Practical difficulties with Measurements

Electrochemical sensors are subject to a number of influences, some of which can be corrected and some of which must be accepted. The most common causes of deviation are pressure, temperature, age and time from calibration. There are also effects caused by the amount of use, but these are here not especially relevant.

Pressure: The sensors are not so much sensitive to pressure, although an increase in pressure will cause a slight increase in signal. The effects of pressure fluctuations are much more marked and will lead to a short term increase in signal, often a very marked increase. These can come about due to blockages in the gas outlets at the base of the instrument or due to not changing the filters. These effects can only be avoided by avoiding the pressure fluctuations. The by far most common cause is blocking of the outlets. The instrument is fitted with rubber feet to keep the base off the ground, but these can sink into soft surfaces such as sand and care must sometimes be taken for this reason.

Temperature: As can be seen for the data sheets, the sensors are constructed and tested for a reproducible result at a standard temperature of 20°C. There will be increasing deviation at elevated or reduced temperatures. This can be partially aided by the electronic correction factor in the instrument and also by calibrating at the temperature you will be measuring at. This will certainly reduce the error appreciably, although there is a certain loss of repeatability that cannot be compensated fully.

Age: The sensors do suffer a loss of signal with time. This is dependent on many factors such as temperature and humidity of storage, amount of use and concentration of gas measured. The loss of signal will make recalibration necessary on the one hand and reduce the resolution of the response on the other hand. The loss of resolution will naturally have an affect on accuracy and repeatability, since small fluctuations will automatically have a larger effect. Again, these effects are difficult to remove or compensate. The most important item being regular calibration to ensure the best accuracy possible under the circumstances. Flushing all the gas out of the system after use and performing a zero calibration during use will all help this matter. Exceeding the measuring range on a sensor will generally not damage it permanently, but will probably require a lengthy period before the sensor returns to zero. For this reason it is important to allow it to reach zero naturally and not force the instrument to accept the new zero point and continue measuring. In extreme cases there may be damage to the sensor, but this can usually be used again after calibration. The lifetime will, however, be shortened.

The time after calibration will naturally also effect accuracy. Most of the points above also apply in this case. There can be no fixed rules for calibration. Legal requirements vary from 2 years to 6 months, although there are applications where the instrument is checked before every measurement. 2 years is probably more wishful thinking than anything else, but most areas accept 1 year as a good standard for people who are using the equipment around one or two times per day on relatively clean equipment. The 6 month requirement is relatively new here and is generally ignored from laziness, lack of knowledge or disinterest. To a great extent it depends on the accuracy required and the availability of calibration equipment. The cross-sensitivity calculation in the instruments ensures that the value shown for the gases is very much independent of the other gases present. These effects are shown roughly in the data sheets for the sensors, but will vary between two sensors, as will the signal itself, making calibration of all the factors essential. If there are two sensors fitted that have a very high cross-sensitivity for each other's gas, then calibration of these two components will usually need to be carried out more frequently since a small change in the response of one sensor can have a large effect on the reading of the other sensor. A typical example of this problem is SO_2 and H2S, where these effects are particularly obvious. SO_2 and NO2 are another similar, if less extreme case. When measuring a mixture of gases and comparing the results to a different instrument that does not have this calculation, there may well be a big difference in readings between the two. The effect can be roughly calculated using the cross-sensitivity data given in the sensor data sheets.

Calibration gas: A bottle of calibration gas contains a known concentration of the gas under investigation in a carrier, usually nitrogen or artificial air. Calibration gas also has an accuracy in any quality, and this must be borne in mind when treating the results of measurement statistically. Another important factor is the life of the gas. Many manufacturers quote a standard shelf life for the gas, but this is not generally the case, some gases deteriorate much more quickly than others. A calibration gas containing carbon monoxide in nitrogen should keep almost indefinitely with very little change in the concentration, but many of the more exotic gases will be nearly useless after 6 months. There is no way of checking this except to return a bottle for measurement if the readings are suspicious. Steel bottles tend to keep the gas longer than aluminium ones. Although we all learned in school that perfect gases will mix perfectly in a given container, this cannot be held to be true for real gases under high pressures. The gases will separate according to their molecular weights with the result that the lightest gas will congregate at the top of the cylinder and be predominant in a sample extracted. This will then change the mixture in the cylinder permanently as well as leading to working with an incorrect concentration of gas in the first place. It is therefore necessary to mix the gases periodically by rolling the bottles, or at least laying them down for a few days and then storing them up right again. The mixing is also a slow process similar to the original separation. Regular changes of position between lying and standing are better than a single attempt to mix the gases quickly. The mixture is not a liquid, but also not a perfect gas, so all processes are somewhat slow. Generally there is a maximum storage temperature quoted for the gases, which should be adhered to as far as possible. Higher temperatures will generally accelerate the breakdown of gases or the formation of other, undesirable compounds. A gas cannot be defined as NOx since this is not a single gas but a mixture of gases. Nitrogen can form a whole series of oxides with greatly varying properties, molecular weights and stabilities. There will always be a tendency for these compound to form an equilibrium based more on temperature and pressure than on the desires of someone to have a specific calibration gas!

The methane sensor is an infrared sensor and should not vary greatly in response with time. It is nevertheless good practice to check that this is the case when calibrating the other sensors. In this model of the analyser the sensor is designed to be zeroed manually after the automatic zero has been carried out for the other sensors. This is done with the manual calibration of the oxygen sensor under GAS SENSORS. This is a good practice anyway for any measurements that require a high accuracy of this sensor. The zero enables effects due to temperature changes to be cancelled.

One of the problems that can occur with any instrument is the ingestion of water. Although this instrument is fitted with a dryer it is still possible to get some water into the gas chambers of the instrument. This does not usually cause any permanent damage, although it should be avoided whenever possible. The main problem is to remove the water afterwards. This will generally involve removing the sensors affected and drying them off wit ha cloth or by blowing. Do not use compressed air. This will almost certainly rupture the membrane of the sensor and render it useless. Industrial compressed air furthermore contains oil and other impurities which will clog the orifices of the sensor.

When all the water has been removed the analyser should be simply left running to dry out the system naturally. The time necessary will depend very much on local temperature and humidity. Hot, dry air will obviously dry the system more quickly. The infrared sensors are not damaged by water directly, but there may be a certain fogging of light source and detector due to dirt in the water. This is basically irreversible, but will be partly compensated by the zero calibration. The extra filters and orifices protect the infrared sensors against most normal accidents of this nature.

The calibration procedure is described in the operating manual. The important points to remember are adequate flushing of the system between calibration gases. 10 to 15 minutes is a good suggestion. The instrument must be running at a constant temperature and it is good to manually zero the sensors before starting. Do not use this function during calibration to cover up any zero errors. These are most likely caused by inadequate flushing. A few parts per million can be ignored, but it is good practice to check the signal from the sensor since it will not show a negative value on the main display, but it is visible on the calibration screens. Once the reading is stable and near the usual zero value (this does not mean that it will show zero on the signal), the next sensor can be calibrated.

The sensors used are generally the 5 series sensors from City Technology Ltd. In certain cases and for certain gases, the 3 series sensors are used, since not all gases are presently available in the 5 series package. There is not practical difference between the two except for the package form. Signals and lifetimes are very much the same. In general the oxygen sensor can be expected to last about two years and the toxic sensors around three years. As with all factors this will depend on ambient temperature and amount of use. Signs that the oxygen sensor will shortly become defective are unstable values in fresh air or under a gas known to be constant. It is very often the case that they simply go to error and require replacement. If this occurs much earlier than expected then the probable cause is water in the system. The toxic sensors do not give advance warning of the end of their useful life, but they can be said to be viable until the signal at a specific concentration has dropped to half of the new value. This can be calculated roughly from the calibration certificate supplied with the instrument or from the calibration values obtained after changing a sensor. New sensors seem to need to be calibrated twice before they give a stable reading, generally with a wait of one or two days between calibrations. There is no obvious logical reason for this, it is purely our experience.

When measuring CO_2 for specific emission targets such as the Kyoto Protocol it is important to remember that there is a certain ambient concentration of carbon dioxide present. The actual ambient level will vary from country to country and area to area as well as being weather dependent. The ambient CO_2 will be present in the air used for combustion and will naturally be in the flue gases measured. Theoretically, this is not part of the CO_2 emission from that burner, it is CO_2 that has already been measured or estimated as part of the emission from another burner or process.

In general, good improvements to efficiency can be made by regular measurement of the emitted gases, in addition to any requirement for monitoring that may be imposed. This is, obviously, only the case when the readings are used and not just collected as a record. High emissions of hydrocarbons and carbon monoxide are generally not necessary and it is usually possible to find a use for the energy wasted in this way. The same is true of low efficiency levels. A regular monitoring scheme will easily pay for itself within a short time in most industrial environments, purely due to the saving in fuel, without consideration of the ecological impact of the toxic emissions.