Tech/App Note 6

Calibration of EC Sensors for Highly Reactive Gases

Introduction

UNI single-gas and POLI multi-gas monitors offer electrochemical (EC) sensors for some gases that are highly reactive. Calibration of such instruments requires special procedures because the gases:

- are often highly toxic
- may react with or be adsorbed on to connecting tubing
- may corrode regulators used on gas cylinders
- are sometimes too unstable to be available in a cylinder

POLI Multi-gas Meter

UNI Single-gas Meter

This note describes special procedures that apply to each of the individual reactive gas sensors. In general, avoid personal exposure by working under a hood, in an open outdoor space, and/or wearing personal protective equipment such as a respirator fitting with an appropriate filter cartridge. Also, we recommend using as short tubing connections as possible, and using non-reactive tubing such as PTFE (aka FEP or Teflon©), or PTFE-lined soft tubing such as Norprene©. We do not recommend using a CaliCase system for reactive gas calibrations because of large surface losses.

In some cases it is possible to calibrate with a surrogate gas that is cross-sensitive on the sensor. However, it is always most accurate to calibrate directly with the gas to be measured.

If the user prefers not to perform calibrations themselves, mPower offers the following Calibration Services. Refer to TA-3 Calibration Frequency for suggestions on calibration intervals.

Calibration Services	Part Number
Ozone sensor	M180-0009-SRC
Chlorine Dioxide sensor	M180-0018-SRC
Hydrogen Fluoride sensor	M180-0011-SRC

Ozone (O_3) and Chlorine Dioxide (ClO_2)

These oxidant gases are both highly toxic with TWA's near 0.1 ppm, and therefore their sensors should be calibrated at ≤1 ppm. They are too unstable to be purchased in pressurized gas cylinders and therefore must be generated at the time of calibration. Convenient generators can be purchased for both gases from Advanced Calibration Designs (ACD, Tuscon, AZ http://goacd.com/) for approximately $2100. Advantages are the large amounts of gas generated at the low concentrations required, allowing frequent calibrations and bump checks. The ozone generator is very simple to operate, while the chlorine dioxide generator requires some simple electrolyte preparation. Both generators eventually need calibration themselves by the manufacturer.

ACD Ozone Calibrator used with UNI O_3

Both these sensors can also be calibrated using chlorine (Cl_2) as a surrogate gas, which is available in a cylinder. For ClO_2, 1.0 ppm Cl_2 is appropriate, with the span value set at the 0.6 ppm equivalent concentration. For ozone, 2.0 ppm Cl_2 gives a 0.8 ppm O_3 equivalent, but this cross-sensitivity is somewhat variable and therefore direct ozone calibration is preferred if possible.

Other ozone calibration options are available from Oxidation Technologies (Inwood, IA, https://www.oxidationtech.com/a23-14-calibrator.html). They offer an ozone calibrator for about

$1400, that generates an ozone concentration of 0.8 ppm. The operation is simple but the concentration is not adjustable and depends on the flow rate of the fixed-flow regulator used to supply the air from the adjacent cylinder. This company also supplies an ozone bump checker (Ozone Puffer) for about $450 and ozone sensor calibration services.

Oxidation Technol. Ozone Calibrator

Ozone sensors can also be bump checked using inexpensive commercial sterilizers (e.g., Airthereal https://airthereal.com/collections/ozone-generator) or by holding the UNI up to the lamp of an mPower NEO PID with its probe removed. However, these bump methods (including the Ozone Puffer) tend to generate high concentrations of ozone and do not do a good job of testing whether the instrument responds to ozone at the sub-ppm levels required for good industrial hygiene.

Phosgene ($COCl_2$)

Phosgene is commonly used in plastics manufacture, but is a toxic gas with TWA of 0.1 ppm and a NIOSH 15-minute Ceiling of 0.2 ppm. Because of it's historical use as a chemical warfare agent, it is difficult to purchase in a calibration gas cilinder, and we therefore recommend using chlorine (Cl_2) gas as a surrogate. Chlorine has half the sensitivity of phosgene itself, so 1 ppm Cl_2 gives an ideal span gas setting of 0.50 ppm. As for ozone, a convenient source of 1 ppm Cl_2 is from a gas generator, available from Advanced Calibration Designs (ACD, Tuscon, AZ http://goacd.com/) for approximately $2100. Alternatively, low-concentration Cl_2 gas can be purchased in a cylinder, but here again 1 ppm is either unavailable or has a short shelf-life of only 3 months. 2 ppm Cl_2 is offered with a shelf life up to one year and is therefore the more practical option (mPower P/N M600-0094-000). Note that 2 ppm Cl_2 is equivalent to 1 ppm phosgene, which is at the upper limit of the sensor range. We therefore suggest setting the span value to 0.95 ppm so that the sensor will not display an overrange warning if the reading goes slightly over the span setting during calibration. The 5% discrepancy thus caused is minor and within the expected accuracy of the gas standard.

Hydrogen Fluoride (HF)

HF gas is highly corrosive and toxic, with an OSHA TWA of 3 ppm and an ACGIH TWA of 0.5 ppm. It can be purchased, but is often very expensive (over $1000) and most manufacturers will only supply it in large, non-portable cylinder and require a site safety inspection first. We have found that disposable hydrogen chloride (HCl) cylinders provide a reliable and less expensive surrogate calibration gas. Although HCl is a somewhat easier to handle than HF, it is still corrosive and subject to losses on connecting surfaces, especially in humid conditions. Therefore it is necessary to use a corrosion-resistant (stainless steel) regulator, inert tubing, keep connections as short and dry as possible, and extend the calibration time to saturate surfaces.

The HF sensor gives a transient response to humidity changes that takes a few minutes re-settle close to zero response. The response is positive when changing to drier air and negative when changing to more humid air. Because HCl calibration gas is dry, it is best to allow about 5 minutes of gas exposure to let the humidity reponse decay, leaving only the HCl chemical response.

Proceed as follows:

- Obtain a cylinder of 10 ppm HCl in dry nitrogen
- Set the HF sensor Span Value to the equivalent HF response of 16 ppm (check TA Note 4 for updates)
- Zero in ambient air
- For UNI single gas meters, a 0.3 LPM regulator is adequate if connections are short, allowing gas savings. For POLI, 0.5 LPM is preferred.
- To calibrate, start the HCl gas flow 1-2 minutes before initiating the 3-minute span calibration, for a total of 4-5 minutes, to pre-soak the tubing, instrument housing and sensor.

- After removing the dry calibration gas, the sensor may go into negative alarm while re-equilibrating to ambient humidity over the course of several minutes. Do not re-zero unless the monitor is still reading negative after 15-20 minutes.

Hydrogen Chloride (HCl)

To calibrate this sensor, use a corrosion-resistant (stainless steel) regulator, inert tubing, and keep connections as short and dry as possible. 10 ppm HCl is the most common calibration gas, but 5 ppm is also adequate. For UNI single gas meters, a 0.3 LPM regulator is adequate if connections are short, allowing gas savings. For POLI, 0.5 LPM is preferred. Start the gas flow at least 90 seconds before initiating the 90-second span calibration, for a total of 3 minutes, to pre-soak the tubing, instrument housing and sensor.

Formaldehyde (HCHO)

This gas tends to be unstable in a cylinder and consequently is difficult to obtain, and mPower currently does not offer it. One supplier, Cal Gas Direct does offer it in portable cylinders, albeit with a shelf of only 3 months for low ppm concentrations and 6 months for higher concentrations. We suggest using 8 or 9 ppm (http://www.calgasdirect.com/formaldehyde-ch20/?sort=featured&page=1).

Another option is to use a formaldehyde generator tube supplied by PPM Technologies and sold through Priggen: https://www.priggen.com/Formaldehyde-Calibration-Standard-Tube . This method requires an instrument with a pump and therefore can be used with a POLI but not with the UNI series. These generator tubes are not precise calibration standards but are a good compromise between low cost, convenience for field use and reasonable accuracy for bump testing or calibration checks. They also have limited use, with a maximum of 100 tests or a shelf life of 6 months from the date of manufacture, whichever comes first.

Also possible is to use a permeation tube or diffusion tube from Kin-tek (https://kin-tek.com/). These tubes use a stable solid polymeric form of formaldehyde (paraformaldehyde) which decomposes to formaldehyde when heated. With a fixed temperature and constant gas flow a precise concentration of formaldehyde gas can be obtained. Kin-tek supplies heating gas generators for several thousand dollars, plus about $500 for the paraformaldehyde tube. Thus, this method is not very useful for field operators and has a fairly high cost.

Arsine (AsH_3)

Arsine gas is difficult to obtain in calibration gas cylinders, but cross-sensitive gases including silane (SiH_4), phosphine (PH_3), hydrogen sulfide (H_2S), and sulfur dioxide (SO_2) can be used. One of the first three gases is preferred because their sensitivity is similar to that of arsine itself; however it is again difficult to find these gases at the low concentrations needed to stay within the standard sensor range of 1 ppm. We therefore suggest using 5 ppm SO_2 (P/N M600-0061-000 disposable or M600-0083-000 recyclable) as a convenient calibration gas, while setting the span value to 0.8 ppm. As always, it should be understood that cross-sensitivities can vary from sensor to sensor and with sensor age and therefore calibration with the target gas or one that has similar sensitivity is likely to be more accurate, if such gas is available.