive Ultraviolet (NDUV)

The characteristics of light in the ultraviolet (UV) region of the spectrum (shorter wavelength, higher energy) lead to molecular electronic transitions when the light is absorbed. Absorption of ultraviolet photons excites the electrons of the atoms within the molecule to a higher energy state. The excited electrons quickly lose the energy by returning to the ground state by one of four methods: disassociation, where absorption of high-energy photons can cause the electron to leave the molecule completely, causing it to fragment; re-emission, where an identical photon is re-emitted as the electron decays back to its ground state; fluorescence, where a photon is emitted at a lower frequency than the original absorption as the electron decays back to its ground state, causing the gas to appear to glow; and phosphorescence, which is a similar process to fluorescence, but takes place over a longer time period.

Analysers that are designed to operate in the UV region typically employ the differential absorption technique. Analysers designed to measure $SO_2$ measure UV light absorption at a wavelength in the $SO_2$ absorption band centred at 285nm. This is then compared with the absorption at the wavelength region of 578nm where there is no $SO_2$ absorption. As in the DOAS technique described previously, a reference wavelength is used rather than a reference gas cell.

Differential absorption NDUV instruments have proven to be very reliable in source monitoring applications. This technique has relative freedom from interferences.

## Ultraviolet Fluorescence

Ultraviolet fluorescence analysers for $SO_2$ are based on the absorption of UV light at one specific wavelength by the $SO_2$ molecules, and its re-emission at a different wavelength.

Commercially available instruments contain either a continuous or pulsed source of UV radiation. Filters are used to produce a narrow waveband around 210nm. The light emitted from the excited molecules is first passed through a filter and then to a detector photomultiplier tube. The amount of light received at the specific wavelength is directly proportional to the number of $SO_2$ molecules and is a measure of concentration in the measurement cell, provided the sample flow rate is tightly controlled.

A problem with this measurement principle is the ‘quench effect’ caused by the capture of the emitted radiation from the $SO_2$ molecules by other molecules present in the gas, eg $CO_2$, $O_2$, $N_2$ etc. The quenching effect varies depending on the molecule involved, and it is therefore very difficult to compensate for this effect when the matrix gas containing $SO_2$ has a time-variable composition, eg a boiler flue gas. This effect has limited the use of this type of analyser for emission monitoring purposes, although it has found wide application as an ambient air analyser for $SO_2$ where the matrix gas, ie ambient air, does not vary significantly in composition. UV fluorescence analysers do not suffer the same degree of cross sensitivities as the NDIR systems.

UV fluorescence analysers can be used for emission monitoring purposes at LCPs if a high ratio dilution sampling system as described earlier is used. The dilution results in a matrix gas that has a relatively stable composition and the characteristics of polluted ambient air. This overcomes the variable quench effect of the gas composition, while at the same time maintaining the high selectivity and lack of interferences associated with UV fluorescence. This type of system has found wide acceptance for source monitoring in North America. A point to note, however, is that at low $SO_2$ concentrations in the stack gases, the quality of the dilution air will significantly affect the measurement result.

## Electrochemical Cells

Several portable systems have come on the market in recent years that measure a wide range of flue gas components using electrochemical cells. These have been further developed, in some cases, to extractive systems designed for continuous operation. The cells are fuel cells that use two, three or four electrodes depending on design. A typical three-electrode design has a sensing electrode, a counter electrode and a reference electrode. Gas diffusing to the sensing electrode reacts at the surface by oxidation.

The current generated in the cell is proportional to the $SO_2$ concentration in the gas around the cell. This type of cell displays certain cross sensitivities ($NO_2$ and CO) and the flue gas must be filtered, cooled and the water vapour removed prior to the measurement. The cross sensitivities can be reduced or eliminated by either gas filters or electronic compensation.

Fuel cells are not generally designed for continuous operation and overloading (ie concentration of pollutant above the nominal operating range) will cause significant measurement drift and a delay time before the cell can recover and recommence operation. It would appear that good results could be obtained with an analyser that is designed for intermittent discrete measurements. However, extractive continuous monitors based on this technology for $SO_2$ have not yet been proved in the market. These types of system are inexpensive, simple and rugged, but they have a slow response and a limited cell life.

## Flame Photometric

Flame photometric analysers are specified in Environment Agency Technical Guidance Note M2 for the measurement of total sulphur. The technique is non-selective, and is not specific to $SO_2$. It is therefore rarely used for continuous monitoring.

## Conductivity (conductometric) Analyser

This type of analysis is based on the change of conductivity of an absorbing solution following contact with the flue gas sample and absorption of the $SO_2$. A heated sample line is used to transport flue gas to the analyser. A Teflon sampling head takes a small flow of gas, bringing it into contact with a hydrogen peroxide solution. The solution is transferred to a measurement cell and its conductivity is measured. The accuracy of the measurement depends on the accuracy of flow control for the gas and absorbing solution. The measured $SO_2$ concentration is reported on a dry basis. A similar principle is also used for the measurement of hydrogen chloride.

An analyser has received Type Approval in Germany for the minimum measurement range 0 to 400mg.m$^{-3}$. The main advantages of these analysers are reported as:

- simple, low-maintenance system
- no cooler/condenser is required in the gas sampling system, which eliminates the possibility of sample loss during water vapour removal
- good sensitivity and accuracy, especially at low concentration levels.

The response time, however, is slow and therefore the system is not suitable for transient emissions.

## Chemiluminescence Analysers

Chemiluminescence is the emission of light energy that results from a chemical reaction. It was found in the late 1960s that the reaction of NO and ozone ($O_3$) produced infrared radiation from about 500 to 3000nm.

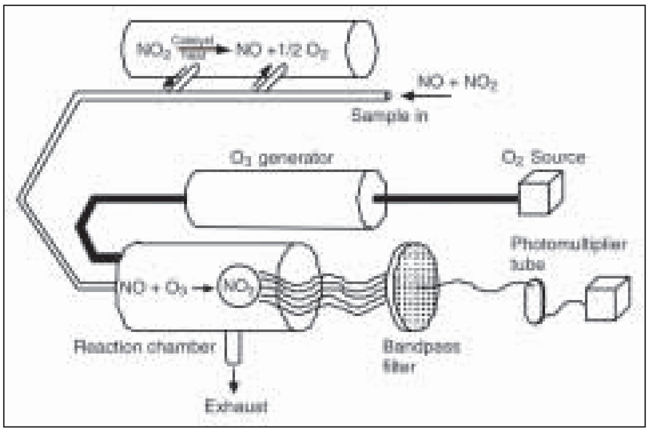

*Figure 6. Chemiluminescence analyser (courtesy of DRC Consultancy Services Ltd)*

Nitrogen dioxide ($NO_2$) does not undergo this reaction and must be reduced to NO before it can be measured by this method. Most commercial analysers contain a converter that catalytically reduces $NO_2$ to NO. The NO (converted from $NO_2$) plus the original NO in the sample is then reacted with $O_3$ as described above to give a total NO + $NO_2$ ($NO_x$) reading.

Chemiluminescence monitors are well established for the monitoring of $NO_x$. In North America they are used with conventional sampling systems and also with high ratio dilution samplers. The method is also well established for ambient air monitoring. These monitors have very low detection limits (of around 0.1 ppm) and a wide range (up to 10,000 ppm), plus a short response time of a few seconds.

## Flame Ionisation Detector

The flame ionisation detector (FID) is the industry standard for the measurement of total hydrocarbons. The FID is capable of sensing most organic compounds and because of its relatively high sensitivity, it has become widely used in environmental applications.

In a typical FID the gas sample enters the base of a combustion chamber, where it is mixed with either hydrogen or a mixture of hydrogen and helium. The mixture is burned in a jet with oxygen at a temperature of around 2100°C. The flame produces ions and free electrons. A current is applied between the burner and a collector plate, and the ions and free electrons increase the current flow in the circuit, which is sensed by an electrometer. The current is approximately proportional to the number of carbon atoms entering the flame, but the response of the detector is slightly different for different types of organic compounds. As a result the detector must be calibrated for the compounds being analysed to achieve the best accuracy.

The extractive sampling arrangement can be either cold or hot. Hot systems provide a more accurate measure of the hydrocarbon content, as there are no losses of sample in chillers or dryers, although they are more difficult to operate continuously because of maintenance requirements. Close-coupled point *in situ* FIDs are available which overcome the problems related to extractive sampling.

The FID is convenient to use in source sampling applications, since it does not respond significantly to other gases in the sample such as $N_2$, water vapour, CO, $SO_2$ and NO. However, organic compounds that contain nitrogen, oxygen or halogen atoms may give a reduced response.

## Photo Ionisation Detector

In a photo ionisation detector (PID), a light in the UV region of the spectrum ionises organic molecules. The major components of the flue gas sample such as $O_2$, CO, $N_2$, $CO_2$ and water vapour are not ionised by the UV source. A typical PID analyser consists of a UV lamp and a pair of electrodes to measure a current proportional to the concentration.

Different molecules require different energies to photo ionise, and the frequency of the light used in the PID may not ionise all of the organic species present in the sample. UV lamps of varying intensities are used to monitor complex mixtures of organic compounds.

PIDs are used in conjunction with gas chromatographs, or alone as portable analysers, where the technique can be used to produce extremely rugged and compact instruments. However, as the PID technique can be non-selective, analysers of this type are usually used as screening devices. For example, portable PIDs are widely used to detect hydrocarbon leaks in oil refineries. Because methane is not ionised by UV light it cannot be detected using this method.

## Gas Chromatography

Gas chromatography (GC) is used to isolate the individual components of a mixture of organic and inorganic compounds from each other for subsequent identification and quantitative analysis. GC is based on the selective distribution of compounds between a stationary and a mobile phase (carrier gas). In the process, the moving gas phase passes over a stationary material that is selected to either absorb or adsorb the organic molecules contained in the sample gas. The stationary phase can be either liquid or solid, and is contained in a long, thin tube, commonly known as a ‘column’. Columns are made from fused silica, glass or stainless steel.

In an ideal column operated under ideal conditions, each molecular species will exit the column at a different time. Selecting the appropriate column and operating it under the appropriate temperature with a suitable carrier gas flow rate will enable separation of the gas sample into its individual components. It should be noted that the technique is not truly continuous.

The compounds separated in a chromatographic column must be detected and quantified. Many types of detectors are available, the most common in source monitoring applications are FID and PID.

Analysers based on the principle of gas chromatography are complex and expensive.

Although portable versions are available, they are not often used for the continuous measurement of organic compounds in emissions to atmosphere from LCPs and waste incinerators.

## Mass Spectrometry

In the technique of mass spectrometry, molecules are ionised by high-energy electrons or by chemical or photo ionisation, and the resultant molecular ions and ion fragments are separated according to their mass-to-charge ratio (m/e). This separation produces a mass spectrum of the different ions generated from the fragmentation of the molecules. The mass spectrum is unique to the original molecule. Different mass separation devices are used such as time-of-flight, quadrupole mass analysers and ion traps. In source testing, the quadrupole mass analyser is most commonly used. With this technique, an oscillating field of radio frequency energy filters ions that have a specific mass-to-charge ratio.

The linear quadrupole mass analyser operates by oscillating the ions in a radio frequency field around four charged cylindrical rods (the quadrupole). Most of the ions passing through the field will oscillate with increasing amplitude and strike the rods, but there will be a combination of field frequency and voltage where ions of a specific m/e ratio will pass through to the detector. The radio frequency is therefore scanned to obtain the mass spectrum. The mass analysers used in mass spectrometers are operated under vacuum, typically $1 \times 10^{-5}$ to $1 \times 10^{-6}$ mmHg, in order to minimize scattering by collision with other ions and molecules. When combined with a gas chromatograph both qualitative and quantitative information can be obtained, since pre-separation in the column can enable the mass spectrometer to analyse each compound individually as it exits the column.

Although portable quadrupole mass spectrometers and gas chromatograph/mass spectrometer combinations are available, owing to their cost and complexity they are seldom used for the continuous monitoring of emissions from LCPs. A mass spectrometer has been used in the UK for the analysis of fuel gas from a crop-fired gasifier.

## Ion-mobility Spectrometry

Ion-mobility spectrometry is a technique similar to time-of-flight mass analysers used in mass spectrometry, except that the analyser operates at ambient pressure, and the ions drift to the detector in an electric field. In this method a radioactive source ionises the sample. The ions then drift in an electric field to an electrometer. The mobility of the ions through the field is dependent on the charge, mass and shape of the molecule. Smaller ions have a greater drift velocity than larger ions, and reach the detector earlier. The resulting instrument signal showing the different ion signals as a function of time looks similar to a chromatogram. Concentrations are determined from the peak heights.

A wide range of gases such as aldehydes, ketones, amines and polyaromatics are said to be measurable by this technique. Use of ion-mobility spectrometry is commonplace for the detection of chemical warfare agents and explosives. The principle has been applied to stack emissions monitoring in the USA, it is not currently used in the UK.

As mentioned earlier, the continuous measurement of organic compounds in flue gases is not required on coal-fired plant in the UK. Carbon monoxide is measured at some installations as an indication of combustion efficiency. Legislation does require the monitoring of organic compounds in emissions from waste incinerators, but the requirement is usually for total rather than speciated organic compounds. Flame ionisation detectors are used for the measurement of total organic compounds as the technique is the standard reference method in the EU. FID systems can be extractive or close-coupled *in situ*.

### Potentiometric Analysis (automated wet analysis by ion-specific electrode)

Several analysers are currently on the market that utilise potentiometric analysis for HCl. A heated sampling system is used to transport a sample of gas to the analyser where it is contacted with a buffered absorbing solution. The solutions that are used include dilute acetic acid/ammonium acetate, dilute citric acid/potassium nitrate and dilute nitric acid. By careful selection of gas and solution flow rates, sufficient enrichment of the $Cl^-$ ion concentration occurs to permit continuous measurement with an ion-specific electrode. The solution is passed to a measurement cell that contains the measurement and reference electrodes. Some early versions of this analyser type required considerable enrichment of the absorbing solution with $Cl^-$ ions and hence worked on a six-minute sampling and analysis cycle. The later versions, with improved flow control, electrodes and buffering solutions can work continuously. These types of analysers will also measure as HCl other inorganic chlorides that are absorbed by the analyser solution. Additionally, cross sensitivities may occur for other halides.

### Derivative Spectroscopy

Derivative spectroscopy involves scanning a spectral absorption peak and obtaining its second derivative or higher derivatives with respect to wavelength at the peak maxima. The derivative peak is measured, and this has the effect of increasing the detection sensitivity of the measurement. In analysers using this technique, either the originating light from the light source is modulated or the light seen at the detector is modulated. This modulation produces a signal at the detector that is dependent on the shape of the absorption curve of the molecules.

Scanning over the absorption spectrum produces harmonics of the absorption line. The second harmonic of the signal is usually used to measure the concentration of the absorbing gas. The amplitude of the second harmonic is proportional to the second derivative of the intensity with respect to the wavelength.

Tuneable diode lasers (TDL) have been used in extractive, path *in situ*, point *in situ* and close-coupled monitoring designs using second derivative detection techniques. A simple diode laser system can employ the differential absorption technique, tuning the laser to different wavelengths by changing the laser temperature or its driving current.

Interferences may influence the measured concentration. This is due to line broadening effects as a result of molecular collisions. Different types of molecule may broaden the absorption line differently.

Modern TDL analysers automatically compensate for this effect using digital filtering techniques. An interesting aspect of the technique is its ability to measure oxygen concentration. As mentioned previously, homoatomic molecules such as $O_2$ do not exhibit unique absorption characteristics in the infrared region of the spectrum. By using the derivative spectroscopic technique however, harmonics are generated which can be detected.

### High Temperature Electrochemical Cells

The electrochemical cell-based analysers previously described are used in extractive systems, and can only be used for the measurement of gas samples at ambient temperature. Point *in situ* electrochemical analysers have been produced, which consist of a probe that can be inserted directly into the stack or duct.

The cell consists of an auxiliary electrode, a reference electrode and a working electrode. The electrolyte used in this design is phosphoric acid, which at ambient temperature is in a semi-liquid form, but becomes less viscous when heated to stack temperature. A polymer film sputtered with metal forms a semi-permeable membrane. The choice of metal determines the gases to which the sensor is sensitive.

These instruments were developed for NO and NO/$SO_2$ monitoring. The presence of HCl in the flue gases results in a much-reduced life expectancy for the cell. However, this can be overcome by the addition of a special chemical filter, which absorbs any HCl before it reaches the sensor.These sensors were widely applied to LCPs in Europe and the USA, and many are still in use. However, they were not successful and are no longer marketed.

## PARTICULATES

Particulate matter (PM) entrained in flue gases from LCPs and waste incinerators is produced by the combustion of fuels or wastes. The size and quantity of particles released depends on the type of fuel and the design of the plant.

In pulverised coal-fired boilers the main source of particulate matter in the flue gas is coal ash. Between 50 and 90% of the coal ash is entrained in the flue gas and carried out of the boiler. The concentration of PM prior to gas treatment would typically be up to 15,000 mg.$m^{-3}$. Commercial PM measurement systems can be classified as follows:

- opacity monitors or transmissometers
- scintillation or received light modulation
- light scattering
- ß-radiation attenuation
- loaded oscillator
- contact charge transfer
- contact acoustical
- electrodynamic induction.

Of the methods listed, opacity monitors, ß-radiation attenuation and light-scattering techniques have had the greatest application and success in meeting continuous monitoring requirements in the EU at the low particulate levels required. The other methods, with the exception of the loaded oscillator, tend to be more qualitative, and are frequently used as alarm monitors or as PM monitors in less demanding applications.

### Opacity Monitors or Transmissometers

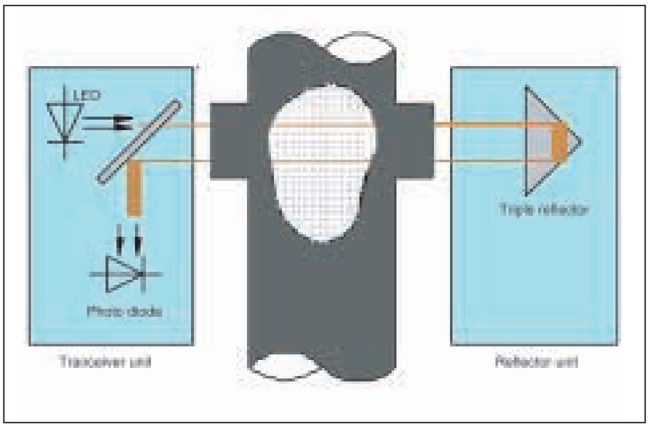

*Figure 7. Dual beam particulate monitor (courtesy of DRC Consultancy Services)*

Opacity monitors or transmissometers are based on the measurement of the optical transmission of a light beam as it passes through the absorbing flue gas stream, which contains particulate matter together with a mixture of gases. As a result of absorption and scattering, the transmitted light beam suffers a reduction in intensity.

As with *in situ* path systems for monitoring gaseous pollutants, transmissometers may be single-pass or double-pass design. Double-pass types use a reflector on the opposite side of the stack or duct so that the light is transmitted twice through the flue gas. Some modern single-pass designs use two identical senders and receivers on each side of the stack to transmit and receive alternately in order to increase sensitivity and reduce the effects of fouling of the optical surfaces. The light sources used include filament bulbs, light emitting diodes and lasers.

The simplest of the transmissometers will produce an opacity that can be correlated with a smoke colour scale, eg the Ringelmann scale. More sophisticated analysers that are equipped with on-line zero and span adjustment can be programmed to produce an output proportional to a mass concentration based on the results of calibration measurements.

Instruments of this type have become a standard feature for emission monitoring at LCPs. Common features include light modulation to compensate for interference of light from other sources (the receiver only recognises light of the correct modulation frequency); air purge systems to keep optical surfaces clean; and automatic zero compensation to compensate for dirt build up on the windows.

Transmissometers are usually of the cross duct design with a sender and receiver on opposite sides of the stack, or with a reflector to pass the light through the flue gas twice. Analysers have been developed in which the light source and detector are carried at opposite ends of a rigid tube. The tube contains a series of slots which allows the passage of PM-laden flue gas through the tube and hence between the light source and detector. This arrangement overcomes some of the problems associated with the cross duct systems with regard to alignment of sender and receiver and differential expansion caused by temperature variations.

Performance standards for transmissometers have been developed in Germany, the USA, and the UK (via the monitoring certification scheme "MCERTS"). Several transmissometers are type-approved in Germany. In the USA, federal opacity standards are based on visual determinations made by trained observers (US EPA Test Method 9). Trained and certified observers view the opacity at the stack exit.

## Scintillation or Received Light Modulation

*Figure 8. Scintillation particulate monitor (courtesy of Dynoptic Systems Ltd)*

In recent years, a variation of the opacity monitor or transmissometer has been developed, which is based on the flicker of the light beam as dust particles pass through it, rather than the overall attenuation. Dust particles passing through the light beam cause the receiver to detect a modulating signal. The fluctuations in the received light (scintillation) are ratioed with respect to the average light intensity at the detector to produce a signal proportional to changes in particulate concentration. Since the fluctuating light intensity and average light intensity are ratioed, fouling of the optics, lamp degradation and detector drift biases cancel out.

The technique has received approval for continuous particulate monitoring in Germany. The technique is not suitable for detecting very low concentrations of particulate.

## Light Scattering

When light is directed toward a particle, the particle may both absorb and scatter the light, deflecting it from its incident path. An opacity monitor or transmissometer measures the intensity of light that is not scattered. Other instruments have been developed to measure the scattered light. The intensity of the scattered light depends on the angle of observation, the size of the particle, its refractive index and shape, and the wavelength of the incident light. Both *in situ* and extractive analysers of this type have been developed. A light beam is passed through the PM-laden flue gas. Absorption and scatter attenuate the light. Light scatter analysers measure the intensity of the scattered light at a predetermined angle to the beam direction. The amount of light scattered in any direction is dependent on the size distribution and shape of the dust particles. Variations in the intensity of the light source and in the sensitivity of the detector are compensated for by the use of a reference beam, in the opposite phase to the measuring beam, on the photoelectric detector.

Scatter light measurement is a more sensitive measurement method for low dust loading. Opacity measurement at low loading is limited by the requirement to measure very small variations in the light received on the axis from the transmitter. Scatter light analysers measure the scatter light only and do not have to deal with small variations in large amounts of transmitted light.

In a similar manner to opacity measurement, calibration is carried out by means of simultaneous determination of PM loading using manual methods and the recording of the analyser output. Special precautions have to be taken to prevent reflection of the light beam from the duct wall interfering with the measurement. Modulation of the light is used to eliminate interference caused by stray light. For zero and span checks, the transmitter and receiver are pivoted to a zeroing chamber, which is an integral part of the analyser mounted on the stack. Filters are then used to simulate known dust loading. Analysers of this design have received type approval in Germany for very low dust levels of 0 to 7mg.m$^{-3}$. Any water droplets present in the gas will influence the measurement. It is also stated in the approval that the measurement volume, ie that area of the flue gas duct or stack that is subjected to the scatter measurement, is approximately 10cm from the side wall. It must be determined during calibration whether this area of the duct is representative of the total flue cross section.

Instruments can be based on the forward scatter, side scatter or back scatter principles, and can be *in situ*, point *in situ* or extractive. One example of an extractive analyser uses an automatic isokinetic sampler to withdraw a sample of flue gas from the duct. The flue gas is heated in a by-pass arrangement and a further sample is taken from the by-pass and passed through the analyser. This system has the advantage that wet flue gases containing water droplets can be sampled and measured. Regular zero and span checking can be carried out internally using check filters. The disadvantages of the system, when compared with opacity monitoring, are that it is a point measurement with no averaging capability over the duct cross section, and the sampling system requires attention in order to maintain isokinetic sampling conditions. This type of analyser is claimed to be more accurate for low PM concentrations of up to 1mg.m$^{-3}$.

## ß-radiation Attenuation

In ß-radiation attenuation devices, flue gas is drawn isokinetically through a probe, to be deposited on a glass fibre filter tape. The filter tape, wound on a roll, moves sequentially so that a spot of particulate matter is collected on the tape over the period that the tape is stationary. The filter tape is then automatically advanced to a sensor, a $^{14}C$ or other radiation source, which emits high-energy electrons or ß rays. The ß radiation is both absorbed and scattered by the collected particles on the tape, depending on the amount and composition of particles present. A detector, typically a Geiger-Müller tube, measures the intensity of the radiation. A reference measurement is provided by passing ß radiation through an unexposed section of tape. If the composition of the particles is relatively constant, the attenuation of the radiation can provide a measure of the thickness of the spot of particulate matter, and hence the mass of material collected. The sampling system is usually heated; therefore cool wet gases can be sampled. The technique has disadvantages, such as the requirement for maintenance of the sampling system and the fact that it is a point measurement. It is not a truly continuous measurement, as only one-minute average values are available as the particulate matter is collected on the tape before being moved on to the sensor. However, these disadvantages can be outweighed in many applications by the possibility of analysing the filter tape at a later date for particulate phase metals content. This gives a good measurement of metals emissions on a semi-continuous basis.

This type of system has a range of 2 to 2000 mg.m$^{-3}$, depending on sampling rates, sampling frequency and integrating times.

## Loaded Oscillator

The frequency of a vibrating oscillator will change if the mass of the vibrating element changes. Electromechanical devices have been developed based on this principle. The technique is one of the most direct means of measuring particle mass apart from direct gravimetric analysis.

Various arrangements have exploited this principle over the years, including devices incorporating piezoelectric crystals and oscillating filters. When gases containing particulate matter are drawn across the vibrating element, the particles adhere to it, thus changing its mass and consequently its frequency of vibration.

The technique has been used successfully for the measurement of particles in ambient air by Tapered Element Oscillating Microbalance (TEOM®). The TEOM®, marketed by Rupprecht & Patashnick Co., Inc. of the USA, has recently been incorporated into an isokinetic probe device for the sampling of hot stack gases. This instrument is intended as a test device to provide compliance testing patterned after US EPA Methods 5 (front half) and 17, ISO 9096, and calibration of PM CEMs according to US EPA Performance Specification 11 & QA Procedure 2. The monitor can be used to measure stack particulate mass concentration continuously at a single point for process assessment and optimisation. The sample duration in this mode is typically 4 to 24 hours depending upon the particulate matter concentration of the source. The use of sample dilution can extend this period. Measurement resolution of 0.2 mg.m$^{-3}$ at a 120-sec averaging time is achievable.

## Contact Charge Transfer

When two materials having different electronic properties make contact, there will be a net transfer of electrons from one material to the other when they are separated. The transfer of charge can occur when a particle impacts on the surface of the other material, or if it comes into contact by sliding and rubbing. The latter effect is known as triboelectricity. The amount of charge transferred depends on other factors besides the electronic properties of the materials, including particle resistivity, the dielectric constant, and the physical conditions of the contact (duration and area of contact, particle deformation etc).

Analysers which use this technique consist of a metal probe which is inserted into the stack or duct. When particles entrained in the flue gas stream impact with the probe, a very small charge is transferred to the probe. This charge is usually measured in picoamperes or nanoamperes. This charge is subsequently amplified in order to produce an electrical output.

The method is influenced by a large number of factors including electrostatic charge on the particles, flue gas velocity, the condition of the sensor surface, particle size and the presence of droplets in the gas stream. This limits the use of the technique for quantitative measurements, and it is mostly used for applications such as the detection of broken bags in baghouses.

### Contact Acoustical

When particles entrained in a gas stream strike a rigid probe they induce a vibration in the probe. Another type of impaction device measures this vibration using a piezoelectric sensor, which counts the number of impacts and measures the energy of the impacts. The signal generated can be used to obtain a mass flow correlation. Particle build-up on the probe, gas streamlining and probe corrosion can affect the instrument response. It has not been applied significantly to the monitoring of particulate releases from LCPs or waste incinerators.

### Electrodynamic Induction

An approach similar to that of the contact charge transfer technique has been developed by PCME Ltd. In this method a charge is induced in a rod, inserted in the flue gas stream, by particles which pass by, rather than impact the rod. As the particles pass the probe an alternating current is induced, which is amplified and measured. The particles that impact the rod will produce a direct current, which is not measured in this technique.

*Figure 9. Electrodynamic induction particulate monitor (courtesy of PCME Ltd)*

The PCME approach avoids the problems associated with sensor surface conditions and particle velocity. Particle composition and size, and electrostatic charge on the particles still affect the measurement. However, particles as small as 0.1µm can be detected. The instrument has been applied to processes where particle characteristics do not change significantly, and has received approval for continuous particulate monitoring in Germany and under the MCERTS scheme in the UK.

## OXYGEN CONTENT

Oxygen ($O_2$) occurs in the flue gases from LCPs and waste incinerators as a result of excess air used during combustion. Economic considerations usually ensure that the concentration is kept as low as possible to minimise flue gas heat losses. A typical concentration at the economiser outlet is usually approximately 2 to 6%. For emission measurement purposes, the actual oxygen concentration of the flue gases at the measurement point must be known so that the measured concentration of pollutant can be referenced to a standard oxygen value, eg, 6% for coal-fired power plant.

The technologies employed for $O_2$ measurement in flue gases are well developed and understood. The following types of $O_2$ analysers are used for plant efficiency monitoring and emission measurement reference value measurement:

- Zirconium oxide analysers; *in situ* and extractive
- Paramagnetic/thermomagnetic analysers
- Electrochemical cells.

## Zirconium Oxide

*Figure 10. Zirconium oxide oxygen analyser (courtesy of Servomex Group Ltd)*

Analysers using zirconium oxide ($ZrO_2$) can either be *in situ*, ie the measurement cell is in the stack; extractive on-stack, ie the cell is mounted on the stack with a sampling probe protruding into the flue gas; or extractive with the cell mounted in an analyser some distance from the stack (requiring sample transfer lines). However, the main MCERTS approved method is *in situ*.

The measurement works on the principle that, in the presence of an electrolyte, a current will flow between solutions or gases containing different concentrations of a chemical species due to a difference in chemical potential.

The characteristics of these analysers can be stated as:

- very accurate and reliable measurement of $O_2$
- a fast response time (for *in situ* measurement) makes it ideal for process control applications
- it is a well-understood technology with examples at most boiler plant (for combustion control)
- it has a low capital cost and low maintenance
- the measurement is on a wet basis: the level of water vapour must be known to calculate the concentration on a dry basis.

This method requires a supply of air, zero and span gas to be available at the measurement site.

## Paramagnetic Analysers

These extractive type analysers make use of the paramagnetic properties of oxygen for the measurement of concentration. Oxygen has a relatively strong permanent magnetic moment, which can be used to influence flow patterns of sample gas within an analyser.

The general characteristics of the extractive paramagnetic analysers can be stated as:

- Accurate and reliable measurement.
- They measure on a dry basis as part of an extractive system, therefore providing correct reference values for other extractive systems.
- They can be installed in the same sampling train as other analysers making use of common components, eg coolers, filters etc. This also ensures that sample contamination by air in-leakage to the sampling system is taken into account.
- They are usually situated adjacent to other analysers, so can be part of an integrated monitoring package.

There are three types of paramagnetic analysers available.

## 1. Thermomagnetic (magnetic wind) analysers

This method uses the temperature dependence of paramagnetism to generate a magnetically induced gas flow (magnetic wind), which is then measured. The sample gas to be analysed flows through a two-chamber system, consisting of sample and reference chambers. The two chambers hold temperature-dependent resistors that form part of a wheatstone bridge. Both chambers have thermodynamically identical conditions. The sample chamber is located in the field of a permanent magnet, while the reference chamber is not. The bridge is connected to a constant current source. If oxygen-free gas flows through both chambers, the thermodynamic conditions in both chambers remain identical. If the gas in the sample chamber contains $O_2$, an enhanced circulatory flow proportional to $O_2$ content is established in the sample chamber. This disturbs the temperature dependent balance of the bridge circuit creating a DC signal proportional to $O_2$ content of the sample gas.

This type of analyser is robust, has a low maintenance requirement and is generally cheaper than other types of paramagnetic analysers. Because of the dependence of the principle on the thermal conductivity and specific heat of the sample gas, the composition of the background gas must be taken into account during calibration. The response time is also relatively slow.

## 2. Differential pressure analysers

If two gases of differing $O_2$ content meet in a magnetic field, a pressure difference exists between them because of their different magnetic properties. This pressure difference can be used to form a pneumatic wheatstone bridge. A reference gas ($N_2$, $O_2$ or air) is introduced into the sample chamber through two channels. One of these reference gas streams meets the sample gas stream under the influence of a pulsed magnetic field. The magnetic field attracts $O_2$ molecules to the outlet of one sample stream and creates a small backpressure, which leads to a small compensating flow in the pneumatic bridge between the two reference streams. This flow is measured by a microflow sensor and is proportional to the $O_2$ content of the sample gas.

This type of analyser operates independently of the thermodynamic properties of the background gases. Compensation measures for vibration and tilt must be incorporated. Several $O_2$ analysers of this type have been type approved in Germany.

## 3. Automatic null-balance analysers

The oxygen molecules in a flowing gas sample will establish a partial pressure gradient in a magnetic field. This gradient can be used to exert a force on a small dumbbell shaped body located within the field. The torque on the dumbbell causes a displacement that is detected by a mirror and photocell assembly, which measures its angular position. Compensation current produced as a function of this position results in an electromagnetic torque counteracting the measurement torque and tries to restore the dumbbell to its original position. This compensation current is proportional to the $O_2$ content of the sample gas.

This measurement principle can achieve high sensitivity and accuracy. Analysers of this type have become a standard for flue gas analysis with many different companies offering versions. Many of them are also type approved in Germany for emission monitoring.

### Electrochemical Fuel Cells

In recent years a wide range of portable flue gas analysers has become available, based on electrochemical fuel cell technology. In certain multi-component analyser applications, $O_2$ measurement is made using one of these cells. A typical cell used for this measurement would be of the metal/air battery type comprising an anode, electrolyte and an air cathode. Reactions take place at the anode and cathode. During this reaction a current is generated which is proportional to the oxygen content of the sample gas. The cross sensitivities of this cell are minimal and the use of gas filters, as used for CO or $SO_2$ measurement with electrochemical cells, are not normally required. Additionally, the problem of overloading (where the concentration is well above the measurement range) that causes problems for other sensors is not a problem for the $O_2$ cell owing to the nature of the combustion process, as $O_2$ concentrations in excess of 21% are not possible. The operating life of the sensor is about 6-18 months, with an average life of 12 months, although cell replacement costs are typically 10% of the initial capital cost.

This type of sensor is not normally designed for continuous operation but has proved ideal for the portable spot check type of instrumentation. Recent advances have led to $O_2$ cells designed for continuous use that have been incorporated into the continuous analysers discussed above. Measurement of $O_2$ would appear to be the most reliable and accurate measurement that can be made with flue gases using fuel cell technology.

## MULTI-COMPONENT SYSTEMS

Most flue gas analysers measure one flue gas component using one of the generic principles described in previous sections. In recent years analysers have become available that can measure more than one component on a continuous basis. In both Germany and the USA, multi-component systems are treated as several analysers for type approval or certification procedures.

*Figure 11. Multi-component gas analyser (courtesy of Land Instruments International Ltd)*

The advantages of the multi-component systems are generally related to cost, both capital and maintenance. There are several types of multi-component systems currently on the market for flue gas analysis. These are:

- non-dispersive photometry with extractive sampling
- dispersive and non-dispersive photometry: *in situ*
- electrochemical cell
- fourier transform infrared analysis.

## ON-LINE EMISSIONS MEASURING TECHNOLOGIES, GENERAL PERFORMANCE ISSUES

Appropriate calibration of instruments is vital if the requirements of the competent authority are to be satisfied. An automated measuring system (AMS) covered by EU Directives, eg 2000/76/EC on the Incineration of Waste and 2001/80/EC on the Limitation of Emissions of Certain Pollutants into the Air from Large Combustion Plants, must have been proved suitable for its measuring task (parameter and composition of the flue gas) by use of the QAL 1 procedure, as specified by EN ISO 14956. In the UK, instruments that are certified under the Environment Agency's MCERTS scheme satisfy this standard. The forthcoming CEN Standard prEN 14181:2003, Stationary source emissions - Quality assurance of automated measuring systems, specifies additional procedures to ensure that the total uncertainty of the results obtained from the AMS meets the specification for uncertainty stated in the applicable regulations. This section outlines the general requirements of the new standard, and also discusses performance issues such as the calibration and validation of monitoring systems.

### PrEN 14181:2003

The draft CEN Standard prEN 14181:2003 specifies four procedures to be used when proving the suitability of AMSs. These are QAL 1, QAL 2, QAL 3 and AST. QAL 1 is a procedure for type testing of sampling and analysis systems. In the UK the requirements of QAL 1 are satisfied by the MCERTS scheme.

### Calibration Gases

In addition to the requirements set out in the preceding section, it is also necessary to regularly challenge analysers with certified reference materials. A critical element of any quality system for AMSs is ensuring that systems of calibration and measurement are traceable to national standards of measurement, and that confidence can be placed in the quality of measurements carried out at all steps in the traceability chain.

All AMSs are susceptible to drift. These effects can be minimised by the strict application of a documented operation and maintenance procedure. Calibration of equipment is a crucial element of this process. From a quality assurance aspect the key element is the frequency of calibration and the use of appropriate certified reference materials, eg calibration gases.

## TECHNIQUES FOR THE CONTINUOUS MEASUREMENT OF GAS FLOW RATE, WATER VAPOUR, TEMPERATURE AND PRESSURE

Gas flow rate monitors were not widely applied to coal-fired LCPs until, in 1993, the US EPA Acid Rain Programme mandated their installation for the calculation of $SO_2$ allowances. The $SO_2$ allowance is an emission rate, expressed in units of tons of $SO_2$ per year, which is calculated from hourly emissions data. These allowances are allocated, banked, sold and traded. Although engineering calculations based on heat balance or process operations may also be used to determine flue gas flows, auditing of these methods is more difficult, and so the US EPA felt that flow monitors would provide the most accurate and traceable means of determining allowances. Across the EU, the dominant method for the determination of mass flow is stoichiometric calculation on the basis of flue gas oxygen content and fuel consumption. Use of direct methods to measure gas velocity are normally not used.

### Principles of Measurement

Instruments used to measure flue gas velocity are essentially *in situ* monitors because a direct measurement of the flue gases must be made. Measurement methods vary from Pitot tubes to the transmission of ultrasonic signals across the stack. Other measurement techniques such as orifice plates, vane anemometers and flow tubes are more suited to the measurement of combustion air, which does not contain particulate matter.

Many of the extractive and *in situ* analysers discussed in the previous sections are capable of measuring the water vapour content of flue gases, together with other determinands. Water vapour is generally measured continuously in order to enable correction of pollutant concentrations to standard reference conditions.

The temperature and pressure of the flue gas is generally measured using thermocouples or resistance thermometers and pressure transducers respectively. Again, the temperature and pressure of the flue gas needs to be known in order to correct to reference conditions.

## Gas Flow Rate

As previously mentioned, calculation is the predominant method used across the EU for estimating flue gas mass release rates. Gas flow rate monitoring techniques that are currently used on some plant for measuring the flow in stacks or ducts are:

- pitot tube
- averaging differential pressure probes
- thermal sensing systems
- ultrasonic flow monitors
- time-of-flight
- balance technique
- stack Venturi
- vortex shedding flow meters
- pneumatic bridge flow meters.

## Pitot Tube

Pitot tubes are the standard reference method for the measurement of stack gas velocity. A Pitot tube consists of two small diameter pipes. One, facing the direction of flow of the gas measures the impact or dynamic pressure of the gas, the other, either parallel to the flow or facing in the opposite direction measures the static pressure. The tubes are connected to a pressure measurement device such as a liquid-in-glass column, or a pressure transducer, and the pressure differential between the dynamic and static tubes is the velocity pressure, $\Delta p$.

For accurate determination of volumetric flow, the temperature, pressure and molecular weight of the flue gases must also be measured. A Pitot tube measures at only one point, although multiple tubes can be used to average a flow distribution across a stack or duct. The dynamic and static tubes can be connected to common chambers where a multipoint average pressure can be obtained. A multipoint average can also be obtained by using an averaging differential pressure probe.

## Averaging Differential Pressure Probes

Averaging probes are modified forms of the Pitot tube, having two or more pressure tappings in a tube. The pressure tappings are located at points across the duct or stack, which correspond to centres of equal areas of the duct or stack cross section. The pressure tappings face the direction of flow of the gas and give an average dynamic pressure over the duct or stack diameter. The static pressure is averaged using ports located in a separate tube positioned at 180° to the dynamic pressure tappings.

An averaging probe averages across only one diameter. If two probes are installed at 90° to each other across the duct or stack sampling plane, the flow measurement is more accurate. Particulate matter and droplets in the flue gas can cause plugging or fouling of the probe. This can be minimized by back purging with compressed air at regular intervals.

## Thermal Sensing Systems

Thermal sensing systems work by the transfer of heat from a heated body to the flowing gas. The gas convects the heat away from the probe and in doing so cools the probe. The greater the flow past the probe, the greater the cooling effect.

In thermal sensing systems used for flow monitoring in ducts and stacks, the heated probe is not allowed to cool. Instead, more power is applied to the sensor to maintain its original temperature. The temperature of this sensor is usually maintained at 25 to 40°C above the flue gas temperature. For heated wire type sensors, the mass flow of the gas is proportional to the amount of power applied.

In order to compensate for fluctuations in temperature of the flue gas, a second sensor is used to measure the flue gas temperature. In a typical design, a platinum resistance wire is wound on a ceramic tube, which is then protected from the abrasive particles in the gas stream by a stainless steel sheath. The heated and temperature sensors are then connected to a bridge circuit that maintains the temperature of the heated sensor at a constant differential above the measured stack temperature. As the moving stack gas cools the sensor, the current through the element is increased in order to keep the temperature differential constant. This current can then be related to the heat lost from the sensor. Velocities down to $0.05 m.s^{-1}$ can be measured using this technique.

The rate of cooling of the heated sensor is dependent on the thermal conductivity of the gas, which is, in turn dependent on the gas velocity and density. As a net result of these effects, thermal sensing instruments produce an output that is proportional to mass flow rather than volumetric flow. Multiple probes of this type can be combined in arrays to measure the average flow rate across large ducts or stacks.

## Ultrasonic Flow Monitors

Ultrasonic flow monitors measure the time that it takes ultrasonic sound pulses to travel with the direction of flow of the stack gas and against the flow of the stack gas. In a typical arrangement ultrasonic pulses in the 50kHz range are transmitted both upstream and downstream of the flow. Two transceivers are located opposite each other on the stack or duct at an angle of typically 45°. In each transceiver a piezoelectric transducer transmits ultrasonic pulses across the path to the opposite transceiver. The speed at which the pulse crosses the stack or duct is dependent on whether it is going with or against the flow.

This method measures the volumetric flow of the gas in actual cubic metres per second. Because the instrument is a path *in situ* system, it is not subject to corrosion and probe fouling problems that may affect in-stack techniques.

## Time-of-flight

The motion of flue gases moving through a stack or duct is turbulent, and turbulent eddies of gases will form. These eddies can contain regions of higher levels of infrared radiation, which can be tracked as they move up the stack. Two broadband infrared detectors are attached to the side of the stack in the direction of flow of the flue gases. The detectors detect infrared radiation emitted from hot gas molecules.

## Balance Technique

In the balance technique the force exerted by the gas flowing in the duct or stack on a probe inserted in the gas stream is measured using a strain gauge.

## Stack Venturi

By designing a constriction between two tapered sections of duct or stack, a large

Venturi can be constructed. A ring of pressure tappings installed before the constriction is used to measure the upstream static pressure, and a ring of pressure tappings around the constriction measures the lower static pressure. The pressure differential between the two rings can be used to calculate the flue gas flow rate.

This approach produces excellent results, but fabrication costs can be high, and additional fan horsepower is required to move the flue gases through the restriction, resulting in higher running costs.

### Vortex Shedding Flow Meters

Vortex shedding flow meters consist of a bar or strut running across the flow diameter, creating turbulence downstream, and an ultrasonic sensor. For given conditions, the number of vortices created downstream of the flow obstruction is proportional to the gas flow rate. The vortex frequency can be measured by means of ultrasonic sensing. An ultrasonic beam is passed through the vortex pattern and is modulated by the vortices. The modulating index should be proportional to the gas velocity.

### Pneumatic Bridge Flow Meters

Pneumatic bridge flow meters are based on a probe with two openings that is inserted into the flow. One of the openings points against the flow direction while the other is 180° in the other direction. Purge gas, eg $N_2$, flows to both openings via channels, which are connected internally by a tube forming a ‘pneumatic bridge’. Flowing flue gas causes a pressure difference between the two openings at the end of the probe and an imbalance is created in the connections connected by the bridge. This imbalance causes a small flow of purge gas in the bridge, which is detected by a change in the temperature gradient in the bridge (thermoelectric sensors).

### Water Vapour Content

Water vapour in flue gases from LCPs arises both from the free water contained in the fuel and as a product of combustion. The normal concentration range is 5-6% water vapour for coal-fired LCPs.

Minimum performance standards have been published in Germany, and the UK (via the MCERTS scheme) for water vapour analysis in flue gases. No specific performance specification has yet been published in the USA. However, as part of the measurement system to determine $SO_2$ mass emission rates, strict requirements are in place for the performance of the whole measurement system. For example, if $SO_2$ is measured on a dry basis, flue gas flow measured on a wet basis and flue gas water vapour content measured continuously, the relative accuracy of the total measurement of mass emission is specified. The measurement problems associated with water vapour include impacts from the high concentration involved and the requirement to maintain high temperatures to avoid condensation in any sampling system used with an extractive system.

The analysers that have been developed for continuous water vapour concentration measurement are based on:

- non-dispersive IR photometry (NDIR)
- dispersive photometry *in situ*
- automatic psychrometry.

### Non-dispersive IR Photometry with Extractive Sampling

The analysis method is similar to that used for gases such as $SO_2$. The main difference is associated with the higher concentration levels and the requirement to heat the whole measurement system to avoid condensation.

A wide range of NDIR analysers is available that can measure water vapour. However, the usual quoted measurement ranges are well below those encountered in flue gases. Their main application has been in process analysis applications in industry. There is very little information on commercial applications of NDIR to the measurement of water vapour at LCP applications. The exception is a multi-component analyser based on NDIR GFC, with a long path length, that is type-approved in Germany for water vapour with the measurement range 0-40%.

### Dispersive Photometry *in situ*

Both path *in situ* and point *in situ* analysers are available for the measurement of water vapour. Systems based on DOAS and GFC are commonly employed. The main advantage of measuring water vapour *in situ* is that all the problems associated with heated sampling and the heated analysers are avoided.

### Automatic Psychrometry

The psychrometry principle measures the water vapour content of a gas by measuring two temperatures; the dry gas temperature in a conventional temperature measurement element and the wet gas temperature, which is measured by a temperature-sensing element in contact with a wet fabric material. The wet temperature is lower than the dry temperature owing to the evaporation of liquid from the wet element. The evaporation rate, and hence the temperature difference, is a function of the humidity of the gas, and hence the water vapour content. This analyser has recently received type approval in Germany for LCP applications.

### Temperature and Pressure

The temperature and pressure of flue gas will differ at different points across the stack or duct, especially if the gas flow is stratified. One way to obtain a measurement of the true flue gas temperature and pressure is to carry out a multi-point survey of the stack or duct in accordance with the positional requirements of ISO 10780:1994. A point, which is representative of the average temperature and pressure, can then be selected and permanent temperature and pressure sensors installed at this position. It should be noted that unshielded thermocouples/ resistance thermometers could be affected by radiation from hot surfaces, and heat losses to relatively cooler surfaces such as duct walls. In this case the use of shielded sensors or suction pyrometers should be considered.

In emission monitoring applications temperature is usually measured using thermocouples or resistance thermometers. Pressure can be measured using liquid-in-glass manometers, but it is more usual to use electronic pressure transducers, so that remote indication and recording is possible.

## CARBON-IN-FLY-ASH MONITORS

The level of unburnt carbon in fly ash from coal-fired LCPs is an important consideration for combustion efficiency as well as ash utilisation. The presence of unburnt carbon in fly ash has been shown to be a function of furnace design, coal quality, the pulverised fuel preparation, and heat release rate. Boilers are designed to take these factors into consideration. However, ever tightening emission legislation in the EU has forced many utilities to switch coal supplies and install low-$NO_x$ burners. Higher carbon-in-ash levels have been the result of these changes in coal quality and the staged combustion characteristics associated with low-$NO_x$ burners. Over the past few years, several instruments for the on-line sampling and determination of the unburnt carbon content of ash samples have been developed. However, to date they have not been widely used in the EU, despite potential uses for combustion optimisation and as an aid in fly ash utilisation.

On-line performance optimisation of the combustion process requires a timely and reliable analysis of fly ash. Presently, most utilities monitor fly ash unburnt carbon levels by manually obtaining fly ash samples from the precipitator ash hoppers or flue gas streams and sending the samples to a laboratory for analysis. Depending on the analytical procedures used, and the location of the laboratory, the results of the analysis may not be available for up to 24 hours. This delay can significantly hinder the combustion optimisation process. Another problem associated with sampling is the difficulty in ensuring that the sample analysed is representative. If the sample is not representative, its analysis will not provide a true indication of the combustion conditions in the furnace. In some cases operators rely on CO levels to indicate combustion performance, and to provide a warning of potential combustion problems. Higher than normal CO levels may result from inadequate fuel/air distribution. However, increased CO levels are not always a precursor of higher unburnt carbon levels.

## Principles of Measurement

Carbon-in-ash measurement technologies fall into two categories: extractive and non-extractive systems. Extractive systems remove fly ash from the flue gas stream and perform the analysis, whereas non-extractive systems infer the unburnt carbon level from measurements directly from the flue gas stream.

Recently, several technologies for the on-line sampling and determination of the unburnt carbon content of ash samples have been developed and marketed. Infrared, capacitance and microwave-based systems are some of the technologies that have been employed.

## Extractive Systems

In extractive systems a sample of fly ash is extracted from the duct isokinetically and transported to a collection cell for analysis. Either single point sampling or multi-point sampling systems are available. In multi-point systems, samples are withdrawn sequentially from each point, typically for five to ten minutes, and each sample is analysed separately. Analysis of the samples is by various techniques. In one technique the ash sample is subjected to microwaves. The sample absorbs microwave radiation to different degrees, depending on the amount of carbon in the sample. In another technique the isokinetically extracted sample is exposed to infrared light, whose reflection is used to estimate the residual carbon content of the sample. In this system a new sample is collected and analysed typically every two to three minutes.

In the SEKAM on-line carbon-in-ash monitor marketed by Clyde Pneumatic Conveying, the isokinetically extracted sample is passed between two capacitance sensors, which measure the capacitance of the ash. The capacitance varies depending on the carbon content of the sample.

In the TEOM® Series 4200 Combustion Efficiency Monitor from Rupprecht and Patashnick, flue gas, drawn isokinetically from the plant duct, passes through a filter cartridge in the TEOM® mass transducer, where the fly ash is deposited and weighed. After weighing the fly ash sample at the sample station, the monitor moves the mass transducer to a furnace station using a pneumatically driven, linear slide mechanism. The furnace heats the sample to convert any residual fly ash carbon into $CO_2$. During the oxidation process, the instrument supplies the furnace with $CO_2$-free air, and channels the furnace output to an infrared $CO_2$ detector. After the heating phase is complete, the unit's microprocessor uses the initial sample mass and readings from the $CO_2$ sensor to calculate automatically the percentage of carbon in the fly ash sample, thus determining the loss on ignition of the sample.

### Non-extractive Systems

The operating principle of the FOCUS Unburned Carbon Module from Applied Synergistics, is based on the premise that unburnt carbon exiting the furnace of coal-fired LCPs will be hotter than the surrounding gases and carbon-free ash. Therefore, the carbon and carbon-laden particles will emit higher levels of radiant energy in the near infrared wavelength range. Infrared video cameras are positioned along the wall of the furnace, and these provide an image of these hotter particles as white spots. An image processor to determine the rate at which hot particles traverse the field of view then processes these images. A unit-specific equation is applied to the particle rate in order to estimate unburnt carbon as a percent of total ash.

## ISSUES FOR COAL GASIFICATION AND WASTE INCINERATION PLANT

### Coal Gasification Plant

*Figure 12. Puertollano IGCC (courtesy of Elcogas SA)*

The drive to develop cleaner coal technologies across the world has resulted in a number of systems based on coal gasification. None of these operates on a truly commercial basis, but they are of a scale that allows realistic conclusions to be drawn on the emissions from this type of plant. Expressed simply, when coal is brought into contact with steam and oxygen, thermochemical reactions produce a fuel gas, largely CO and hydrogen, which when combusted can be used to power gas turbines. The most developed gasification processes are the Integrated Coal Gasification Combined Cycle (IGCC) power generating systems that are presently being developed and operated in Europe and the USA.

A number of demonstration units, mainly around 250$MW_e$ size are being operated in Europe and the USA. Most of these units use entrained flow and are oxygen blown, but one is based on a fluidised bed, and is air blown. The 235$MW_e$ unit at Buggenum in the Netherlands started up in 1993. The three plant operating in the US are located at: Wabash River in Indiana; Polk Power near Tampa in Florida and Piñon Pine in Nevada. The largest gasification unit currently operating is at Puertollano in Spain and has a capacity of 330$MW_e$.

The emissions of particulates, $NO_x$ and $SO_2$ from IGCC units are inherently low and are expected to meet, and possibly better, all current standards. On most units, sulphur is produced in elemental form as a by-product and sulphur removal efficiencies of more than 99% are achievable. Particulate entrained in the syngas product material would damage the gas turbine and so it is removed by filtration, either at low temperature after cooling of the gas, or at high temperature using specialised media such as ceramic candle filters. Particulate emissions from gasification plant are consequently very low.

The requirement for monitoring emissions from gasification plant is therefore broadly similar to that for more conventional coal-fired plant. The lower concentrations of the pollutant species will require greater precision and accuracy from CEM technologies installed on gasification plant, as compared with conventional coal-fired plant, but comparable with new pulverised coal-fired plant and plant retrofitted to meet the very latest environmental legislation. UK manufacturers are developing and improving their product lines to meet these more demanding measurement limits and so should be equally well-placed to supply to new gasification plant as they are commissioned and constructed around the world.

### Waste Incineration Plant

The role of waste incineration differs across the world. While in the industrialised countries in Europe as well as in Japan, the USA and Canada, the proportion of waste burned in waste incineration plant can be very high (up to 100%), in most developing countries landfill is the more common waste management practice. The technology of waste incineration encompasses the destruction of municipal wastes and hazardous wastes, the incineration of sewage sludge, and specialised applications such as the destruction of medical wastes and crematoria operations. Many of the incineration plant in the first three categories operate with energy recovery.

The thermal treatment of solid municipal waste mostly takes place in plant equipped with grate firing systems, in pyrolysis, gasification or fluidised bed plant, or in plant using a combination of these processes. Residual municipal waste (domestic refuse, commercial waste similar to domestic refuse, bulky waste, road sweepings, market waste, etc) is delivered to grate furnaces as a heterogeneous mixture of wastes. The combustible components account for approximately 40-60% of the total mass processed.

The principal system used for the incineration of sewage sludge is fluidised-bed combustion. Most plant are stationary fluidised-bed furnaces, but there are also multiple-hearth furnaces and multiple-hearth fluidized-bed furnaces in use.

Currently, the use of waste in plant other than waste incineration plant is gaining in importance as a waste management option. The object of co-incinerating high-calorific waste as substitute fuel (so-called waste for energy recovery) in production (eg cement works, brick manufacture, blast furnace), in power plant (eg use of sewage sludge in coal-fired power plant) and industrial boilers is the substitution of regular fuel (coal, fuel oil, etc) and the reduction of energy costs.

Legislation around the world, especially in the EU, the USA and Japan, places strict limits on the emissions of pollutants from waste incineration plant. In addition to the conventional emissions of $NO_x$, $SO_2$ and particulates, operators are required to monitor the concentrations of species such as hydrogen chloride and dioxins. This market sector is an important and growing area for UK CEM manufacturers.

## LEGISLATIVE DRIVERS FOR THE MARKETPLACE

Environmental legislation has been cited by CEM manufacturers as being the primary driver for their market. Important regions of market activity include the EU, the USA, Japan, Australia and the Developing World. Brief notes on the key legislation for the EU and the USA follow.

## The European Union

The primary environmental legislation addressing emissions from industrial processes is Integrated Pollution Prevention and Control (IPPC), which is embodied in EC IPPC Directive of 1996 (96/61/EC). All industrial installations covered by Annex I of the Directive are required to obtain an authorisation (permit) from the authorities in each of the EU countries in which they are based. Unless a process has a permit, it is not allowed to operate. The permits must be based on the concept of Best Available Techniques (BAT), which is defined in Article 2 of the Directive. It is recognised that in many cases BAT means radical environmental improvements and sometimes it will be very costly for companies to adapt their plants to BAT. Consequently if stringent BAT rules were imposed on industry many EU jobs could be jeopardised, and therefore, the Directive allows these installations an eleven-year long transition period to achieve compliance, beginning on the day that the Directive entered into force.

The air pollutants included in the IPPC Directive are:

- $SO_2$ and other sulphur compounds
- $NO_x$ and other nitrogen compounds
- Carbon monoxide
- VOC
- Metals and their compounds
- Dust (particulate matter)
- Asbestos (suspended particulates, fibres)
- Chlorine and its compounds
- Fluorine and its compounds
- Arsenic and its compounds
- Cyanides
- Substances and preparations which have been proved to possess carcinogenic or mutagenic properties or properties which via the air may affect reproduction
- Polychlorinated dibenzodioxins and polychlorinated dibenzofurans.

The total emissions allowable from each Member State are addressed by the National Emissions Ceilings Directive (NECD) for acidifying and ozone-forming air pollutants. This Directive (2001/81/EC) sets limits (Emissions Limits Values - ELV) for each member state for $SO_2$, $NO_x$, VOC and ammonia ($NH_3$). The NECD provides binding national ceilings for 2010 along with EU-wide aggregate, but non-binding limits for $SO_2$, $NO_x$ and VOCs. Aggregate emissions of these pollutants are to be reduced between 1990 and 2010 as follows: $SO_2$ by 77%, $NO_x$ by 51%, VOC by 54% and $NH_3$ by 14%.

For the coal-fired power generation sector, the legislation governing emissions to air is the Large Combustion Plant Directive (LCPD (2001/80/EC)) which was originally intended to set emission standards for new plant larger than $50MW_{th}$ irrespective of the fuel used. The Directive includes emission ceilings and reduction targets for plant in each Member State, specifically for emissions of $SO_2$ and $NO_x$. Since its inception the Directive has been the subject of a number of derogations, eg plant operating for less than 2200 hours per year, and a newly revised Directive sets emission limit values for existing plant and tightens up the requirements for new plant. Within the LCPD plant is categorised by age to reflect achievable performance and differences between BAT for plant of different ages:

- Existing plant - licensed before 1 July 1987
- New plant - licensed after 1 July 1987 but before 27 November 2002 (and operational before 27 November 2003)
- New plant - licensed after 27 November 2003.

Emissions from waste incineration plant are addressed in the EC's "Waste Incineration Directive (2000/76/EC). This Directive supersedes and extends the scope of earlier legislation, and in addition to including the incineration of non-toxic municipal waste, its scope extends to the incineration of non-toxic non-municipal waste (such as sewage sludge, tyres and hospital waste) and toxic wastes not covered by Directive 94/67/EC (such as waste oils and solvents). Simultaneously, the Directive is intended to incorporate technical progress made on monitoring incineration-process emissions into the existing legislation, and to ensure that the international commitments entered into by the Community are met in terms of pollution reduction, particularly those setting limit values for the emissions of dioxins, mercury and dusts arising from waste. In order to guarantee complete waste combustion, the Directive requires all plants to keep the incineration or co-incineration gases at a temperature of at least 850°C for at least two seconds. If hazardous wastes with a content of more than 1% of halogenated organic substances, expressed as chlorine, are incinerated, the temperature has to be raised to 1100°C for at least two seconds. The limit values for incineration plant emissions to atmosphere are set out in Annex V to the Directive. They include heavy metals, dioxins and furans, CO, dust, total organic carbon (TOC), hydrogen chloride (HCl), hydrogen fluoride (HF), $SO_2$, NO and $NO_2$. With the practice of co-firing waste with coal becoming increasingly common in Europe, in countries such as Austria, Finland and the Netherlands, new limits for co-firing plant have been developed. These limits are calculated using the "mixing rule" which is defined within the Waste Incineration Directive where the formula takes into account the heat input of the coal and of the waste as well as the different oxygen reference values.

The environmental policies of the EU as set and administered by the European Commission are the main instruments for protecting the environment and achieving sustainable development. Twelve countries within Central and Eastern Europe are poised to join the Union in 2004 and ten of these countries need to fulfil the economic and political conditions known as the 'Copenhagen criteria' in order to join. These include adopting the common rules, standards and policies that make up the body of EU law. Full membership will lead to significant benefits and the European Commission is assisting these countries in adopting the body of EU laws, providing a full range of assistance to improve their infrastructure and economy.

## Specific Considerations for the United Kingdom

The UK is currently investigating its preferred strategy for implementing the LCPD, and in June 2003 Defra issued a Consultation Paper setting out the way the UK should implement the revised Directive, the background to the decisions that need to be taken, and the options. One of the central decisions that has to be taken is whether the UK should adopt the Emission Limits Value (ELV), or the National Emissions Reduction Plan (NERP) approach to regulate pre-1987 plant, an option allowable within the Directive. If the NERP approach were taken, plants would operate within a 'national plan' that would set a ceiling for each pollutant. Some plants would emit more than would be allowed by application of the ELV, others less. A refinement made possible by a national plan is that emissions trading for $NO_x$ and $SO_2$ would operate. This has the advantage of allowing operators additional flexibility in their investment decisions, and offers scope for greater efficiency in meeting the requirements of the LCPD by encouraging operators to develop innovative solutions that might not occur to the regulator.

## The United States Market

The USA is highly regulated in respect of emissions to the environment. Environmental laws are policed by the Environmental Protection Agency (EPA). EPA works to develop and enforce regulations that implement environmental laws enacted by Congress.  EPA is responsible for researching and setting national standards for a variety of environmental programmes, and delegates to states and tribes the responsibility for issuing permits and for monitoring and enforcing compliance.  Where national standards are not met, EPA can issue sanctions and take other steps to assist the states and tribes in reaching the desired levels of environmental quality.

The EPA uses a variety of methods to gather information on air pollution from vehicle exhausts, power plants, industrial facilities and small businesses.  Models, sampling, emissions tests and release reports all contribute to the Agency's ability to protect the nation's environmental health, set achievable goals and develop new initiatives for combating pollution.  Once it has gathered and compiled this information, the Agency makes it available to the public through the Toxics Release Inventory, National Emission Inventory, the Aerometric Information Retrieval System and other sources.

More than a dozen major statutes or laws form the legal basis for the programmes of the Environmental Protection Agency.  The Federal laws that enforce air quality control are the Clean Air Act (CAA) of 1970, CAA Amendments of 1977, and CAA amendments of 1990. The Clean Air Act is the comprehensive Federal law that regulates air emissions from area, stationary, and mobile sources. This law authorises the US EPA to establish National Ambient Air Quality Standards (NAAQS) to protect public health and the environment.  The goal of the Act was to set and achieve NAAQS in every state by 1975. The setting of maximum pollutant standards was coupled with directing the states to develop state implementation plans (SIPs) applicable to appropriate industrial sources in the state.  The Act was amended in 1977 primarily to set new goals (dates) for achieving attainment of NAAQS since many areas of the country had failed to meet the deadlines. The 1990 amendments to the Clean Air Act were in large part intended to meet unaddressed or insufficiently addressed problems such as acid rain, ground-level ozone, stratospheric ozone depletion and air toxics.

Although the Clean Air Act is a federal law covering the entire country, the states do much of the work to enforce the Act. For example, a state air pollution agency holds a hearing on a permit application by a power or chemical plant or fines a company for violating air pollution limits.  Under this law, EPA sets limits on how much of a pollutant can be in the air anywhere in the US. This ensures that all Americans have the same basic health and environmental protections. The law allows individual states to have stronger pollution controls, but states are not allowed to have weaker pollution controls than those set for the whole country.

The law recognizes that it makes sense for states to take the lead in carrying out the Clean Air Act, because pollution control problems often require special understanding of local industries, geography, housing patterns, etc.

States have to develop state implementation plans (SIPs) that explain how each state will do its job under the Clean Air Act. A state implementation plan is a collection of the regulations a state will use to clean up polluted areas. The states must involve the public, through hearings and opportunities to comment, in the development of each state implementation plan. EPA must approve each SIP, and if a SIP is not acceptable, EPA can take over the enforcing of the Clean Air Act in that state.

The US government, through EPA, assists the states by providing scientific research, expert studies, engineering designs and money to support clean air programmes.

## STANDARDS REVIEW

Standard reference methods are essential for the effective measurement and control of air pollution.  Such standards are developed at national, European and world level.  The robustness and fitness for purpose of these standards is a function of the accumulated expertise and experience of the people who work together in committee to produce them. Where internationally derived standards are binding on the UK, as European (EN) standards are, it is particularly important that they should recognise UK interests and sensitivities.  BSI manages the UK input to new standards via its technical committees and the UK experts they nominate to CEN and ISO working groups.  The Comite Europeen de Normalisation (CEN) is currently working on a set of standards for performance criteria and performance testing for Continuous Monitors. Its aim is to develop a set of European standard measurement methods for the pollutants controlled by the Waste Incineration Directive (WID), Large Combustion Plant Directive (LCPD) and Solvent Directive (SD). This work, carried out by Technical Committee 264 (TC264) of CEN, is applicable to a wide range of emission sources, including LCPs, and is particularly concerned with the standardisation of calibration and validation for CEM methodologies across Europe.

Emissions from LCPs in the USA are regulated by the Clean Air Act 1990 and the associated regulations. Until recently emission limits and monitoring requirements for the American equivalent of LCPs were given in the Code of Federal Regulations Title 40, Part 60 (4OCPR Pt60), Subparts D, Da, Db, Dc and Part 75 (40CPR Pt75) which deal specifically with fossil fuel fired steam generating units. For example, subpart Da describes the requirements for steam generating units with a thermal input in excess of 73MW$_{th}$. Emission limits are expressed in terms of nanogrammes per joule of energy input (ng.J$^{-1}$). The limit for $SO_2$ at coal- and oil-fired boilers with a thermal input as above is 520ng.J$^{-1}$. This figure is roughly equivalent to 585mg.m$^{-3}$. Monitoring requirements vary according to the size and age of the particular facility. There is a requirement for the installation of continuous monitors for a wide range of LCPs (in particular the newer ones). Parameters to be monitored include $SO_2$, $NO_x$, diluent ($CO_2$ or $O_2$) and opacity. Performance specifications are given for these monitors in Appendix B 40 CPR Pt 60. Standard reference methods are given in Appendix A of the same regulation.

## MARKET POTENTIAL FOR EMISSIONS MEASURING TECHNOLOGIES

The UK CEM manufacturers interviewed during this study were asked for details of their current markets, and where they thought the most promising opportunities lay in the near future.  Overall, current activity is strongest in the UK, USA, mainland Europe and the Far East.  In the foreseeable future, opportunities are thought to exist in the Accession Countries to the EU, the Middle East, South America and the developing markets in China and Russia. The manufacturers were unanimous in citing legislation as the principal driver for CEM market development, closely followed by “ability to pay”.  This latter consideration was thought to be the most important barrier to extending their activities further in the developing world.  An exception exists, however, for projects financed by the international funding agencies (World Bank, Asian Development Bank, European Bank for Reconstruction and Development etc). A particular concern voiced by some companies was the lack of protection for their intellectual property, especially in the Far Eastern markets and it was suggested that the Government should continue to press for better protection in regions lacking appropriate and policed legislation.

## PRIORITY AREAS FOR UK RESEARCH AND DEVELOPMENT

Working with established technologies, the UK CEM companies main RD&D focus is to address ever lower emission limits by improving limits of detection, better repeatability, improvements to detector technology and the incorporation of up-to-date electronics and software. Some specific areas raised by users and regulators during this study, for which further RD&D is recommended, included:

- continuous measurement of $PM_{2.5}$ condensables
- development of monitoring techniques to meet future requirements
- better measurement systems for PCDD, PCDF, PAH & PCBs
- measurement of $CO_2$ mass release
- flow monitoring for measurement of pollutant mass release
- size speciated particulate measurement ($PM_{10}$, $PM_{2.5}$)
- direct measurement of $N_2O$
- better techniques for the measurement of $SO_3$.

## CONCLUSIONS

1. Although the size of the UK market for CEM equipment is relatively large, UK manufacturers compete with UK-based distributors of equipment manufactured overseas. As a result, the share of the market that UK manufacturers currently hold is relatively small. Annual sales by UK companies for CEM equipment account for approximately £3.4 million. Sales to countries outside the UK by UK manufacturers are approximately £12.4 million per annum.
2. Apart from new techniques for particulate monitoring, in general there are very few new technologies currently available or being developed. UK manufacturers tend to refine well-proven technologies to meet lower limits of detection using up-to-date electronics, and also concentrate limited R&D budgets on developing better data processing and reporting electronics and software in order to satisfy the reporting requirements of the environmental regulators.
3. Given the costs of R&D and equipment certification, smaller manufacturers find it increasingly difficult to maintain innovation in equipment technology and would welcome some form of Government support for these activities.
4. Users find the need to maintain several devices at different locations in plant an inconvenience, and would greatly prefer a single instrument to cover all regulatory requirements. Extractive systems have proved to be maintenance intensive, and many end-users are planning to replace ageing extractive analysers with either point *in situ* or *in situ* analyser systems.
5. Future potential markets were identified as the EU Accession Countries, the Far East, especially China, the Middle East, South America and Southern Africa.
6. Manufacturers, users and regulatory authorities all recognised the value of certifying schemes such as TUV in Germany and MCERTS in the UK for CEM technologies. However, the UK CEM business manufacturing base is small compared with international competitors. This leads to pressure on budgets for certification against competing needs, eg for R&D. In Germany, Umwelt Bundes Amt (UBA) underwrites the costs of certification. A similar scheme in the UK would be appreciated by manufacturers.

## RECOMMENDATIONS

1. Manufacturers felt the application of the UK MCERTS scheme within Accession Countries would widen the market for

UK companies and they would welcome Government support for the translation of the UK scheme.
2. Some of the companies interviewed had taken part in UK Government-sponsored trade missions and found them invaluable in developing new markets. They would welcome further opportunities for focused trade missions to developing market areas such as the Accession Countries, Middle East, Far East, and South America.
3. A particular concern voiced by some companies was the lack of protection for their intellectual property, especially in the Far Eastern markets. Government should continue to press for better protection in regions lacking appropriate and policed legislation.
4. The future requirements of regulators and end-users include continuous sampling of dioxins, furans, PAH and PCBs, continuous monitoring of mass releases of carbon dioxide for emissions trading, continuous flow monitoring of flue gases so that pollutant mass releases can be more accurately reported, continuous particulate emissions measurement methods which are not sensitive to changes in particle size and composition, or to changes in flue gas conditions, and can size speciate, eg for $PM_{10}$ and $PM_{2.5}$. Continuous measurement of mercury, $N_2O$ and $SO_3$ were also identified as important technologies. These future requirements will provide significant opportunities for UK companies, provided that sufficient R&D resources are available to develop and bring to market techniques to satisfy these requirements.
5. The largest single market driver was identified as legislation, and manufacturers wished to encourage greater participation in the MCERTS scheme, with a view to it being mandatory and rigorously enforced by the regulatory authorities in the near future.

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