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 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 (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 is sensitive to humidity changes and therefore should be zeroed and calibrated at close to the same humidity as the measurements. To calibrate, the desired HCl concentration is about 1 ppm, which is the equivalent of 5 ppm HF. We recommend obtaining a cylinder of 10 ppm HCl in dry nitrogen and diluting that 10-fold using ambient air, in a Tedlar© gas bag. This procedure serves the dual purpose of reducing the HCl concentration and increasing the humidity close to ambient conditions.

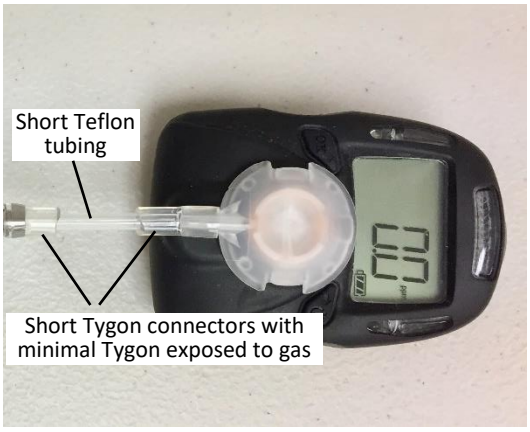
Proceed as follows:

- Obtain a large-volume syringe such as a 1-Liter Hamilton syringe (Hamilton P/N 86312).
- Obtain a 3-Liter gas bag, preferably made of Tedlar© or equivalent (P/N M490-0061-000).
- Obtain a cylinder of 10 ppm HCl in air or nitrogen (P/N M600-0054-000).
- Prepare 1 ppm HCl by diluting the cylinder gas 10:1 with ambient air using a large-volume syringe. For example, place 0.2 liters of 10 ppm HCl into the bag and then add 1.8 liters of ambient air (at the measurement humidity). Massage the bag for several seconds to ensure good mixing.

Gas dilution system using a Tedlar gas bag and a high-volume syringe

- Attach the gas bag outlet to the calibration cap using as short a connection of tubing as reasonably possibly (~5 cm). This could be 5 cm of Norprene flexible Teflon-coated tubing, or use 5 cm of 3 mm i.d. x 4 mm o.d. Teflon tubing and two 1.5-cm sections of Tygon to connect to the calibration cap on one side and the gas bag on the other.

Overview showing weight on gas bag



Exploded view showing tubing connections

HF sensor calibration set-up using HCl standard gas

- Measure the relative humidity of the ambient air used to dilute the HCl gas, and set the UNI Span gas concentration according to the following table. (These settings compensate for the humidity effect on the HF sensor, assuming a temperature of about 20-25°C or 68-77°F).

%RH	Span Setting	%RH	Span Setting	%RH	Span Setting	%RH	Span Setting
10	5.5 ppm	30	6.5	50	7.5	70	8.5
15	5.8	35	6.8	55	7.8	75	8.8
20	6.0	40	7.0	60	8.0	80	9.0
25	6.3	45	7.3	65	8.3	85	9.3

- Zero the instrument in ambient humidity air.
- Span calibrate with the 1 ppm HCl in humid air from the gas bag. 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. Place a small object such as a mobile phone on top of the gas bag to ensure a steady gas flow during calibration.

- **NOTE**: When screwing the stainless-steel regulator into the cylinder, be sure to open the valve before beginning. If the valve is closed while attaching the regulator, small amounts of air and moisture can be injected back into the cylinder, compromising the gas quality and reducing the shelf life.
- To further ensure gas quality, it is recommended to dedicate a single regulator by keeping it attached to the HCl calibration gas and not to removing it until the cylinder is empty or expired.

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. 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.