Technical Note

THORNTON

Leading Pure Water Analytics

Ozone Sensor
Polarization and Calibration Recommendations

Technical Note TN-0132

System Configuration

A pharmaceutical water ozonation system typically uses three ozone measurement points:

1. Following the ozone generator or ozonated water storage tank
2. Following the UV ozone destruct unit to confirm no ozone is going to distribution
3. At the end of the distribution loop to verify that adequate levels of ozone have reached the end during sanitization with the UV light off

A semiconductor ultrapure water system generally does not shut down for sanitization and omits the 3rd measurement point.

Sensor Requirements

Polarographic ozone sensors such as those provided by Mettler-Toledo Thornton require a period of polarization at first startup *in the presence of ozonated water* before they develop a signal. They require additional time to achieve stability. During polarization, readings can remain at zero as long as an hour after ozone is first introduced and then the sensor signal will rise to its steady-state response level where calibration can be performed. If a large volume holding tank is in the recirculation loop, additional time may be needed for its ozone concentration to stabilize.

It is necessary for Mettler-Toledo Thornton ozone sensors to be powered in the presence of > 0.05 ppm ozone for at least 2 hours, or > 0.5 ppm for at least 30 minutes to achieve full polarization. This must be accomplished before performing a calibration and using the measurement results.

Once the sensors have been polarized, that condition will be held for long periods even when measuring zero ozone. Re-polarization is necessary only if power is off the sensor for more than a few minutes or if the electrolyte or membrane are replaced. The amount of time needed for re-polarization depends on the length of time the sensor was not polarized (length of time the probe was disconnected from the measuring circuit or was disassembled). The following can be used as an estimate for re-polarization timing but the basic requirement is that the reading is stable before calibration.

Unpolarized time	Re-polarization time*
< 5 min	2 x unpolarized time
5 - 15 min	4 x unpolarized time
*in ozone concentration > 0.05 ppm	

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System and Measurement Operation
Polarization of sensors at measurement points 2 and 3 above is problematic because there should be no ozone present there during normal operation. The recommended procedure to start up and operate the measurements is to run a system sanitization (ozone destruct UV light off) that exposes all 3 sensors to > 0.05 ppm ozone for at least 2 hours, or > 0.5 ppm for at least 30 minutes to achieve full polarization as noted above.

Alternatively, if the sensor flow housings are mounted in close proximity, it may be possible to temporarily place the point 2 and 3 sensors, one at a time, into the flow housing for point 1 sample without disconnecting any sensor electrical connections. This allows polarization of those sensors in ozonated water during normal operation.

Span Calibration
Colorimeter measurements are used as the standards for ozone measurement. Colorimeters have limited accuracy but are more accurate as a percentage of reading at higher concentrations. It is therefore recommended to calibrate the span during sanitization at a relatively high level such as > 0.25 ppm, if possible. (Span calibration must not be performed at points where the ozone has been removed by UV.)

Because the polarographic measurement method used in Mettler-Toledo Thornton sensors has excellent linearity, a similar percent of reading accuracy is provided at lower levels. (This is also common practice with dissolved oxygen sensors that are calibrated in air but are used to measure at ppb levels.) For example, if a calibration is performed based on a colorimetric ozone measurement of 0.25 ppm with an uncertainty of ± 0.05 ppm or ± 20% of reading, the polarographic system can provide an accuracy near ± 20% of reading at 0.05 ppm or ± 0.01 ppm.

Span calibration should be performed near the end of a sanitization cycle when the ozonation rate and measurements are high and stable. Because of the rapid decay of ozone in samples and the limited repeatability of the ozone colorimetric method, it is good practice to take at least 2 colorimeter measurements to establish consistency and to take a third one if a significant deviation is found between the first two. For calibration, use only the average of two measurements that are within reasonable agreement.

Measurement points immediately before and immediately after the UV unit are typically close together and should read the same when the UV unit is off. Therefore one point can be calibrated to match the colorimetric result and then the second point can be calibrated to match the first point. A separate colorimetric measurement must be made for the point 3 end of distribution loop span calibration since normal ozone decay going through the distribution loop will cause a significant drop in the concentration.

Zero Calibration
The zero calibration can be performed at any time by removing the sensor from the flow housing and exposing it to air for at least 10 minutes. The instrument should give a stable reading at zero or at the single digit ppb level before initiating the calibration.

Maintenance
Sensor maintenance is normally required more frequently on the point 1 sensor which is exposed to ozone continuously. The need for electrolyte change is usually indicated by a downward drift in ozone reading. However, when automatic PID control is based on the

point 1 measurement, the controller will increase the ozonation rate to maintain the reading at the setpoint. Then the symptoms will be an increasing ozonation rate and colorimetric measurements that are consistently increasing above the on-line instrument reading.

When upward drift occurs or when electrolyte change alone will not restore the signal level and stability, then the membrane should be changed. If the sensor signal drifts upward but PID control is used, the control action will decrease the ozonation rate to compensate and the symptom will be decreasing ozonation rate and colorimetric measurements that are consistently decreasing below the on-line instrument reading.

Once experience has been gained with a particular ozonation system, a sensor maintenance schedule can be established to minimize process interruption.

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