ELECTROCHEMISTRY: AN ACCEPTABLE TECHNOLOGY FOR MONITORING EMISSIONS OF TOXIC GASES IN ACCORDANCE WITH EU DIRECTIVES

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Introduction

The European Union has adopted directives on the incineration of waste and on emissions to air from large combustion plants. These directives require that monitoring of emissions be carried out in accordance with CEN standards or, where these are not available, suitable ISO standards, national standards or international standards.

The latest standards do not prescribe specific measurement techniques; they state requirements for various measurement parameters. This means that plant operators are free to adopt novel methods as they become available, rather than waiting for changes in the laws. Even in the USA, notoriously shy of new CEM developments, the EPA's Environmental Technology Verification Program (ETV) "was created to accelerate the entrance of new environmental technologies into the domestic and international marketplace."

Some authorities within the EU still reject the use of electrochemical cells for toxic gas measurements. This can no longer be justified when a number of instruments based on this technology have been approved by respected authorities. The latest analysers employing Advanced Dual Sensor Technology (ADST) have minimal drift and include sophisticated self-checking algorithms. They have demonstrated high reliability in a wide range of applications including coal- and gas-fired boilers, incinerators and gas turbines.

Electrochemical Cells (1)

Electrochemical toxic gas sensors are micro fuel cells, designed to be maintenance-free and stable for long periods. They have a direct response to volume concentration of gas rather than partial pressure.

The simplest form of electrochemical toxic sensor comprises two electrodes: sensing and counter, separated by a thin layer of electrolyte. This is enclosed in a plastic housing that has a small capillary to allow the gas to reach the sensing electrode, and includes pins which are electrically attached to both electrodes and allow easy external interface (Figure 1). Gas diffusing into the sensor is either oxidized or reduced at the sensing electrode and, coupled with a corresponding (but converse) counter reaction at the other electrode, a current is generated through the external circuit. Since the rate of gas entry into the sensor is controlled by the capillary diffusion barrier, the current generated is proportional to the concentration of gas present outside the sensor and gives a direct measure of the toxic gas present.

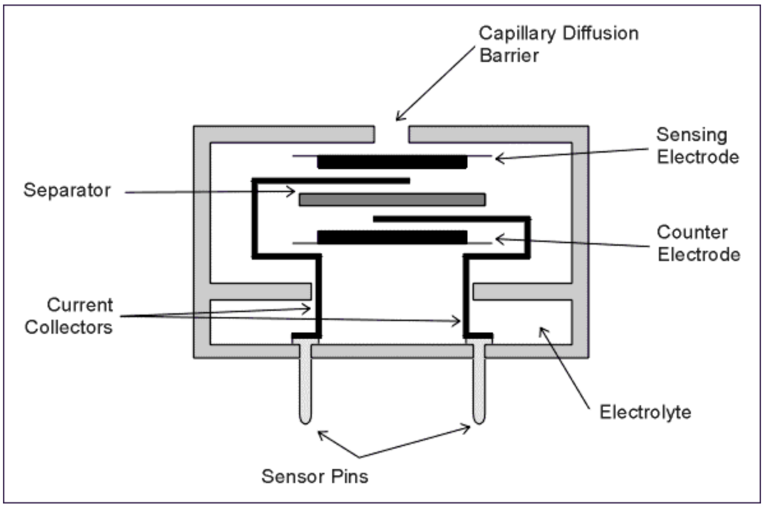

Figure 1 – Toxic Gas Sensor

The central feature of the design is the gaseous diffusion barrier, which limits the flow of gas to the sensing electrode. All of the target gas is therefore able to react as it reaches the electrode surface, and the electrode still has electrochemical activity in reserve.

The reactions that take place at the electrodes in a carbon monoxide sensor are:

Sensing: $CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$

Counter: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

And the overall reaction is: $CO + \frac{1}{2}O_2 \rightarrow CO_2$

Similar reactions take place for all other toxic gases that are capable of being electrochemically oxidized or reduced.

From the reaction at the counter electrode, it is evident that oxygen is required for the current generation process to take place. This is usually provided in the sample stream by air diffusing to the front of the sensor, or by diffusion through the sides of the sensor.

Two-electrode sensors are the simplest form of toxic gas sensors. However they have limited measuring range due to polarization of the counter electrode. This polarization effect can be eliminated by using a third, reference, electrode with a stable potential in the sensor design. In these sensors the sensing electrode is held at a fixed potential relative to the reference electrode (from which no current is drawn) so both maintain a constant potential. The counter electrode is still free to polarize, but has no effect on the sensing electrode and does not limit the sensor in any way.

Three-electrode sensors are the most widely used design of electrochemical sensors for detecting toxic gases. Despite this there are some applications where the 3-electrode design proves inadequate. For example cross-interfering gases or zero-offset changes with temperature can compromise their overall performance. By introducing a fourth 'auxiliary' electrode, accurate sensor performance can be maintained while also allowing the simultaneous measurement of two gases.

Fixed and Portable Alarm Systems

Electrochemical sensors for toxic gases have their origin in the need for personal and workplace monitoring. Numerous manufacturers can provide hand-held instruments for monitoring the local ambient air. Electrochemical cells are light in weight and have low power consumption, making them ideal for battery operation. Their simplicity and inherent reliability makes them very appropriate as continuously operating safety monitors for workplaces where toxic gas leaks are likely to occur. One corollary of these applications is that electrochemical cells used for monitoring emissions from chimney stacks actually work better as pollution levels reduce. This contrasts with systems based on spectroscopic methods which tend to suffer from low signal-to noise ratios when Emission Limit Values are reduced.

Figure 2 – Crowcon TXgard Detectors

Portable Gas Analysers

Manufacturers of portable gas analysis equipment appreciate the advantages provided by electrochemical technology. Equipment can be made light enough to be easily carried up a vertical ladder, and the power consumption can be kept low enough to provide a full 8-hour working day without the need for a mains power supply. Today's portable analysers can measure as many as nine separate gas components simultaneously, and with the benefit of microprocessor control can perform all of the necessary calculations required for emissions monitoring and combustion control.

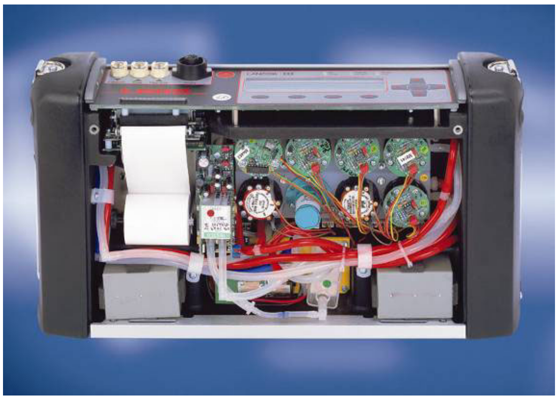

Figure 3 – Land Instruments LANCOM III

ETV Technology Verification Programme

In the USA, EPA's Environmental Technology Verification (ETV) Program develops testing protocols and verifies the performance of innovative technologies that have the potential to improve protection of human health and the environment. ETV was created to accelerate the entrance of new environmental technologies into the domestic and international marketplace.

The ETV Center lists eight types of portable NO_x analyser which it has tested for performance (2). Seven of these instruments use electrochemical cells to perform their measurements.

EU Legislation

The European Union has adopted two very significant directives on emissions. They are:

Directive 2000/76/EC on the incineration of waste
Directive 2001/80/EC on the emissions from large combustion plants

These directives require that monitoring of emissions to air be carried out in accordance with CEN standards or, where these are not available, suitable ISO standards, national standards or international standards. The existing standards are inconsistent and of variable quality and usefulness.

There are two CEN standards for continuous monitoring: EN 12619 and EN 13526 (3, 4). They both concern Total Organic Carbon emissions, and they specify that the measuring technique must be Flame Ionisation Detection. But there are no equivalent standards for other gaseous pollutants. Instead, it is necessary to look to the available ISO standards:

ISO 10849 concerns continuous monitoring of Oxides of Nitrogen (5). Several measurement techniques are described in it, but no specific technique is required provided the analyser meets the stated performance requirements.

ISO 12039 is a continuous monitoring standard for Carbon Monoxide (6). It gives performance requirements for measuring systems, and specifically states that electrochemical cell techniques are applicable for measuring CO concentrations in flue gases.

ISO 7935 covers SO_2 monitoring (7). No specific measuring technique is required, but the analyser must meet the stated performance characteristics.

Both CEN and ISO are working hard to produce a set of standards with common attributes and requirements. If these standards specify only the required performance and not the specific measurement techniques then instrument manufacturers and plant operators are free to adopt novel methods as they become available, rather than waiting for changes in the national laws.

Continuous Flue Gas Monitoring

In order to use electrochemical cells for continuous measurement of toxic gas emissions, it is important to ensure that their electrolytes remain in the proper balance. Oxygen and water are essential mediators in the electrochemical process, and must be present in the proper proportions. Portable analysers work well because they are only used to make measurements for short periods. Between measurements, the cells are exposed to ambient air and this allows the electrolyte balance to recover. A number of quasi-continuous electrochemical analysers operate by periodically switching ambient air to the sensors, thus allowing them to recover. During this period, the outputs are usually held constant. The duty cycle can be better than 90%, depending upon the application. (Figure 4).

Figure 4 – Autoflame EGA

Figure 5 – Testo Model 360

Analysers of this type have been certified for continuous NO_x monitoring in accordance with the German guideline VDI 33962 (Figure 5).

Dual-Sensor Technology (DST)

In order to make a truly continuous measurement using electrochemical cells, it is necessary to have two cells per measured gas component. In principle, one of the pair is used for measuring while the other is fed with ambient air to restore its electrolyte balance. In fact, the switching has to be slightly more complicated, to allow time for the resting sensor to respond to the sample gas before the measuring sensor is switched over to air. Typical times are 35 minutes for measurement and 30 minutes for air, with a 5 minute settling period. The resultant sensor output waveforms are shown in Figure 6. At all times, one or other of the cells is measuring the gas concentration. The microprocessor renders the switching process invisible to the operator, and ensures that the output signal remains representative of the pollutant concentration.

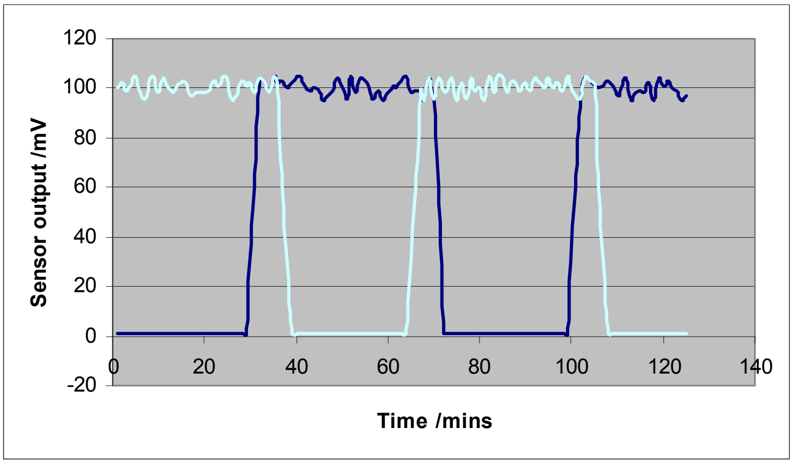

Figure 6 – Sensor outputs; dual sensor system.

Advanced Dual-Sensor Technology (ADST)

In the USA, the regulatory authorities are continually reducing emission limit values. Already permits with ELVs of 1 or 2 ppm have been issued for gas turbine utilities. In order to make accurate measurements at these very low levels, it is essential to minimise thermal drift effects. This is achieved by placing the cells in a temperature-controlled environment.

Figure 7 – Land Instruments FGA950E

Continuous monitoring electrochemical analyser systems using DST or ADST have been in use on a wide variety of plants since 1994. The main area of application was always intended to be gas turbines, where the low levels of pollution are ideally suited to electrochemical technology.

However, once the simplicity and reliability of the equipment had been demonstrated on combined-cycle and simple-cycle gas turbines which were being built in great numbers during the last decade, there was inevitably pressure to make the product available for use on more demanding applications. Before this could be done successfully, it was necessary to demonstrate that electrochemical systems could be relied upon to produce acceptable results.

Approval Testing

In 1998 in Germany, the Umweltbundesamt recorded its approval of an electrochemical analyser system for monitoring Carbon Monoxide, Oxides of Nitrogen, and Oxygen on plants subject to the 13th and BImSchV and TA Luft (9). This equipment has since been used on coal-fired power stations and large internal-combustion engine power plants on sites around the world.

An improved analyser system, using ADST, was approved for measurement of CO, NO, NO_2, SO_2, CO_2 and O_2 in 2003 (10). This has been installed and used successfully on a number of gas turbine sites. A more robust sample handling system has been incorporated, allowing the equipment to be used on applications generating high concentrations of sulphuric acid in the flue gas.

Figure 8 – Land Instruments FGA^{II}

Monitoring Certification Scheme (MCERTS)

The MCERTS Certification Scheme is managed by the UK Environment Agency. MCERTS aims to improve the quality of monitoring data delivered by operators of regulated processes. Quality data is dependent upon proper use of suitable methods, standards, services and equipment, trained and qualified personnel, effective planning, quality assurance and quality control.

The scheme assures users of certified instruments and services that they meet performance standards set out in current international standards and the growing requirements of EU Directives, and that they comply with relevant national regulations and requirements. It enables instrument manufacturers and service providers to assure customers that their instruments and services are suitable for the customers' requirements.

MCERTS for Continuous Emissions Monitoring Systems (CEMs) covers:

Extractive stack emission-monitoring instruments, where a sample of the stack gas is drawn from the stack, generally through a sample conditioning line, into the measuring cell; and

Cross-stack or *in-situ* emissions monitoring instruments, where measurements of the target species are made within the gaseous atmosphere of the stack or duct.

There are currently (May 2004) thirty-four different Continuous Monitoring Systems certified under the MCERTS scheme. Of these, nine use the electrochemical measuring technique (11).

Conclusions

Electrochemical cells can provide a reliable, accurate, and economical method of continuously measuring pollutant concentrations in the gaseous emissions from industrial processes.

Independent laboratory and field testing has shown that well-designed analyser systems that use electrochemical sensors, can meet all relevant National and International standards of performance.

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