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.

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

Calibrations with a Surrogate Gas is Less Accurate

In some cases, it is possible to calibrate with a surrogate gas that is cross-sensitive on the sensor. This is especially helpful when the target gas is unstable, unavailable or very costly. However, it is always most accurate to calibrate directly with the gas to be measured. For example, an ETO sensor can be calibrated using 100 ppm CO gas while setting the span value to 62.5 ppm. In a series of tests with ETO UNI's calibrated with CO and tested with 10 ppm ETO, we expect readings of 10 ppm but obtained the following readings: 7.8, 9.3, 11.2, 11.7, 13.2, and 14.5. Thus, the readings are around 10 ppm, but because cross-sensitivities vary from sensor to sensor, there could be as much as a factor of 2 variation in response between the CO-calibrated sensors. Therefore, it is always preferable to calibrate with the gas of interest, and the user should be aware of the possible errors introduced by using a surrogate gas.

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 Advanced Calibration Designs generators can be purchased for both gases either directly from ACD (http://goacd.com/) or through mPower for approximately $3100.

ACD Ozone Calibrator used with UNI O_3

Gas Generator	Part Numbers Needed
Ozone 0.2-1.0 ppm	750-0202-00 and 750-0202-02
Chlorine Dioxide 0.5-5.0 ppm	750-0202-00 and 750-0202-01 and 510-0206-00

Advantages are the large amounts of gas generated at the low concentrations required, allowing frequent calibrations and bump checks. The ozone generator is very easy to operate, while the chlorine dioxide generator requires some simple electrolyte preparation. Both generators eventually need calibration themselves by the manufacturer.

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 0.4 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 its historical use as a chemical warfare agent, it is difficult to purchase in a calibration gas cylinder, 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 $3100. Alternatively, low-concentration Cl_2 gas can be purchased in a cylinder, 1 ppm is available, albeit with a short shelf-life of only several 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.

NOTE: Be sure to use a corrosion-resistant, stainless-steel regulator with Cl_2 gas cylinders as chlorine can react with the regulator and cause low sensor response with low-ppm Cl_2 cylinders and regulator corrosion with high-ppm Cl_2 cylinders. Similarly, Cl_2 calibrations cannot be performed using mPower docking stations because losses occur.

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 and most manufacturers will only supply it in large, non-portable cylinder and require a site safety inspection first.

HF Generator We now offer an HF Generator for calibration of UNI MP100 diffusion monitors (PN 006-0003-001). The generator has a digital concentration display and the output is typically in the range 3 to 12 ppm, depending on temperature. Therefore, it should be allowed to equilibrate at the ambient temperature for at least a half hour before use. It has an opening/cradle that fits a UNI monitor and a 1-year service life. The HF gas is generated by diffusion and therefore the calibrator cannot be used with pumped instruments, nor will it work with other diffusion instruments that do not fit snugly into the cradle. Because the gas is generated slowly, we recommend a 4-minute calibration time to allow the generator to equilibrate, after the UNI is placed on top and the value opened.

NO$_2$ Gas NO$_2$ is a convenient surrogate gas for calibration for both UNI and POLI. We recommend using 10 ppm NO$_2$ while setting the span value to 8 ppm HF. On special request, NO$_2$ can even be used to calibrate HF sensors using a docking station (check with mPower). We caution, however, that cross-sensitivities vary, as with all surrogate gases. Variations are commonly within 20%, but differences of up to 50% can occur. One advantage of NO$_2$ is that its response is much faster than actual HF (t_{90} of ~20s compared to 90s for HF) and therefore a full calibration can be completed within 1 minute compared to 3-4 minutes for HF. The normal span countdown is 180 seconds for the HF UNI, but to save NO$_2$ gas one can start the span and wait until the countdown reaches 60 seconds before opening the regulator. This gives the same results as a full 3 minutes of applied NO$_2$.

HCl Gas HCl is a preferred surrogate gas because it is chemically similar to HF and therefore cross-sensitivities are not likely to vary as much as other gases like NO$_2$. However, of late we have found it difficult to find a good source of portable, stable hydrogen chloride (HCl) cylinders, and therefore we are not recommending HCl use at this time. If the user can find their own reliable source, we suggest proceeding as described below:

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 response 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 (stainless steel) regulator is adequate if connections are short, allowing gas savings. For POLI, 0.5 LPM is preferred.
- To calibrate, start the HCl gas flow 2 minutes before initiating the 3-minute span calibration, for a total of 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 3 minutes seconds before initiating the 90-second span calibration, for a total of 4.5 minutes, to pre-soak the tubing, instrument housing and sensor. **CAUTION**: As noted above for HF, we have had difficulty finding a supplier of stable HCl gas in a disposable cylinder recently. Be sure to check the HCl concentration by an independent method such as gas detection tubes before calibrating with HCl gas.

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.