

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



UNI Single-gas Meter

POLI Multi-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
Calibration and testing set-up	M180-0011-SRC
Calibration and testing service, per sensor or gas	M180-0009-SRC

* Must order one set-up M180-0011-SRC plus one M180-0009-SRC for each monitor

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 (O₃) and Chlorine Dioxide (ClO₂)

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.

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



ACD Ozone Calibrator
used with UNI O₃

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.

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 6-month 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 valve opened.



NO₂ Gas NO₂ is a convenient surrogate gas for calibration for both UNI and POLI. We recommend using either 5 ppm NO₂ while setting the span value to 6 ppm HF or 10 ppm NO₂ and setting the span value to 13 ppm. NO₂ can even be used to calibrate HF sensors using a docking station. 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 NO₂ is that its response is much faster than actual HF (t₉₀ 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 NO₂ 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 NO₂. When using a docking station the full 180 second calibration is automatic and can't be changed.

Cl₂ Gas Cl₂ is a convenient surrogate gas for calibration for both UNI and POLI. We recommend using 10 ppm Cl₂ while setting the span value to 8 ppm HF. A 1-minute pre-soak with flowing Cl₂ gas is helpful but not absolutely necessary to get a slightly better calibration. Cl₂ cannot currently be used for calibrations on docking stations. Again, we caution that cross-sensitivities vary, that variations of 20% are common, and differences of up to 50% can occur.

HCl Gas HCl is in principle a good surrogate gas because it is chemically similar to HF. However, it requires long exposure times to condition the regulator (30 minutes for the first calibration) and therefore we do not recommend using this gas. In addition, has inconsistent cross-sensitivities and it is difficult to find a good source of portable, stable hydrogen chloride (HCl) cylinders,

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 preferred calibration gas. For UNI single gas meters, a 0.3 LPM regulator is adequate if connections are short, allowing gas savings. We currently no longer offer HCl sensors in POLI monitors, but for legacy users in a POLI, a 0.5 LPM stainless steel corrosion-resistant is preferred, or use a demand-flow regulator (DFR). *On the first use of the day, it is necessary to condition the regulator by flowing gas for about 30 minutes before initiating the 2-minute calibration.* For subsequent calibrations (within the same 8-hour working day) after conditioning, with the same or different instruments, start the gas flow at least 3 minutes before initiating the 2-minute span calibration, for a total of 5 minutes. **CAUTION:** As noted above for HF, we have had difficulty finding a supplier of stable HCl gas in a disposable cylinder. Be sure to check the HCl concentration by an independent method such as gas detection tubes before calibrating with HCl gas. At present we recommend using HCl cylinders within no more than 3 months of their manufacture, as we have not found suppliers in the US whose HCl concentrations in disposable cylinders last longer than that, despite longer expiration time claims. Note also that at least 10 liters of gas are needed for the first calibration because of the long (30-minute) initial conditioning times.

To summarize for HCl:

- 1) UNI only
- 2) Order 10 ppm HCl gas shortly before use and expect no more than 3-month shelf life.
- 3) Be sure to have at least 10 liters of gas per calibration day.
- 4) Precondition the stainless steel 0.3 LPM regulator for 30 minutes of gas flow before calibrating.
- 5) Subsequent calibrations the same day require only 3 minutes of preconditioning.
- 6) Do not use surrogate gases or docking stations.

Alternatively, one can obtain HCl sources from generator suppliers such as Kin-Tek, albeit at high cost. Advanced Calibration Designs (ACD, Tuscon, AZ <http://goacd.com/>) provides bump test equipment for ppm level HCl gas monitors, but does not offer precise HCl calibrators. Look for an HCl generator coming soon, similar to the HF generator described above, for UNI HCl monitors.

We currently do not recommend the use of surrogate calibration gases because of very large discrepancies found in cross-sensitivities.

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.