EFFLUENT GAS MONITORING

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Summary

Effluent gases are continuously monitored using electro-optical monitors, yielding almost real time concentrations, with delays related only with the transfer to the sensor and analysis proper. Accuracy depends on frequent calibration and absence of disturbing interferences.

Numerous inorganic and organic compounds can be identified and measured using infrared (or other) spectrophotometric methods combining adequate selectivity with high sensitivity. In spectrochemical analysis the intensity is measured of electromagnetic radiation emitted or absorbed (A.A.S.) at a specific wavelength, after initial excitation of the analyte by an external source of energy.

Ultra-violet light Fluorescence is used to measure SO_2. Chemiluminescence analyzers are commonly used for nitrogen oxides (NO, NO_2) and the zirconia detector is the most frequently utilized electrochemical sensor, measuring oxygen in gases.

1. Survey

Effluent gas monitoring is important to ascertain compliance with emission codes, detect deviations from optimal operating conditions and defects of air pollution control equipment.

Gas chromatographic separation (see Emission *Sampling and Analysis*) allows analyzing air and flue gases with a periodicity, dictated basically by the duration of the partition process on the chromatographic column. Trace contaminants can also be monitored provided the detector is sufficiently sensitive to allow direct detection. If not, preliminary enrichment on absorption tubes is required. Mass spectrometers allow virtually continuous monitoring of a wide range of ion masses, including those typical for flue gas compounds.

The use of continuous electro-optical monitors yields almost real time concentrations with delays only related with the transfer to the sensor and analysis proper. Accuracy depends on frequent calibration and the absence of disturbing interferences. Other compounds, present at extremely low concentrations, need prior enrichment to enhance the original concentrations to levels well above detection limits, before an analysis can be performed successfully.

Therefore automatic sampling systems have been developed, tested, and calibrated to collect pollutants or hazardous substances, gathering samples over a certain time period for eventual analysis at off-site or on-site laboratories. Analysis yields concentrations, averaged over the sampling period.

The following table gives an overview of the most common techniques used for the control of gaseous substances:

Analytical technique	Examples of compounds to be measured
Infra Red (IR) absorption	Inorganic gases and vapors, e.g. CO, CO_2, SO_2, NO, NH_3, H_2O Numerous organic substances such as methane, olefins, aromatics, chloroform …
Ultraviolet (UV) absorption	SO_2, NO, NO_2, Cl_2
Absorption of a visible light beam (VIS)	NO_2, Cl_2
Ultraviolet (UV) Fluorescence	SO_2
Chemoluminescence	NO, NO_2, O_3
Thermal conductivity detection (TCD)	CO_2, NH_3, H_2, methane, organic substances
Flame Ionization Detection (FID)	Total Organic Compounds (TOC)Individual organic substances, after GLC-separation
Electrochemical cells	O_2, CO, SO_2, NO, NO_2
Zirconium oxide sensors	O_2
Paramagnetism	O_2
Total Organic Carbon	All combustible organic compounds
Explosimeter	All combustible organic compounds

Table 1: Analytical techniques and examples of compounds measured

In another approach, monitors and detectors are required for assessing safety aspects as well as detecting inappropriate occupational conditions, ensuring that the workforce cannot be exposed to toxic gases, vapors, or aerosols, explosive, or oxygen deficient conditions.

Testing is often based on absorption tubes, supplied by companies such as Draeger, Auer and 3M.

2. Occupational Hazard Monitoring Methods

2.1. Survey

Safety managers in industrial plants are required to carry out a formal safety assessment of all potential hazards, identify risks to personnel and ensure that suitable safety equipment and working procedures are in place to minimize those risks. Already at relatively low concentrations certain poisonous gases, generally invisible and often odorless, can prove fatal to personnel whereas flammable gases may cause explosion and fire, leading to extensive damage.

Certain gases readily combust if a mixture of the gas with air comes into contact with a source of ignition. This ignition source could be a flame, a spark or a heated surface. The Lower Explosive Limit (LEL) is the lowest concentration of flammable gas in air that will burn. For most flammable gases, this level is less than 5 % by volume of their mixture with air. Flammable gas detectors measure the concentration of a flammable gas from 0-100 % of its LEL.

It is therefore crucial to have advanced warning of the presence of explosive gas mixtures. In the oil and gas industries, and anywhere where petroleum fuels are used or stored, there is a high risk of flammable hydrocarbons being present in the atmosphere.
An EU directive places a requirement on users and installers to complete a risk assessment on their plant in which they identify the nature of the flammable materials present, the scale of any possible explosion, the probability of ignition and the training and marking requirements so that all personnel are aware of the hazard. All of these points need to be recorded in an explosion protection document and the use of the standard EN 50073 will be helpful in declaring that an appropriate approach has been taken with this risk assessment.

Many gases have detrimental physiological effects even at low levels. Depending on the nature of the gas and the level and time of exposure, effects vary from a mild headache, to dizziness, unconsciousness and in extreme cases death. Toxic gases are usually measured in parts per million (ppm). In industrial environments, the most common toxic gas is carbon monoxide, and hydrogen sulfide, characterized by its rotten eggs smell at low concentrations.

Maximum Exposure Levels (MELs) are for the more dangerous substances. Exposure in these cases should be as low as possible and certainly never above the MEL. Occupational Exposure Standards (OESs) are for less dangerous materials where a safe exposure level can be set in which workers can work day after day.

2.2. Gas Detection Systems

An important aspect of this re-assessment must be an evaluation of the existing gas detection systems, which form a first line of defense against gas hazards.
A fixed gas detection system, linked to remote detectors in hazardous areas of the plant, allows safety officers to monitor gas concentrations from a single control point. Programmable alarm levels and emergency safety procedures, such as plant evacuation or shutdown, and sprinkler systems, can be triggered automatically by microprocessor controlled command and control centers.

In broad terms, equipment, which is already certificated to comply with the latest CENELEC standards on explosion protection, will be able to be made compliant with the EU directive.

As well as the obvious hazards of flammable gas concentrations leading to explosions and toxic gas build-ups leading to poisoning, there is an equal or greater hazard in industry from the depletion of oxygen within confined spaces.

Infrared detectors operate in inert atmospheres suitable for use in confined spaces where oxygen depletion might limit the effectiveness of an explosimeter (pellistor) detector and are immune to poisoning effects. Infrared detectors have a fail-safe design. If the detector becomes obscured or fails, no infrared radiation is recorded and alarm signals are activated. Infrared detectors are available in either a fixed-point format, in which gas diffuses into the detector, or open-path format, in which distances of tens or even hundreds of meters separate source and detector. In this way, a line-of-sight beam is formed and a gas cloud passing through the beam will be detected.

Oxygen detectors used in industrial safety applications typically utilize an electrochemical sensor, which contains a lead wool material in contact with electrodes and electrolyte. When oxygen is allowed to diffuse into this material the electrochemical reaction causes a current to flow. Such sensors are very reliable, but once all of the lead has been consumed the sensor needs to be replaced.

Any gas that can be oxidized or reduced electrochemically can be detected by means of a fuel cell-based electrochemical sensor. Fuel cells are electric batteries that consume gas from outside rather than solid or liquid materials within. Electrochemical sensors are miniaturized fuel cells that react to low concentrations of gas to produce a current that is linearly proportional to the gas concentration.

Galvanic electrochemical sensors may detect other gases. In these sensors, electrodes or electrolyte within the fuel cell are used up in the electrochemical reaction. The life span of these sensors is therefore governed by the amount of gas that they absorb.

Solid-state sensors that use heated semiconductor materials are also available, e.g. the Sulphistor, a hybrid device, most useful for hot environments (temperature exceeding 45° C) or where there is a continuous high background of hydrogen sulfide. Under such conditions electrochemical sensors may be unsuitable.

Guidance can also be obtained from the Health and Safety executives' publications, such as the Control of Substances Hazardous to Health Regulations (COSHH), the Confined Space Working Regulations, Occupational Exposure Standards (EH40) and general guidance - from the Health and Safety at Work Regulations.
A comprehensive description on choosing the correct gas measurement system for an application can be found in part 4 of the European standard norm EN 45544-41.

2.3. Colorimetric Techniques

2.3.1. Lambert-Beer's law

Colorimetric Analytical Techniques are a range of analysis methods based on a measurement of the wavelength and the intensity of electromagnetic radiation in the visible region of the spectrum and used extensively for identification and determination of concentrations of substances that absorb light, i.e. organic and inorganic colored compounds. The methods are quantitative and measures are based on **Lambert-Beer's law**, whereby Lambert's law relates the amount of light absorbed and the distance it travels through an absorbing medium and Beer's law relates light absorption and the concentration of the absorbing substance. The two laws are combined in the equation:

$$\log I_0/I \quad = \quad k\, c\, d\,, \qquad (1)$$

where

I_0 = intensity of the incident beam of light,

I = transmitted intensity,

c = the concentration of absorbing substance,

d = the distance through the absorbing solution, and

k = a constant, dependent upon the absorbing substance, the wavelength of light used, and the units used to specify c and d.

This expression is applied when comparing intensities of radiation transmitted through layers of different thickness of two solutions of the same absorbing substance, one with a known concentration, the other unknown. If the same incident intensity is used and the thickness of the two solutions is so adjusted that the transmitted intensities are equal, then the concentration of the unknown (c_2) can be expressed by the ratio of the thicknesses of the two solutions, d_1/d_2, times the known concentration (c_1). If a photoelectric cell instead of the eye is used to compare intensities, the instrument is called a photoelectric colorimeter.

In colorimetry, frequently the entire visible spectrum (white light) is used, and consequently the complementary color of the one absorbed is observed as transmitted light. If monochromatic light or a narrow band of radiation is used, the instrument is called a ***spectrophotometer***. It is also often employed in the ultraviolet and infrared regions. The spectrophotometer has largely replaced the ***colorimeter***. Most chemical elements and a numerous compounds may be determined, frequently at concentrations smaller than one part in several hundred million parts of solution.

2.3.2. Detector Tubes

Detector Tubes make use of a chemical reaction between the target gas and a chemical, contained in a tube and dispersed over an inert adsorbent, e.g. silica gel. This reaction causes a characteristic color change, which is a measure of the concentration of the target gas.

A fixed volume of gas sample is aspired down the tube using a hand pump or sample pump and as it passes it reacts. Tubes may be used over a limited range of concentrations, by passing gas over them and using the supplied correction factor.

To monitor at widely different levels different tubes must be used. Detector tubes are available for a wide range of substances and gas concentrations. Some tubes contain multiple layers so that known interfering gases can be removed, before passing over the main test reagent. With this type it may be necessary to operate the pump a number of times in clean air, after the sample has been taken, to ensure none of the target gas is held up in the pre-cleaning layer.

Monitoring over an extended time period is also possible in order to produce an average exposure such as an 8 hr value for health and safety purposes.

Detector tubes are supplied as calibrated units that are sealed until use. They have a "use by" date, which should be at least 2 years from purchase.

Other gases present may cause false readings. Suitable information regarding this should be supplied with the tubes. Temperature and humidity will also affect the reading.

2.3.3. Colorimetric (Paper Tapes)

A paper tape is impregnated with a chemical that will react with the target gas to give a color change. The degree of color change is detected using an optical system and the effect compared to predetermined curves stored in the memory, allowing a concentration to be determined.

The flow rate of sample gas to the tape and the speed the tape moves past the optical detector are precisely controlled to maintain an accurate reading. The tape is held in a cassette and gradually unrolls past the detector. Typical cassettes may provide 2 to 4 weeks monitoring.

Since providing zero and sample gases may be very difficult for low ppm measurements the manufacturer provides stain cards, prepared from known gas concentrations during machine manufacture. These may be placed in the optical system as an original calibration.

2.4. Explosimeters or Pellistors

A Pellistor detector consists of a matched pair of elements, one of which is an active catalytic detecting element and the other a compensating element. Each element consists of a coil of very fine platinum wire embedded in a bead of alumina.

Flammable gas contacting the catalytic surface of the detecting element is oxidized, causing a rise in temperature, which increases the resistance of the platinum coil. There is no such change in the compensating element. The output signal of the detector is based on the imbalance between the two resistances.

Pellistor sensors give accurate readings under adverse environmental conditions, as any change in ambient temperature, humidity or pressure impacts equally on both elements. Pellistor sensors require the presence of oxygen in order to operate. However, they can be poisoned or inhibited by silicones, sulfides, chlorine, halogenated hydrocarbons and lead. The detectors require regular cleaning and calibration, increasing the costs of maintenance.

2.5. Total Organic Carbon

2.5.1. Operating Principles

The ***total (amount of) organic carbon (TOC)*** in off-gases can be measured using a FID detector, without prior gas chromatographic separation into individual compounds. The technique is only used as an off-line monitoring system.

A small stream of the gases to be monitored is led into a tiny flame, burning the organic compounds present. The flame is maintained with a steady flow of hydrogen, alone or mixed with helium, in a microburner, using oxygen as an oxidant. The required high purity, oil free gases are supplied from gas bottles or from a small, dedicated water electrolysis unit.

The FID-flame sits in between two electrodes, generating an electric field. Burning pure hydrogen in hydrocarbon free air and oxygen produces negligible numbers of carbon or other ions. However, as soon as organic molecules are introduced, the nature of the flame changes dramatically: combustion creates a large number of carbon-based ions. Such flames are easily detected since they supply additional electric conductivity (the same principle is applied in flame monitoring, to detect a potentially dangerous loss of ignition in furnaces or boilers).

In FID-detectors a polarizing high voltage is applied between two electrodes, one positioned around the burner jet and the other associated with the burner body. This produces an electrostatic field. Positive ions migrate to the grounded collector electrode, and negative ions migrate to the positively charged high voltage electrode. Ionization current, directly proportional to the hydrocarbon concentration in the flame is thus created between the electrodes; the electrometer amplifier can thus measure this concentration over many decades.

In order to prevent losses of high molecular weight compounds by their condensation or adsorption to the walls, the flame ionization detector is built into a heated oven. This also prevents the condensation of water vapor and ensures a highly reliable performance in the analysis of trace levels in air and other gases.

Calibration factors mainly depend upon the number of carbon-hydrogen (C-H) bonds present in the organics to be monitored. As a first approximation the FID-detector yields a similar response for all hydrocarbons with their concentration expressed in weight units, e.g. in µg Nm^{-3}. As each organic compound has a different potential for creating carbon ions in the excited state, the sensitivity also depends upon the structure and composition of the substances. Compounds containing oxygen or heteroatoms have a somewhat lower response factor, of the same order of magnitude. For an accurate determination of specific compounds, however, calibration remains mandatory.

When using pure hydrogen as a fuel, the readout of some detectors can be influenced by variations in oxygen concentration. This effect also depends upon the nature of the organics to be detected.

Therefore it is better to use well-defined calibration gas mixtures. For measuring gases with a high concentration of oxygen, e.g. in solvent laden air, a calibration gas mixture containing a standard 21 % oxygen is recommended. Likewise, when measurements are performed in nitrogen, it is better to use calibration mixtures without oxygen.

Oxygen influences can also be minimized by selecting the right mixture of fuel and combustion air, or by using as a fuel a mixture of helium/hydrogen instead of pure hydrogen; the latter leads to higher detection limits because a larger volume of fuel (about five times more) is needed.

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Biographical Sketches

Johan Versieren has studied Agricultural Engineering at the University Ghent (1982) and performed additional studies and a specialization on environment, 1987 – 1989, at the Institute “Universitaire Instelling”, Antwerpen. He has been responsible, during the last 13 years, for the air monitoring section of the laboratory SGS-Ecocare Belgium. He Started in 1998 his own Environmental Laboratory specialized in air pollution monitoring, as well as emissions and immissions.
Since 1990 he is licensed in Vlaanderen for Environmental Impact Assessments (sections air, water and soil). He is also licensed for Environmental Coordinator.

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).

Kathleen Schroyens has studied Industrial Engineer in Chemistry (1998) at the KAHO – Ghent.

Since 1999 she is working as scientific collaborator at the Chemical Engineering department of the Vrije Universiteit Brussel. Kathleen Schroyens is collaborating in projects for the European Union (MINIDIP, Haloclean) and The Flemish Government, AMINAL, preparing an inventory of all waste or product streams, derived from thermal processes that are contaminated with dioxins, performing (succinct) risk analysis and devising the measures required in order to monitor and control such streams'. She is also a collaborator in smaller assignments concerning dioxins emissions of MSWI and other industrial plants.